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The kinetic energy problem in density-functional theory

Doktori (PhD) értekezés

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Contents

1. Introduction

Since its birth in 1964, density-functional theory [1-6] has become a major tool in describing electronic systems, which, thirty-four years after, was honoured with a Nobel prize in chemistry for *W. Kohn*, one of its founders. The essence of density-functional theory, namely, the idea of replacing the many-electron wave function with the density distribution of the electrons as basic variable, from which all properties of an electron system can be determined, was established in a paper by *Hohenberg* and *Kohn* [1], giving a sound theoretical ground to theories based on the statistical approach of *Thomas* and *Fermi* [7-12]. A year later *Kohn* and *Sham* [2] proposed one-particle Schrödinger equations with a local effective potential (not as in Hartree-Fock theory [13], which is, in addition, approximate by nature) for determining the density, which made it possible for density-functional theory to become useful in practice and, also, justified self-consistent field calculations using local, density-dependent potentials, induced by the work of *Slater* [14-18]. Since then density-functional theory, originally a non-relativistic ground-state theory, has gone through much development, now being formalized rigorously [19-22] and having finite-temperature [23-26], excited-state [27-32], time-dependent [33-40] and relativistic [41-45] generalizations and, also, being extended to magnetic external potentials [46-48].

In the present work, the non-interacting kinetic energy part of the energy functional of density-functional theory, the lack of knowledge of which being a substantial problem, is investigated. In Chapters 2-4 the basics of non-relativistic ground-state density-functional theory are described, which forms the ground of the investigations by the author and co-workers in Chapters 5-7, each of them representing a different approach of the problem of the non-interacting kinetic energy of density-functional theory. First, however, it is worth saying some words about density-functional theory without any mathematics for a better view on the subject.

As mentioned above, the idea of density-functional theory is to determine the different properties of electronic systems without recourse to wave functions, which are the basic variables of traditional quantum mechanics. The wave function is an abstract entity, which is not an observable and has no direct physical meaning. Further, it is a complex function and has N variable, N being the number of particles of the system it corresponds, which makes it so difficult to determine for many-electron systems. In quantum mechanics the quantities characterizing a quantum system are functionals of the wave function and for determining the wave function of a ground-state system quantum mechanics has a minimum principle for the energy functional. However, because of the complexity connected with the nature of the wave function, most practical calculations in quantum chemistry and solid state physics are approximative by nature, one of the most applied approaches being the well-known Hartree-Fock method, which constructs the wave function of a many-electron system from one-particle orbitals in single determinant form, treating exchange exactly this way but ignoring correlation between particles.

Density-functional theory, on the contrary, takes the density distribution of the electrons, which, itself, is also a functional of the wave function, as the basic quantity from which all properties of a ground-state electron system can be obtained, establishing the electron density as a quantity containing all information about an electron system, beside being an observable in itself, which can be measured by diffraction experiments, and so readily visualized. The electron density is a real, even positive, one-variable function of position in space, which gives the power of density-functional theory to be so useful not just conceptually but also as a calculational tool. The replacement of wave function by single-particle density is made possible by the Hohenberg-Kohn theorems, which constitute a one-to-one correspondence between wave functions and single-particle densities, establishing the wave function as a functional of the density, and give an energy minimizing procedure for determining the density for a ground-state system. Through this wave function–density relationship different functionals of wave function lead to different density-functionals, the most substantial of them being the energy density-functional, the position of minimum of which for given N gives the ground-state density of an N-electron system.

However, the nature of the wave function–density relationship, embracing the complexity due to the multi-variable character of the wave function, is highly complex, giving a substantial problem in density-functional theory, namely, to obtain the exact forms of the density-functionals, restricting density-functional theory to be an approximative practical tool though being exact in principle. To reduce the approximative character and increase accuracy the concept of a non-interacting reference system has been introduced into density-functional theory, defining for each electron system a non-interacting Fermion system which has the same particle density as its interacting correspondent, since the kinetic energy of this non-interacting reference system, which is the so-called non-interacting kinetic energy and gives the major part of the kinetic energy of the interacting system, can be treated exactly by considering it directly as a functional of the single-particle orbitals of the non-interacting reference system and minimizing the energy with respect to these orbitals to determine them, that is taking the N single-particle orbitals as basic variables, instead of the density itself. The equations resulting from the minimization procedure, the so-called Kohn-Sham equations, are one-particle Schrödinger equations with a common, local effective potential, containing the external potential acting on the electron system and all exchange-correlation effects. Separating the Hartree potential, that is, the classical Coulombic part, only a relatively small part of the energy density-functional remains to be approximated, which makes density-functional theory so effective in practical calculations. This method has the advantage over the Hartree-Fock approach to have a local, density dependent effective potential, which, in addition, does not exclude correlation effects. However, the introduction of orbitals means a step backward on the road to using the electron density as basic variable in determining ground-state properties, which gets more and more disadvantageous with increasing number of electrons, thus further investigations towards a pure density-functional theory remain of great importance.

2. Density-functionals

Density-functional theory is based on the two Hohenberg-Kohn theorems [1], the first of which states that the external potential $v(\vec{r})$ acting on an *N*-electron system is determined by the ground-state density distribution $\rho(\vec{r}) = \langle \psi | \hat{\rho}(\vec{r}) | \psi \rangle$ of the electrons ($\hat{\rho}(\vec{r})$ being the density operator) within a trivial additive constant. Hence, with $v=v[\rho]$ and $N = N[\rho] = \int \rho(\vec{r}) d\vec{r}$, the ground-state wave function of the system is also a functional of $\rho(\vec{r})$:

$$\psi=\psi[\rho] , \tag{2.1}$$

which can be extended to all *N*-representable densities (densities obtainable from antisymmetric wave functions) through Levy's constrained-search formulation [19,22]:

$$\rho \to \psi: \quad \rho[\psi] = \rho, \quad T[\psi] + V[\psi] = F[\rho] , \tag{2.2}$$

where

$$\rho[\psi] = \langle \psi | \hat{\rho}(\vec{r}) | \psi \rangle , \tag{2.3}$$

$$F[\rho] = \min_{\tilde{\psi} \to \rho} \{ T[\tilde{\psi}] + V[\tilde{\psi}] \} , \tag{2.4}$$

$$T[\tilde{\psi}] = \langle \tilde{\psi} | \hat{T} | \tilde{\psi} \rangle , \tag{2.5}$$

with $\hat{T}$ being the kinetic enegy operator, and

$$V[\tilde{\psi}] = \langle \tilde{\psi} | \hat{V} | \tilde{\psi} \rangle \tag{2.6}$$

with $\hat{V}$ being the operator of the interaction between the electrons (throughout, the wave functions are normalized and antisymmetric). The mapping $\psi = \psi[\rho]$, defined by

Eq.(2.2), is an inverz of the mapping $\rho = \rho[\psi]$, given by definition of ρ. With Eq.(2.2) density-functionals can be defined from functionals of wave function:

$$A[\rho] = A[\psi[\rho]], \tag{2.7}$$

for example, the energy density-functional and its components,

$$E[\rho]=F[\rho]+\int \rho(\bar{r})v(\bar{r})d\bar{r} =T[\rho]+V[\rho]+\int \rho(\bar{r})v(\bar{r})d\bar{r} \ . \tag{2.8}$$

It is important to note that the mapping

$$\psi \ \rightarrow \ \rho \ \rightarrow \ \psi' \tag{2.9}$$

is not an identity since generally a ρ can result from many normalized antisymmetric functions ψ but $\psi[\rho]$ of Eq.(2.2) gives the one that minimizes $T[\tilde{\psi}]+V[\tilde{\psi}]$, therefore a functional of ψ leads to a different functional of ψ if applying the mapping Eq.(2.9) to its variable, ψ, that is,

$$A[\psi] = A[\rho[\psi]] \tag{2.10}$$

does not hold generally [49].

3. Determination of the density

For determining the ground-state density $\rho(\vec{r})$ of an N-electron system in an external field $v(\vec{r})$, density functional theory has its own variational principle, based on the second Hohenberg-Kohn theorem [1] which says that the energy functional $E[\rho]$ takes its minimum over N-particle densities for the real density of the ground-state system, from which it follows that variations of $E[\rho]$ conserving the particle number

$$N = \int \rho(\vec{r}) d\vec{r} \tag{3.1}$$

must vanish for the ground-state density of the system (N,v):

$$\delta_N E[\rho] = 0 \ , \tag{3.2}$$

that is

$$\frac{\delta E[\rho]}{\delta_N \rho(\vec{r})} = 0 \tag{3.3}$$

($\frac{\delta}{\delta_N \rho(\vec{r})}$ denotes functional differentiation with respect to $\rho(\vec{r})$ while keeping N fixed) [50]. The constraint on the variations in Eq.(3.2) can be resolved by a Lagrange multiplier, μ, ensuring the fulfilment of Eq.(3.1):

$$\delta\{E[\rho] - \mu(\int \rho(\vec{r}) d\vec{r} - N)\} = 0 \ , \tag{3.4}$$

from which

$$\frac{\delta E[\rho]}{\delta \rho(\vec{r})} = \mu \ , \tag{3.5}$$

or

$$\frac{\delta F[\rho]}{\delta\rho(\vec{r})}+v(\vec{r})=\mu \quad , \tag{3.6}$$

arises, which, if knowing $F[\rho]$, can be used formally to get $\rho(\vec{r};\mu)$, then using Eq.(3.1) μ can be determined, thus obtaining the ground-state density of the system (N,v).

The variational principle Eq.(3.2) makes the elimination of wave functions complete in density-functional theory. However, the exact explicit form of $F[\rho]$ is not known, because of the complexity of the mapping Eq.(2.2), therefore approximations have to be used.

4. The non-interacting kinetic energy, T$_s$

The concept of the non-interacting kinetic energy is introduced in density-functional theory to eliminate the problem of not knowing a major part of $E[\rho]$. It is defined as a functional of the density by [19]

$$T_s[\rho] = \min_{\psi_D \to \rho} T[\psi_D] \ , \tag{4.1}$$

ψ_D denoting single-determinant wave functions: $\psi_D = \psi_D(u_1,...,u_N)$. $T_s[\rho]$ can also be written as $T_s[\rho] = T[\psi_D[\rho]]$ [49] but $\psi_D[\rho]$, of course, is not the $\psi[\rho]$ of Eq.(2.2):

$$\rho \to \psi_D: \quad \rho[\psi_D] = \rho, \quad T[\psi_D] = T_s[\rho] \ . \tag{4.2}$$

Introducing $T_s[\rho]$ makes it possible to get one-particle Schrödinger equations, the so-called Kohn-Sham equations [2,21,22],

$$-\tfrac{1}{2}\nabla^2 u_i(\vec{r}) + v_{KS}(\vec{r})\,u_i(\vec{r}) = \varepsilon_i\, u_i(\vec{r}) \qquad i=1,...,N\,, \tag{4.3}$$

for determining $\rho(\vec{r})$, instead of using the pure density-functional equation

$$\frac{\delta T_s[\rho]}{\delta\rho(\vec{r})} + v_{KS}(\vec{r}) = \mu \ , \tag{4.4}$$

with

$$v_{KS}(\vec{r}) = \frac{\delta(E[\rho] - T_s[\rho])}{\delta\rho(\vec{r})} \ . \tag{4.5}$$

The Kohn-Sham equations result from minimizing directly the functional

$$E[u_1,u_1^*,\ldots,u_N,u_N^*] = T_s[u_1,u_1^*,\ldots,u_N,u_N^*] + E[\rho] - T_s[\rho]\,, \tag{4.6}$$

with

$$T_s[u_1,u_1^*,\ldots,u_N,u_N^*] = \int \sum_{i=1}^{N} u_i^*(\vec{r})\left(-\tfrac{1}{2}\nabla^2\right)u_i(\vec{r})\,d\vec{r} \tag{4.7}$$

and

$$\rho[u_1,u_1^*,\ldots,u_N,u_N^*] = \sum_{i=1}^{N} u_i^*(\vec{r})\;u_i(\vec{r}) \quad , \tag{4.8}$$

(under normalization constraints) [21], for the minimum $\left\{u_i(\vec{r})\right\}_{i=1}^{N}$ of which

$$T_s\,[u_1,\ldots,u_N] = T_s[\rho[u_1,\ldots,u_N]] \quad , \tag{4.9}$$

that is

$$E\,[u_1,\ldots,u_N] = E[\rho[u_1,\ldots,u_N]] \quad . \tag{4.10}$$

In the Kohn-Sham formulation of density-functional theory the major part of the kinetic energy, thus, is treated exactly, only the remaining part in $F[\rho]$,

$$F[\rho]\ -T_s[\rho]=T[\rho]\ -T_s[\rho]+V[\rho]=T_c[\rho]+V[\rho] \tag{4.11}$$

has to be approximated, which makes density-functional theory so useful in quantum chemistry and solid-state physics.

5. Direct investigation of $T_s[\rho]$

Though the Kohn-Sham formulation of density-functional theory makes it possible to determine the ground-state density and the corresponding ground-state energy without the knowledge of the non-interacting kinetic energy density-functional, its investigation remains of substantial importance, since in the Kohn-Sham formulation single-particle wave functions are the basic variables instead of the density itself, which, although being already a significant simplification of the wave-mechanical many-body problem, does not fully utilize the possibilities implied in the Hohenberg-Kohn theorems. There have been several attempts to find $T_s[\rho]$ or construct generally applicable approximations to it but with little succes. Exact forms of $T_s[\rho]$ are known only for the two boundary cases of the electron number, N, namely, for the case of a single electron or electron pair,

$$T_W[\rho] = \tfrac{1}{8}\int \frac{|\nabla\rho(\vec{r})|^2}{\rho(\vec{r})}\, d\vec{r} \ , \tag{5.1}$$

and for the case of N tending to infinity [51],

$$T_{TF}[\rho] = C_F \int \rho(\vec{r})^{5/3}\, d\vec{r} \tag{5.2}$$

with $C_F = \tfrac{3}{10}(3\pi^2)^{2/3}$. The functional Eq.(5.1) is the so-called Weizsäcker functional, which was originally obtained by *Weizsäcker* [52] as a correction to the Thomas-Fermi formula [7,8], Eq.(5.2), which is exact for the homogeneous electron gas, being derived in a semiclassical statistical approach, to extend its validity to electron systems with small inhomogeneity. Later it was shown [53-56] how a term, one ninth of the Weizsäcker functional, arises as the second-order correction to $T_{TF}[\rho]$ in a so-called density-gradient expansion of $T_s[\rho]$, which is valid for slowly varying densities, placing the Weizsäcker functional as an inhomogeneity correction onto sound theoretical ground:

$$T_s[\rho] = T_{TF}[\rho] + \sum_{i=1}^{\infty} T_{2i}[\rho] \tag{5.3}$$

with

$$T_2[\rho] = \tfrac{1}{9} T_W[\rho], \tag{5.4}$$

$$T_4[\rho] = \frac{1}{1800 C_F} \int \rho(\vec{r})^{1/3} \left\{ \left(\frac{\nabla^2 \rho(\vec{r})}{\rho(\vec{r})} \right)^2 - \frac{9}{8} \left(\frac{\nabla^2 \rho(\vec{r})}{\rho(\vec{r})} \right) \left(\frac{\nabla \rho(\vec{r})}{\rho(\vec{r})} \right)^2 + \frac{1}{3} \left(\frac{\nabla \rho(\vec{r})}{\rho(\vec{r})} \right)^4 \right\} d\vec{r} \tag{5.5}$$

[56] and higher-order terms also derivable explicitly ($T_6[\rho]$ having been obtained as well [57]). Though strictly being valid only in the limit of slowly varying densities, numerical studies have demonstrated that the gradient expansion of $T_s[\rho]$ truncated at fourth-order can give good approximation, e. g., it can reproduce the Hartree-Fock kinetic energy within 1% for most atoms when Hartree-Fock densities are employed [58]. However, $T_6[\rho]$ and higher-order terms in Eq.(5.3) diverge because of the long-range behaviour of atomic densities [59]. Also does $\frac{\delta T_4[\rho]}{\delta \rho(\vec{r})}$ as the distance from the nuclei tends to infinity, instead of being convergent, which spoils the purely DFT use of the fourth-order gradient expansion, which includes determining $\rho(\vec{r})$ through the Euler equation Eq.(4.4). Because of these inappropriate properties, attempts have been made to get accurate expressions for $T_s[\rho]$ by leaving the fourth- and higher-order terms in Eq.(5.3) and weighting the Weizsäcker term,

$$T_s[\rho] = T_{TF}[\rho] + \lambda T_W[\rho], \tag{5.6}$$

or correcting $T_{TF}[\rho]$ with other terms depending on $\rho(\vec{r})$ and $\nabla\rho(\vec{r})$ (e.g., [60]). For atoms a factor between Weizsäcker's value (λ=1) and the gradient expansion value (λ=1/9), namely, λ=1/5 has been found to lead to a sensible improvement over the other two cases in ground-state energies [61]. However, it has been argued that the Weizsäcker term, instead of being a correction term, should be considered in full as a key component of $T_s[\rho]$ [62-68] and it is the Thomas-Fermi term which should be modified,

$$T_s[\rho] = T_W[\rho] + \gamma\, T_{TF}[\rho] \tag{5.7}$$

(e.g., with the electron number dependent $\gamma(N) = \left(1-2N^{-1}\right)\left(1-C_0N^{-1/3}+C_1N^{-2/3}\right)$ [66], proposed for atoms and atomic ions), or replaced by a nonlocal functional of $\rho(\vec{r})$,

$$T_s[\rho] = T_W[\rho] + T_{nl}[\rho] \;. \tag{5.8}$$

$T_W[\rho]$, as mentioned above, gives the exact non-interacting kinetic energy for a system composed of only one electron or two electrons in the same spatial state. Also, it guarantees the correct exponential decay of the electron density in atoms and metal surfaces, as well as the Kato cusp condition [69,70], and it is a lower bound of $T_s[\rho]$ and describes the leading term in the linear response of a homogeneous electron gas under short wavelength perturbations [71,68]. The following investigation goes in the direction of Eq.(5.8) by proposing a method to get analytical expressions for $T_s[\rho]$, assuming it in the form

$$T_s[\rho] = \int t\left(\rho(\vec{r}), \nabla\rho(\vec{r}), \nabla\nabla\rho(\vec{r}), \ldots\right) d\vec{r} \;, \tag{5.9}$$

from equations relating $T_s[\rho]$ and its functional derivatives with respect to $\rho(\vec{r})$ [72], which, taking the virial theorem of density-functional theory and a first-order homogeneity restriction for $T_s[\rho]$ as basic requirements to be satisfied, yields expressions of the form Eq.(5.8), leading to a new kind of density-gradient expansion for the non-interacting kinetic energy, in which the leading term is $T_W[\rho]$.

To describe the method, the kinetic energy density $t(\vec{r})$ will be restricted to be a function of ρ and its first derivative with respect to $\vec{r}$, $\nabla\rho$, only, that is

$$T_s[\rho] = \int t\big(\rho(\vec{r}), \nabla\rho(\vec{r})\big) d\vec{r} \ . \tag{5.10}$$

Under this restriction, the most general expression for $T_s[\rho]$ allowed by two equations relating $T_s[\rho]$ and $\frac{\delta T_s[\rho]}{\delta\rho(\vec{r})}$, namely,

$$T_s[\rho] = -\frac{1}{2}\int \rho(\vec{r})\vec{r}\nabla\frac{\delta T_s[\rho]}{\delta\rho(\vec{r})} d\vec{r} \tag{5.11}$$

and

$$T_s[\rho] = \int \rho(\vec{r})\frac{\delta T_s[\rho]}{\delta\rho(\vec{r})} d\vec{r} \ , \tag{5.12}$$

will be derived. Eq.(5.11) is a straightaway consequence of the exact $T_s[\rho]$ being homogeneous of degree two in coordinate scaling [73], and yields the virial theorem of density-functional theory through the density-functional Euler equation, Eq.(4.4). Eq.(5.12) describes functionals homogeneous of degree one in $\rho(\vec{r})$ and, though its validity for the exact $T_s[\rho]$ [74] has been shown to be wrong [49,75], can be true for functionals giving T_s for certain particle numbers, as in the case of $T_W[\rho]$, and also, is a reasonable assumption since, for expressions like the terms in the gradient expansion Eq.(5.3), it forces the convergence for both $t(\vec{r})$ and $\frac{\delta T_s[\rho]}{\delta\rho(\vec{r})}$, the lack of which is an essential problem with the terms in Eq.(5.3). The result arising from these equations with Eq.(5.10) will be found to be a generalization of the Weizsäcker kinetic energy functional. Though this generalization, leading to the Weizsäcker functional times a constant after rotational invariance considerations, does not extend the range of systems for which it works as an exact functional and including higher-order derivatives of ρ has already been found to be necessary to get better approximations [58,76-81], the method described below can be useful in deriving expressions for $T_s[\rho]$ involving other equations as well as basis for the calculations and starting from less restrictive assumptions for $t(\vec{r})$ (allowing dependence on higher-order derivatives of ρ as well) to get more generally valid non-interacting kinetic energy density functionals.

Mathematical formulation

Before focusing on the equations to be taken as main criteria in the derivation, first an explanation of the notation used in the following needs to be given. The derivative of a functional of the form (5.10) with respect to $\rho(\vec{r})$ is given by [82]

$$\frac{\delta T_s}{\delta \rho} = \frac{\partial t}{\partial \rho} - \sum_{q=x,y,z} \frac{\partial}{\partial q} \frac{\partial t}{\partial \frac{\partial \rho}{\partial q}} = \frac{\partial t}{\partial \rho} - \nabla \frac{\partial t}{\partial \nabla \rho} \tag{5.13}$$

which means that $\frac{\delta T_s}{\delta \rho}$ is a function of ρ and its first and second derivatives with respect to $\vec{r}$:

$$\frac{\delta T_s}{\delta \rho(\vec{r})} = g\big(\rho(\vec{r}), \nabla \rho(\vec{r}), \nabla\nabla \rho(\vec{r})\big) \ , \tag{5.14}$$

where $\nabla\nabla$ is not the usual Laplace operator, ∇^2, with scalar multiplication between the ∇ operators but

$$\nabla\nabla \equiv \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix} \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) = \begin{pmatrix} \frac{\partial^2}{\partial x^2} & \frac{\partial^2}{\partial x \partial y} & \frac{\partial^2}{\partial x \partial z} \\ \frac{\partial^2}{\partial x \partial y} & \frac{\partial^2}{\partial y^2} & \frac{\partial^2}{\partial y \partial z} \\ \frac{\partial^2}{\partial x \partial z} & \frac{\partial^2}{\partial y \partial z} & \frac{\partial^2}{\partial z^2} \end{pmatrix} \tag{5.15}$$

that is multiplication of matrices appears, which can be seen by applying the chain rule of differentiation when differentiating $\frac{\partial t}{\partial \frac{\partial \rho}{\partial q}}$ with respect to q (q= x,y,z):

$$\nabla \frac{\partial t(\rho, \nabla \rho)}{\partial \nabla \rho} = \frac{\partial}{\partial x} \frac{\partial t}{\partial \frac{\partial \rho}{\partial x}} + \ldots = \frac{\partial^2 t}{\partial \rho \partial \frac{\partial \rho}{\partial x}} \frac{\partial \rho}{\partial x} + \sum_{q=x,y,z} \frac{\partial^2 t}{\partial \frac{\partial \rho}{\partial q} \partial \frac{\partial \rho}{\partial x}} \frac{\partial^2 \rho}{\partial x \partial q} + \ldots =$$

$$= \frac{\partial^2 t}{\partial \rho \partial \frac{\partial \rho}{\partial x}} \frac{\partial \rho}{\partial x} + \frac{\partial^2 t}{\partial \frac{\partial \rho}{\partial x} \partial \nabla \rho} \frac{\partial \nabla \rho}{\partial x} + \ldots = \frac{\partial^2 t}{\partial \rho \partial \nabla \rho} \nabla \rho + \left(\frac{\partial^2 t}{\partial \nabla \rho^2} \nabla \right) \nabla \rho \ .$$

Taking an arbitrary function $f(\vec{r}\,)$,

$$\int f(\vec{r}\,') \frac{\delta^2 T}{\delta \rho(\vec{r}\,) \delta \rho(\vec{r}\,')} d\vec{r}\,' = f(\vec{r}\,) \frac{\partial}{\partial \rho} \frac{\delta T}{\delta \rho(\vec{r}\,)} - \nabla \left(f(\vec{r}\,) \frac{\partial}{\partial \nabla \rho} \frac{\delta T}{\delta \rho(\vec{r}\,)} \right) +$$

$$+ \nabla\nabla \left(f(\vec{r}\,) \frac{\partial}{\partial \nabla\nabla \rho} \frac{\delta T}{\delta \rho(\vec{r}\,)} \right) . \tag{5.16}$$

Using Eq.(5.13),

$$\int f(\vec{r}\,') \frac{\delta^2 T}{\delta \rho(\vec{r}\,) \delta \rho(\vec{r}\,')} d\vec{r}\,' = f(\vec{r}\,) \left(\frac{\partial^2 t}{\partial \rho^2} - \frac{\partial}{\partial \rho} \nabla \frac{\partial t}{\partial \nabla \rho} \right) - \nabla f(\vec{r}\,) \nabla \frac{\partial^2 t}{\partial \nabla \rho^2} -$$

$$- \nabla\nabla f(\vec{r}\,) \frac{\partial^2 t}{\partial \nabla \rho^2} , \tag{5.17}$$

where

$$\nabla \frac{\partial t}{\partial \nabla \rho} = \frac{\partial^2 t}{\partial \rho \partial \nabla \rho} \nabla \rho + \frac{\partial^2 t}{\partial \nabla \rho^2} \nabla\nabla \rho \ , \tag{5.18}$$

$$\nabla \frac{\partial^2 t}{\partial \nabla \rho^2} = \frac{\partial^3 t}{\partial \rho \partial \nabla \rho^2} \nabla \rho + \frac{\partial^3 t}{\partial \nabla \rho^3} \nabla \nabla \rho \ , \tag{5.19}$$

with

$$\frac{\partial^2 t}{\partial \nabla \rho^2} \nabla \nabla \rho \equiv \sum_{q=x,y,z} \frac{\partial^2 t}{\partial \frac{\partial \rho}{\partial q} \partial \nabla \rho} \frac{\partial \nabla \rho}{\partial q} = \left(\frac{\partial^2 t}{\partial \nabla \rho^2} \nabla \right) \nabla \rho \ , \tag{5.20}$$

$$\frac{\partial^3 t}{\partial \nabla \rho^3} \nabla \nabla \rho \equiv \left(\frac{\partial^3 t}{\partial \frac{\partial \rho}{\partial x} \partial \nabla \rho^2} \nabla \nabla \rho, \frac{\partial^3 t}{\partial \frac{\partial \rho}{\partial y} \partial \nabla \rho^2} \nabla \nabla \rho, \frac{\partial^3 t}{\partial \frac{\partial \rho}{\partial z} \partial \nabla \rho^2} \nabla \nabla \rho \right) =$$

$$= \left(\frac{\partial^3 t}{\partial \nabla \rho^3} \nabla \right) \nabla \rho \tag{5.21}$$

and

$$\nabla \nabla f(\vec{r}) \frac{\partial^2 t}{\partial \nabla \rho^2} = \left(\frac{\partial^2 t}{\partial \nabla \rho^2} \nabla \right) \nabla f(\vec{r}) \tag{5.22}$$

as can be seen by substituting the components of the vectors and the elements of the two dimensional $\frac{\partial^2 t}{\partial \nabla \rho^2}$ and the three dimensional $\frac{\partial^3 t}{\partial \nabla \rho^3}$ matrices into Eqs.(5.17)-(5.22) and doing some algebraic manipulation on them as was shown for Eq.(5.18) previously. Generally, it can be said that differentiating matrices $\underline{M}(\rho(\vec{r}), \nabla \rho(\vec{r}), \nabla \nabla \rho(\vec{r}), ...)$ with respect to $\vec{r}$, ρ, $\nabla \rho$, $\nabla \nabla \rho$, ... can be done formally in the same way as for scalar functions, keeping in mind the meaning of the symbols appearing this way.

Homogeneity in ρ and virial theorem as criteria

With the help of Eq.(5.17), the first derivative of Eq.(5.12) with respect to $\rho(\vec{r})$,

$$\int \rho(\vec{r}\,')\frac{\delta^2 T_s}{\delta\rho(\vec{r})\delta\rho(\vec{r}\,')}d\vec{r}\,' = 0 \ , \tag{5.23}$$

and that of Eq.(5.11), the first of a hierarchy of equations obtainable by successive functional differentiations [83],

$$\frac{\delta T_s}{\delta\rho(\vec{r})} = -\tfrac{1}{2}\vec{r}\nabla\frac{\delta T_s}{\delta\rho(\vec{r})} - \tfrac{1}{2}\int \rho(\vec{r}\,')\vec{r}\,'\nabla'\frac{\delta^2 T_s}{\delta\rho(\vec{r})\delta\rho(\vec{r}\,')}d\vec{r}\,' , \tag{5.24}$$

can be used to get partial differential equations for $t(\rho,\nabla\rho)$.

First let $f(\vec{r})$ be $\rho(\vec{r})$, then Eq.(5.17) yields

$$\int \rho(\vec{r}\,')\frac{\delta^2 T_s}{\delta\rho(\vec{r})\delta\rho(\vec{r}\,')}d\vec{r}\,' = -\left(\nabla\rho\frac{\partial^3 t}{\partial\nabla\rho^3} + \rho\frac{\partial^3 t}{\partial\rho\partial\nabla\rho^2} + \frac{\partial^2 t}{\partial\nabla\rho^2}\right)\nabla\nabla\rho + $$

$$+\rho\frac{\partial^2 t}{\partial\rho^2} - \rho\nabla\rho\frac{\partial^3 t}{\partial\rho^2\partial\nabla\rho} - \left(\nabla\rho\right)^2\frac{\partial^3 t}{\partial\rho\partial\nabla\rho^2} , \tag{5.25}$$

which, with the condition (5.23), gives two equations because $\rho(\vec{r})$ can be arbitrary and t is a function of ρ and $\nabla\rho$ only so the multipliers of $\nabla\nabla\rho$ must vanish together:

$$\nabla\rho\frac{\partial^3 t}{\partial\nabla\rho^3} + \rho\frac{\partial^3 t}{\partial\rho\partial\nabla\rho^2} + \frac{\partial^2 t}{\partial\nabla\rho^2} = 0 \tag{5.26}$$

and

$$\left(\nabla\rho\right)^2\frac{\partial^3 t}{\partial\rho\partial\nabla\rho^2} + \rho\nabla\rho\frac{\partial^3 t}{\partial\rho^2\partial\nabla\rho} - \rho\frac{\partial^2 t}{\partial\rho^2} = 0 \ . \tag{5.27}$$

Applying an integration by part in Eq.(5.24),

$$\frac{\delta T_s}{\delta\rho(\vec{r})} = -\tfrac{1}{2}\vec{r}\nabla\frac{\delta T_s}{\delta\rho(\vec{r})} + \tfrac{1}{2}\int\left(3\rho(\vec{r}\,') + \vec{r}\,'\nabla'\rho(\vec{r}\,')\right)\frac{\delta^2 T_s}{\delta\rho(\vec{r})\delta\rho(\vec{r}\,')}d\vec{r}\,' \text{ , } \quad (5.28)$$

and using Eq.(5.23),

$$\frac{\delta T_s}{\delta\rho(\vec{r})} = -\tfrac{1}{2}\vec{r}\nabla\frac{\delta T_s}{\delta\rho(\vec{r})} + \tfrac{1}{2}\int\vec{r}\,'\nabla'\rho(\vec{r}\,')\frac{\delta^2 T_s}{\delta\rho(\vec{r})\delta\rho(\vec{r}\,')}d\vec{r}\,' \quad . \qquad (5.29)$$

Now, let $f(\vec{r})$ equal $\vec{r}\nabla\rho(\vec{r})$,

$$f(\vec{r}) = \vec{r}\nabla\rho(\vec{r}) \quad , \qquad (5.30)$$

then

$$\nabla f(\vec{r}) = \nabla\rho(\vec{r}) + \vec{r}\nabla\nabla\rho(\vec{r}) \quad , \qquad (5.31)$$

$$\nabla\nabla f(\vec{r}) = 2\nabla\nabla\rho(\vec{r}) + \vec{r}\nabla\nabla\nabla\rho(\vec{r}) \quad . \qquad (5.32)$$

Substituting Eqs.(5.30)-(5.32) into Eq.(5.17), then inserting the result and Eq.(5.13) into Eq.(5.29),

$$\tfrac{1}{2}\nabla\rho\frac{\partial^3 t}{\partial\nabla\rho^3}\nabla\nabla\rho + \tfrac{1}{2}(\nabla\rho)^2\frac{\partial^3 t}{\partial\rho\partial\nabla\rho^2} - \nabla\rho\frac{\partial^2 t}{\partial\rho\partial\nabla\rho} + \frac{\partial t}{\partial\rho} = 0 \qquad (5.33)$$

arises which can be split into two equations,

$$\tfrac{1}{2}\nabla\rho\frac{\partial^3 t}{\partial\nabla\rho^3} = 0 \qquad (5.34)$$

and

$$\tfrac{1}{2}(\nabla\rho)^2\frac{\partial^3 t}{\partial\rho\partial\nabla\rho^2} - \nabla\rho\frac{\partial^2 t}{\partial\rho\partial\nabla\rho} + \frac{\partial t}{\partial\rho} = 0 \quad , \qquad (5.35)$$

for the same reasons as in the previous case.

Eqs.(5.26)-(5.27) and Eqs.(5.34)-(5.35) are four partial differential equations from which $t(\rho,\nabla\rho)$ can be determined. From Eq.(5.34) follows that $\frac{\partial^2 t}{\partial\nabla\rho^2}$ does not depend on $\nabla\rho$ that is

$$\frac{\partial^2 t}{\partial\nabla\rho^2} = \hat{c}(\rho)\,, \tag{5.36}$$

from which

$$t = \tfrac{1}{2}\hat{c}(\rho)(\nabla\rho)^2 + \vec{c}(\rho)\nabla\rho + c(\rho)\ \ , \tag{5.37}$$

where $\hat{c}(\rho)$, $\vec{c}(\rho)$ and $c(\rho)$ are a matrix, a vector and a scalar function of ρ only, respectively. Inserting this expression for *t* into Eq.(5.35),

$$\frac{\partial c(\rho)}{\partial\rho} = 0 \tag{5.38}$$

arises which means that c is independent of ρ as well:

$$c(\rho) = k\ \ . \tag{5.39}$$

Now applying the equations emerged from the homogeneity restriction on $T_s[\rho]$, Eq.(5.26) with Eq.(5.36) leads to

$$\rho\frac{\partial\hat{c}(\rho)}{\partial\rho} = -\hat{c}(\rho)\,, \tag{5.40}$$

from which

$$\hat{c}(\rho) = \hat{k}\rho^{-1} \tag{5.41}$$

follows with $\hat{k}$ being a constant matrix. However, Eq.(5.27) does not give any further information about $t(\rho,\nabla\rho)$: it is not independent from the other three equations. Thus,

$$t(\rho,\nabla\rho) = \tfrac{1}{2}\hat{k}\nabla\rho\nabla\rho\,\rho^{-1} + \vec{c}(\rho)\nabla\rho + k \tag{5.42}$$

has been obtained from Eqs.(5.23) and (5.24).

Direct use of Eq.(5.12) leads to

$$\int \left(\vec{c}(\rho(\vec{r}))\nabla\rho(\vec{r}) + k \right) d\vec{r} = 0 \tag{5.43}$$

so the result for $T_s[\rho]$ is

$$T_s[\rho] = \int \tfrac{1}{2} \hat{k} \nabla\rho \nabla\rho \, \rho^{-1} d\vec{r} \,, \tag{5.44}$$

assuming Eq.(5.10). Eq.(5.44) is a generalization of Weizsäcker's kinetic energy functional, including mixed products of the functions $\frac{\partial\rho}{\partial q}$ ($q=x,y,z$) as well beside the usual $|\nabla\rho|^2$ part. Since $\hat{k}$ is related with a second derivative matrix by a scalar multiplier, Eq.(5.41), it must be symmetric because of the irrelevance of the order of differentiating t with respect to the variables $\frac{\partial\rho}{\partial q}$ ($q=x,y,z$). Furthermore, requiring t to be invariant under arbitrary rotation of the frame of reference, the diagonal elements of $\hat{k}$ must be equal and the non-diagonal elements must be zero, thus

$$\hat{k} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix} , \tag{5.45}$$

that is

$$t = \tfrac{1}{2} a |\nabla\rho|^2 \rho^{-1} \tag{5.46}$$

which means that one system is needed to fix parameter a. Choosing a one-electron system, a=1/4, obtaining Weizsäcker's functional, but for different systems a can be different, that is Eq.(5.44) cannot be the form of a more general non-interacting kinetic energy functional.

Conclusion

Taking the virial theorem of density-functional theory and the homogeneity of T_s in $\rho(\vec{r})$ as basic conditions to be satisfied, an analytical expression for the functional $T_s[\rho]$ has been derived under the assumption that the kinetic energy density *t* is a function of ρ and $\nabla\rho$. In the derivation the first functional derivatives of the relations Eqs.(5.11) and (5.12), Eqs.(5.24) and (5.23), were used in order to obtain pure differential equations without integration. Since the highest order derivative of the density, $\nabla\nabla\rho$, appears only explicitly, as a multiplier of the terms being functions of ρ and $\nabla\rho$ only because of the condition (5.10), each of the two equations can be split into a couple of partial differential equations for *t* to get enough equations to yield a solution for $t(\rho,\nabla\rho)$. The result, Eq.(5.44), is a formal generalization of Weizsäcker's functional. That the Weizsäcker functional has been found to be a special case of this solution, however, is natural since $T_W[\rho]$ itself satisfies the three conditions (5.10)-(5.12).

That the functional obtained does not serve the exact $T_s[\rho]$ means the exact $T_s[\rho]$ cannot have a form of the kind (5.10). Also, Eq.(5.44) does not present any progress concerning the number of systems to which it is applicable as an exact kinetic energy functional. However, the method described here can be useful in finding more general expressions for $T_s[\rho]$, making less strict assumptions for $t(\vec{r})$: $t(\vec{r},\rho,\nabla\rho,\nabla\nabla\rho,\ldots)$, which, of course, may require one to involve further relations for $T_s[\rho]$ in order to have enough equations to obtain an explicit analytical form for it.

In summary, in this chapter a method is proposed to get the most general analytical expression for the non-interacting kinetic energy density-functional, derivable from equations relating $T_s[\rho]$ and its functional derivatives taken as basic criteria to be fulfilled, assuming $T_s[\rho]$ in the form Eq.(5.9). Also, a simple mathemathical formalism to handle multiple spatial derivatives of ρ in functional differentiations in a compact way is proposed, which makes calculations much easier. To make understanding better the method proposed is described through applying it under the assumption Eq.(5.10) and taking the virial theorem and Eq.(5.12) as basic conditions to be satisfied. As a result the Weizsäcker functional has been found for $T_s[\rho]$, which, of course, may be quite trivial, however, the way it is obtained demonstrates how one can get new expressions for $T_s[\rho]$, involving higher-order derivatives of $\rho(\bar{r})$ as well, by applying this method.

6. Differential equations for the density

In the previous chapter the non-interacting kinetic energy density-functional is investigated explicitly with the goal of replacing the Kohn-Sham method and the use of orbitals by the pure density-functional procedure for the calculation of ground-state properties, which includes the use of the Euler equation Eq.(3.6), or Eq.(4.4), for determining the ground-state density. Another way of treating the problem of not knowing $T_s[\rho]$ is to investigate Eq.(3.6), or some derivative of it, directly, without the separation of $T_s[\rho]$, which means the construction of equations for the density, containing the external potential $v(\vec{r})$ as a parameter, from which $\rho(\vec{r})$ can be determined for a given $v(\vec{r})$. Several studies along this direction have been made, *N. H. March* being a leading figure in this area [84-92]: differential equations for the ground-state densities of different electron systems have been set up, containing $v(\vec{r})$ implicitly. The investigation in the following sections in this chapter follows in these footsteps by constructing differential equations for $\rho(\vec{r})$ for different cases.

6.1 Differential equation for the density in a generalized local approach

March have derived the non-linear second-order differential equation [85]

$$\frac{\nabla^2\rho}{\rho}-\frac{1}{3}\left(\frac{\nabla\rho}{\rho}\right)^2=\frac{\rho^{1/3}}{l_1}\ , \tag{6.1}$$

with l_1=(1/4)(π/3)$^{1/3}$, satisfied by the ground-state electron density of the Thomas-Fermi atom [10-12], for which the Euler equation Eq.(3.6) has the form

$$\frac{\delta T_{TF}\left[\rho\right]}{\delta\rho(\vec{r})}+\int\frac{\rho(\vec{r}\,')}{\left|\vec{r}-\vec{r}\,'\right|}d\vec{r}\,'+v(\vec{r})=\mu_{TF}\ , \tag{6.2}$$

the second term coming from the classical Coulomb repulsion. Eq.(6.1) has subsequently been extended [86] to include Dirac’s exchange [9] and Gell-Mann–Brueckner correlation [93] (obtained for a high-density homogeneous electron liquid):

$$\left(l_1\rho^{-1/3}-l_2\rho^{-2/3}-l_3\rho^{-1}\right)\frac{\nabla^2\rho}{\rho}-\left((1/3)l_1\rho^{-1/3}-(2/3)l_2\rho^{-2/3}-l_3\rho^{-1}\right)\left(\frac{\nabla\rho}{\rho}\right)^2=1\,, \tag{6.3}$$

where $l_2=(1/4)(3\pi^2)^{-2/3}$ and $l_3=(1-ln2)(12\pi^3)^{-1}$. Recently, *March* has made a proposal [87,89] for a generalization along this path to include interaction between electrons in full, proposing the shape

$$\frac{\nabla\rho}{\rho}\cdot\nabla S(\rho)+\frac{\nabla^2\rho}{\rho}S(\rho)=1 \tag{6.4}$$

for the differential equation that describes inhomogeneous electron systems, which can be considered as a generalized local density approximation (GLDA). The form of $S(\rho)$ in the Thomas-Fermi model is explicitly

$$S_{TF}(\rho)=l_1\rho^{-\frac{1}{3}}\ , \tag{6.5}$$

while with the introduction of exchange and Gell-Mann–Brueckner correlation one has

$$S_{TFxc}(\rho)=l_1\rho^{-\frac{1}{3}}+l_2\rho^{-\frac{2}{3}}+l_3\rho^{-\frac{3}{3}}\ . \tag{6.6}$$

The proposal is now to assert, but strictly for finite systems, that $S(\rho)$ can be generalized from Eq.(6.6) to read [87]

$$S(\rho)=\sum_{i=1}^{\infty}l_i\rho^{-\frac{i}{3}}\ . \tag{6.7}$$

Because of the lack of knowledge of the coefficients l_i (i >3) in the GLDA form Eq.(6.7), in the following known densities of closed shell atoms Kr and Xe will be used as input in order to extract forms of $S(\rho)$ [88]. Naturally, the function thus obtained will be somewhat different for different atoms. Nevertheless, the calculations will show that $S(\rho)$ has the same basic shape, on the basis of which an attempt will be made to represent the limit of large numbers of electrons by an approximate form. In the concluding section the possibility will be discussed that a form of $S(\rho)$ obtained this way, inserted into Eq.(6.4), could lead to a differential equation which is of useful accuracy in describing the ground-state density $\rho(\vec{r})$ in neutral homonuclear assemblies, and in particular in clusters having many electrons.

Analytical solution in terms of the density for a spherically symmetric system

For spherically symmetric systems Eq.(6.4) has the form

$$-q(r)\frac{\partial S\left(\rho(r)\right)}{\partial r}+\left(\frac{\rho''(r)}{\rho(r)}-\frac{2}{r}q(r)\right)S\left(\rho(r)\right)=1 \ , \qquad (6.8)$$

where $q(r)=-\dfrac{\rho'(r)}{\rho(r)}$ is the local wavenumber introduced earlier by *Nagy and March* [94], and the prime ’ denotes differentiation with respect to r. This is a first-order differential equation for $S(r)$ which can be solved analytically:

$$S(r)=\frac{N(r)}{r^2\rho'(r)}=-\frac{1}{q(r)}\frac{N(r)}{r^2\rho(r)} \ , \qquad (6.9)$$

where

$$N(r) = \int_0^r r^2 \rho(r) dr \ . \tag{6.10}$$

If $r \to \infty$ $N(r)$ is proportional to the number of electrons N: $4\pi N(r) \to N$.

Taking into account that asymptotically [95]

$$\rho(r) \sim A r^p \exp(-Qr) \ , \tag{6.11}$$

where $Q = 2\sqrt{2I}$ with I being the first ionization potential, and $q(r \to \infty) = Q$ [94],

$$S(r) \sim N(4\pi A)^{-1} \frac{\exp(Qr)}{r^{p+2}\left(\frac{p}{r} - Q\right)} \tag{6.12}$$

can be obtained for the asymptotic behaviour of $S(r)$ via integrations by parts since $\int_0^r r^2 \rho dr = N/(4\pi) - \int_r^\infty r^2 \rho dr$. (The $const. \cdot r^{-n}$ -like parts beside the $\exp(r) \cdot r^{-m}$-like one can be neglected.) Eq.(6.12) also means that

$$\lim_{r \to \infty} S(r) = -\infty \ . \tag{6.13}$$

On the other hand, using l'Hospital's rule,

$$\lim_{r \to 0} S(r) = 0 \tag{6.14}$$

and, the $r \to 0$ limit of the second part of the left hand side of Eq.(6.8),

$$\lim_{r \to 0} \left(\frac{\nabla^2 \rho(r)}{\rho(r)} S(r) \right) = \frac{2}{3} \tag{6.15}$$

are obtained.

Numerical results for closed-shell atoms

Using analytical Hartree-Fock densities computed from wave functions from *Koga et al.* [96] S is calculated and plotted in Fig.1 and 2 as a function of radial distance r for the closed shell atoms Kr and Xe. As can be seen from Figs.1 and 2 (which is an enlargement of Fig.1 for smaller radial distances from the nucleus), $S(r)$ has a roughly monotonically decreasing behaviour, and reflects the electronic shell structure of atoms with its positions of local minima or pairs of inflection points: the $S(r)$ curve of Kr has four 'shells' while the curve for Xe has five. (Similar properties also hold for Ne and Ar.)

Since the density $\rho(r)$ in each atom decreases monotonically from its value $\rho(0)$ at the nucleus, $S(r)$ can be translated into $S(\rho)$, the curves obtained in this way being shown in Fig.3 for Kr and Xe. Also in Fig.3, curves are plotted for Ne and Ar in order to display the dependence on the number of electrons in the closed shell series. As is also expected on the basis of Eqs.(6.13) and (6.14) and the results for the shape of $S(r)$, from

$$\lim_{\rho\to 0} S(\rho) = -\infty \tag{6.16}$$

$S(\rho)$ roughly monotonically increases tending to zero as $\rho\to\rho(0)$,

$$\lim_{\rho\to\rho(0)} S(\rho) = 0 \ . \tag{6.17}$$

In accord with what is expected, namely that these curves of $S(\rho)$ should tend to a limit for large numbers of electrons, the curves for Kr and Xe are closer to each other than for the other pairs of atoms. These two curves have six intersections (that is common points) while the other pairs have only two or none. The six intersection points of the

$S(\rho)$ curves of Kr and Xe, displayed in Fig.4, make it possible to estimate the shape of a function of ρ, which can be considered as an approximation to $S(\rho)$ in the limit of large electron numbers. Fig.5 exhibits an example for this estimating $S(\rho)$ with a simple *ln* curve, $S(\rho)=0.563\ln(\ln(\rho)+1.5)-1.042$.

It may be worth noting that if p in Eq.(6.11) equals zero (or r^p is neglected beside exp($-Qr$)) an asymptotic formula can be obtained for $S(\rho)$. Inverting Eq.(6.11) to get $r(\rho)$ then inserting it into Eq.(6.12),

$$S(\rho) \sim -N(4\pi)^{-1} Q \frac{1}{\rho(\ln\rho - \ln A)^2} \tag{6.18}$$

arises for low densities, which can be useful in finding analytic forms for $S(\rho)$.

Conclusion

Eq.(6.4) is the proposed generalized local density approximation, where $S(\rho)$ is represented by the infinite series of Eq.(6.7) for the finite systems this present investigation solely has been concerned with. Because of the lack of knowledge of all but the first three coefficients (see Eq.(6.6)) in the form Eq.(6.7), forms of $S(\rho)$ have been extracted numerically for closed shell atoms, and these are presented in Fig.3.

As for future directions, the form of $S(\rho)$ for neutral systems with large numbers of electrons proposed here may afford a route to calculating the density from the (now partial) differential equation Eq.(6.4), given $S(\rho)$, say in large homonuclear clusters such as Si. Of course, here directional bonding is important, and it remains to be seen whether the universality of functionals underlying density functional theory is an adequate basis for expecting that $S(\rho)$ derived from neutral closed shell atoms can be taken over to apply to homonuclear complexes with large numbers of electrons. Naturally, even for given $S(\rho)$, the task of solving Eq.(6.4) for a multicentre molecule or cluster remains formidable, and probably basis sets plus a suitable 'least squares' reformulation of Eq.(6.4) may be essential for progress.

Nevertheless the approach advocated here seems to be a step towards attaining a long-term goal of density functional theory: namely a differential equation to be solved directly for the ground-state electron density $\rho(\bar{r})$, without recourse to wave functions. The present proposal, as stressed above, should come into its own for homonuclear multicentre complexes with many electrons, though, of course, the entire proposal is within the general framework afforded by the non-relativistic many-electron Schrödinger equation.

Figures

Fig.1: $S(r)$ for Kr and Xe in the $0< r <3$ region, the origin being on the nucleus itself (in a.u.).

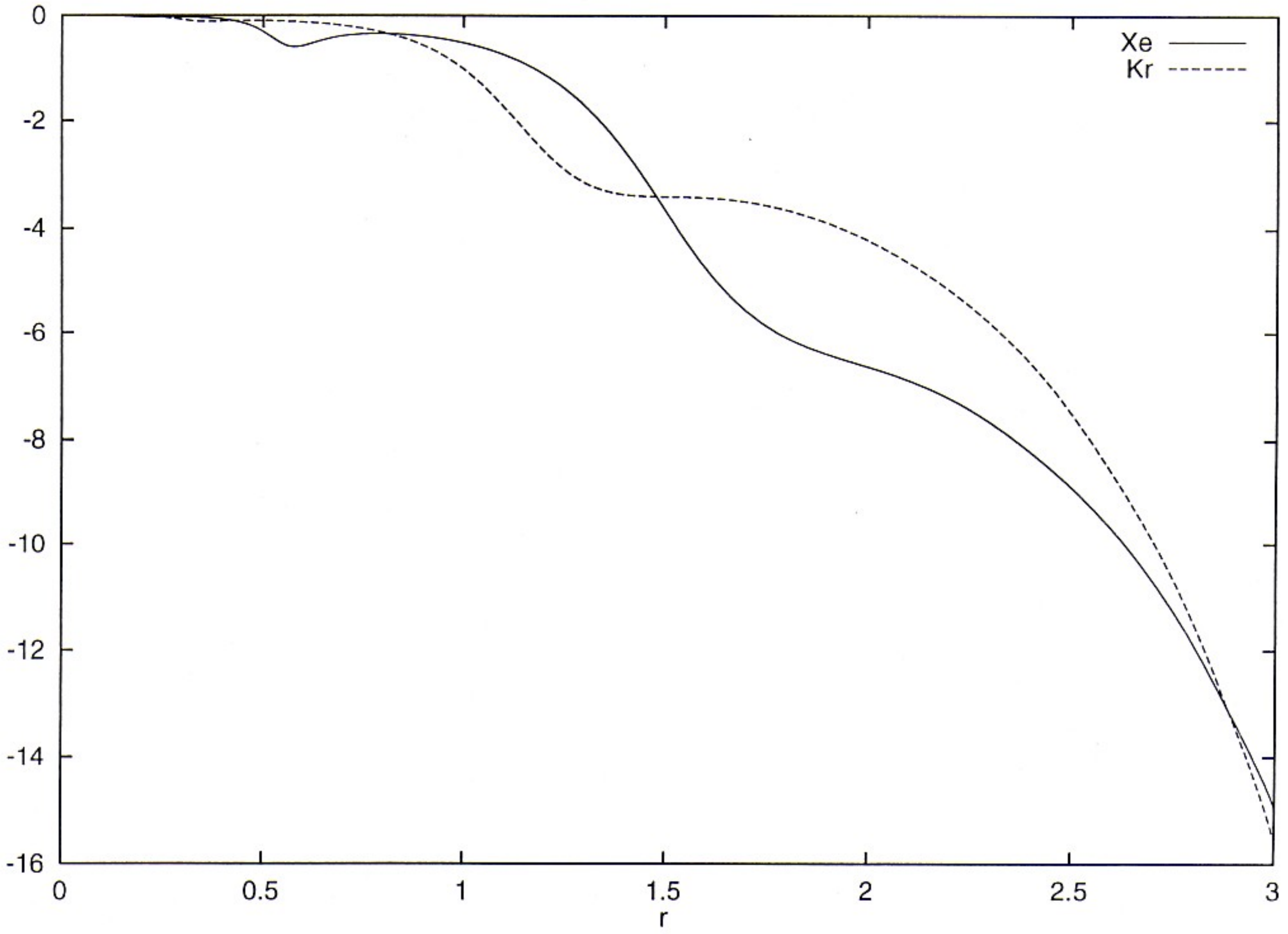
Fig.2: $S(r)$ for Kr and Xe in the $0<r <0.45$ region, the origin being on the nucleus itself (in a.u.).

Fig.3: $S(\rho)$ for Ne, Ar, Kr and Xe, the origin being on the nucleus itself (in a.u.).

Fig.4: $S(\rho)$ vs. $\ln(\rho)$ for Kr and Xe, with their intersection points (the nuclei are at r=0).

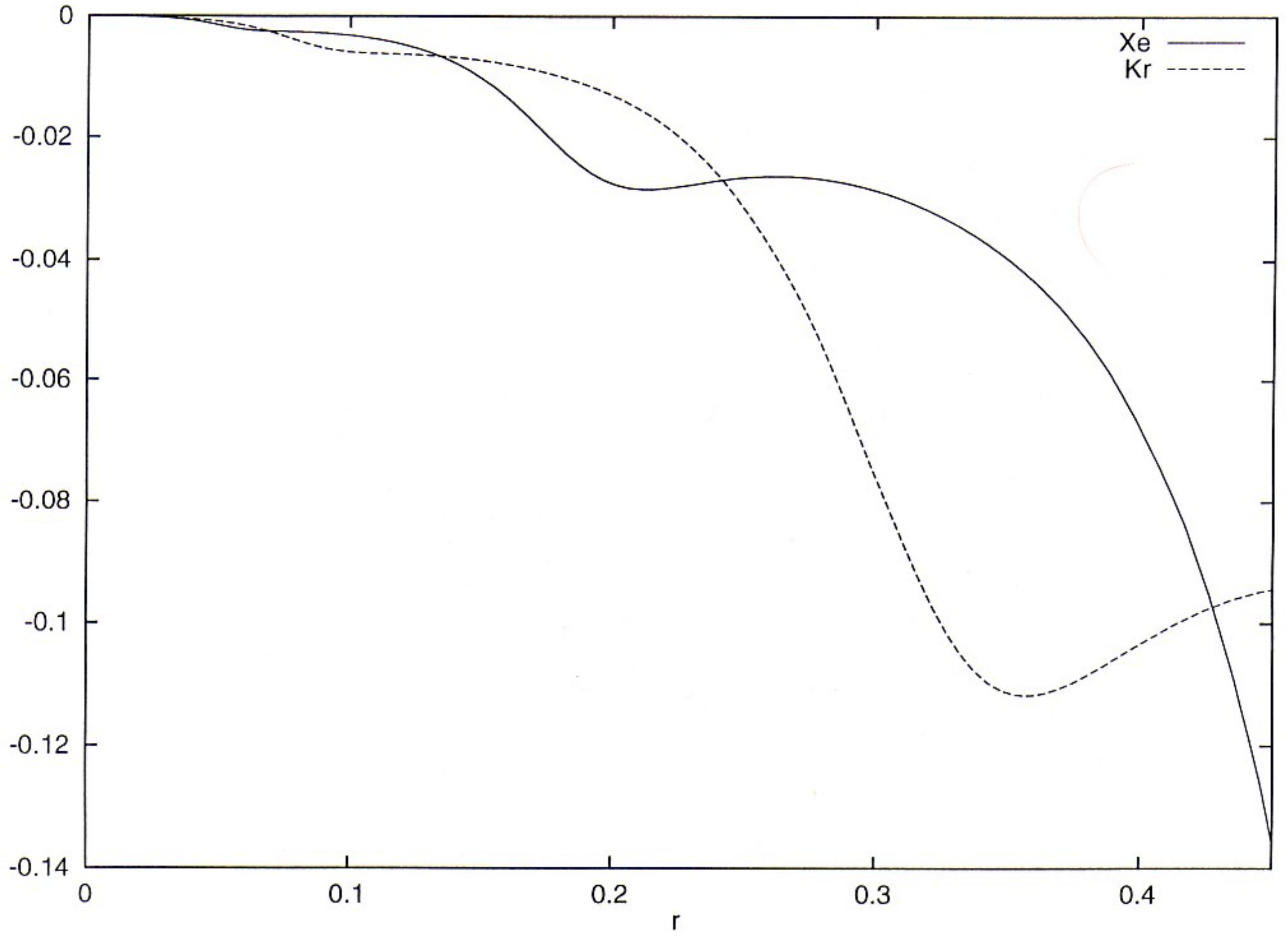
Fig.5: An estimation for $S(\rho)$ of large numbers of electrons,

$S(\rho)=0.563\ln(\ln(\rho)+1.5)-1.042$ vs. $\ln(\rho)$.



Xe
Kr
0
-2
-4
-6
-8
-10
-12
-14
-16
0
0.5
1
1.5
2
2.5
3
r

1.



Xe
Kr
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-0.04
-0.06
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-0.1
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-0.14
0
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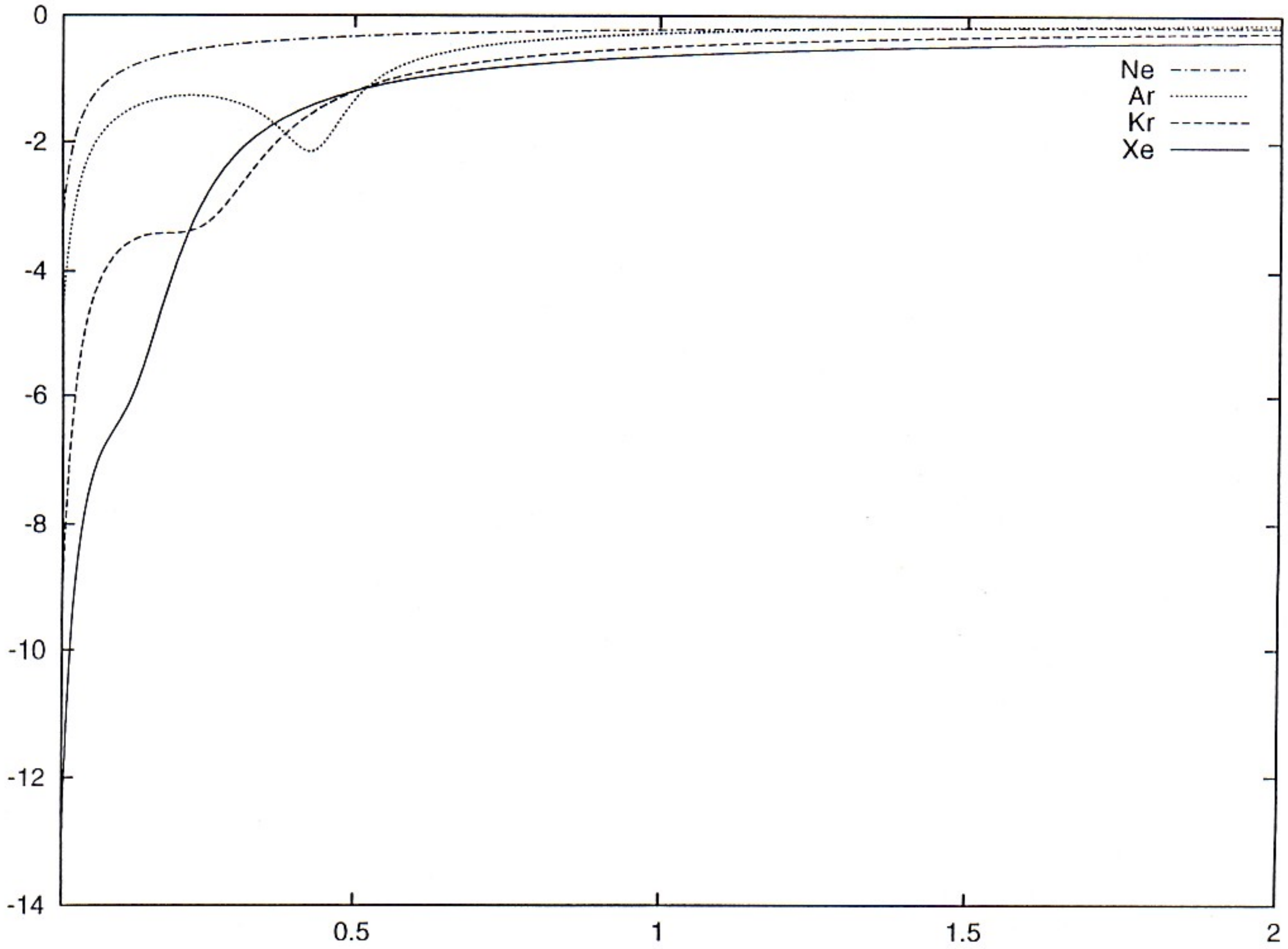
0.2
0.3
0.4
r

2.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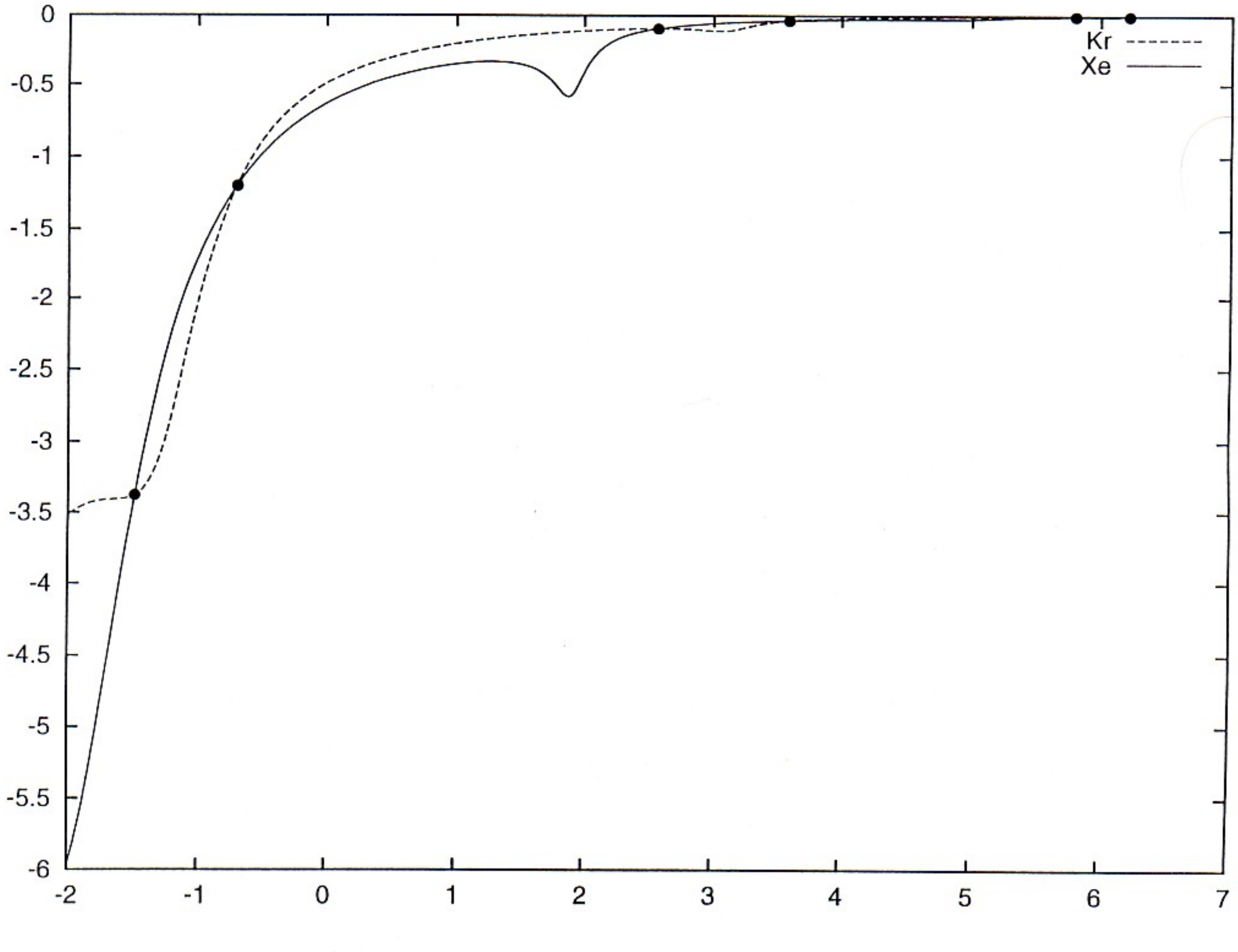
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Kr
Xe

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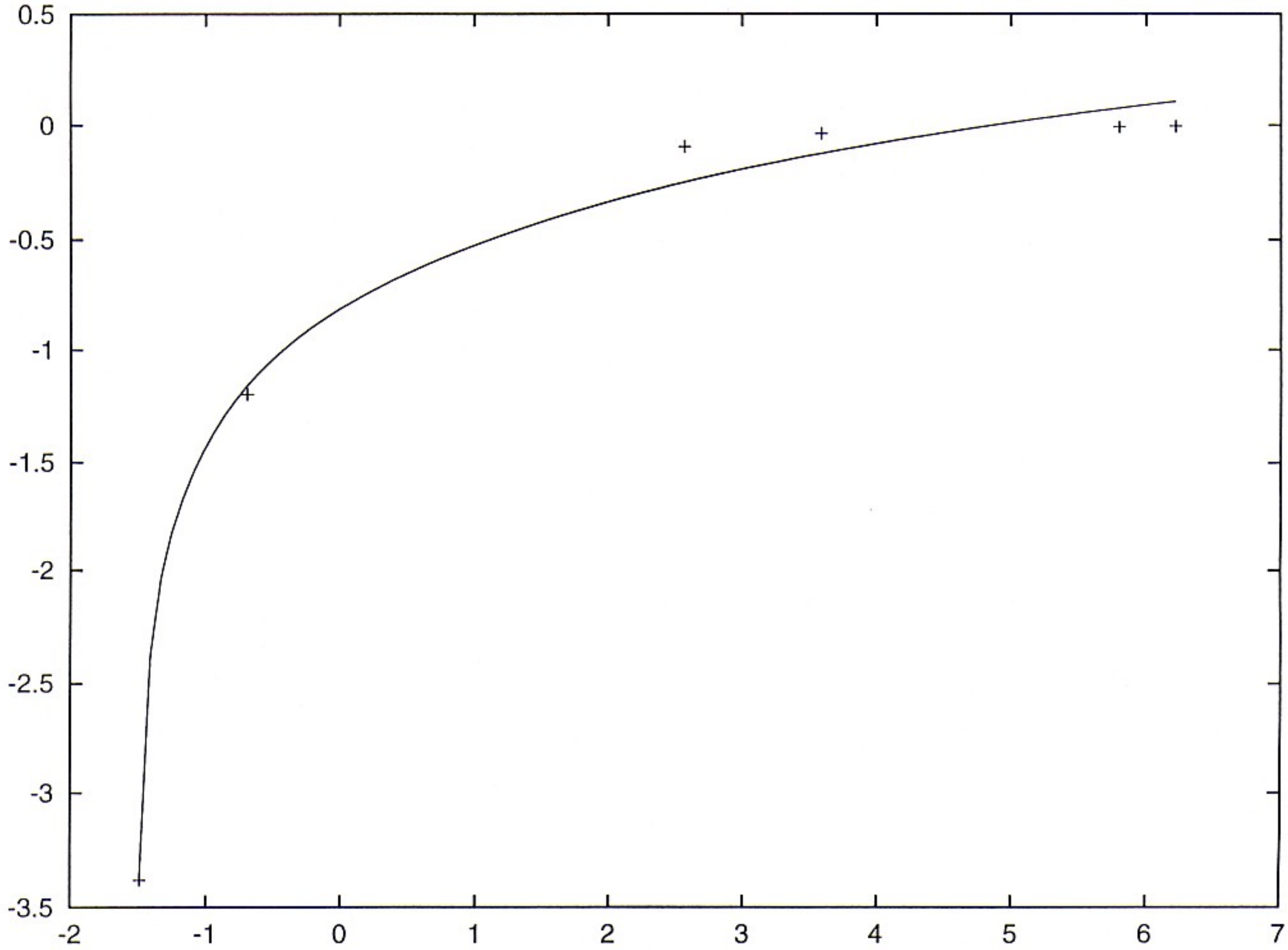

5.

6.2 Differential equations for two-electron systems

In this section homogeneous linear third-order differential equations for the ground-state electron densities $\rho(\vec{r})$ of two two-electron systems with explicitly known densities are derived [90,91], which gives an insight of the nature of a general equation for the ground-state electron density, at least for two-electron systems, and can be a good basis for further investigations into this direction, as this homogeneous linear third-order character has already been shown to be general for two-electron systems with weak electron-electron Coulomb repulsion $\lambda \frac{1}{|\vec{r}_1 - \vec{r}_2|}$ ($\lambda \ll 1$) [92].

Differential equation for the electron density of a two-electron Hookean atom

The two-electron Hookean atom, first applied by *Kestner and Sinanoğlu* [97] to gain insight into electron correlation in atoms, is characterized by the Hamiltonian

$$H = -\tfrac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) + \tfrac{1}{2}k\left(\vec{r}_1^{\,2} + \vec{r}_2^{\,2}\right) + \frac{1}{\left|\vec{r}_1 - \vec{r}_2\right|} \tag{6.19}$$

(written in atomic units), that is in a Hookean atom the electrons move under the influence of their Coulomb interaction but the attractive Coulomb potential produced by the nucleus of a real atom is replaced by an isotropic harmonic oscillator potential.

The Schrödinger equation with the Hamiltonian Eq.(6.19) has an exact analytical solution for the ground-state for a particular choice of the spring constant *k*, namely for *k*=1/4, as shown by *Kais et al.* [98,99], from which the ground-state density is

$$\rho(r) = C\exp(-r^2/2)\left\{\left(\frac{\pi}{2}\right)^{1/2}\left[\frac{7}{4}+\frac{1}{4}r^2+\left(r+\frac{1}{r}\right)erf(2^{-1/2}r)\right]+\exp(-r^2/2)\right\}, \qquad (6.20)$$

where $C = 2\pi^{3/2}(8+5\pi^{1/2})^{-1}$, $r = |\bar{r}|$ and *erf* denotes the error function. Writing Eq.(6.20) in the form

$$2^{-1/2}C^{-1}\frac{r}{1+r^2}\exp(r^2/2)\rho(r) =$$

$$= \frac{\pi^{1/2}}{2}\frac{r}{1+r^2}\left[\frac{7}{4}+\frac{1}{4}r^2+\left(\frac{2}{\pi}\right)^{1/2}\exp(-r^2/2)\right]+\frac{\pi^{1/2}}{2}erf(2^{-1/2}r) \qquad (6.21)$$

and differentiating with respect to *r* (′),

$$C^{-1}[(1+r^4)\rho(r)+(r+r^3)\rho'(r)] = \frac{1}{4}\left(\frac{\pi}{2}\right)^{1/2}(7-4r^2+r^4)\exp(-r^2/2)+2\exp(-r^2) \,. (6.22)$$

In the next steps two further differentiations are applied in order to eliminate exp(-r^2) and exp(-r^2/2) from Eq.(6.22) to get a homogeneous differential equation. One further differentiation yields then

$$C^{-1}[4r^3\rho(r)+(2+3r^2+r^4)\rho'(r)+(r+r^3)\rho''(r)] =$$

$$= \frac{1}{4}\left(\frac{\pi}{2}\right)^{1/2}(-15r+8r^3-r^5)\exp(-r^2/2)-4r\exp(-r^2), \qquad (6.23)$$

with the use of which first, e. g., exp(-r^2) may be eliminated from Eq.(6.22):

$$C^{-1}[(2r+2r^3)\rho(r)+(2+3r^2)\rho'(r)+r\rho''(r)] = \frac{1}{4}\left(\frac{\pi}{2}\right)^{1/2}(-r+r^3)\exp(-r^2/2). \qquad (6.24)$$

Of course, now using the obtained Eq.(6.24), exp(-r^2) and exp(-r^2/2) both could be eliminated from Eq.(6.22) to get a second-order differential equation, but this would be a complicated non-linear differential equation. Instead, differentiating once more,

$$C^{-1}[(2+6r^2)\rho(r)+(8r+2r^3)\rho'(r)+(3+3r^2)\rho''(r)+r\rho'''(r)] =$$

$$= \frac{1}{4}\left(\frac{\pi}{2}\right)^{1/2}(-1+4r^2-r^4)\exp(-r^2/2), \qquad (6.25)$$

and eliminating exp($-r^2/2$) by using Eq.(6.24), a homogeneous linear third-order differential equation is obtained for the ground-state electron density of the two-electron Hookean atom with the harmonic oscillator spring constant being 1/4:

$$(-r^2+r^4)\rho'''(r)+(-2r-4r^3+4r^5)\rho''(r)+(2-13r^2-4r^4+5r^6)\rho'(r)+(-10r^3+2r^7)\rho(r)=0\,. \quad (6.26)$$

Constructing this differential equation follows in the footsteps of the works by *March et al.* in which differential equations for the ground-state electron density were derived for different cases, namely for the case of particles moving independently in a linear harmonic oscillator potential [84], for the self-consistent Thomas-Fermi atom [85], Eq.(6.1), and for its generalization to include exchange and Gell-Mann–Brueckner correlation [86], Eq.(6.3). Except for the first case, these differential equations are non-linear and second-order. However, the differential equation

$$\tfrac{1}{8}\rho'''(r)+(k^{1/2}N-\tfrac{1}{2}kr^2)\rho'(r)+\tfrac{1}{2}kr\rho(r)=0\ , \quad (6.27)$$

for an arbitrary number N of non-interacting Fermions moving in one-dimension in a common, harmonic oscillator potential and filling the lowest energy levels in accordance with the Pauli Exclusion Principle, shows substantial similarity to Eq.(6.26): both of them are homogeneous linear third-order differential equations. It would, of course, be of considerable interest for future progress if Eq.(6.26) had a generalization to arbitrary numbers N of interacting electrons.

Differential equation for electron density of He-like ions for large atomic number

In the previous section, a differential equation for the ground-state electron density in a Hookean atom with two electrons repelling coulombically was derived for one particular spring constant. Here the corresponding problem for the ground-state of He-like ions of atomic number Z will be treated for sufficiently large Z.

The starting point is the work of *Schwartz* [100,101] who gave the ground-state electron density of He-like ions for large Z in the form

$$\rho(r) = 2\frac{Z^3}{\pi}\exp(-2Zr)\left[F(r) - < F >\right], \tag{6.28}$$

where, putting $Zr=y$,

$$ZF(r) = \frac{5}{8}y - \frac{1}{8} - \frac{1}{4}\exp(-2y) - \frac{3}{16}\frac{\exp(-2y)-1}{y} + \frac{3}{8}\int_0^y \frac{\exp(-2x)-1}{x}dx, \tag{6.29}$$

and the quantity $<F>$ has the explicit form

$$< F >= \frac{1}{Z}\left(\frac{19}{32} - \frac{3}{8}\ln 2\right). \tag{6.30}$$

Following the method described in the case of the Hookean atom it can be shown that $\rho(r)$ given by Eqs.(6.28)-(6.30) also satisfies a differential equation which is linear, third-order and homogeneous:

$$P_3(r)\rho'''(r) + P_2(r)\rho''(r) + P_1(r)\rho'(r) + P_0(r)\rho(r) = 0, \tag{6.31}$$

where $P_i(r)$ (i=0,1,2,3) are polynomials. To get to the form Eq.(6.31), first, after writing Eq.(6.28) in the right form:

$$\frac{2\pi}{Z^2}\exp(2y)\rho(r) = \frac{5}{2}y + \frac{3}{4}\frac{1}{y} - \frac{1}{2} - Z < F > - \left(1 + \frac{3}{4}\frac{1}{y}\right)\exp(-2y) + \frac{3}{2}\int_0^y \frac{\exp(-2x)-1}{x}dx, \tag{6.32}$$

a differentiation with respect to *r* (’) is applied to get rid of the integration:

$$\frac{2\pi}{Z^2}\left(\frac{\rho'(r)}{Z}+2\rho(r)\right)=\left(\frac{5}{2}-\frac{3}{2}\frac{1}{y}-\frac{3}{4}\frac{1}{y^2}\right)\exp(-2y)+\left(2+3\frac{1}{y}+\frac{3}{4}\frac{1}{y^2}\right)\exp(-4y)\,. \quad (6.33)$$

In the next steps two further differentiations are applied in order to eliminate exp(-2*y*) and exp(-4*y*) from Eq.(6.33). Before carrying these out, Eq.(6.33) is written in the form

$$\frac{2\pi}{Z^2}\left(\frac{\rho'(r)}{Z}+2\rho(r)\right)=D(y)\exp(-2y)+E(y)\exp(-4y) \quad (6.34)$$

with the notation $D(y)=\frac{5}{2}-\frac{3}{2}\frac{1}{y}-\frac{3}{4}\frac{1}{y^2}$, $E(y)=2+3\frac{1}{y}+\frac{3}{4}\frac{1}{y^2}$ being introduced for simplicity. Differentiation of Eq.(6.34) with respect to *r* yields

$$\frac{2\pi}{Z^2}\left(\frac{\rho''(r)}{Z^2}+2\frac{\rho'(r)}{Z}\right)=\left(D'(y)-2D(y)\right)\exp(-2y)+\left(E'(y)-4E(y)\right)\exp(-4y) \quad (6.35)$$

($'$ denoting differentiation with respect to *r* in the case of $\rho(r)$, with respect to *y* otherwise), with the use of which first exp(-2*y*) is eliminated from Eq.(6.34):

$$\frac{2\pi}{Z^2}\left(D(y)\frac{\rho''(r)}{Z^2}+\left(4D(y)-D'(y)\right)\frac{\rho'(r)}{Z}+\left(4D(y)-2D'(y)\right)\rho(r)\right)=F(y)\exp(-4y)\,, \quad (6.36)$$

with $F(y)=D(y)\left(E'(y)-2E(y)\right)-D'(y)E(y)$ being introduced. Differentiating once more,

$$\frac{2\pi}{Z^2}\left(D(y)\frac{\rho'''(r)}{Z^3}+4D(y)\frac{\rho''(r)}{Z^2}+\left(4D(y)+2D'(y)-D''(y)\right)\frac{\rho'(r)}{Z}+\left(4D'(y)-2D''(y)\right)\rho(r)\right)=$$

$$=G(y)\exp(-4y) \quad (6.37)$$

with $G(y)=F'(y)-4F(y)$, and eliminating exp(-4*y*) by using Eq.(6.36), a homogeneous linear third-order differential equation is obtained for $\rho(r)$:

$$D(y)F(y)\frac{\rho'''(r)}{Z^3}+D(y)\left(4F(y)-G(y)\right)\frac{\rho''(r)}{Z^2}+$$

$$+\big((4D(y)+2D'(y)-D''(y))F(y)-(4D(y)-D'(y))G(y)\big)\frac{\rho'(r)}{Z}+$$

$$+\big((4D'(y)-2D''(y))F(y)-(4D(y)-2D'(y))G(y)\big)\rho(r)=0, \quad (6.38)$$

where the polynomials $P_3 = D(y)F(y)/Z^3$, $P_2 = D(y)\big(4F(y)-G(y)\big)/Z^2$, $P_1 = \big((4D(y)+2D'(y)-D''(y))F(y)-(4D(y)-D'(y))G(y)\big)/Z$ and $P_0 = (4D'(y)-2D''(y))F(y)-(4D(y)-2D'(y))G(y)$, after some algebraic manipulation and simplification (which may be carried out by using an algebraic computer program), can be given explicitly as

$$P_3(r) = (-9y^2-36y^3-40y^4)/Z^3, \quad (6.39)$$

$$P_2(r) = 2(-9y-54y^2-144y^3-160y^4)/Z^2, \quad (6.40)$$

$$P_1(r) = 2(9-138y^2-360y^3-400y^4)/Z \quad (6.41)$$

and

$$P_0(r) = 4(9+18y-48y^2-144y^3-160y^4) \quad (6.42)$$

with $y=Zr$. That constructing a differential equation of the form (6.31) for the density given by Eqs.(6.28)-(6.30) has been possible follows from the analytical form of the density itself, namely being composed from exponential functions and polynomials in the following way:

$$\rho(r) = d\exp(a(r))\left(A(r)+B(r)\exp(a(r))+C(r)\int_0^{d'r}\big(b(r')\exp(a(r'))+c(r')\big)dr'\right) \quad (6.43)$$

where $a(r)$, $b(r)$, $c(r)$, $A(r)$, $B(r)$ and $C(r)$ are polynomials and d and d' are constants determined by the force constant of the external potential, as in the case of the Hookean atom as well.

It must be emphasized that while Eq.(6.31) with the polynomials Eqs.(39-42) is an exact equation satisfied by the Schwartz density $\rho(r)$ for He-like ions, given explicitly by Eqs.(6.28)-(6.30) above, it is, of course, only valid asymptotically in the limit of large *Z*. Nevertheless, any differential equation embracing the neutral He atom corresponding to *Z*=2, valid for general *Z*, must plainly reduce asymptotically to the form given by Eq.(6.31) with Eqs.(39-42). As can be seen readily, in the *r*=0 limit this differential equation, Eq.(6.31) with Eqs.(39-42), gives Kato's theorem [69],

$$\rho'(0) + 2Z\rho(0) = 0\,. \tag{6.44}$$

It is worth noting that a screening constant, α, was introduced [102,101] in order to split the Hamiltonian into one-electron terms

$$-\frac{1}{2}\nabla^2 - \frac{(Z-\alpha)}{r}, \tag{6.45}$$

for each electron, plus a perturbation which is

$$\frac{1}{r_{12}} - \frac{\alpha}{r_1} - \frac{\alpha}{r_2}, \tag{6.46}$$

with the use of which a more general form of the density Eqs.(6.28)-(6.30) has been derived with the constant α being included. The density given by Eqs.(6.28)-(6.30) is a special case of this generalized expression, corresponding to α=0. For general α the expressions

$$P_3(r) = (24\alpha y - (9-72\alpha)y^2 - (36-96\alpha)y^3 - (40-64\alpha)y^4)/(Z-\alpha)^3, \tag{6.47}$$

$$P_2(r) = 2(36\alpha - (9-168\alpha)y - (54-336\alpha)y^2 - (144-384\alpha)y^3 - (160-256\alpha)y^4)/(Z-\alpha)^2, \tag{6.48}$$

$$P_1(r) = 2(9+144\alpha+528\alpha y - (138-912\alpha)y^2 - (360-960\alpha)y^3 - (400-640\alpha)y^4)/(Z-\alpha) \tag{6.49}$$

and

$$P_0(r) = 4(9+72\alpha+(18+240\alpha)y - (48-384\alpha)y^2 - (144-384\alpha)y^3 - (160-256\alpha)y^4) \tag{6.50}$$

can be obtained for the polynomials $P_i(r)$ in Eq.(6.31), following the method described above.

While the differential equation given by Eq.(6.31) with Eqs.(39-42) is the main result of the present section, it is worth recalling that *Hall et al.* have generalized the Schwartz density Eqs.(6.28)-(6.30) to the off-diagonal first-order density matrix $\gamma_1(\vec{r}\,',\vec{r})$ [102,101], which is beginning to assume major importance in relation to first-principles density functional theory [103-105]. This matrix γ_1 has the form

$$\gamma_1(\vec{r}\,',\vec{r}) = \gamma_0(\vec{r}\,',\vec{r})\left[F(r') + F(r) - 2 < F >\right] \tag{6.51}$$

where $F(r)$ and $<F>$ are defined by Eqs.(29) and (30), respectively, while $\gamma_0(\vec{r}\,',\vec{r})$ is given by

$$\gamma_0(\vec{r}\,',\vec{r}) = \frac{Z^3}{\pi}\exp\{-Z(r'+r)\}\,. \tag{6.52}$$

With the use of the diagonal forms $\rho(r)$ and $\rho_0(r)$ corresponding to the off-diagonal Eqs.(6.51) and (6.52), respectively, Eq.(6.51) can be rewritten in the form

$$\gamma_1(\vec{r}\,',\vec{r}) = \frac{\rho(r')}{2}\left(\frac{\rho_0(r)}{\rho_0(r')}\right)^{\frac{1}{2}} + \frac{\rho(r)}{2}\left(\frac{\rho_0(r')}{\rho_0(r)}\right)^{\frac{1}{2}}. \tag{6.53}$$

In connection with the studies in Refs.(103-105), mentioned above, Eq.(6.53) is of interest in expressing the off-diagonal density matrix $\gamma_1(\vec{r}\,',\vec{r})$ for He-like ions of large Z in terms of *(a)* its diagonal density $\rho(\vec{r})$, satisfying the differential equation (6.31) with P_i as in Eqs.(39-42) and *(b)* the simple known function $\rho_0(r)=\gamma_0(\vec{r},\vec{r})$ given in Eq.(6.52), which can be regarded as a functional of the density $\rho(\vec{r})$ on the basis of Kato's theorem, Eq.(6.42), that is the $Z[\rho]$ relationship.

Thus, in the asymptotic limit of large Z for the He-like ions, Eq.(6.53) gives the interacting off-diagonal density matrix $\gamma_1(\vec{r}\,',\vec{r})$ explicitly in terms of the ground-state electron density $\rho(\vec{r})$ in a simple form with the help of which the kinetic energy density $t(r)$ defined in terms of $\gamma_1(\vec{r}\,',\vec{r})$ by

$$t(r) = \frac{1}{2}\nabla_{\vec{r}\,'} \cdot \nabla_{\vec{r}}\ \gamma_1(\vec{r}\,',\vec{r})\Big|_{\vec{r}\,'=\vec{r}} \tag{6.54}$$

can be calculated and given as a functional of the density:

$$t(r) = \frac{1}{4}\rho'(r)\frac{\partial}{\partial r}\{\ln\rho_0(r)\} - \frac{1}{8}\rho(r)\left(\frac{\partial}{\partial r}\{\ln\rho_0(r)\}\right)^2 = -\frac{1}{2}Z\rho'(r) - \frac{1}{2}Z^2\rho(r)\,. \tag{6.55}$$

It is of some interest to use Eq.(6.55) to extract the correlation kinetic energy functional $T_c[\rho]$ for the He-like ions at large Z. Using, for this two-electron case,

$$T[\rho] = T_W[\rho] + T_c[\rho]\,, \tag{6.56}$$

where the Weizsäcker kinetic energy is given by

$$T_W[\rho] = \frac{1}{8}\int \frac{\rho'^2(r)}{\rho(r)}d\vec{r}\,, \tag{6.57}$$

and removing Z with the use of Kato's theorem,

$$T_c[\rho] = -T_W[\rho] - \frac{1}{2}\left[\frac{\rho'(r)}{\rho(r)}\right]_{r=0}\int \frac{\rho(r)}{r}d\vec{r} - \frac{1}{8}\left\{\left[\frac{\rho'(r)}{\rho(r)}\right]_{r=0}\right\}^2\int \rho(r)d\vec{r}\,. \tag{6.58}$$

In summary, in this section for the large Z limit of He-like ions *(i)* the differential equation (6.31), with P_i as in Eqs.(39-42) (and Eqs.(47-50)), for the ground-state electron density $\rho(r)$, *(ii)* a simple expression, Eq.(6.53) for the off-diagonal first-order density matrix $\gamma_1(\vec{r}\,',\vec{r})$ in terms of the diagonal density $\rho(r)$ and *(iii)* the correlation kinetic energy functional $T_c[\rho]$ given by Eq.(6.58) are presented.

7. Local temperature

The non-interacting kinetic energy, being an essential concept in density-functional theory, is of great importance to be investigated not just as a functional of the density but from other aspects as well. The quantitative study of it and related quantities, such as is the local temperature [106-110] as well, can help to get a deeper understanding of its nature, and can show how it is useful in describing electronic systems, there being a continuing interest in characterizing electronic structure and chemical reactivity by various local properties [109-125] defined within the framework of density functional theory. In describing the shell srtuctures of atoms much attention was focused on the radial density function, $n(\vec{r})=4\pi r^2\rho(\vec{r})$ with its positions of minima shown to be physically significant in several respects [111-113], e.g., in separating atomic shells [111-114]. However, in this respect the Politzer average local ionization energy index $\bar{I}(\vec{r})$ [115-122] has been proved to be a better tool as it shows a stepwise decreasing behaviour with the inflection points serving as effective boundaries between electronic shells in the elements up to krypton [116] (even to xenon with some exception in the second transition series [117]), whereas the radial density does not distinguish between the M and N shells [111-114]. $\bar{I}(\vec{r})$ (in the case of molecules plotted on well-defined molecular surfaces) has also been found to provide a quantitative indicator of reactivity toward electrophiles in a variety of chemical systems as small $\bar{I}(\vec{r})$ values correspond to sites most reactive to electrophilic reagents [115,118-122]. Another useful concept for characterizing chemical reactivity describing the soft-soft interactions between the reagents is the local softness, $s(\vec{r})=\left(\frac{\partial\rho(\vec{r})}{\partial\mu}\right)_{v(\vec{r})}$ or the Fukui function, $f(\vec{r})=\left(\frac{\partial\rho(\vec{r})}{\partial N}\right)_{v(\vec{r})}$ [123-125] proportional to $s(\vec{r})$ ($s(\vec{r})=f(\vec{r})S$ with S being the global softness) with the left (right) derivative corresponding to a reactivity index $f^{-}(\vec{r})$ ($f^{+}(\vec{r})$) for an electrophilic (nucleophilic) attack [123]. For the hard-hard interactions between reacting molecules, the molecular electrostatic potential [126], $V(\vec{r})=\sum_{A}\frac{Z_A}{|\vec{r}-\vec{R}_A|}-\int\frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,'$ is used frequently in the study of electrophilic attacks [125,127-129].

Beside these local properties, the local temperature $T(\vec{r})$ proposed by *Ghosh et al.* [106] attracts attention also as a possible tool to describe atomic structure and chemical reactivity [109,110], since it has been found in atoms to behave similarly to the Politzer average local ionization energy index: $T(\vec{r})$ decreases in a nearly piecewise constant manner with increasing radial distance from the nucleus with the roughly constant regions corresponding to electronic shells, and $\frac{3}{2}kT(\vec{r})$ is approximately the same as $\bar{I}(\vec{r})$ far from all nuclei [109]. Here, the study of the local temperature and its comparison with the Politzer average local ionization energy index will be extended to molecules [110]. Along various spatial directions $T(\vec{r})$ and $\bar{I}(\vec{r})$ will be computed and plotted for the molecules O_2, CO, CO_2, C_2H_2, C_2H_4, HCN, using Hartree-Fock wave functions.

Local temperature and Politzer's average local orbital energy index

While the Politzer average local ionization energy index (the absolute value of the Politzer average local orbital energy index) can be interpreted as the average energy needed to remove an electron from a point in the space of an atom or molecule, the local temperature can be considered as the local kinetic energy of an electron moving in the Kohn-Sham potential of an atom or molecule, since it is defined by [106]

$$T_s = \int t(\bar{r})d\bar{r} = \int \tfrac{3}{2}\rho(\bar{r})kT(\bar{r})d\bar{r}\,, \tag{7.1}$$

where T_s is the non-interacting kinetic energy, $\rho(\bar{r})$ is the electron density and k is the Boltzmann constant. Because of ambiguity in the kinetic energy density $t(\bar{r})$ the definition of $T(\bar{r})$ is not unique either.The ambiguity in $t(\bar{r})$ appears in the form of an additive part $c\nabla^2 g(\bar{r})$ with c being an arbitrary number and $g(\bar{r})$ being an arbitrary well behaved function:

$$t(\bar{r}) = \frac{1}{8}\sum_i \frac{\left|\nabla\rho_i(\bar{r})\right|^2}{\rho_i(\bar{r})} + c\nabla^2 g(\bar{r}), \tag{7.2}$$

where $\rho_i(\bar{r})=|u_i(\bar{r})|^2$ with $u_i(\bar{r})$ being the one-electron orbitals. With $g(\bar{r})=\rho(\bar{r})$ one can get, for example, $t(\bar{r}) = -\frac{1}{2}\sum_i u_i^* \nabla^2 u_i$ $(c=-\frac{1}{4})$, which is perhaps the most obvious expression for $t(\bar{r})$, or the formula favoured in the original Ghosh-Berkowitz-Parr theory [106]: $t(\bar{r}) = \frac{1}{8}\sum_i \frac{\left|\nabla\rho_i\right|^2}{\rho_i} - \frac{1}{8}\nabla^2\rho$. However, the mathematically simplest (c=0) form,

$$t(\bar{r}) = \frac{1}{2}\sum_i \left|\nabla u_i\right|^2 = \frac{1}{8}\sum_i \frac{\left|\nabla\rho_i\right|^2}{\rho_i} \tag{7.3}$$

was found to be the most appropriate one [109] as it has several advantages on its side. Most importantly, it makes the local temperature everywhere positive. Also, a study concerning information entropy favours Eq.(7.3) [108].

Thus the formula Eq.(7.3) is taken for defining $T(\vec{r})$:

$$\frac{3}{2}\rho(\vec{r})kT(\vec{r}) = \frac{1}{8}\sum_i \frac{\nabla\rho_i \nabla\rho_i}{\rho_i}. \tag{7.4}$$

As pointed out in Ref.(109), Eq.(7.4) yields

$$\tfrac{3}{2}kT(\vec{r}) \approx \tfrac{1}{2}Z^2 \qquad \text{(near a nucleus)} \tag{7.5}$$

and

$$\tfrac{3}{2}kT(\vec{r}) \approx E_I \qquad \text{(far from all nuclei)} \tag{7.6}$$

with E_I being the ionization energy, and a more or less monotonic decrease of $T(\vec{r})$ can be expected from the value given by Eq.(7.5) to the value given by Eq.(7.6).

The Politzer average local orbital energy index is defined as

$$\bar{\varepsilon}(\vec{r}) = \sum_i \frac{\rho_i(\vec{r})\varepsilon_i}{\rho(\vec{r})} \tag{7.7}$$

with the ε_i being the orbital energies, and can be considered as the local energy per electron. Originally the average local ionization energy index $\bar{I}(\vec{r})$ proposed by *Politzer et al.* was used:

$$\bar{I}(\vec{r}) = \sum_i \frac{\rho_i(\vec{r})|\varepsilon_i|}{\rho(\vec{r})} = |\bar{\varepsilon}(\vec{r})| = -\bar{\varepsilon}(\vec{r}). \tag{7.8}$$

Eq.(7.7) gives [109]

$$\bar{\varepsilon}(\vec{r}) \approx \varepsilon_{1s} \qquad \text{(near a nucleus)} \tag{7.9}$$

and

$$\bar{\varepsilon}(\vec{r}) \approx -E_I \qquad \text{(far from all nuclei).} \tag{7.10}$$

From Eqs.(7.5) and (7.9)

$$\frac{-\bar{\varepsilon}(\vec{r})}{\frac{3}{2}kT(\vec{r})} \approx \frac{-\varepsilon_{1s}}{\frac{1}{2}Z^2} \qquad \text{(near a nucleus)} \tag{7.11}$$

can be obtained, and from Eqs.(7.6) and (7.10)

$$\frac{-\bar{\varepsilon}(\vec{r})}{\frac{3}{2}kT(\vec{r})} \approx 1 \qquad \text{(far from all nuclei)} \qquad (7.12)$$

arises.

These relations suggest that $-\bar{\varepsilon}(\vec{r})$ and $\frac{3}{2}kT(\vec{r})$ have similar behaviour, which is confirmed by the study of the two functions, on the basis of plotting the computed values of them, reported below.

Numerical study

For the calculations Hartree-Fock $u_i(\vec{r})$ orbitals and Hartree-Fock ε_i orbital energies obtained from the Gamess program package [130] were used [131]. Since reporting numerical values for $T(\vec{r})$ and $-\bar{\varepsilon}(\vec{r})$ is not the goal of this study, only the behaviour of these functions is examined, employing Hartree-Fock orbitals and energies calculated using finite, Gaussian, basis sets is satisfying, keeping in mind, of course, that the gradient of an orbital like these does not give appropriate values near a nucleus so neither does the local temperature obtained this way.

Various spatial directions are chosen along which $T(\vec{r})$ and $-\bar{\varepsilon}(\vec{r})$ are calculated and plotted: one of them is the direction of a bond in the actual molecule and the others are parallel or perpendicular to it, all of them being in the same plane. Figs.(3)-(9) display some of the resulted $T(x)$ and $-\bar{\varepsilon}(x)$ ($I(x)$) curves. The curves of the two functions for the carbon and oxygen atoms (Figs.(1) and (2), respectively) are also included for comparison purposes.

From the values of $T(\vec{r})$ and $-\bar{\varepsilon}(\vec{r})$ plotted along various directions going through a nucleus it can have been seen that near a nucleus they show behaviour caused by the free atom corresponding to that nucleus, and far from all nuclei they give the familiar constancy found in the case of atoms but, of course, with different values (ionization energies). Figs.(3) and (4) for the molecules O_2 and CO_2 in an equilibrium state along the molecular axes and Figs.(1) and (2) for the atoms C and O illustrate this. These results were expected as well on the basis of Eqs.(7.5) and (7.6) and Eqs.(7.9) and (7.10).

The regions for which the atoms that a molecule consists of do not serve as models are the bond regions of the molecule. To study the functions $T(\bar{r})$ and $-\bar{\varepsilon}(\bar{r})$ in these regions they were examined along several directions crossing these areas, the most useful of which are the directions perpendicular to the bonding axis and going through the midpoint of the bond. In Figs.(5)-(9) $T(y)$ and $-\bar{\varepsilon}(y)$ curves along directions of this kind are plotted for the CO, CC and CN bonds of the molecules CO, CO_2, C_2H_2, C_2H_4, HCN, in an equilibrium state, with the origins being in the midpoints of the bonds. From these one can see a more significant difference between $T(\bar{r})$ and $-\bar{\varepsilon}(\bar{r})$. While $-\bar{\varepsilon}(y)$ shows relatively simple, monotonically decreasing behaviour (except in the case of ethylene), $T(y)$ has some local minima and local maxima following each other, that is $T(\bar{r})$ seems to be more 'sensitive' to bonds. Furthermore the behaviour of $T(\bar{r})$ differs according to whether the bond examined is a double or a triple one: for the molecules CO_2 and C_2H_4 it has relatively deep 'valleys' at the axes of the double bonds (for C_2H_4 a clear minimum) whereas in the case of CO and C_2H_2 these deep valleys disappear and also cannot be seen for the triple bond of HCN, moreover, there are global maxima at the triple bonds of C_2H_2 and HCN.

Conclusion

The local temperature and the Politzer average local orbital energy index, as in atoms [109], have been found to behave similarly, except for the bond regions. Moreover near a nucleus they show behaviour that charaterizes the atom the nucleus of which this is when the atom is not bound to other atoms, and they are proportional far from all nuclei. So these two local properties reflect the structures of molecules and also characterize chemical reactivity as $\bar{I}(\vec{r})$ has been proved already to be a quantitative indicator in this respect [118-122], thus, because of the similarity, $T(\vec{r})$, apart from the bond regions, can serve the same purpose: low local temperature corresponds to molecular sites most reactive toward electrophiles, as do small $\bar{I}(\vec{r})$ values.

In the bond regions of molecules the local temperature has been found to be more sensitive to bonding electron clouds than the Politzer average local orbital energy index. The $T(\vec{r})$ function seems to distinguish between double bonds and triple bonds in its behaviour, although this suggestion has to be confirmed by calculations using various basis sets and extending the study to other molecules as well.

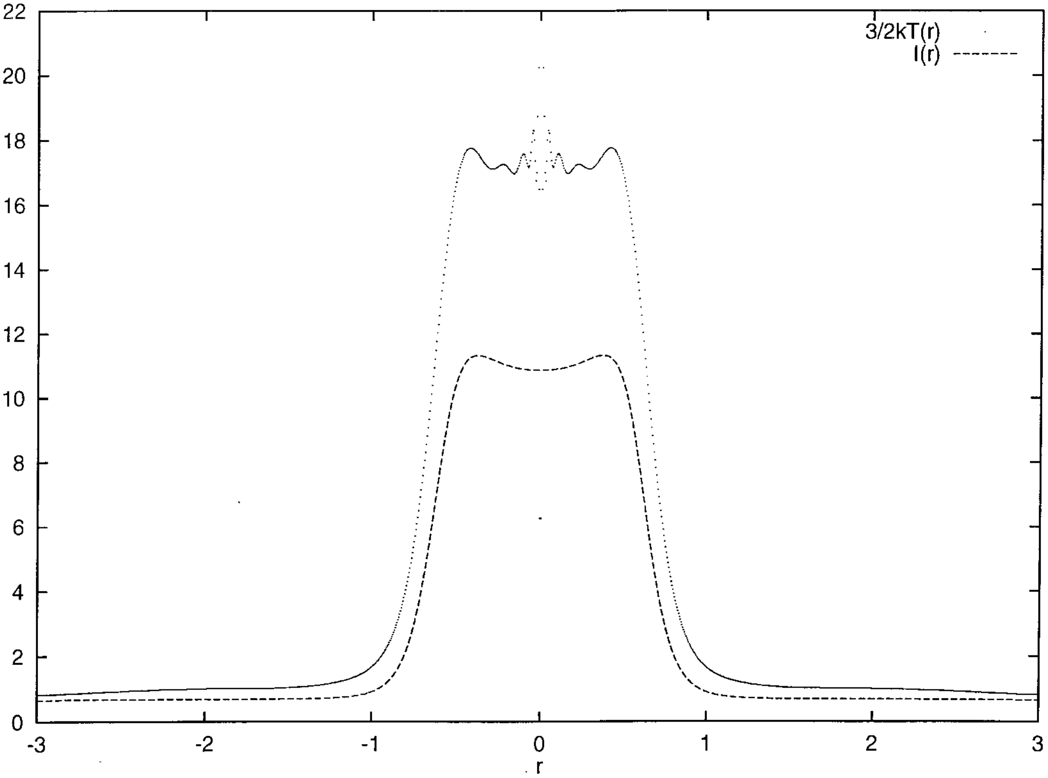

Figure 1. $\frac{3}{2}kT(\mathbf{r})$ and $\bar{I}(\mathbf{r})$ for the C atom along a direction crossing the nucleus, with the origin being on the nucleus itself (in au).

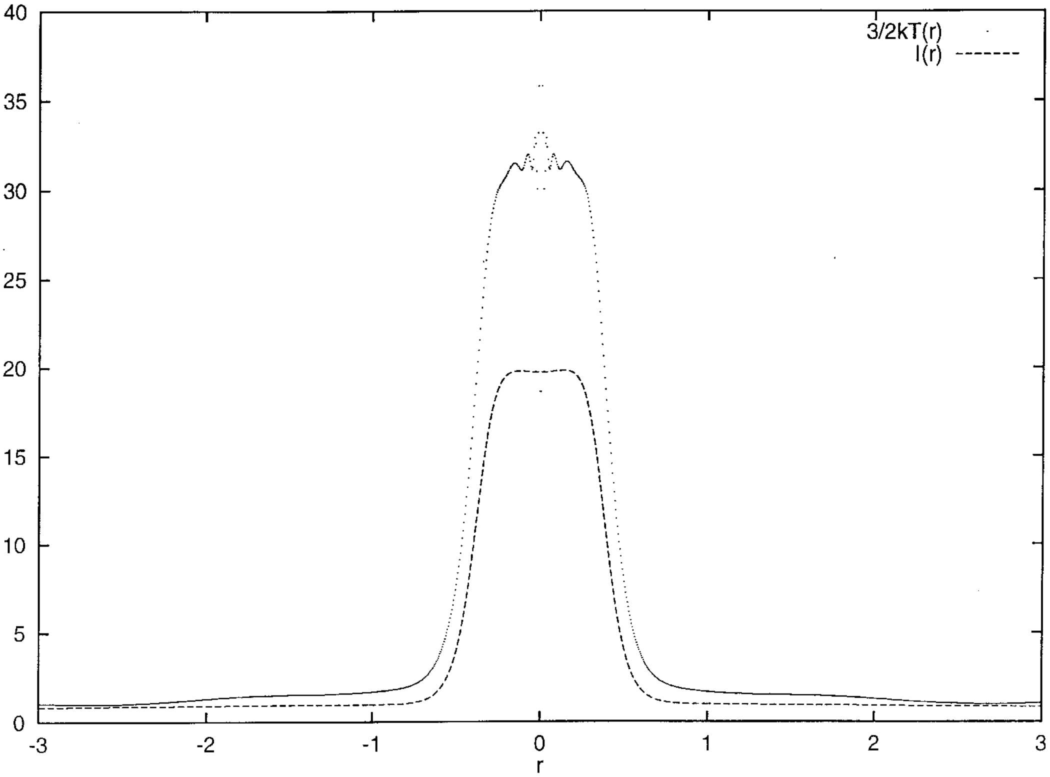

Figure 2. $\frac{3}{2}kT(\mathbf{r})$ and $\bar{I}(\mathbf{r})$ for the O atom along a direction crossing the nucleus, with the origin being on the nucleus itself (in au).

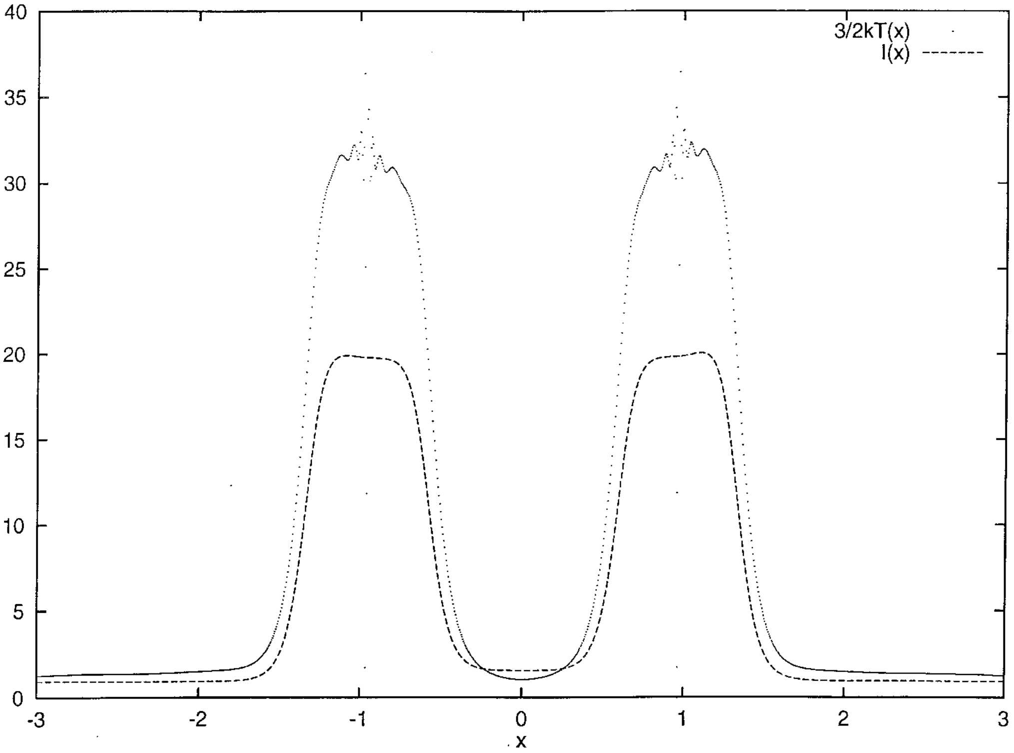

Figure 3. $\frac{3}{2}kT(\mathbf{r})$ and $\bar{I}(\mathbf{r})$ for the O_2 molecule along the molecular axis, with the origin being in the midpoint of the OO bond (in au); the nuclei are at the cusps.

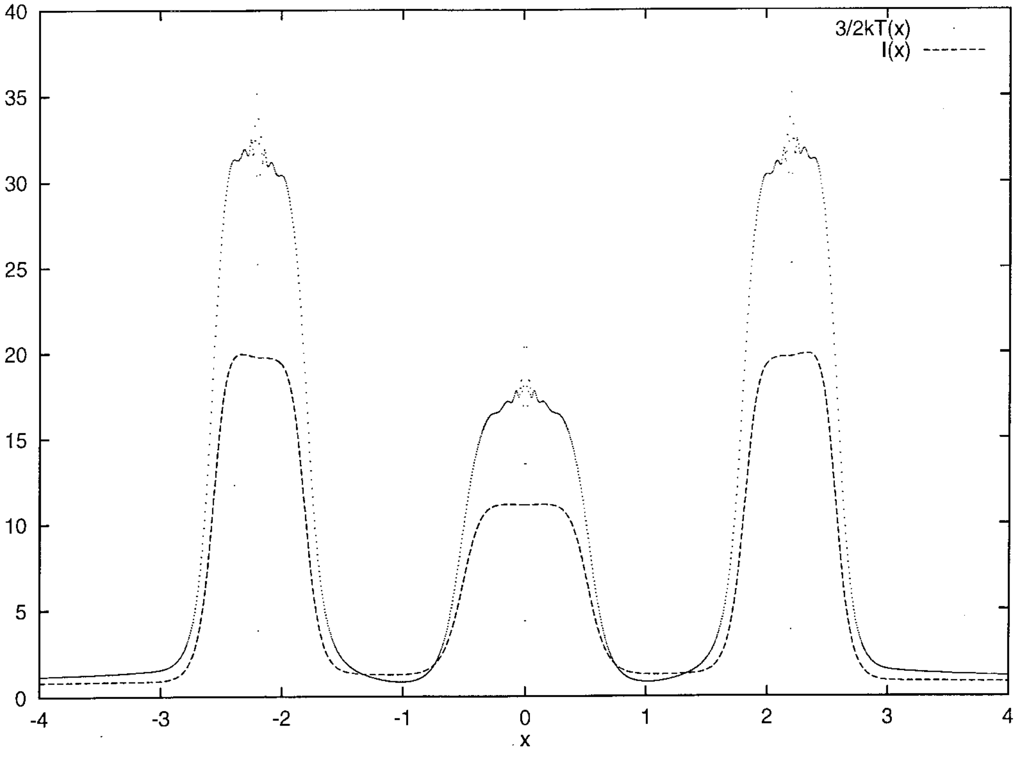

Figure 4. $\frac{3}{2}kT(\mathbf{r})$ and $\bar{I}(\mathbf{r})$ for the CO_2 molecule along the molecular axis, with the origin being in the nucleus of C (in au); the nuclei are at the cusps.

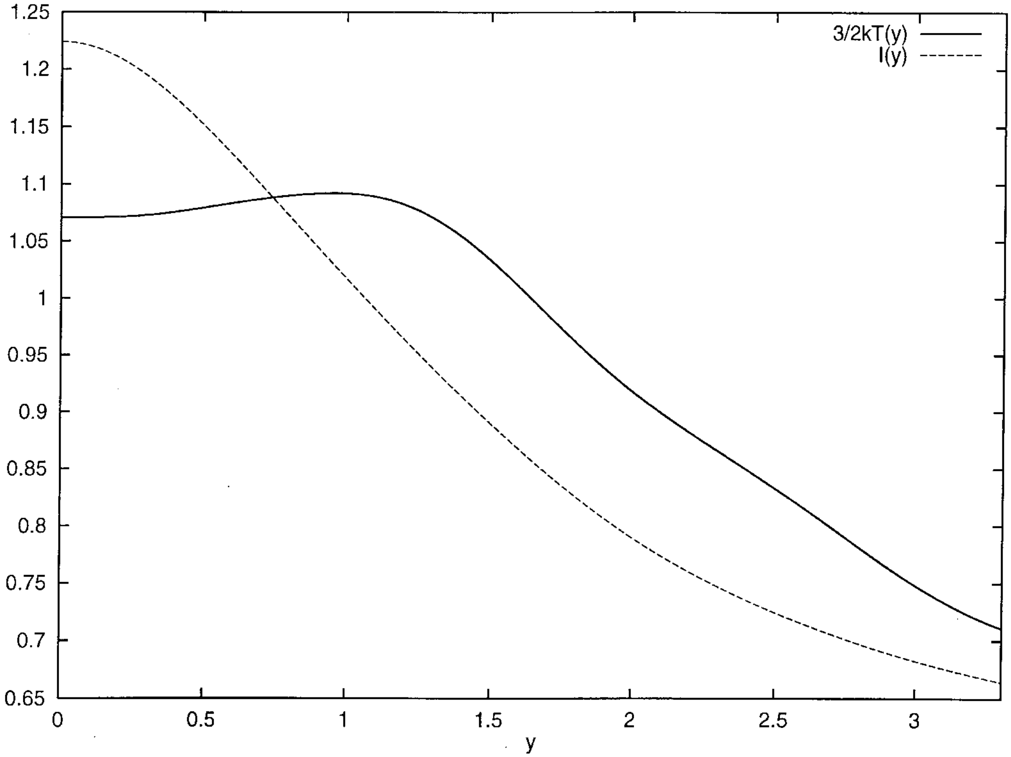

Figure 5. $\frac{3}{2}kT(\mathbf{r})$ and $\bar{I}(\mathbf{r})$ for the CO molecule along a direction perpendicular to the molecular axis and crossing the midpoint of the CO bond, with the origin being in this point itself (in au).

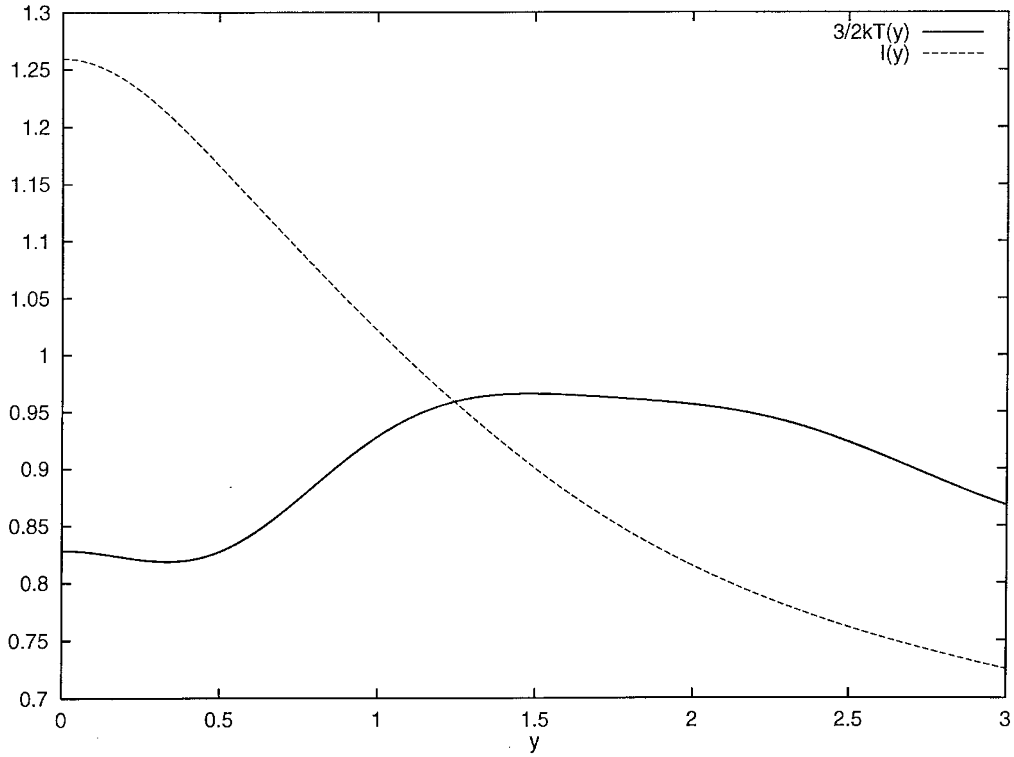

Figure 6. $\frac{3}{2}kT(\mathbf{r})$ and $\bar{I}(\mathbf{r})$ for the CO_2 molecule along a direction perpendicular to the molecular axis and crossing the midpoint of one of the CO bonds, with the origin being in this point itself (in au).

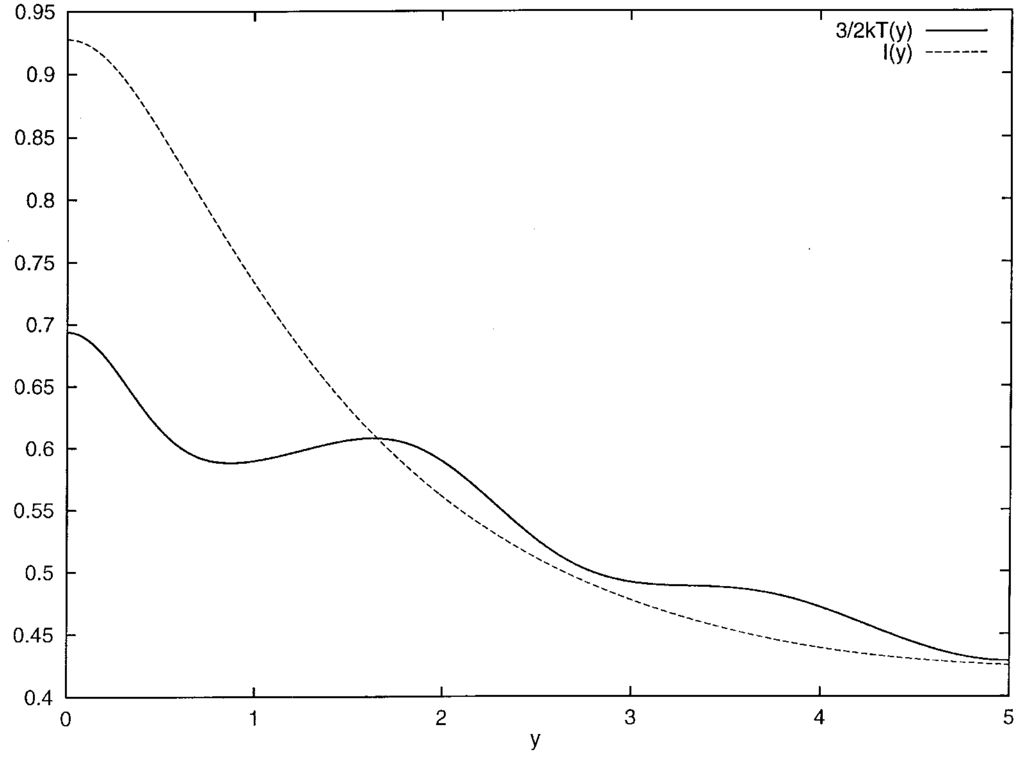

Figure 7. $\frac{3}{2}kT(\mathbf{r})$ and $\bar{I}(\mathbf{r})$ for the C_2H_2 molecule along a direction perpendicular to the molecular axis and crossing the midpoint of the CC bond, with the origin being in this point itself (in au).

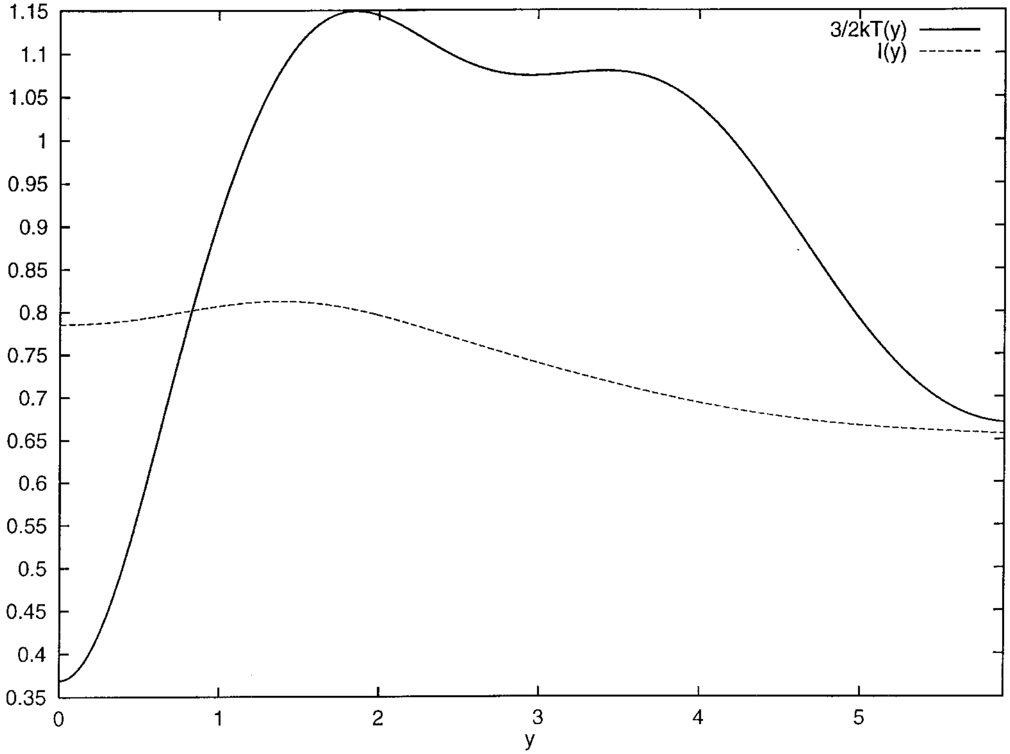

Figure 8. $\frac{3}{2}kT(\mathbf{r})$ and $\bar{I}(\mathbf{r})$ for the C_2H_4 molecule along the direction perpendicular to the molecular axis in the molecular plane and crossing the midpoint of the CC bond, with the origin being in this point itself (in au).

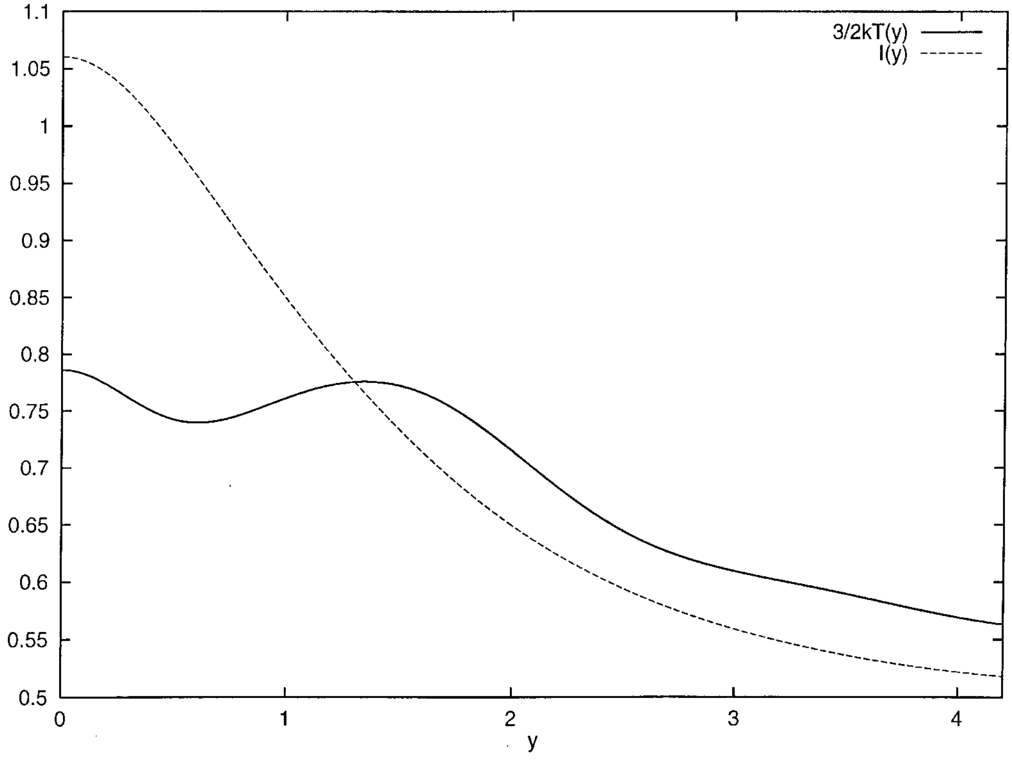

Figure 9. $\frac{3}{2}kT(\mathbf{r})$ and $\bar{I}(\mathbf{r})$ for the HCN molecule along a direction perpendicular to the molecular axis and crossing the midpoint of the CN bond, with the origin being in this point itself (in au).

8. Summary

In the previous chapters the non-interacting kinetic energy problem of density-functional theory has been investigated from different aspects. In Chapter 5 a method, with a mathematical formalism for the simple handling of multiple spatial derivatives in functional differentiation, was proposed [72] to get the most general expression for $T_s[\rho]$ allowed by equations relating $T_s[\rho]$ and its functional derivatives with respect to $\rho(\bar{r})$, assuming that the non-interacting kinetic energy density is simply a function of $\rho(\bar{r})$ and its spatial derivatives, which can lead to new density-gradient expansions for $T_s[\rho]$. In Chapter 6 three differential equations for the ground-state electron density in different cases were set up as a part of the investigation of a general equation, containing $T_s[\rho]$ implicitly, from which $\rho(\bar{r})$ can be determined for given external potential $v(\bar{r})$. The first one, Eq.(6.4) with Eq.(6.7), studied in detail for spherically symmetric systems [88], is a generalization of a differential equation for the ground-state electron density of the Thomas-Fermi atom along a direction shown by its extension to include exchange and Gell-Mann–Brueckner correlation, which can be considered as a generalized local density approximation. The other two differential equations, Eq.(6.26) and Eq.(6.38), are constructed from explicitly known ground-state electron densities for a two-electron Hookean atom [90] and for He-like ions of large atomic number [91], and have the common character of being linear, third-order and homogeneous, which has already been found to be the case for independent Fermions moving in a common, linear harmonic oscillator potential and shown to be a general feature of systems composed of two weakly interacting electrons. In Chapter 7 the local temperature $T(\vec{r})$, which is the average local non-interacting kinetic energy per electron, was studied in molecules [110]. It was found that $T(\vec{r})$ reflects the structures of molecules and, apart from bond regions, characterizes chemical reactivity, low local temperature corresponding to molecular sites most reactive toward electrophiles, further, seems to be quite sensitive to bonding electron clouds, distinguishing between double bonds and triple bonds in its behaviour.

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Összefoglaló

A disszertáció a sűrűségfunkcionál elmélet kinetikus energia problémájával foglalkozik különböző megközelítésekben. E probléma a kölcsönhatásmentes kinetikus energia mint az elektronsűrűség funkcionálja ismeretének hiányát jelenti, amelynek következtében egyrészecskés hullámfüggvények használata szükséges, hogy a sűrűségfunkcionál elmélet alkalmazhatóvá váljék atomok és molekulák elektronszerkezetének leírására. Az első négy fejezet bevezető jellegű, az elmélet alapjainak rövid ismertetését adja, talajt teremtve a következő három fejezethez, amelyek mindegyike más-más szempontból közelít a kölcsönhatásmentes kinetikus energia problémájához.

Az ötödik fejezet közvetlenül a $T_s[\rho]$ kölcsönhatásmentes kinetikus energia sűrűségfunkcionált kutatja, egy módszert ismertetvén $T_s[\rho]$-ra és funkcionális deriváltjaira vonatkozó egyenletek által megengedett legáltalánosabb alak megtalálására azon feltétel mellett, hogy a kölcsönhatásmentes kinetikus energia-sűrűség tisztán $\rho(\vec{r})$-nak és $\rho(\vec{r})$ deriváltjainak függvénye, amely újfajta sűrűség-gradiens sorokhoz vezethet $T_s[\rho]$-ra. A módszer mellett a használhatóságát igazán lehetővé tevő matematikai formalizmus is bevezetésre kerül a többszörös gradiensek funkcionális deriválásban való tömör kezelésére. A módszer leírása egy viszonylag egyszerű esetre való alkalmazásával történik, mégpedig azon feltétel mellett, hogy a kölcsönhatásmentes kinetikus energia-sűrűség csak $\rho(\vec{r})$-nak és $\rho(\vec{r})$ első deriváltjának a függvénye; $T_s[\rho]$ által kielégítendő egyenletként pedig a sűrűségfunkcionál elmélet viriáltételét és egy $T_s[\rho]$-t elsőfokú homogén

funkcionálként jellemző összefüggést véve. A viriáltétel a sűrűségfunkcionál elmélet Euler-egyenletén keresztül a $T_s[\rho]$-ra vonatkozó egyik legelemibb követelmény, ami a kölcsönhatásmentes kinetikus energia koordinátaskálázásbeli másodfokú homogén voltából adódik; a ρ-ban való elsőfokú homogenitási megszorítás pedig –bár általánosan nem igaz $T_s[\rho]$-ra– biztosíthatja $T_s[\rho]$ és funkcionális deriváltja konvergenciáját, ami $T_s[\rho]$ hagyományos gradiens sorfejtésének egyik legalapvetőbb hiányossága. Ezen feltételek mellett a jól ismert, csak egy elektron vagy elektronpár esetén egzakt Weizsäcker kinetikus energia funkcionál egy általánosítása adódik mint a lehető legáltalánosabb kifejezés $T_s[\rho]$-ra, mely rotációs invariancia megkövetelésével magára a Weizsäcker funkcionálra redukálódik, azonban $\rho(\vec{r})$ magasabb fokú deriváltjaira is kiterjesztve a számításokat –tehát enyhítve a kölcsönhatásmentes kinetikus energia-sűrűségre vonatkozó megszorításon–, újfajta sűrűséggradiens sor nyerhető $T_s[\rho]$-ra, amelyben a vezető tag a Weizsäcker funkcionál a Thomas-Fermi kinetikus energia funkcionál helyett.

A hatodik fejezet három, az alapállapoti elektronsűrűségre vonatkozó differenciálegyenletet állít fel különböző esetekre, ami egy általános, $T_s[\rho]$-t impliciten tartalmazó egyenlet irányába történő kutatás részének tekinthető, amelyből adott $v(\vec{r})$ külső potenciálhoz meghatározható $\rho(\vec{r})$, mindehhez a sűrűségfunkcionál elmélet Euler-egyenlete adván elméleti alapot. Az első –részletesen gömbszimmetrikus rendszerek esetében vizsgált– differenciálegyenlet egy, a Thomas-Fermi atom alapállapoti elektronsűrűségére vonatkozó differenciálegyenlet egy általánosítása a kicserélődésre és Gell-Mann-Brueckner-féle korrelációra történt kiterjesztés által szolgáltatott minta mentén az elektronok közti kölcsönhatás minél teljeskörűbb figyelembevételére, ami egyfajta általánosított lokális közelítésnek tekinthető. A differenciálegyenlet alapvető része a sűrűség különböző hatványaiból álló $S(\rho)$ sor, amelynek együtthatói azonban –az első hármat kivéve– ismeretlenek, ezért $S(\rho)$ közelítése szükséges. A közelítés nagyfokú pontossággal ismert elektronsűrűségű, zárt héjú atomok alapján történik, nevezetesen a legnagyobb elektronszámú Kr és Xe atomot alapul véve, lévén a differenciálegyenlet várhatóan minél nagyobb elektronszám esetén nyújthat megfelelő közelítést a végtelenbe tartó rendszám határesetében egzakt Thomas-Fermi egyenletből történt származtatásából kifolyólag. A fejezetben felállított másik két differenciálegyenlet egy kételektronos Hook atom illetve nagy rendszámú He típusú ionok expliciten ismert alapállapoti elektronsűrűségéből van megszerkesztve, és egyaránt homogén lineáris harmadrendű differenciálegyenlet, amely vonás már a lineáris harmonikus oszcillátor potenciáltérben mozgó független fermionok alapállapoti sűrűségeloszlása esetében is meglévőnek bizonyult és általánosan jellemző két gyengén kölcsönható elektron esetében is. Emellett még egy egzakt kifejezés is levezetésre kerül a kinetikus energia sűrűségfunkcionálra egy, az elsőrendű sűrűségmátrixot a sűrűség függvényében megadó –szintén itt levezetett– összefüggésből.

Végül, a hetedik fejezet a $T(\vec{r})$ lokális hőmérsékletet, azaz az egy elektronra jutó átlagos lokális kölcsönhatásmentes kinetikus energiát vizsgálja molekulákban. A vizsgálat főként numerikus úton, az O_2, CO, CO_2, C_2H_2, C_2H_4 és HCN molekulák alapján, Hartree-Fock adatokat használva történik. Megállapítható, hogy $T(\vec{r})$ visszatükrözi a molekulák szerkezetét, és –legalábbis a kötési tartományokon kívül– jellemzi a kémiai reaktivitást: alacsony lokális hőmérséklet az elekrofilek felé legreaktívabb részekhez tartozik a molekulában. Ezenfelül $T(\bar{r})$ igen érzékenynek mutatkozik a kötő elektronfelhőre, viselkedésével megkülönböztetvén kettős és hármas kötéseket.