Attainable accuracy in the numerical integration of the Thomas–Fermi kinetic-energy functional using a modeled electron density

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In the Hohenberg and Kohn formation of the density-functional theory of an electronic system, the basic variable is the electron (number) density. This quantity, however, is not known. For this reason, in an actual calculation, one has to resort to an approximate electron (number) density in order to evaluate the integral occurring in the Hohenberg and Kohn density-functional framework. This poses the question: what is the accuracy beyond which one cannot penetrate in the numerical evaluation of the integrals? The present work attempts to provide an answer to this question by considering the Ne atom as an example and using the simplest energy-density functional, namely the Thomas–Fermi functional. In this functional, composed of three terms, there is only one term, the kinetic-energy functional, that has to be evaluated numerically. The evaluation of this integral is done by modeling the electron (number) density of the Ne atom and resorting to Simpson's compound rule. Following this, an error bound for the integral is established. This is the central result of this paper.

1. Introduction

In the Hohenberg and Kohn [1] formulation of density-functional theory, the (nondegenerate) ground-state energy of an electronic system, such as an atom, or a molecule, is a unique functional of the respective electron (number) density. This quantity, however, is not known so, in a particular calculation, one has to resort to an approximation to the electron (number) density. In a previous work [2], the author used the Thomas–Fermi (TF) energy-density functional [3] and carried out variational calculations of the total atomic binding energy using the Ne atom as an example. In the work mentioned, the electron (number) density of the Ne atom is modeled by using hydrogen-like one-electron wave functions (with the 2s radial function orthogonalized to the 1s radial function). In the TF energy-density functional [3] the kinetic-energy functional can only be evaluated by resorting to numerical integration. The integration technique used in ref. [2] is the compound Simpson's rule [4]. In applying this rule, the integration interval is divided into a number of equal subintervals (or panels) and Simpson's (three-point rule) is applied to each. The numerical integration raises a question: what is the attainable

accuracy beyond which one cannot penetrate? An investigation of this question is the purpose of the present work.

This paper is organized as follows: in section 2, the theoretical framework of ref. [2] is briefly outlined. In section 3, the error estimate of the numerical integration is presented.

All quantities used in the present work are expressed in atomic units (the unit of energy is the hartree, the unit of length is the bohr).

2. Theoretical framework

The TF total-energy functional [3] of an atom is the sum of three terms: the kinetic-energy functional, the functional describing the (attractive) interaction of the electrons with the atomic nucleus, and the functional describing the classical (or the direct) part of the (repulsive) interaction among the electrons. One can then write

$$E_t^{TF}[\rho] = E_k^{TF}[\rho] + E_{ne}[\rho] + E_{ee}[\rho], \tag{1}$$

where ρ is the electron (number) density, and the superscript and subscripts have obvious meanings. It is seen from eq. (1), that it reflects the spirit of the Hohenberg and Kohn [1] formulation of density-functional theory.

The TF kinetic-energy functional, for an atom of spherically symmetric electron distribution, such as the Ne atom, is given [3] by

$$E_k^{TF}[\rho] = \tfrac{3}{10}(3\pi^2)^{2/3} \int_0^\infty \rho^{5/3}\, 4\pi r^2\, dr. \tag{2}$$

The functional describing the (attractive) interaction of the N electrons of an atom with the nucleus of atomic number ζ_n is given [3] by

$$E_{ne}[\rho] = -\int_0^\infty V_n \rho\, 4\pi r^2\, dr, \tag{3}$$

where

$$V_n = \zeta_n/r \tag{4}$$

is the potential of the nucleus with r denoting the distance from the atomic nucleus. For a neutral atom, such as the Ne atom considered in this work, one has $N = \zeta_n = 10$.

The functional describing the classical (or direct) part of the (repulsive) interaction among the N electrons is, in general, described [3] by

$$E_{ee}[\rho] = \tfrac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r - r'|}\, dr\, dr', \tag{5}$$

where $\rho(r)\, dr$ and $\rho(r')\, dr'$ are the charges contained in volume elements dr and

d$\mathbf{r}'$, respectively, and $|\mathbf{r} - \mathbf{r}'|$ is the distance between the volume elements. The factor $1/2$ occurs to avoid double counting.

Equation (5) can also be written [3] as

$$E_{ee}[\rho] = -\tfrac{1}{2} \int_0^\infty V_e \rho \, 4\pi r^2 \, dr, \tag{6}$$

where V_e denotes the potential of the N electrons. This quantity, upon making a choice for ρ, is determined from Poisson's equation

$$\frac{d^2}{dr^2}(r V_e) = 4\pi \rho r \tag{7}$$

by integrating it twice with the boundary condition

$$r V_e \rightarrow -N \quad \text{as} \quad r \rightarrow \infty. \tag{8}$$

The next step is the making of a choice for the electron (number) density. In previous calculations of the author [2] this choice was made in such a way that the electron (number) density (1) is finite at the atomic nucleus, (2) exhibits an exponential decay with the distance from the nucleus, and (3) its associated radial electron (number) density,

$$D = 4\pi r^2 \rho, \tag{9}$$

exhibits the extrema associated with the shell structure of an atom.

For the Ne atom of electron configuration $(1s)^2(2s)^2(2p)^6$, the electron (number) density is constructed [2] as

$$\rho = 2\rho_{1s} + 2\rho_{2s} + 2\rho_{2p_{+1}} + 2\rho_{2p_0} + \rho_{2p_{-1}}, \tag{10}$$

where the subscripts refer to the respective hydrogen-like densities. Substitution of the one-electron wave functions [5] into eq. (10) leads to

$$\rho = \frac{1}{4\pi}[2R_{1s}(Z_1)^2 + 2\mathscr{R}_{2s}(Z_1, Z_2)^2 + 6R_{2p}(Z_3)^2]. \tag{11}$$

In eq. (11), the quantities $R_{1s}(Z_1)$ and $R_{2p}(Z_3)$ denote the normalized radial parts of hydrogen-like wave functions, namely [5]

$$R_{1s}(Z_1) = 2Z_1^{3/2} e^{-Z_1 r} \tag{12}$$

and

$$R_{2p}(Z_3) = \frac{1}{2\sqrt{6}} Z_3^{3/2} (Z_3 r) e^{-Z_3 r/2}. \tag{13}$$

In eq. (11), the (script) function $\mathscr{R}_{2s}(Z_1, Z_2)$ is obtained from an unnormalized hydrogen-like 2s radial wave function, namely from [5]

$$R_{2s}^{un}(Z_2) = (2 - Z_2 r) e^{-Z_2 r/2} \tag{14}$$

that is orthogonalized by the Gram–Schmidt procedure [6] to an unnormalized hydrogen-like 1s radial wave function, namely to [5]

$$R_{1s}^{un}(Z_1) = e^{-Z_1 r}.$$ (15)

The result of the Gram–Schmidt procedure [6] is [#1]

$$\mathcal{R}_{2s}(Z_1, Z_2) = \mathcal{N}[R_{2s}^{un}(Z_2) + \mathcal{K} R_{1s}(Z_1)],$$ (16)

where the (script) constants $\mathcal{N}$ and $\mathcal{K}$ are obtained from the integrals [#2]

$$\int_0^\infty \mathcal{R}_{2s}(Z_1, Z_2)^2 r^2 \, dr = 1,$$ (17)

and

$$\int_0^\infty R_{1s}(Z_1) \mathcal{R}_{2s}(Z_1, Z_2) r^2 \, dr = 0.$$ (18)

For the sake of completeness, it is mentioned here that eqs. (17) and (18) lead to the quantities

$$\mathcal{N} = [8Z_2^{-3} - \mathcal{K}^2]^{-1/2}$$ (19)

and

$$\mathcal{K} = -\left(\frac{8Z_1^{3/2}}{(Z_1 + \frac{1}{2}Z_2)^3} - \frac{12Z_1^{3/2}Z_2}{(Z_1 + \frac{1}{2}Z_2)^4} \right).$$ (20)

(Equations (19) and (20) were not displayed in ref. [2]).

It is important to realize that the orthogonalization of the radial 2s function to the radial 1s function permits the introduction of different variational parameters for the 1s and 2s electrons [7].

Using eq. (11), $E_t^{TF}[\rho]$ in eq. (1) has been minimized with respect to the parameters Z_1, Z_2, and Z_3. The minimization has been carried out by numerical integration based on Simpson's compound rule [4]. An integration interval from 0 to 8 bohr was found to be satisfactory, subdivided into $M = 2048$ equal subintervals (or panels). The minimizing values of the variational parameters Z_1, Z_2, and Z_3, values of the normalization and orthogonalization constants $\mathcal{N}$ and $\mathcal{K}$, and the value of kinetic energy are listed in table 1.

At this point, it is convenient to rewrite eq. (2) as

$$E_k^{TF}[\rho] = \tfrac{3}{10}(\tfrac{3}{4}\pi)^{2/3} \int_{A=0}^{B=8} g(r) \, dr,$$ (21)

[#1] In ref. [2], due to a notational oversight, the function $R_{2s}(Z_2)$ appears in $\mathcal{R}_{2s}(Z_1, Z_2)$. The correct quantity is $R_{2s}^{un}(Z_2)$, where the superscript un stands for unnormalized. All calculations, however, were done with the correct expression for $\mathcal{R}_{2s}(Z_1, Z_2)$.

[#2] Equation (18) can also be expressed by $\mathcal{K} = -\int_0^\infty R_{2s}^{un}(Z_2) R_{1s}(Z_1) r^2 \, dr$.

Table 1
Minimizing values of the variational parameters Z_1, Z_2, and Z_3, values of the normalization and orthogonalization constants $\mathcal{N}$ and $\mathcal{K}$, and the value of the kinetic energy E_k. The last column is a check on the virial theorem, given [3] by VT $= (E_{ne} + E_{ee})/E_k = -2$.

Z_1	Z_2	Z_3	$\mathcal{N}$	$\mathcal{K}$	E_k(au)	VT
10.52	2.34	6.63	1.2803	−0.1196	128.91	−2.0004

where the integrand is given by

$$g(r) = r^2[2R_{1s}(Z_1)^2 + 2\mathcal{R}_{2s}(Z_1, Z_2)^2 + 6R_{2p}(Z_3)^2]^{5/3} . \tag{22}$$

It is known from calculus that the remainder associated with the integral in eq. (21) is given [4] by

$$R_M = -\frac{(B-A)^5}{180M^4} g^{(4)}(\xi); \quad A < \xi < B , \tag{23}$$

where the superscript on g refers to the fourth derivative of g. With g defined in eq. (22), the fourth derivative can be calculated analytically.

The central question is: what is the attainable accuracy of the numerical integration by Simpson's compound rule? For this technique, the maximum error is given [4] by

$$|E| \leqslant \frac{(B-A)^5}{180M^4} \max_{A \leqslant r \leqslant B} |g^{(4)}(r)| . \tag{24}$$

To investigate the quantity $\max |g^{(4)}(r)|$, a successively refined tabulation of $|g^{(4)}(r)|$ has been carried out in the interval $A \leqslant r \leqslant B$. It was found that $|g^{(4)}(r)|$ has several maxima (and minima, of no interest here). The maxima are tabulated in table 2. The maximum of $|g^{(4)}|$ at $x = 0$ is included in table 2 only for the sake of completeness. The remainder, as defined in eq. (23), does not include the limit. What does one conclude then from table 2? The most pessimistic conclusion is that the integral in eq. (21) cannot be obtained to an accuracy greater than 2.566×10^{-4}. This conclusion, of course, pertains to the case of $M = 2048$. A doubling of the number of subintervals (or panels) would introduce a factor of $1/16$, that would lead to an attainable accuracy of 1.604×10^{-5} in the most pessimistic case. In density-functional theory, one would rarely desire such an accuracy. As to the other maxima of $|g^{(4)}(r)|$ in table 2, no problem arises. They permit much smaller errors than an error of the order of 10^{-4}.

In rounding out the present discussions, one more point should be brought out. There is also a roundoff error $|R|$. In practice, the roundoff error is usually negligible [8] but with high speed computers there is the temptation to use a very large number of subintervals. The use of a very large value for M may take the roundoff error out of the negligible category.

Table 2
Maxima of $|g^{(4)}(r)|$ as a function of r in the $A \leqslant r \leqslant B$ interval. The last column gives the error $|E|$, as defined in eq. (24).

r (au)	$\max|g^{(4)}(r)|$	$|E|$
0	6.264123×10^{10}	6.482×10^{-1}
0.202930	2.479880×10^{7}	2.566×10^{-4}
0.692266	3.776076×10^{4}	3.907×10^{-7}
2.776234	1.586347×10^{0}	1.642×10^{-11}
3.977615	$1.90853 \ \times 10^{-1}$	1.975×10^{-12}

In closing it is, perhaps appropriate to quote Davis and Rabinowitz [8]: "error analysis is the tithe that intelligence demands of action, but it is rarely paid."

References

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