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Application of a recent kinetic-energy functional in a variational density-functional calculation of the total atomic binding energy

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Recently DePristo and Kress [Phys. Rev. A **35**, 438 (1987)] have presented a Padé approximation formula for the kinetic-energy functional of a many-electron system, such as an atom. This functional has been adopted in the present work in variational density-functional calculations of the total atomic binding energy, using the Ne atom as an example. For this atom similar calculations have been done earlier by the author using the sum of the first two terms of the gradient expansion of the kinetic-energy functional. The total-energy functional used in the present work contains the kinetic-energy term, the term describing the interaction of the electrons with the atomic nucleus, the term describing the interaction among the electrons, and the exchange-energy term. The electron (number) density of the Ne atom is modeled by using hydrogenlike one-electron wave functions (with the $2s$ function orthogonalized to the $1s$ function) containing three variational parameters. The result of the present calculations is compared with the previous calculations of the author and it is concluded that the DePristo-Kress Padé approximation formula for the kinetic-energy functional gives a better agreement with the Hartree-Fock kinetic energy for the Ne atom than the sum of the first two terms of the gradient expansion of the kinetic-energy functional.

I. INTRODUCTION

Recently, DePristo and Kress¹ presented a Padé approximation formula for the kinetic-energy functional of an atom. Also recently, Perdew and Wang Yue² presented an expression for the exchange-energy functional of a many-electron system. Both of these functionals have been adopted in the present work in variational density-functional calculations of the total atomic binding energy of the Ne atom. For this atom similar calculations have been done earlier by Csavinszky,³ who approximated the kinetic-energy functional by the first two terms of its gradient expansion.

In the present calculations, as in the previous one,³ the electron (number) density of the Ne atom is constructed

from hydrogenlike one-electron wave functions⁴ (with the $2s$ function orthogonalized to the $1s$ function) containing three variational parameters. With this electron (number) density, the total-energy functionals have been minimized with respect to the three variational parameters.

The present work is organized as follows. In Sec. II the theoretical framework is briefly outlined, in Sec. III the results of the present and previous³ calculations are compared, and in Sec. IV the conclusions are presented. All quantities are expressed in atomic units.⁵

II. THEORY

The total-energy functionals used in the present work are composed of four terms: the kinetic-energy functional, the functional describing the attractive (Coulomb) in-

TABLE I. Values of the parameters entering into the kinetic-energy functional of DePristo and Kress (Ref. 1).

	$i=0$	$i=1$	$i=2$	$i=3$	$i=4$
a_i	1	0.950 00	14.281 11	-19.579 62	26.647 77
b_i	1	-0.050 00	9.998 02	2.960 85	

TABLE II. Values of the variational parameters and the normalization and orthogonalization constants. (The values given with a superscript G have been calculated to a higher accuracy than those in Ref. 3.)

Z_1^G	Z_1^P	Z_2^G	Z_2^P	Z_3^G	Z_3^P	\mathcal{N}^G	\mathcal{N}^P	\mathcal{H}^G	\mathcal{H}^P
9.7956	9.7022	2.9198	1.9845	7.1228	6.7897	1.7950	0.99247	-0.10508	-0.25268

teraction of the electrons with the nucleus, the functional describing the repulsive (Coulomb) interaction among the electrons, and the exchange-energy functional. One can then write

$$E_t(\rho) = E_k(\rho) + E_{ne}(\rho) + E_{ee}(\rho) + E_x(\rho), \quad (1)$$

where ρ is the electron (number) density.

For the kinetic-energy functional DePristo and Kress¹ give the Padé approximation formula

$$E_k^P(\rho) = \int \tau_0(\rho) P_{4,3}(x) dv, \quad (2)$$

where $\tau_0(\rho)$ is the expression familiar from the Thomas-Fermi theory,⁶ namely,

$$\tau_0(\rho) = \frac{3}{10} (6\pi^2)^{2/3} \rho^{5/3}, \quad (3)$$

and $P_{4,3}(x)$ is defined¹ by

$$P_{4,3}(x) = \frac{\sum_{i=0}^4 a_i x^i}{\sum_{i=0}^3 b_i x^i}. \quad (4)$$

In Eq. (4) the variable x is defined¹ by

$$x = \tau_2(\rho) / \tau_0(\rho), \quad (5)$$

where $\tau_2(\rho)$ is the so-called Weizsäcker⁷ inhomogeneity correction, as modified by Kompaneets and Pavlovskii⁸ and by Kirzhnits,⁹ namely,

$$\tau_2(\rho) = \frac{1}{72} \int \frac{(\nabla\rho) \cdot (\nabla\rho)}{\rho} dv. \quad (6)$$

The quantities a_i and b_i , occurring¹ in Eq. (4), are listed in Table I.

The functional describing the attractive (Coulomb) interaction of the N electrons with the nucleus of atomic number ζ is given⁶ by

$$E_{ne}(\rho) = - \int V_n \rho dv, \quad (7)$$

where

$$V_n = \zeta / r, \quad (8)$$

with r denoting the distance from the atomic nucleus. For a neutral atom, such as Ne, $N = \zeta$.

The functional describing the repulsive (Coulomb) interaction among the N electrons is given⁶ by

$$E_{ee}(\rho) = - \frac{1}{2} \int V_e \rho dv, \quad (9)$$

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

$$\frac{d^2(rV_e)}{dr^2} = 4\pi\rho r, \quad (10)$$

by integrating it twice with the boundary condition

$$rV_e \rightarrow -N \text{ as } r \rightarrow \infty. \quad (11)$$

The exchange-energy functional, as obtained by Perdew and Wang Yue,² is given by

$$E_x(\rho) = \int \rho^{4/3} F(s) dv, \quad (12)$$

where $F(s)$ is defined² by

$$F(s) = (1 + 1.296s^2 + 14s^4 + 0.2s^6)^{1/15}, \quad (13)$$

with

$$s = \frac{|\nabla\rho|}{2k_F\rho} \quad (14)$$

and

$$k_F = (3\pi^2\rho)^{1/3}. \quad (15)$$

The next step is the making of a choice for the electron (number) density ρ . In the present work, as in the previous one,³ the choice for ρ is made in such a way that this quantity is (1) finite at the atomic nucleus, (2) exhibits an exponential decay with the distance r from the nucleus, and (3) the associated radial-electron (number) density exhibits the atomic-shell structure.

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

$$\rho = \frac{1}{4\pi} [2R_{1s}(Z_1)^2 + 2R_{2s}(Z_1, Z_2)^2 + 6R_{2p}(Z_3)^2]. \quad (16)$$

In Eq. (16), $R_{1s}(Z_1)$ and $R_{2p}(Z_3)$ are the radial parts of hydrogenlike radial wave functions, given⁴ by

$$R_{1s}(Z_1) = 2Z_1^{3/2} e^{-Z_1 r} \quad (17)$$

and

$$R_{2p}(Z_3) = \frac{1}{2\sqrt{6}} Z_3^{5/2} r e^{-(1/2)Z_3 r}, \quad (18)$$

TABLE III. Values of the energy components and the total energy. (The values given with a superscript G have been calculated to a higher accuracy than those in Ref. 3.)

E_k^G	E_k^P	E_{ne}^G	E_{ne}^P	E_{ee}^G	E_{ee}^P	E_x^G	E_x^P	E_t^G	E_t^P
130.57	129.67	-315.13	-309.53	66.29	62.12	-12.31	-11.94	-130.57	-129.66

TABLE IV. Values of the electron (number) densities at the nucleus. The HF value has been calculated with the double- ζ wave functions of Ref. 12.

$\rho^G(r=0)$	$\rho^P(r=0)$	$\rho^{\text{HF}}(r=0)$
608.50	609.04	617.17

while $\mathcal{R}_{2s}(Z_1, Z_2)$ is a hydrogenlike radial $R_{2s}(Z_2)$ function,⁴ namely,

$$R_{2s}(Z_2) = \frac{1}{2\sqrt{2}} Z_2^{3/2} (2 - Z_2 r) e^{-(1/2)Z_2 r}, \quad (19)$$

orthogonalized to the $R_{1s}(Z_1)$ function. This procedure, that permits the introduction of different variational parameters for the different n, l electrons, has been suggested by Csavinszky.¹⁰

The $\mathcal{R}_{2s}(Z_1, Z_2)$ function is given by

$$\mathcal{R}_{2s}(Z_1, Z_2) = \mathcal{N}[R_{2s}(Z_2) + \mathcal{H}R_{1s}(Z_1)], \quad (20)$$

where the constant \mathcal{N} is determined from the normalization condition

$$\int \mathcal{R}_{2s}(Z_1, Z_2)^2 r^2 dr = 1, \quad (21)$$

and the constant \mathcal{H} is obtained from the orthogonalization condition

$$\int R_{1s}(Z_1) \mathcal{R}_{2s}(Z_1, Z_2) r^2 dr = 0. \quad (22)$$

Using Eq. (12), Eq. (1) has been evaluated by numerical integration, based on Simpson's rule.¹¹ The results of the computations, based on the DePristo-Kress¹ kinetic-energy functional and the Perdew-Wang Yue² exchange-energy functional are displayed in Tables II and III.

Using the first two terms of the gradient expansion of the kinetic energy, namely,

$$E_k^G(\rho) = \frac{3}{10} (6\pi^2)^{2/3} \int \rho^{5/3} dv + \frac{1}{72} \int \frac{(\nabla\rho) \cdot (\nabla\rho)}{\rho} dv \quad (23)$$

in Eq. (1), the minimization of this expression has been carried out again by numerical integration based on Simpson's rule.¹¹ The results of the calculations, based on Eq. (23) and the Perdew-Wang Yue² exchange-energy functional, are displayed in Tables II and III. In these tables the superscript G refers to the gradient expansion approximation for the kinetic-energy functional, while the superscript P refers to the Padé approximation for the kinetic-energy functional.

III. DISCUSSION

Table I displays the values of the parameters a_i and b_i , entering into the Padé approximation formula¹ for the kinetic-energy functional.

Table II displays the values of the variational parameters Z_1^P , Z_2^P , and Z_3^P , the values of the normalization constant \mathcal{N}^P , and the orthogonalization constant \mathcal{H}^P , obtained by using Eq. (2) in Eq. (1).

Table III contains the values of the energy components

and the total energy E_t^P obtained by using Eq. (2) in Eq. (1).

Table II also displays the values of the variational parameters Z_1^G , and Z_2^G , and Z_3^G , and the values of the normalization constant \mathcal{N}^G , and the orthogonalization constant \mathcal{H}^G , obtained by using the sum of Eqs. (3) and (6) in Eq. (1). Table III also contains the values of the energy components and the total energy E_t^G obtained by using the sum of Eqs. (3) and (6) in Eq. (1).

It is instructive to compare $E_k^P = 129.67$ a.u. (from Table III) with $E_k^G = 130.57$ a.u. (also from Table III) with the near-Hartree-Fock (HF) value, $E_k^{\text{HF}} = 128.55$ a.u., of Clementi and Roetti.¹² The comparison shows that E_k^P is in better agreement with E_k^{HF} than E_k^G . It is also instructive to compare $E_t^P = -129.66$ a.u. (from Table III) with $E_t^G = -130.57$ a.u. (also from Table III) with the near-Hartree-Fock value of $E_t^{\text{HF}} = -128.55$ a.u., as given by Clementi and Roetti.¹² The comparison shows that E_t^P is in better agreement with E_t^{HF} than E_t^G .

It is also interesting to note that Perdew and Wang Yue² find that the exchange energy calculated for the Ne atom with the near-Hartree-Fock density of Clementi and Roetti¹² is $E_x^{\text{HF}} = -12.22$ a.u. This is compared with $E_x^P = -11.94$ a.u. (from Table III) and $E_x^G = 12.31$ a.u. (also from Table III). The comparison shows that E_x^G is in better agreement with E_x^{HF} than E_x^P .

Another test of the quality of the kinetic-energy functionals is based on a comparison of the electron (number) densities at the nucleus. Such a comparison is valuable because it involves a local property, in contrast to the comparison of total energies that involves a global property. Electron (number) densities at $r=0$ are listed in Table IV. The HF value has been calculated with the double- ζ wave functions of Clementi and Roetti.¹²

The values of $\rho^G(r=0)$ and $\rho^P(r=0)$ are just about the same and, what is more significant, both differ only about 2% from the HF value. This fact shows that one can obtain good results with a modeled electron (number) density.

IV. CONCLUSION

As far as the total binding energy of the Ne atom is concerned, the Padé approximation formula of DePristo and Kress¹ for the kinetic-energy functional leads to a better agreement with the near-Hartree-Fock total-energy value than the value obtained by using the sum of the first two terms of the gradient expansion of the kinetic-energy functional. It would be tempting to add to this sum the next term of the gradient expansion of the kinetic-energy functional, derived by Hodges.¹³ This would probably lead to a better agreement with E_t^{HF} . This author, however, believes that Tal and Bader¹⁴ have conclusively shown that the kinetic-energy functional can have only two terms in its gradient expansion.

One can then ask: What is the next step? Undoubtedly, work will be done in the future to further improve the kinetic-energy functional, on the one hand, and the exchange-energy functional, on the other hand.

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