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Conjoint gradient correction to the Hartree-Fock kinetic- and exchange-energy density functionals

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Becke [J. Chem. Phys. **84**, 4524 (1986); Phys. Rev. A **38**, 3098 (1988)] has shown that the Hartree-Fock exchange energy for atoms (and molecules) can be excellently represented by a formula $K=2^{1/3}C_x\int\sum_\sigma\rho_\sigma^{4/3}(\mathbf{r})[1+\beta G(x_\sigma)]d\mathbf{r}$, where C_x is the Dirac constant, β is a constant, $G(x)$ is a function of the gradient-measuring variable $x_\sigma=|\nabla\rho_\sigma|/\rho^{4/3}$, and the summation is over spin densities ρ_σ. Becke recommends $G(x_\sigma)=x_\sigma^2/[1+0.0253x_\sigma\sinh^{-1}(x_\sigma)]$. It is demonstrated that the kinetic energy can be represented with comparable accuracy by the formula $T=2^{2/3}C_F\int\sum_\sigma\rho_\sigma^{5/3}(\mathbf{r})[1+\alpha G(x_\sigma)]d\mathbf{r}$, where C_F is the Thomas-Fermi constant, α is a constant, and $G(x)$ is just the same function that appears in the formula for K. Recommended values, obtained by fitting data on rare-gas atoms, are $\alpha=4.4188\times10^{-3}$, $\beta=4.5135\times10^{-3}$. The best α-to-β ratio, 0.979, is close to unity, and calculations with $\alpha=\beta=4.3952\times10^{-3}$ are shown to give remarkably accurate values for both T and K. It is briefly discussed how the above-noted equations for K and T can both result from scaling arguments and a simple assumption about the first-order density matrix.

I. INTRODUCTION

Gradient expansions for the kinetic energy and exchange energy of a nonhomogeneous but nearly homogeneous electronic system are well known. With $C_F=\frac{3}{10}(3\pi^2)^{2/3}=2.8712$ and $C_x=\frac{3}{4}(3/\pi)^{1/3}=0.7386$ the Thomas-Fermi and Dirac coefficients, such expansions can be written

$$T[\rho]=2^{2/3}C_F\int\sum_\sigma\rho_\sigma^{5/3}(\mathbf{r})(1+\alpha x_\sigma^2+\cdots)d\mathbf{r} \tag{1}$$

and

$$K[\rho]=2^{1/3}C_x\int\sum_\sigma\rho_\sigma^{4/3}(\mathbf{r})(1+\beta x_\sigma^2+\cdots)d\mathbf{r}\ , \tag{2}$$

where α and β are constant and the quantity

$$x_\sigma=\frac{|\nabla\rho_\sigma(\mathbf{r})|}{\rho_\sigma^{4/3}(\mathbf{r})} \tag{3}$$

measures the deviation from homogeneity at each $\mathbf{r}$; $\rho(\mathbf{r})$ is the electron density at $\mathbf{r}$. Summations are over spin σ, with x_σ defined using the electron density ρ_σ for electrons of spin σ. Specifically, $2^{2/3}C_F\alpha=\frac{1}{72}$ [1] and $2^{2/3}C_x\beta=0.001\,667$ [2], so that

$$\alpha/\beta=2.1435 \tag{4}$$

for the nearly homogeneous electron gas. When one tries to apply Eqs. (1) and (2) to atoms and molecules as components of energy functionals, one meets many difficulties. Both series diverge, and the accuracy when the series are truncated at zero or second order is poor by any contemporary standard.

However, a recent innovation by Becke [3,4] shows much promise. He suggested replacing all of the second- and higher-order terms in the above formula for K by a single function of x, call it $G(x)$. Then

$$K[\rho]=2^{1/3}C_x\int\sum_\sigma\rho_\sigma^{4/3}(\mathbf{r})[1+\beta G(x_\sigma)]d\mathbf{r}\ , \tag{5}$$

which is necessarily approximate because exact representation of all of the higher-order terms in this way is not to be expected. Becke tried several forms for $G(x)$. Arguing from recently discovered long-range properties of the exchange kernel [5], he finally came to, from among others, the form

$$G(x)=\frac{x^2}{1+\gamma\sinh^{-1}(x)}\ , \tag{6}$$

where γ is a constant. Numerical results are very good; Becke recommends $\gamma=0.0253$ and $\beta=4.5135\times10^{-3}$ [4].

In the present paper we carry out a complementary study of $T[\rho]$, assuming that there exists a good approximation for it of the form

$$T[\rho]=2^{2/3}C_F\int\sum_\sigma\rho_\sigma^{5/3}(\mathbf{r})[1+\alpha G(x_\sigma)]d\mathbf{r}\ . \tag{7}$$

We test this hypothesis in Sec. II, again using Eq. (6) for $G(x)$.

That the $G(x)$ in Eqs. (5) and (7) might be more or less the same could be conjectured on inspection of Eqs. (1) and (2): The sums of the terms $x^2+\cdots$ in the two equations could be close to the same. A formal argument supporting this assumption is given in Sec. III. We note the fact that usually it is the combination $T-K$ in which we are interested.

II. RESULTS

In Table I are given the Hartree-Fock (HF) kinetic energies and exchange energies for the rare-gas atoms He, Ne, Ar, Kr, and Xe. These are taken from literature [6]. The fits that follow are least-squares fits of percentage deviations from these values. The various quantities in Eqs. (5) and (7) are determined by numerical integration.

TABLE I. Exchange and kinetic energies for rare-gas atoms. Numbers in parentheses are percentage errors.

	K_{HF}[a]	K_0	K_{calc}[b]	T_{HF}[a]	T_0	T_{calc}[c]
He	1.026	0.884	1.025 (−0.10)	2.861 68	2.560 54	2.858 61 (−0.11)
Ne	12.11	11.03	12.14 (0.25)	128.547	117.761	128.393 (−0.12)
Ar	30.18	27.86	30.15 (−0.10)	526.814	489.947	527.715 (0.17)
Kr	93.89	88.62	93.87 (−0.02)	2752.05	2591.23	2753.96 (0.07)
Xe	179.1	170.6	179.0 (−0.06)	7232.14	6857.70	7238.15 (0.08)

[a] True values, from HF wave functions of Ref. 6.

[b] From Eqs. (5) of present text, $\beta=4.5135\times10^{-3}$; rms percentage is 0.14%.

[c] From Eq. (7) of present text, $\alpha=4.4188\times10^{-3}$; rms percentage is 0.13%.

TABLE II. $T-K$ calculations for rare-gas atoms. Numbers in parentheses are percentage errors.

			$(T-K)_{\mathrm{calc}}$	
	$(T-K)_{\mathrm{HF}}$[a]	$(T-K)_0$[b]	One parameter[c]	Two parameter[d]
He	1.836	1.677	1.835 (−0.03)	1.833 (−0.18)
Ne	116.44	106.73	116.23 (−0.15)	116.25 (−0.16)
Ar	496.63	462.09	497.41 (0.16)	497.55 (0.19)
Kr	2658.2	2502.6	2659.4 (0.04)	2660.1 (0.07)
Xe	7053.0	6687.1	7057.3 (0.06)	7059.1 (0.09)

[a] Actual values, calculated from Ref. 6.

[b] $T-K$ using Hartree-Fock wave functions and the local density approximation.

[c] From Eqs. (5) and (7) with $\alpha=\beta=4.3952\times10^{-3}$; rms percentage is 0.13%.

[d] T and K from Eqs. (5) and (7) with $\alpha=4.4188\times10^{-3}$, $\beta=4.5135\times10^{-3}$; rms percentage is 0.15%.

TABLE III. Exchange and kinetic energies for first-row atoms. Numbers in parentheses are percentage errors.

			One parameter[a]		Two parameter[b]	
	T_{HF}[c]	K_{HF}[c]	T_{calc}	K_{calc}	T_{calc}	K_{calc}
He	2.8617	1.026	2.8570 (−0.16)	1.022 (−0.34)	2.8584 (−0.11)	1.025 (−0.10)
Li	7.4327	1.781	7.4567 (0.32)	1.769 (−0.70)	7.4616 (0.39)	1.776 (−0.29)
Be	14.573	2.667	14.584 (0.07)	2.649 (−0.71)	14.592 (0.13)	2.659 (−0.31)
B	24.529	3.744	24.384 (−0.59)	3.757 (0.35)	24.397 (−0.54)	3.730 (−0.38)
C	37.688	5.045	37.443 (−0.65)	5.016 (−0.57)	37.559 (−0.34)	5.033 (−0.26)
N	54.401	6.596	54.416 (0.03)	6.572 (−0.39)	54.422 (0.03)	6.589 (−0.11)
O	74.809	8.174	74.578 (−0.76)	8.147 (−1.06)	74.276 (−0.71)	8.172 (−0.03)
F	99.409	10.00	98.642 (−0.77)	9.989 (−0.11)	98.936 (−0.48)	10.02 (0.20)
Ne	128.55	12.11	128.34 (−0.17)	12.11 (0.01)	128.39 (−0.12)	12.14 (0.25)

[a] From Eqs. (7) and (5) with $\alpha=\beta=4.3952\times10^{-3}$. For T, rms percentage is 0.47%; rms percentage is 0.45% for K.

[b] From Eqs. (7) and (5) with $\alpha=4.4188\times10^{-3}$, $\beta=4.5135\times10^{-3}$. For T, rms percentage is 0.39% and rms percentage is 0.24% for K.

[c] True values, from HF wave functions of Ref. 6.

TABLE IV. $T-K$ calculations for first-row atoms. Numbers in parentheses are percentage errors.

			$(T-K)_{\mathrm{calc}}$	
	HF[a]	LDA[b]	One parameter[c]	Two parameter[d]
He	1.836	1.677	1.835 (−0.03)	1.833 (−0.16)
Li	5.652	5.141	5.689 (0.65)	5.686 (0.60)
Be	11.906	10.817	11.935 (0.25)	11.933 (0.22)
B	20.785	18.800	20.668 (−0.56)	20.667 (−0.57)
C	32.634	29.555	32.427 (−0.63)	32.526 (−0.33)
N	47.805	43.584	47.844 (0.08)	47.831 (0.05)
O	66.635	60.555	66.431 (−0.81)	66.104 (−0.80)
F	89.409	81.408	88.653 (−0.84)	88.937 (−0.53)
Ne	116.44	106.73	116.23 (−0.18)	116.25 (−0.16)

[a] Actual HF values of $T-K$, from HF wave functions of Ref. 6.

[b] $T-K$ using HF wave functions and the local-density approximation (LDA).

[c] Calculated Eqs. (5) and (7) with $\alpha=\beta=4.3952\times10^{-3}$; rms percentage is 0.54%.

[d] From Eqs. (5) and (7) with $\alpha=4.4188\times10^{-3}$, $\beta=4.5135\times10^{-3}$; rms percentage is 0.45%.

Results for kinetic energies determined from Eq. (7) are given in Table I. We find $\alpha=4.4188\times10^{-3}$ in Eq. (7), 1.4501 times the value obtained by Hodges [1]. The rms percentage deviation is 0.13%. Also given in Table I are the exchange energies determined from Eq. (5) with $\beta=4.5135\times10^{-3}$, which is 3.173 times the value obtained by Sham [2]. The rms percentage deviation is 0.14%.

These empirical values of α and β predict the ratio

$$\alpha/\beta=0.979\ . \tag{8}$$

Remarkably, this number is seen to be close to 1.

Now we turn to the quantity $T-K$, which is the combination of T and K that enters the total energy. Table II gives $T-K$ values determined in two ways. First (last column), α and β values are taken from the independent fits of T and K described above: $\alpha=4.4188\times10^{-3}$ and $\beta=4.5135\times10^{-3}$. In the second calculation of $T-K$, we arbitrarily use the ratio unity, taking $\alpha=\beta$. We obtain $\alpha=\beta=4.3952\times10^{-3}$ and the $T-K$ values shown in the next-to-last column. Little seems to have been lost in employing this simplification, which reduces the fitting to one parameter. Agreement with true values is very good indeed.

For calculation of T alone we recommend $\alpha=4.4188\times10^{-3}$; for calculation of K alone we recommend $\beta=4.5135\times10^{-3}$, while for calculation of $T-K$ we recommend $\alpha=\beta=4.3952\times10^{-3}$.

III. DISCUSSION

As a test of this formulation, in Table III we present values of T and K computed for first-row atoms using the two sets of α and β values recommended above. Hartree-Fock values are given for comparison. Again, we give the values of $T-K$ in Table IV. The results are highly promising. Note the number of parameters involved–only one for the second calculation.

To try to understand better how it can be that to such good accuracy we can use the same $G(x)$ in Eqs. (5) and (7), we may start from formulas for T and K obtained from exact formulas in terms of the first-order density matrix [7]. Namely, exactly (total density is used for convenience),

$$T=\tfrac{3}{2}\int\frac{\rho(\mathbf{r})}{\beta(\mathbf{r})}d\mathbf{r} \tag{9}$$

and

$$\begin{aligned} K&=\pi\int\int s\,ds\,d\mathbf{r}\,\rho^2(r)\left[1+\frac{s^2}{\beta(\mathbf{r})}+\cdots\right]\\ &=\pi\int\int s\,ds\,d\mathbf{r}\,\rho^2(\mathbf{r})\Gamma(\mathbf{r},s)\ , \end{aligned} \tag{10}$$

where $\beta(\mathbf{r})$ is defined by Eq. (9)—its reciprocal is two-thirds of the exact kinetic-energy density per electron.

With $\beta_0(\mathbf{r})=5[3\pi^2\rho(\mathbf{r})]^{-2/3}$, the Thomas-Fermi formula, we may write

$$\frac{1}{\beta(\mathbf{r})}=\frac{1}{\beta_0(\mathbf{r})}[1+F(\mathbf{r},0)]\ , \tag{11}$$

defining $F(\mathbf{r},0)$ thereby. Then

$$T=T_0+\tfrac{3}{2}\int\frac{\rho(\mathbf{r})}{\beta_0(\mathbf{r})}F(\mathbf{r},0)d\mathbf{r} \tag{12}$$

and

$$\begin{aligned} \Gamma(\mathbf{r},s)&=1-\frac{s^2}{\beta_0(\mathbf{r})}[1+F(\mathbf{r},0)]+\cdots\\ &=\Gamma_0(\mathbf{r},s)-\frac{s^2}{\beta_0(\mathbf{r})}F(\mathbf{r},0)+\cdots\\ &=\Gamma_0(\mathbf{r},s)-\frac{s^2}{\beta_0(\mathbf{r})}F(\mathbf{r},s)\ , \end{aligned} \tag{13}$$

where Γ_0 is the Thomas-Fermi Γ and $F(\mathbf{r},s)$ is defined as indicated by grafting onto $F(\mathbf{r},0)$ higher-order terms in s. Consequently,

$$K=K_0+\pi\int\int\frac{\rho^2(\mathbf{r})}{\beta_0(\mathbf{r})}F(\mathbf{r},s)s\,ds\,d\mathbf{r}\ . \tag{14}$$

Now change the variable s to the variable $t=s^2/\beta_0(\mathbf{r})$, giving $F(\mathbf{r},s)=G(\mathbf{r},t)$. Equations (12) and (14) become

$$T=T_0+A\int\rho^{5/3}(\mathbf{r})G(\mathbf{r},0)d\mathbf{r}\ , \tag{15}$$

$$K=K_0+B'\int\rho^{4/3}(\mathbf{r})d\mathbf{r}\int G(\mathbf{r},t)t\,dt\ , \tag{16}$$

where A and B' are constants. These formulas are exact. If we now assume that, to a good approximation,

$$\int_0^\infty G(\mathbf{r},t)t\,dt=\text{const}\times G(\mathbf{r},0)\ , \tag{17}$$

Eq. (16) becomes

$$K=K_0+B\int\rho^{4/3}(\mathbf{r})G(\mathbf{r},0)d\mathbf{r}\ , \tag{18}$$

where B is a constant. Equations (18) and (15) are of the form of Eqs. (5) and (7), with $G(\mathbf{r},0)$ playing the role of $G(x)$.

This argument is, of course, more or less formal. The evidence for "conjointness" we have presented is in large part empirical. What seems to be the case, for whatever reason, is that as soon as one separates T and K integrands into properly scaling parts $\rho^{5/3}$ and $\rho^{4/3}$, respectively, and the scale-invariant "rest," the "rest" may be assumed to be very similar for T and K.

March and Santamaria also have recently begun to study conjointness [8].

Results of comparable accuracy have been obtained for molecules and will be presented elsewhere.

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