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Challenge of creating accurate and effective kinetic-energy functionals

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The accuracy and effectiveness of various kinetic-energy functionals in providing total noninteracting kinetic energies, atomization kinetic energies, and equilibrium properties is evaluated. Employing converged Kohn-Sham densities, we assess various kinetic-energy functionals in a non-self-consistent manner. It is found that the gradient expansion, the Pearson-Gordon local truncation scheme, and the [4/3]-Padé approximant of DePristo and Kress provide reliable estimates for the total noninteracting kinetic energy. The estimates for the atomization kinetic energy and equilibrium geometries are, however, far from being reliable for chemical applications

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I. INTRODUCTION

Density-functional theory (DFT) is one of the most powerful and commonly used tools to calculate equilibrium properties of atoms, molecules, and solids [1–4]. The formal framework of DFT is provided by the Hohenberg-Kohn theorems [5], that prove the existence of a one-to-one mapping between the ground-state electron density $\rho(\vec{r})$ and external local potential $v(\vec{r})$ that differ by more than a constant. As a consequence, a variational expression for the ground-state energy in terms of the electron density is obtained. Modern implementations of DFT are, however, based on the Kohn-Sham method [6]. Here, a major portion of the kinetic energy (the noninteracting kinetic energy T_S) [1,2] is calculated in terms of the Kohn-Sham orbitals and not as a functional of the density. It is only the exchange-correlation energy E_{XC} , a functional of the electron density, that has to be approximated. The constrained minimization of energy with respect to the Kohn-Sham orbitals yields the ground-state energy of the system.

The search for an accurate density-functional approximation to T_S remains an unsolved problem. Such a functional would facilitate the direct minimization of the ground-state energy with respect to the electron density, and hence the calculation of Kohn-Sham orbitals would not be required. This would reduce the computational complexity of DFT calculations immensely.

Efforts to obtain a simple and accurate expression for the noninteracting kinetic energy in terms of $\rho(\vec{r})$ may be traced back to Thomas [7] and Fermi [8]. In the Thomas-Fermi approximation, the noninteracting kinetic energy (T_S) is written as

$$T_S = c_0 \int d^3 r \rho^{5/3}(\vec{r}), \tag{1}$$

where $c_0 = (3/10)(3\pi^2)^{2/3}$ (in atomic units). Some of the subsequent improvements of this idea are, for instance, the gradient expansion [2] and partial resummations [2,1] of the gradient expansion. However, the search for an approximate noninteracting kinetic energy functional, which provides results accurate enough for chemical applications, is still on.

In this paper, we evaluate the merits of various kinetic-energy functionals. Previous tests of kinetic-energy functionals focused primarily on the ability of approximate functionals to reproduce the total noninteracting kinetic energy of atoms [9–15] and extended systems [12,13,16,17]. Exceptions are Ref. [18], where the second-order gradient approximation has been tested for atomization processes, and Ref. [19], where atomization energies have been studied using the gradient expansion up to fourth order. In this work, we focus on the ability of various approximate kinetic-energy functionals to describe chemical transformations such as atomizations and changes in the bond lengths, in addition to evaluating the accuracy when the total noninteracting kinetic energy is calculated.

In Sec. II, we introduce various functionals proposed in the literature and discuss modifications thereof. Our test calculations, in Sec. III, include determining total kinetic energies and atomization kinetic energies $\Delta T_S = T^{\mathrm{atoms}} - T^{\mathrm{molecule}}$ as well as evaluating T_S as a function of the bond length for various molecules belonging to the G2 set [20]. In Sec. IV, we present our conclusions.

II. KINETIC-ENERGY FUNCTIONALS

The Thomas-Fermi approximation to the noninteracting kinetic energy can be systematically refined by utilizing not only the local density but also spatial derivatives of the local density. The resulting partially integrated gradient expansion (simplified using Green's theorem under the assumption that $\rho(\vec{r}) \to 0$ as $|\vec{r}| \to \infty$ on an appropriate surface) is [1,2]

$$T_S[\rho] = \int d^3 r [t_S^{(0)}(\vec{r}) + t_S^{(2)}(\vec{r}) + t_S^{(4)}(\vec{r}) + \cdots], \tag{2}$$

where

$$t_S^{(0)}(\vec{r}) \equiv c_0 \rho^{5/3}, \tag{3}$$

$$t_S^{(2)}(\vec{r}) \equiv c_2 \frac{|\vec{\nabla}\rho|^2}{\rho}, \tag{4}$$

$$t_S^{(4)}(\vec{r}) \equiv c_4 \rho^{1/3}\left[\left(\frac{\vec{\nabla}^2\rho}{\rho}\right)^2 - \frac{9}{8}\frac{\vec{\nabla}^2\rho}{\rho}\left(\frac{\vec{\nabla}\rho}{\rho}\right)^2 + \frac{1}{3}\left(\frac{\vec{\nabla}\rho}{\rho}\right)^4\right]. \tag{5}$$

c_0, c_2, and c_4 are known constants (see, e.g., [2]). Although the gradient expansion can, in principle, be derived up to arbitrary high orders [21,22], this does not imply that the calculated noninteracting kinetic energies can be systematically improved. In fact, all sixth- and higher-order terms of the gradient expansion diverge for atoms and molecules as $r \rightarrow \infty$ [23,2]. Here, r is the distance from the center of mass of the molecule. One way around this divergence problem of the gradient expansion, for exponentially decreasing densities, is provided by the local truncation scheme of Pearson and Gordon [9], where the kinetic-energy functional is written as

$$T_S^{\mathrm{PG}}[\rho] = \int d^3r\left[\left(\sum_{l=0}^{l_{\max}-1} t_S^{(2l)}(\vec{r})\right) + \frac{1}{2}t_S^{(2l_{\max})}(\vec{r})\right]. \tag{6}$$

$l_{\max} \equiv l_{\max}(\vec{r})$ is determined such that $t_S^{(2l_{\max})}(\vec{r})$ is the smallest (in absolute value) term of the gradient expansion at point $\vec{r}$. We have also tried other truncation criteria but found the above criterion to be quite effective, as will be shown in the Results section.

A conceptually elegant kinetic-energy functional was obtained by Baltin [24]. In this author's work, a partial resummation of the gradient expansion including all the terms involving powers of $\vec{\nabla}\rho$ leads to an approximation that is exact if the external potential is a linear function.

Another important kinetic-energy functional, the von Weizsäcker kinetic-energy functional [25],

$$T_S^{\mathrm{vW}} = \tfrac{1}{8}\int d^3r \frac{|\vec{\nabla}\rho(\mathbf{r})|^2}{\rho(\mathbf{r})}, \tag{7}$$

is considered exact [1,2,26–28] in the limit of rapidly varying electron densities. This functional is simply nine times the second-order term in Eq. (4) and gives the exact kinetic energy for one electron systems. It provides a rigorous lower bound to the *true* kinetic energy [2]. It may be noted that the sum of the Thomas-Fermi and the von Weizsäcker term provides a rigorous upper bound to the total kinetic energy of noninteracting particles in one dimension [2].

The gradient expansion becomes exact in the slowly varying limit where s is small [$s \equiv |\vec{\nabla}\rho|/2k_F\rho$, $k_F \equiv (3\pi^2\rho)^{1/3}$] and the von Weizsäcker functional is exact [1,2,26–28] in the limit of rapidly varying electron densities with large s values. Taking these limits into account, DePristo and Kress [11] constructed a smooth [4/3]-Padé approximant [29],

$$t_S^{[4/3]}(\vec{r}) = t_S^{(0)}(\vec{r})\frac{1+0.95x+a_2x^2+a_3x^3+9b_3x^4}{1-0.05x+b_2x^2+b_3x^3}, \tag{8}$$

where $x = t_S^{(2)}/t_S^{(0)}$, and $t_S^{(0)}$ and $t_S^{(2)}$ are defined in Eqs. (3) and (4). Of the eight parameters in the Padé approximant above, four were determined from physical limits. The other four parameters (a_2, a_3, b_2, and b_3) were determined by fitting the functional to the total kinetic energies of inert gas elements [11]. (The fitted parameters obtained in Ref. [11] are $a_2 = 14.281\,11$, $a_3 = -19.579\,62$, $b_2 = 9.998\,02$, and $b_3 = 2.960\,85$.) This method, along with the local truncation scheme described above, provides the best results [2] for the noninteracting kinetic energy of atomic systems.

Another class of functionals, based on the linear-response theory, has been actively studied by many groups [12,13,16,17]. These functionals depend on averaged values of the density of the system, which are significant for certain metallic and extended systems. However, an average density has little physical significance [12] for molecular systems, due to the rapidly varying nature of the electron density in molecules. As a result, this method has found applications in metallic and extended systems [17]. In this paper, we study molecular systems and hence do not discuss the merits of these functionals.

III. RESULTS AND DISCUSSION

To study the effectiveness of the functionals discussed in the preceding section, we perform Kohn-Sham calculations on a number of small molecules selected from the G2 set [20], using uncontracted $6-311+G(3df,2p)$ basis sets. We obtain the electron densities and the associated ''exact'' noninteracting kinetic energies from the Kohn-Sham orbitals. The self-consistent densities are then used to calculate approximate kinetic energies with the above-described functionals. In all cases, the Kohn-Sham calculations are performed with the Becke 1988 exchange [30] functional and the Perdew-Wang 1991 (PW91) correlation [31] functional. Our implementation of the approximate kinetic-energy functionals is based on a development version of the GAUSSIAN [32] suite of programs.

The functionals depending on the Laplacian of the electron density sometimes yield slowly decaying and oscillating approximations to the noninteracting kinetic-energy density. In these cases, it is necessary to employ large grids in order to integrate the kinetic energy density accurately. A 400-point Euler-Macloren quadrature for the radial integration [33,34] and 5000-point Gauss-Legendre quadrature [35] for the angular integration were used in our work. This grid results in integrations precise to within 1 mHartree.

A. Total noninteracting kinetic energies

In Tables I and II, we present results for the total noninteracting kinetic energy. In Table I, we see that while the Thomas-Fermi functional yields large errors for molecules and atoms, these results are improved by the inclusion of the second- and fourth-order gradient corrections. From Table I, it is also clear that the nth-order local truncation scheme interpolates between the gradient expansions up to nth-order. As a consequence, this functional provides improved results at the fourth-order level compared to $T_S^{(024)}$.

Table II shows that the von Weizsäcker functional always yields a lower bound to the total noninteracting kinetic energy, which is consistent with the discussion in Ref. [2].

TABLE I. Exact noninteracting kinetic energies and errors in approximate kinetic energies. In all calculations, converged Kohn-Sham orbitals and densities obtained within the Becke88-PW91 approximation are employed.

	Exact	$T_S^{(0)}$[a]	$T_S^{(02)}$[b]	$T_S^{(024)}$[c]	$T_S^{\mathrm{PG}_{02}}$[d]	$T_S^{\mathrm{PG}_{024}}$[e]
H	0.500	−0.044	0.011	0.032	−0.019	0.015
B	24.548	−2.506	−0.058	0.476	−1.287	−0.093
C	37.714	−3.731	−0.154	0.600	−1.949	−0.064
N	54.428	−4.993	−0.097	0.904	−2.554	0.193
O	74.867	−6.990	−0.546	0.765	−3.778	−0.772
F	99.485	−9.093	−0.933	0.659	−5.025	−0.464
H_2	1.151	−0.142	−0.014	0.033	−0.084	−0.006
HF	100.169	−9.016	−0.920	0.639	−4.979	−0.456
H_2O	76.171	−7.074	−0.692	0.565	−3.893	−0.317
CH_4	40.317	−3.773	−0.140	0.619	−1.967	0.086
NH_3	56.326	−5.292	−0.400	0.587	−2.856	−0.106
BF_3	323.678	−29.052	−2.641	2.454	−15.869	−1.114
CN	92.573	−8.940	−0.687	0.978	−4.823	−0.181
CO	112.877	−10.694	−0.911	1.036	−5.813	−0.322
F_2	199.023	−18.367	−2.201	0.925	−10.301	−1.259
HCN	92.982	−8.925	−0.658	1.008	−4.802	−0.150
N_2	109.013	−10.487	−0.916	0.999	−5.711	−0.333
NO	129.563	−12.342	−1.240	0.962	−6.803	−0.574
O_2	149.834	−14.186	−1.527	0.965	−7.870	−0.772
O_3	224.697	−21.636	−2.699	1.028	−12.183	−1.500
Ave. Abs.[f]		9.364	0.872	0.812	5.128	0.439

[a] Thomas-Fermi approximation.

[b] Second-order gradient approximation.

[c] Fourth-order gradient approximation.

[d] Second-order locally truncated scheme.

[e] Fourth-order locally truncated scheme.

[f] Average of the absolute errors.

However, a comparison of the results obtained using the von Weizsäcker functional with those obtained using the Thomas-Fermi functional (in Table I) leads to the conclusion that while the von Weizsäcker functional is more accurate for systems with a smaller numbers of electrons, the Thomas-Fermi functional is more accurate for atomic systems with larger numbers of electrons. This is consistent with the discussion in Ref. [37] where it is shown that the Thomas-Fermi functional is exact for atoms in the limit of large atomic numbers. Furthermore, for all the cases studied here, the sum of Thomas-Fermi and von Weizsäcker functionals, i.e., T_S^{TFW} in Table II, yields an upper bound to the noninteracting kinetic energy. While it is rigorously shown [2] that this is true in one dimension, our results seem to indicate that it may be true for Coulomb systems in three dimensions as well. Furthermore, the functional $T_S^{\mathrm{vW}+C(N)\mathrm{TF}}$ [2,14,15] interpolates between the von Weizsäcker functional and the T_S^{TFW} functional. The interpolation is done using a particle-number-dependent function $C(N)$ which is obtained [2,14] by modifying the derivation of the Thomas-Fermi functional to account for a finite number of particles. This yields [14]

$$C(N)=\left(1-\frac{2}{N}\right)\left[1-\frac{a_o}{N^{1/3}}+\frac{a_1}{N^{2/3}}\right], \tag{9}$$

with $a_o=1.314$ and $a_1=0.0021$ [14]. It is clear from Table II that while $T_S^{\mathrm{vW}+C(N)\mathrm{TF}}$ is reasonably accurate for atoms and singly bonded molecules, the errors encountered for F_2, BF_3, and for multiply-bonded systems are, however, very large.

In Table II, we also present results obtained from the Baltin functional [24]. This functional has been the object of great interest [10,12,13]; however, to the best of our knowledge, this is the first paper in which the Baltin functional has been applied to molecules. For all the cases studied, the Baltin functional has always overshot the exact T_S (see Table II).

The [4/3]-Padé approximant, which interpolates between the second-order gradient expansion and the von Weizsäcker functional, yields noninteracting kinetic energies with an accuracy similar to that of the second-order gradient expansion (Table II). Hence, it may be concluded that most of the s values sampled during a total noninteracting kinetic energy calculation for atoms and molecules are not, in fact, within the large-s region where the von Weizsäcker functional is considered accurate.

It is interesting to discuss the differences between the [4/3]-Padé approximant and the Baltin functional. Both functionals have the correct behavior for large and for zero s [11,24]. However, Table II indicates that the Padé approxi-

TABLE II. Exact noninteracting kinetic energies and errors in approximate kinetic energies. In all calculations, converged Kohn-Sham orbitals and densities obtained within the Becke88-PW91 approximation are employed.

	Exact	T_S^{vW}[a]	T_S^{TFW}[b]	$T_S^{\mathrm{vW}+C(N)\mathrm{TF}}$[c]	T_S^{B}[d]	$T_S^{[4/3]}$[e]
H	0.500	−0.000	0.456	0.142	0.527	0.012
B	24.548	−2.521	19.521	0.551	22.487	−0.361
C	37.714	−5.517	28.465	0.770	32.536	−0.483
N	54.428	−10.364	39.070	0.711	44.181	−0.399
O	74.867	−16.872	51.005	0.617	57.332	−0.717
F	99.485	−26.043	64.349	−0.116	71.673	−0.843
H_2	1.151	−0.000	1.009	0.000	1.182	−0.017
HF	100.169	−27.301	63.852	1.179	70.906	−0.733
H_2O	76.171	−18.731	50.367	2.858	56.394	−0.707
CH_4	40.317	−7.615	28.929	3.803	32.847	−0.345
NH_3	56.326	−12.302	38.731	3.643	43.688	−0.548
BF_3	323.678	−85.981	208.645	75.968	232.094	−2.280
CN	92.573	−18.298	65.335	12.949	74.104	−1.100
CO	112.877	−24.825	77.358	15.041	87.205	−1.201
F_2	199.023	−53.527	127.129	26.591	141.419	−1.907
HCN	92.982	−18.583	65.474	14.211	74.223	−1.047
N_2	109.013	−22.879	75.647	15.560	85.583	−1.282
NO	129.563	−29.646	87.574	17.852	98.577	−1.484
O_2	149.834	−35.906	99.741	20.932	111.915	−1.697
O_3	224.697	−54.268	148.794	47.125	167.004	−2.884
Ave. Abs.[f]		23.559	67.073	13.031	75.294	1.002

[a] von Weizsäcker.

[b] Thomas-Fermi plus von Weizsäcker.

[c] von Weizsäcker plus particle-number-dependent parameter times Thomas-Fermi. See text for details.

[d] Baltin's functional.

[e] [4/3]-Padé approximant.

[f] Average of the absolute errors.

mant provides significantly better results. This would indicate that the Padé approximant, for most systems considered here, models the intermediate s behavior better than the Baltin functional. A plausible explanation for this may be found in Fig. 1, where we study the enhancement factor $F(s(\vec{r}))$ of various functionals as a function of s. $F(s(\vec{r}))$ is defined by the relation

$$T_S^{\mathrm{app}}[\rho]=\int d^3r\, t_S^{(0)}(\vec{r})F^{\mathrm{app}}(s(\vec{r})). \tag{10}$$

In this equation, T_S^{app} stands for the particular functional of interest. Note that in general the enhancement factor may be a function of other variables, such as the reduced Laplacian of the density, in addition to being a function of s. The Baltin enhancement factor is oscillatory for small values of s (<0.25), but as s increases, it very quickly approaches the enhancement factor of the von Weizsäcker functional. The enhancement factor of the Padé approximant, on the other hand, remains close to the enhancement factor of the second-order gradient expansion and in fact shows a dip in the physically important range of s [36]. The functional $T_S^{\mathrm{vW}+C(N)\mathrm{TF}}$ (plotted setting the number of electrons at $N=15$) approaches the von Weizsäcker functional for large s. However, it does not yield the correct Thomas-Fermi limit for small s. The Padé approximant remains close to the gradient expansion for a larger range of s values compared to the other functionals in the figure, and this is the reason for the greater accuracy of the Padé approximant. Although, it is not obvious from the figure, the [4/3]-Padé approximant does approach the von Weizsäcker results as $s\rightarrow\infty$. This, of course, is not the case for the nth-order gradient expansion.

To summarize, the best results for the total noninteracting kinetic energy are obtained from the locally truncated fourth-order gradient approximation, the second-order and the fourth-order gradient expansions, and the [4/3]-Padé approximant. Note that a finite-order gradient expansion has the incorrect asymptotic behavior for large s, since it does not approach the von Weizsäcker functional in this limit. The success of the gradient expansion, however, indicates that the large s behavior may have little or no consequence in the calculation of total noninteracting kinetic energies. The [4/3]-Padé approximant also provides results that are of similar accuracy as those obtained from the gradient expansions and the local truncation scheme. Another interesting fact to be noted from Tables I and II is that the particle-number-dependent functional $T_S^{\mathrm{vW}+C(N)\mathrm{TF}}$ provides better results for total noninteracting kinetic energies than the corre-

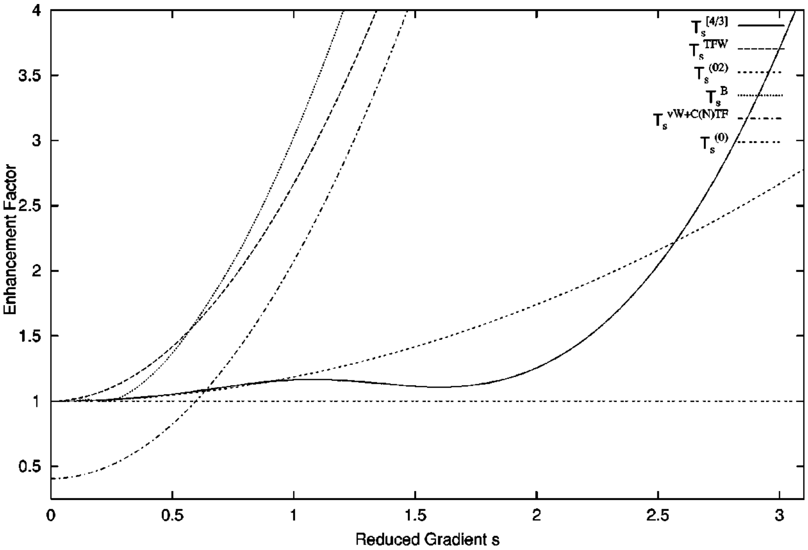

FIG. 1. Enhancement factors for various kinetic-energy functionals.

sponding functionals that are independent of particle number (i.e., T_S^{TFW}). The particle-number-dependent functionals, however, often have the big disadvantage of being size inconsistent (as is the case for $T_S^{\mathrm{vW}+C(N)\mathrm{TF}}$), i.e., the noninteracting kinetic energy of two isolated subsystems A and B depends on whether one calculation is performed for $A+B$ or two calculations are performed for A and B separately.

It is important to note that the above results are obtained when accurate, converged densities are inserted into the functionals. This does not imply that the functionals themselves yield satisfactory results when used in a self-consistent manner.

B. Atomization energies

In applications, the calculation of energy changes upon chemical transformations is of great importance. Therefore, we use approximate and exact noninteracting kinetic energies to study noninteracting kinetic-energy contributions to atomization energies.

Unlike in the case of total kinetic energies, the addition of gradient corrections to the Thomas-Fermi ansatz did not improve the results for atomization energies. In fact, in most cases inclusion of even the second-order gradient correction worsens the results compared to the Thomas-Fermi functional (Table III). The second-order local truncation scheme, though, improves on the full second-order (i.e., $T_S^{(02)}$) result. Similarly, inclusion of the fourth-order terms with local truncation criterion is found to improve on the full fourth-order expansion (i.e., $T_S^{(024)}$). The local truncation scheme interpolates between the Thomas-Fermi and corresponding nth-order gradient expansion (as in the case of total energies). The gradient expansion itself yields progressively poorer results. These findings are to be contrasted with calculations performed for slowly varying systems [38,39] where gradient expansions of increasing order systematically improve the results.

The von Weizsäcker functional does not yield a lower bound to the change in the noninteracting kinetic energy upon atomization (as it did for the total noninteracting kinetic energies), and the T_S^{TFW} functional does not provide an upper bound. Further, the $T_S^{\mathrm{vW}+C(N)\mathrm{TF}}$ functional does not interpolate between the von Weizsäcker and T_S^{TFW} results and provides results that are worse than those obtained from T_S^{vW} or from. T_S^{TFW} An explanation for this might be that the particle-number-dependent factor, $C(N)$ in $T_S^{\mathrm{vW}+C(N)\mathrm{TF}}$, was originally derived for atomic systems [14]. The Baltin functional provides results that were comparable to those provided by the von Weizsäcker and T_S^{TFW} functionals. The [4/3]-Padé approximant yields results comparable to the Thomas-Fermi and local truncation schemes. As in the case of the noninteracting kinetic energy, our calculations indicate that the values of s sampled during the atomization energy calculation are outside the region where the von Weizsäcker functional is considered accurate.

To summarize, the results, shown in Table III, are not as encouraging as those for the total noninteracting kinetic energies in Tables I and II. None of the methods tested is accurate enough for chemical applications. The best results are obtained with the Thomas-Fermi functional, the [4/3]-Padé approximant, and the locally truncated second-order expansion. For ‘‘noncongested’’ [40] molecules such as HF, H_2O, and CH_4, the Thomas-Fermi or the locally truncated gradient expansions provided encouraging results. In these systems the orbital nodality problem [40], which causes density functionals to fail badly, is less severe compared to typical multiply bonded systems.

C. Equilibrium properties and behavior with change in bond length

To illustrate the behavior of the various kinetic-energy functionals upon changes in bond length, we calculated approximate and exact kinetic energies using the converged Kohn-Sham densities at various bond lengths. In Fig. 2, we present results for N_2. (A similar behavior was found for other multiply bonded molecules, such as NO, hence only N_2 is presented.) Note that all the curves are shifted such that they have the same kinetic energy at the equilibrium bond

TABLE III. Exact atomization kinetic energies and errors in approximate atomization kinetic energies. All calculations use converged Kohn-Sham orbitals and densities within the Becke88-PW91 approximation. Abbreviations as in Tables I and II.

	Exact	$T_S^{(0)}$	$T_S^{(02)}$	$T_S^{(024)}$	$T_S^{\mathrm{PG}_{02}}$	$T_S^{\mathrm{PG}_{024}}$
H_2	−0.150	0.053	0.036	0.031	0.046	0.036
HF	−0.183	−0.121	−0.002	0.052	−0.065	0.011
H_2O	−0.304	−0.004	0.168	0.264	0.077	0.183
CH_4	−0.602	−0.136	0.031	0.109	−0.058	0.043
NH_3	−0.397	0.166	0.337	0.413	0.245	0.350
BF_3	−0.674	−0.733	−0.216	−0.001	−0.493	−0.171
CN	−0.431	0.216	0.436	0.526	0.320	0.447
CO	−0.297	−0.027	0.211	0.468	0.086	0.227
F_2	−0.053	0.181	0.336	0.393	0.251	0.340
HCN	−0.340	0.156	0.419	0.528	0.280	0.433
N_2	−0.157	0.501	0.723	0.809	0.604	0.731
NO	−0.268	0.360	0.598	0.707	0.472	0.608
O_2	−0.100	0.206	0.436	0.565	0.314	0.444
O_3	−0.097	0.667	1.062	1.267	0.850	1.076
Ave. Abs.		0.252	0.358	0.442	0.297	0.364

	Exact	T_s^{vW}	T_S^{TFW}	$T_S^{\mathrm{vW}+C(N)\mathrm{TF}}$	T_S^{B}	$T_S^{[4/3]}$
H_2	−0.150	0.000	−0.097	0.284	−0.128	0.041
HF	−0.183	1.258	0.953	−1.153	1.294	−0.098
H_2O	−0.304	1.859	1.551	−1.957	1.991	0.015
CH_4	−0.602	2.098	1.360	−2.464	1.796	−0.089
NH_3	−0.397	1.938	1.707	−2.504	2.073	0.185
BF_3	−0.674	5.330	3.923	−75.766	5.412	−0.610
CN	−0.431	2.416	2.201	−11.468	2.613	0.217
CO	−0.297	2.436	2.112	−13.655	2.663	0.001
F_2	−0.053	1.440	1.568	−26.824	1.927	0.222
HCN	−0.340	2.701	2.518	−12.588	3.021	0.177
N_2	−0.157	2.150	2.493	−14.138	2.778	0.483
NO	−0.268	2.410	2.502	−16.524	2.935	0.368
O_2	−0.100	2.163	2.269	−19.698	2.749	0.263
O_3	−0.097	3.653	4.222	−45.276	4.991	0.733
Ave. Abs.		2.275	2.105	17.449	2.597	0.250

length (which is the point where all the curves in the figure intersect). The gradient approximations (including the local truncation schemes) appear to reproduce the general behavior of the exact curve to a reasonable degree. The slopes of these approximate curves at equilibrium, are, however, off by at least 25%.

We then use the approximate kinetic energies calculated above to get the approximate total energies at the respective geometries. This is done by replacing the exact noninteracting kinetic energies with approximate kinetic energies in the expression for the Kohn-Sham ground-state energy. It is found that the total energy calculated using the Thomas-Fermi kinetic-energy functional always decreases with increasing internuclear distances. This is consistent with the nonbinding theorem [41,42,1]. Furthermore, none of the functionals has a local minimum at or close to the equilibrium geometry. The asymptotic behavior for large internuclear distances is also found to be not in agreement with the exact results, which further substantiates the unsatisfactory atomization-energy results in Table III. We conclude that equilibrium properties (such as force constants) obtained using approximate functionals may be inaccurate.

IV. CONCLUSIONS

In this paper, we examined the potential of various kinetic-energy functionals for providing chemically relevant results for molecular systems. Among other functionals, we have considered the gradient expansion, the Pearson-Gordon local tuncation scheme, the von Weizsäcker functional, the Baltin partial resummation of the gradient expansion, and the [4/3]-Padé approximation of Ref. [11].

We found that while the total noninteracting kinetic energy of atoms and molecules may be estimated with reasonable accuracy, the differential kinetic energy of processes such as atomization is not well approximated by current functionals for T_S. Equilibrium properties, such as force constants and equilibrium geometries are far from being considered chemically relevant.

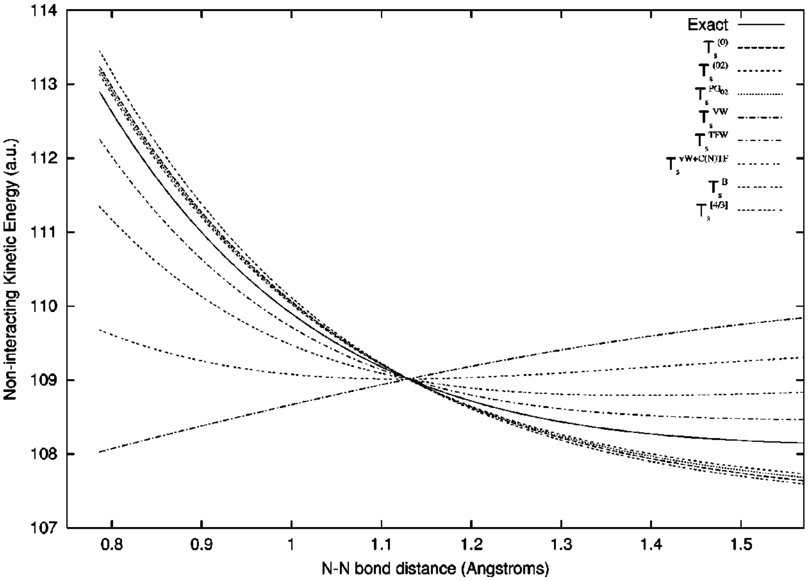

FIG. 2. Kinetic energy of N_2 as a function of the bond distance.

For the case of the total noninteracting kinetic energy, the best results were obtained with the locally truncated fourth-order gradient expansion, the second- and fourth-order gradient expansion, and the [4/3]-Padé approximants. These results indicate that the asymptotic behavior of a functional for large s is not very significant in calculating the noninteracting kinetic energy because on average the s values of atoms and molecules are not very large. Hence, to further improve the performance of these functionals (in the calculation of total energies), it is necessary to understand the behavior of the noninteracting kinetic energy for intermediate values of s. A good starting point for this might be the [4/3]-Padé approximant or the local truncation scheme in which the intermediate-s behavior is determined empirically.

The best results for atomization energies were obtained from the Thomas-Fermi functional, the [4/3]-Padé approximant, and the second-order local truncation scheme. Again, the similarity of the results obtained from the Thomas-Fermi functional and the [4/3]-Padé approximant indicate that, as in the case of the total noninteracting kinetic energy, the large-s limit (where the von Weizsäcker functional is considered [26,2,27,28,1] exact) is not significant. Hence, further improvement in the atomization results may be expected from a better understanding of the behavior of the noninteracting kinetic energy for intermediate values of s. Our calculations have been carried out in a non-self-consistent manner. Self-consistent calculations would suffer from the severe deficiency of missing shell structure [2] and are thus likely to produce even worse results than those reported here.

Recently [43], a method has been developed, in which a linear combination of a variety of functionals is considered and the coefficients of this linear combination are optimized to fit a data set containing exact kinetic-energy values. This method is interesting since a family of functionals may now be developed in the form

$$T_s[\rho]=\int d\vec{r}[\Theta(\mathbf{s}-\mathbf{s_0})t_{s,1}(\vec{r})+\Theta(\mathbf{s_0}-\mathbf{s})t_{s,2}(\vec{r})], \quad (11)$$

where $\Theta(\mathbf{s}-\mathbf{s_0})$ is a smooth approximation to the step function. $\{t_{s,i}(\vec{r})\}$ may be chosen such that $t_{s,i}$ most accurately describes the behavior in the relevant range of s. [For the expression in Eq. (11), the functional $t_{s,1}$ may be considered accurate in the region $s\in[0,s_0]$, while the functional $t_{s,2}$ may be accurate in $s\in[s_0,\infty)$.] This form may, of course, be generalized to include more than two functionals. Fitting functionals in this fashion may lead to further insight into the correct behavior of $T_s[\rho]$ for intermediate s.

The accuracy of the Thomas-Fermi functional and the second-order gradient expansion in the near-homogeneous limit, may allow their use in methods involving ''partitioning schemes'' for complex systems [44,45]. Investigating the use of the [4/3]-Padé approximants in such partitioning methods may also lead to fruitful results.

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