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Toward an All-Around Semilocal Potential for Electronic Exchange

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Abstract: We test local and semilocal approximations of the exchange potential for a variety of systems including atoms, molecules, and atomic chains. In particular, we focus on a recent universal extension of the Becke−Johnson exchange potential [Räsänen, E.; Pittalis, S.; Proetto, C. R. *J. Chem. Phys.* **2010**, *132*, 044112]. It is shown that when this potential is used together with the Becke−Roussel approximation to the Slater potential [Becke, A. D.; Roussel, M. R. *Phys. Rev. A* **1989**, *39*, 3761−3767], a good overall agreement is obtained with experimental and numerically exact results for several systems, and with a moderate computational cost. Thus, this approximation is a very promising candidate in the quest for a simple and all-around semilocal potential.

1. Introduction

Density-functional theory[1,2] (DFT) has become the standard tool both in quantum chemistry and in atomic, molecular, and solid-state physics. The practical applicability of DFT crucially depends on the approximation for the exchange-correlation (xc) energy functional. The "Jacob's ladder" of functionals developed in the past few decades[3] has posed the following well-known problem: by climbing successive rungs of the ladder, one increases the accuracy of the functional, but one also increases substantially the computational burden of the method. Finding a balance between accuracy and efficiency, together with *universality* (which

is the ideal ability to deal equally well with any kind of system), has remained a major challenge in DFT.

As the simplest density functionals, occupying the first two rungs of Jacob's ladder, the local density approximation (LDA) and generalized-gradient approximations (GGA) are numerically efficient and surprisingly accurate for many (strongly inhomogeneous) systems. However, both of these families of functionals exhibit well-known failures in the calculation of, e.g., band gaps of semiconductors and insulators,[4] the response to electric fields,[5] etc. The problems are particularly dramatic in systems where long-range interactions play a crucial role, i.e., elongated molecules and atomic chains.[6−13] The main origin for these errors is the wrong (exponential) asymptotic behavior and the lack of derivative discontinuity in the xc potential.

Climbing the ladder further, the optimized-effective-potential (OEP) method[14−16] or its simplification within the Krieger−Li−Iafrate (KLI) approximation[17] provide, in principle, access to the *exact* exchange energy and potential within DFT. Thus, as long as the electronic correlation is not significant, OEP and KLI are free from the failures mentioned above. However, as nonlocal orbital functionals,

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they are computationally demanding and therefore usable only for systems containing a small number of particles.

To bridge the gap between the GGA and OEP, meta-GGAs[18,19] are appealing candidates. They supplement the GGA by further semilocal information through the kinetic-energy density and/or the Laplacian of the density, and, in some cases, also through the paramagnetic current density. Recently, Räsänen, Pittalis, and Proetto[20] (RPP) developed a meta-GGA for the exchange part of the xc potential. The RPP potential introduces a number of important constraints and features (see below) and performs well for, e.g., non-Coulombic systems and atomic chains. It is based on the Becke−Johnson (BJ) potential[21]—a simple meta-GGA close to the OEP accuracy for atoms—but, in contrast to BJ, the RPP potential is fully gauge-invariant, exact for any one-particle system, and has the correct asymptotic behavior for any N-particle system.

Also, other modifications to the BJ potential have been suggested to improve the performance for atomic chains[22] and band gaps.[23] In fact, the latter modification[23] allows the calculation of band gaps of semiconductors and insulators with an error on the same order of GW calculations, but at a very small fraction of the GW computational time.

In this paper, we test the RPP potential,[20] used together with the Becke−Roussel (BR) approximation to the Slater potential,[24] for a large variety of systems. We compare this approximation to the BJ one, also complemented by the BR potential. In order to allow for a comparison to experimental reference data, we have added to the above exchange potentials the correlation within the LDA. We compare the results also against the LB94 potential of van Leeuwen and Baerends[25] (a GGA with correct asymptotic behavior also including correlation). Moreover, for completeness, we include results calculated with standard LDA and GGA functionals. As a reference, we use experimental or high-quality ab initio data. In some cases, the performance of the exchange potentials alone, i.e., without the addition of correlation, is compared to the exact-exchange OEP results. The combination of RPP and BR potentials is found to yield the best overall performance of the tested approximations, and thus it provides a promising step toward an all-around semilocal exchange potential in DFT.

2. Theory

2.1. Exact Exchange. In a majority of atomic, molecular, and solid-state systems, the electronic exchange gives, in absolute terms, a much larger contribution to (most) observables than the correlation. Therefore, in practical applications, the exchange is the most important term to be approximated in the functional. The exact exchange energy in Hartree atomic units (au) is written as

$$E_x[\rho_\sigma] = -\frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{j,k=1}^{N_\sigma} \int d^3 r \int d^3 r' \frac{\varphi_{j\sigma}^*(\mathbf{r})\, \varphi_{k\sigma}^*(\mathbf{r'})\, \varphi_{j\sigma}(\mathbf{r'})\, \varphi_{k\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r'}|} \quad (1)$$

and its functional derivative gives the Kohn−Sham (KS) exchange potential as $v_{x\sigma}(\mathbf{r}) = \delta E_x/\delta\rho_\sigma(\mathbf{r})$. These quantities

can be rigorously calculated with the OEP method[14−16] through an integral equation that has to be solved together with the KS equations.

At this point, it is useful to write the (KS) exchange potential as a sum

$$
\begin{aligned}
v_{x\sigma}(\mathbf{r}) &= v_{x\sigma}^{SL}(\mathbf{r}) + \Delta v_{x\sigma}^{OEP}(\mathbf{r}) \\
&= v_{x\sigma}^{SL}(\mathbf{r}) + \Delta v_{x\sigma}^{KLI}(\mathbf{r}) + \Delta v_{x\sigma}^{OS}(\mathbf{r})
\end{aligned}
\quad (2)
$$

where

$$v_{x\sigma}^{SL}(\mathbf{r}) = -\sum_{j,k=1}^{N_\sigma} \int d^3 r' \frac{\varphi_{j\sigma}^*(\mathbf{r})\, \varphi_{k\sigma}^*(\mathbf{r'})\, \varphi_{j\sigma}(\mathbf{r'})\, \varphi_{k\sigma}(\mathbf{r})}{\rho_\sigma(\mathbf{r})|\mathbf{r} - \mathbf{r'}|} \quad (3)$$

is the Slater potential, i.e., the average of the Fock potential felt by the electrons, and $\Delta v_{x\sigma}^{OEP}(\mathbf{r})$ is the exact (OEP) contribution,[14−16] which can be decomposed into the Krieger−Li−Iafrate[17] (KLI) part and the orbital shifts. Apart from, e.g., atomic chains,[6] the orbital shifts in a ground-state calculation are usually of minor importance and therefore neglected, leading to so-called KLI approximation. This relieves the computational burden of solving the integral equation, but the tedious integrals in the Slater potential are still to be calculated. Therefore, even within the KLI approximation, the efficiency of an OEP calculation is far from that of semilocal functionals.

2.2. Becke−Johnson Potential. The BJ potential[21] is a simple approximation to the OEP contribution in eq 2:

$$\Delta v_{x\sigma}^{OEP}(\mathbf{r}) \approx \Delta v_{x\sigma}^{BJ}(\mathbf{r}) = C_{\Delta v}\sqrt{\frac{\tau_\sigma(\mathbf{r})}{\rho_\sigma(\mathbf{r})}} \quad (4)$$

where

$$\tau_\sigma(\mathbf{r}) = \sum_{j=1}^{N_\sigma} |\nabla \varphi_{j\sigma}(\mathbf{r})|^2 \quad (5)$$

is (twice) the spin-dependent kinetic-energy density, and $C_{\Delta v} = \sqrt{5/(12\pi^2)}$. The BJ potential is exact for the hydrogen atom and for the homogeneous electron gas, and regarding quantum chemistry applications, it has several beneficial properties. First, it yields the atomic step structure in the exchange potential (which was the main motivation for the approximation) very accurately.[21] Second, it has the derivative discontinuity for fractional particle numbers.[22]

To improve the numerical efficiency of this potential, one often also replaces the Slater potential $v_{x\sigma}^{SL}(\mathbf{r})$ with the Becke−Roussel potential.[24] This is again a meta-GGA potential, written in terms of $\nabla^2 \rho_\sigma$ and of τ_σ, that reproduces to a very high precision the Slater potential for atoms.

2.3. Universal Extension to Becke−Johnson. The main limitations of the BJ potential are that it is not gauge-invariant and that it is not exact for *all* one-particle systems. Both limitations were recently removed in the extension by RPP,[20] which proposed the form

$$\Delta v_{x\sigma}^{OEP}(\mathbf{r}) \approx \Delta v_{x\sigma}^{RPP}(\mathbf{r}) = C_{\Delta v}\sqrt{\frac{D_\sigma(\mathbf{r})}{\rho_\sigma(\mathbf{r})}} \quad (6)$$

where

$$D_\sigma(\mathbf{r}) = \tau_\sigma(\mathbf{r}) - \frac{1}{4}\frac{|\nabla\rho_\sigma(\mathbf{r})|^2}{\rho_\sigma(\mathbf{r})} - \frac{|\mathbf{j}_{p\sigma}(\mathbf{r})|^2}{\rho_\sigma(\mathbf{r})} \tag{7}$$

describes the local curvature of the exchange (Fermi) hole.[26] This quantity has already been useful in the derivation of several functionals[24,27−31] and is the key ingredient of the electron-localization function,[32−34] a standard tool used to analyze bonding in electronic systems. Finally, the spin-dependent paramagnetic current density is defined as

$$\mathbf{j}_{p\sigma}(\mathbf{r}) = \frac{1}{2i}\sum_{j=1}^{N_\sigma}\{\varphi_{j\sigma}^*(\mathbf{r})[\nabla\varphi_{j\sigma}(\mathbf{r})] - [\nabla\varphi_{j\sigma}^*(\mathbf{r})]\varphi_{j\sigma}(\mathbf{r})\} \tag{8}$$

The RPP approximation is gauge-invariant, and it is exact for *all* one-particle systems. Furthermore, it has a correct asymptotic limit for finite N-electron systems (except on nodal surfaces of the highest occupied orbitals[35,36]). The universality of the approach, whose principles have also been shown to work in two dimensions,[37] is reflected in a resulting potential that can be applied reasonably well to any kind of system. For example, the RPP potential has been seen to reproduce well the KLI potential in hydrogen chains in electric fields and in Hooke's atoms subject to magnetic fields.[20] The present study aims at further evaluating the capability of this approximation for atoms, small molecules, and atomic chains.

3. Numerical Procedure

The evaluation of the Slater part in the BJ[21] and RPP[20] potentials is computationally more demanding than the evaluation of the correction terms $\Delta v_{x\sigma}^{BJ}$ and $\Delta v_{x\sigma}^{RPP}$. Nevertheless, as already pointed out by Becke and Johnson,[21] it is possible to approximate the Slater part by using the semilocal Becke−Roussel (BR) exchange-energy functional.[24] In this way, the cost of evaluating the full BJ and RPP potentials becomes similar to that of a usual LDA or GGA. To avoid any ambiguity, we will hereafter denote the BJ and RPP potentials, where the Slater part was replaced by the BR potential, as BJBR and RPPBR, respectively.

When using experimental results as a reference, it is necessary to add a correlation contribution to the BJBR and RPPBR potentials for a proper comparison. We use the correlation in the LDA level within the Perdew−Wang[38] (PW) form. The results are compared also to the standard LDA—with the PW parametrization for the correlation part; the GGA of Perdew, Burke, and Ernzerhof[39] (PBE); and the GGA of van Leeuwen and Baerends[25] (LB94)—again using the PW parametrization for the LDA part of the potential. In all cases, we have applied the potentials self-consistently in the KS-DFT framework. Although, in the case of PBE, the correlation functional used is not the same as in the other cases, we expect this fact to result in negligible differences in the quantities and systems studied in this work.

In the case of atoms and hydrogen chains, calculations are also performed using *exchange-only* potentials. Results are then compared with exact-exchange OEP data available in the literature. Besides the BJBR and RPPBR potentials, we also performed these calculations using the exchange part of the LDA (xLDA) and of the PBE (xPBE).

It is important to bear in mind that BJ, RPP, and LB94 are such approximations to the exchange (or xc) potential that are not functional derivatives of corresponding exchange (or xc) *energies*.[40] Here, we focus on fairly standard quantities that may be accessed without the computation of total energies. These quantities include ionization potentials and electronic affinities of atoms, ionization potentials and dipole polarizabilities of small molecules, and longitudinal polarizabilities of hydrogen chains. We believe that these benchmarks provide us with a fairly complete view on the properties of different approximations considered in this work.

All of the single-atom calculations are performed with the APE code,[41] while molecules and atomic chains are dealt with the octopus code.[42] In the latter case, the electron−ion interaction is handled through norm-conserving pseudopotentials generated with APE for each functional and approximation studied in this work.

4. Results

4.1. Atoms. First, we consider single atoms and focus on the ionization energies and electron affinities (see Table 1). There are several ways to estimate these quantities within DFT. The most direct one is to calculate the differences in total energy of both the neutral atom and its anion and cation, respectively. In this way, traditional LDA and GGA functionals usually yield quite good ionization potentials. Electron affinities are more complicated as often LDAs and GGAs fail to bind the extra electron.

The other approach, the one used in this work, is to look at the KS eigenenergy of the highest occupied atomic orbital (HOMO), which should be equal to the negative of the ionization potential. The electron affinity is computed simply from the ionization potential of the respective anion. This method samples much better the quality of the potential, and it is particularly sensitive to the asymptotic description of the potential.

As known from previous studies,[25] the LDA and PBE perform poorly for the ionization potential: the mean absolute error (last row of Table 1) is larger than 40% for this set of atoms. The result indicates the crucial role of the correct asymptotic behavior in the exchange potential. The decay of the xc potential is properly described by the LB94 potential showing good performance. For the same reason, good results have been obtained also with KLI-CS—a combination of KLI[17] for the exchange and the Colle−Salvetti[43] functional for the correlation—as reported by Grabo and Gross.[44] It seems that RPPBR-PW is slightly more accurate than the original BJBR-PW potential. When compared against exact-exchange OEP results,[45] xLDA and xPBE perform poorly, while BJBR and RPPBR perform better, the latter again being more accurate.

As noted already by Becke and Johnson,[21] the BJ exchange potential goes asymptotically to a finite (nonzero) constant. In principle, this constant only redefines the zero of orbital energy and should have no implication in the quality of the results, but it has to be taken into account when computing the ionization potential. This can be done by subtracting the

Table 1. Ionization Potentials from the Highest Occupied Kohn−Sham Orbital (in au)[a]

atom	xLDA	xPBE	BJBR	RPPBR	OEP[b]	LDA	PBE	LB94	KLI-CS[c]	BJBR-PW	RPPBR-PW	expt.[d]
He	0.517	0.553	0.857	0.924	0.918	0.570	0.585	0.851	0.945	0.922	0.982	0.903
Li	0.100	0.109	0.254	0.183	0.196	0.116	0.111	0.193	0.200	0.276	0.201	0.198
Be	0.170	0.182	0.355	0.300	0.309	0.206	0.201	0.321	0.329	0.401	0.338	0.343
B	0.120	0.128	0.279	0.226		0.151	0.143	0.296	0.328	0.321	0.260	0.305
C	0.196	0.204	0.399	0.332		0.227	0.218	0.401	0.448	0.440	0.366	0.414
N	0.276	0.285	0.526	0.451	0.571	0.309	0.297	0.510	0.579	0.567	0.486	0.534
O	0.210	0.224	0.391	0.383		0.272	0.266	0.516	0.559	0.472	0.450	0.500
F	0.326	0.339	0.564	0.526		0.384	0.376	0.647	0.714	0.636	0.588	0.640
Ne	0.443	0.456	0.743	0.686	0.851	0.498	0.491	0.788	0.884	0.810	0.745	0.792
Na	0.097	0.103	0.247	0.178	0.182	0.113	0.106	0.205	0.189	0.270	0.197	0.189
Mg	0.142	0.149	0.313	0.252	0.253	0.175	0.168	0.291	0.273	0.357	0.287	0.281
Al	0.086	0.092	0.227	0.160		0.111	0.102	0.216	0.222	0.263	0.188	0.220
Si	0.144	0.150	0.320	0.237		0.170	0.160	0.290	0.306	0.356	0.267	0.300
P	0.203	0.210	0.416	0.324	0.392	0.231	0.219	0.369	0.399	0.453	0.355	0.385
S	0.174	0.182	0.349	0.305		0.229	0.219	0.410	0.404	0.420	0.362	0.381
Cl	0.254	0.262	0.469	0.400		0.305	0.295	0.491	0.506	0.533	0.453	0.477
Ar	0.334	0.343	0.592	0.506	0.591	0.382	0.373	0.577	0.619	0.652	0.557	0.579
Δ(%)	43	41	13.8	8.5		41	42	3.7	5.7	14.4	7.4	

[a] The last row shows the mean absolute error in percentage with respect to exact-exchange and experimental results for exchange potentials and combined exchange and correlation potential, respectively. [b] From the work of Engel and Vosko.[45] [c] From the work of Grabo and Gross.[44] [d] Experimental results taken from Ratzig and Smirnov.[46]

Table 2. Electron Affinities Calculated from the Highest Occupied Kohn−Sham Orbital of the Anion (in au)[a]

atom	LB94	KLI-CS[b]	BJBR-PW	RPPBR-PW	expt.[c]
Li	0.020	0.024		0.036	0.023
B	0.016	0.033			0.010
C	0.049	0.083		0.032	0.046
O	0.077	0.110			0.054
F	0.128	0.208		0.110	0.125
Na	0.023	0.022	0.012	0.036	0.020
Al	0.018	0.024			0.016
Si	0.050	0.065	0.019	0.039	0.051
P	0.061	0.048		0.026	0.027
S	0.098	0.106		0.069	0.076
Cl	0.140	0.174	0.118	0.127	0.133
Δ(%)	29	66	38[d]	28[d]	

[a] The last row shows the mean absolute error in percentage. [b] From the work of Grabo and Gross.[44] [c] Experimental results taken from Ratzig and Smirnov.[46] [d] Mean error calculated for bound solutions only.

Table 3. Ionization Potentials for Molecules Calculated from the Highest Occupied Kohn−Sham Orbital (in eV)[a]

molecule	LDA	PBE	LB94	BJBR-PW	RPPBR-PW	expt.[b]
CS_2	6.93	6.81	11.54	13.08	10.76	10.07
H_2S	6.4	6.3	11.33	12.51	11.05	10.46
C_2H_4	6.92	6.74	11.85	12.71	10.96	10.51
PH_3	6.69	6.64	11.65	12.88	11.62	10.59
NH_3	6.28	6.19	11.55	12.58	11.3	10.8
Cl_2	7.47	7.36	12.3	14.03	11.86	11.48
C_2H_6	8.13	8.15	12.94	15.04	13.33	12
SiH_4	8.53	8.53	13.44	15.44	14.04	12.3
SO_2	8.3	8.09	14.06	15.2	13.29	12.35
H_2O	7.38	7.23	13.2	14.08	12.66	12.62
HCl	8.14	8.04	13.29	14.81	12.83	12.74
N_2O	8.6	8.35	14.48	15.4	13.37	12.89
CH_4	9.46	9.45	14.29	16.69	14.65	13.6
CO_2	9.31	9.05	15.32	16.37	14.2	13.78
CO	9.16	9.09	14.49	16.46	14.47	14.01
H_2	10.28	10.4	15.27	17.92	17.54	15.43
N_2	10.39	10.24	16.94	18.18	16.09	15.58
F_2	9.79	9.54	17.03	17.56	16.18	15.7
HF	9.85	9.65	16.44	17.3	15.69	16.03
Δ(%)	35	36	8.0	19	5.7	

[a] The last row shows the mean absolute error in percentage. [b] Experimental results taken from Grüning et al.[7]

value of the constant, which can be obtained from the asymptotic expansion of the density and the kinetic energy density, from the value of the KS eigenenergy of the HOMO. A perfectly equivalent procedure is to shift the BJ exchange potential so that it goes asymptotically to zero. In the case of spin-uncompensated atoms, the constant depends on spin. Then, it is possible to shift the spin-up and spin-down potentials by different amounts, provided that this does not imply a change in the occupancies of the orbitals. In this work, we have chosen to shift the BJ potential when computing ionization potentials and electron affinities. For some selected cases, we also performed calculations without shifting the potential and verified that the results obtained with both methods were identical.

The electron affinities for our set of atoms are given in Table 2. As is well-known, the LDA and most GGAs do not give bound solutions for most negative ions, so we chose not to include them in the table. In most cases, BJBR-PW failed to give bound solutions for the anions, while for RPPBR-PW, this happened only in a few cases. Considering only the cases where RPPBR-PW gave bound solutions, the

deviation from the exact values was around 28%. It seems that LB94, having a similar overall accuracy, works better for small ions, whereas RPPBR-PW increases its accuracy for larger systems. For example, for the last three atoms in Table 2 (P, S, Cl), RPPBR-PW has an error of only a few percent. Interestingly, KLI-CS results deviate by more than 60% from the exact values. This might be due to the poor compatibility between the exact nonlocal exchange and the correlation part, when the asymptotic regime is strongly dominated by the ionic HOMO.

4.2. Molecules. Next, we test the approximations for a large set of small molecules by computing ionization potentials and static (isotropic) dipole polarizabilities. The ionization potentials are obtained from the HOMO as in the previous section, while the polarizabilites are computed as a derivative of the dipole moment of the system with respect to the applied electric field. The ionization potentials are

Table 4. Static (Isotropic) Dipole Polarizabilities for Molecules (in au)[a]

molecule	LDA	PBE	LB94	BJBR-PW	RPPBR-PW	expt.[b]
CS_2	56.50	56.45	51.72	55.44	55.29	55.28
H_2S	26.21	25.91	21.95	24.24	22.51	24.71
C_2H_4	28.71	28.52	24.93	27.71	25.21	27.7
PH_3	32.29	31.72	27.39	29.99	27.47	30.93
NH_3	15.58	15.45	12.41	13.83	12.32	14.56
Cl_2	32.33	32.21	30.92	31.41	32.39	30.35
C_2H_6	30.17	29.73	27.41	28.23	26.52	29.61
SiH_4	34.03	33.07	30.17	31.11	28.47	31.9
SO_2	27.44	27.53	22.97	25.78	23.68	25.61
H_2O	10.74	10.73	8.28	9.49	8.53	9.64
HCl	18.61	18.47	15.85	17.18	16.21	17.39
N_2O	20.7	20.74	17.42	19.46	18.47	19.7
CH_4	17.77	17.45	15.87	16.46	15.41	17.27
CO_2	18.21	18.24	15.66	17.39	16.16	17.51
CO	13.91	13.87	11.6	13.13	12.29	13.08
H_2	5.87	5.64	5.02	5.27	4.56	5.43
N_2	12.64	12.63	10.79	11.9	11.4	11.74
F_2	8.86	8.97	7.23	8.31	7.73	8.38
HF	6.23	6.27	4.8	5.52	4.89	5.6
$\Delta(\%)$	6.1	5.3	9.8	2.0	8.9	

[a] The last row shows the mean absolute error in percentage.
[b] Experimental results taken from Grüning et al.[7]

listed in Table 3. Interestingly, RPPBR-PW is significantly more accurate than BJBR-PW and deviates less than 6% from the experimental values. LB94 performs also well with a mean absolute error of 8%. In contrast, the LDA and PBE fail in a similar fashion as in the atomic cases considered in the previous section.

For static (isotropic) dipole polarizabilities (see Table 4), the situation is different in the sense that the LDA and PBE perform rather well, which is surprising in view of the fact that the polarization is largely a nonlocal and collective effect. It is noteworthy, however, that the present test set does not include problematic elongated molecules or chains (see next section), for which going beyond LDA (and GGA) is essential.[6−13] For the present cases, BJBR-PW works remarkably well with a mean error of only 2%, whereas RPPBR-PW and LB94 deviate almost 10% from the experiments. Nevertheless, no dramatic failures are obtained by using any of the tested approximations.

4.3. Hydrogen Chains. In Table 5, we show the polarizabilities calculated for hydrogen chains from H_2 up to H_{20}. As the reference results, we use available data from CCSD(T) (coupled-cluster with single and double and

perturbative triple excitations) and MP4 (fourth-order Møller−Plesset perturbation theory).[11] This well-studied system has proved to be a remarkable challenge for DFT.[6,11−13,22] For example, LDA severely overestimates the polarizability, as demonstrated also by our results in Table 5. The error of PBE is slightly smaller. The failure of LDA and PBE to capture the electric response is believed to be due to the inherent self-interaction error.[11,48,49] We find that the mean error of LB94 is almost the same as that of LDA, whereas for BJBR-PW it is smaller. RPPBR-PW has the best performance of all of the tested potentials when compared to MP4, although the mean error is still quite large (27.7%). Possible sources of error in RPPBR-PW (and BJBR-PW) results are the ultranonlocal effects in long chains, which might be beyond reach of any semilocal functionals without *ad hoc* modifications, and the use of LDA for the correlation part. This last point seems to be confirmed by the results obtained without adding a correlation part to the exchange potentials: when comparing the polarizabilities obtained from the exchange-only potentials against exact-exchange OEP results,[6] all of the average errors are reduced, while the overall trend remains the same.

5. Summary and Outlook

In summary, we have tested recently constructed meta-generalized-gradient (meta-GGA) functionals for the exchange potential, in particular, the potential of Räsänen, Pittalis, and Proetto (RPP) and that of Becke and Johnson (BJ), when complemented by the Becke−Roussel (BR) approximation to the Slater potential (denoted in total as RPPBR and BJBR, respectively) and by the correlation in the LDA level. These approximations were compared to the van Leeuwen and Baerends potential (LB94), a GGA that shares some properties with these new meta-GGAs, as well as to standard LDA and GGA functionals. As the reference data, we used experimental results whenever available, numerically exact data, and, in the case of comparing the exchange-only results, the exact-exchange results obtained from the optimized-effective-potential method.

Overall, the RPPBR potential fared best in the present test suite consisting of ionization potentials and electronic affinities of atoms, ionization potentials and dipole polarizabilities of small molecules, and longitudinal polar-

Table 5. Longitudinal Polarizabilities of Hydrogen Chains (in au)[a]

chain	xLDA	xPBE	BJBR	RPPBR	OEP[b]	LDA	PBE	LB94	BJBR-PW	RPPBR-PW	CCSD(T)[c]	MP4[c]
H_2	13.1	12.5	12.4	11.2		12.4	12.0	11.2	11.8	10.8		
H_4	39.6	37.2	36.3	33.3	32.2	37.7	36.1	35.5	34.9	32.4	29	29.5
H_6	76.4	70.7	68.6	63.6	65.6	72.9	69.4	70.5	65.8	61.6	50.9	51.9
H_8	120.6	110.2	106.0	99.0	84.2	115.2	108.8	112.9	101.6	95.8	74.4	76.2
H_{10}	169.9	153.2	146.1	137.1		162.2	152.1	160.5	140.8	132.7		
H_{12}	222.4	199.2	188.4	177.2	138.1	212.2	197.8	211.6	182.1	171.1	124	127.3
H_{14}	277.0	246.1	231.9	218.0		264.0	245.2	264.3	224.1	210.6		155
H_{16}	333.0	294.1	277.5	259.5		317.2	293.4	318.6	267.3	250.5		
H_{18}	389.8	342.5	323.0	301.5		371.1	342.2	373.2	309.8	290.8		205.39
H_{20}	447.3	391.4	367.2	343.6		425.4	391.4	425.0	353.9	331.3		
$\Delta(\%)$	40.6	28.9	24.0	15.4		56.2	46.5	53.8	36.2	27.7		

[a] The last row shows the mean absolute error in percentage, calculated against OEP and MP4 (when available) for exchange only potentials and combined exchange and correlation potentials, respectively. [b] Results from the work of Kümmel et al.[6] [c] The MP4 and CCSD(T) results have been taken from the work of Ruzsinszky et al.[11] apart from the MP4 result for H_{18} taken from Champagne et al.[47]

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izabilities of hydrogen chains. The LB94 potential performed in an appealing fashion in several instances. The BJBR potential gave particularly good results for the calculation of static polarizabilities of small molecules. Desired future developments would include the development of correlation potentials compatible with the RPRBR potential.

In conclusion, the RPPBR potential combines a proper theoretical foundation with very good results for a series of properties of atoms and molecules. Moreover, it is very light from the computational point of view, thus allowing an efficient calculation of large systems. Therefore, we believe that the RPPBR potential is an important step in the quest for a simple and all-around semilocal potential for applications of density-functional theory.

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