REGULAR ARTICLE

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Pseudopotentials for H to Kr optimized for gradient-corrected exchange-correlation functionals

Abstract Pseudopotential parameter sets for the elements from H to Kr using the relativistic, norm-conserving, separable, dual-space Gaussian-type pseudopotentials of Goedecker, Teter, and Hutter (GTH) are presented as optimized for the gradient-corrected exchange-correlation functionals of Becke, Lee, Yang, and Parr (BLYP), Becke and Perdew (BP), and Perdew, Burke, and Ernzerhof (PBE). The accuracy and reliability of the GTH pseudopotentials is shown by calculations for a series of small molecules.

Keywords Goedecker pseudopotentials · Gaussian plane waves method · Quickstep · CP2K · Gradient corrected functionals

1 Introduction

The development of new electronic structure methods accompanied by the rapid development of the computer hardware during the last decades is causing a growing interest to use such methods for the investigation of complex chemical processes. However, the chemical processes of interest often involve heavy elements, in particular transition metals, as a key ingredient. A further complication is possibly introduced by the system size, since large model systems have to be employed in order to take environmental effects properly into account. An all-electron description of all atoms is computationally expensive and often not needed. Moreover, the inclusion of relativistic effects is indispensable for the heavy elements. The employment of effective pseudopotentials is known to be a valid method to reduce the computational effort in such cases, since the chemically inert core electrons are not explicitly considered in the calculation. Furthermore,

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relativistic effects can be included into the pseudopotential parametrization. There are only a few properties like the nuclear magnetic resonance for which an all-electron treatment is inevitable. Also plane waves methods require to employ pseudopotentials, since an expansion of an atomic all-electron density or wavefunction in plane waves is computationally inefficient. Thus, there was always a strong need for efficient pseudopotentials from the very beginning.

This work refers to the relativistic, norm-conserving, separable, dual-space pseudopotentials of Goedecker, Teter, and Hutter (GTH) [1, 2]. These are accurate pseudopotentials which have a compact analytic form based on Gaussian functions, whereas many other pseudopotential types are defined by dense radial grids which have to be tabulated for each atomic kind [3]. The GTH pseudopotential parameter sets for the elements from H to Rn optimized in the framework of the local density approximation (LDA) are already available from [2]. The original idea was to provide only optimized LDA parameter sets for all chemically relevant elements together with the code for the optimization. However, there is still no easy and foolproof recipe for the generation of new parameter sets and an optimization might be cumbersome, since there are often many pitfalls. While the LDA is still often used in condensed matter applications, nowadays most studies of, for instance, (bio-)molecular systems are performed with exchange-correlation functionals based on the generalized gradient approximation (GGA). The aim of this work is to provide the optimized GTH parameter sets for the elements from H to Kr for a couple of often used GGA functionals.

2 Definition of the GTH pseudopotentials

The norm-conserving, separable, dual-space GTH pseudopotentials consist of a local part

$$V_{\text{loc}}^{\text{PP}}(r) = -\frac{Z_{\text{eff}}}{r}\text{erf}\left(\alpha^{\text{PP}}r\right)$$
$$+ \sum_{i=1}^{4} C_i^{\text{PP}}\left(\sqrt{2}\alpha^{\text{PP}}r\right)^{2i-2}\exp\left[-\left(\alpha^{\text{PP}}r\right)^2\right], \quad (1)$$

with

$$\alpha^{\mathrm{PP}} = \frac{1}{\sqrt{2}\, r_{\mathrm{loc}}^{\mathrm{PP}}},$$

and a nonlocal part

$$V_{\mathrm{nl}}^{\mathrm{PP}}(\mathbf{r}, \mathbf{r}') = \sum_{lm} \sum_{ij} \langle \mathbf{r} \mid p_i^{lm} \rangle\, h_{ij}^l\, \langle p_j^{lm} \mid \mathbf{r}' \rangle, \qquad (2)$$

with the Gaussian-type projectors

$$\langle \mathbf{r} \mid p_i^{lm} \rangle = N_i^l\, Y^{lm}(\hat{r})\, r^{l+2i-2} \exp\left[-\frac{1}{2}\left(\frac{r}{r_l}\right)^2\right],$$

where the N_i^l are normalization constants and the $Y^{lm}(\hat{r})$ are spherical harmonics. An advantage of such a pseudopotential definition in real space is that it has an analytic representation in Fourier space, too. This feature is advantageous for methods dealing with both real and Fourier space like plane waves methods. The explicit form of Eqs. (1) and (2) in Fourier space is given in [2]. The attribute dual-space for the GTH pseudopotential stems from this special property. Moreover, a good convergence behavior is achieved both in real and Fourier space by the usage of Gaussian functions. A further advantage of the Gaussian functions is that with atom-centered Gaussian function basis sets the pseudopotential contribution involves only the calculation of two- and three-center overlap integrals over Gaussian functions. The three-center overlap integrals of Eq. (2) reduce to products of two-center overlap integrals because of the separability of the non-local term. There are very efficient recursion schemes [4] to evaluate such integrals. For that reason, the GTH pseudopotentials are optimally suited for the use with the Gaussian plane waves (GPW) method [5–7] which uses Gaussian basis sets for the expansion of the Kohn–Sham orbitals and an auxiliary plane waves basis set for the description of the electronic density.

Relativistic all-electron wavefunctions are used as the reference for the fit of the pseudo wavefunctions and hence all orbitals with an angular momentum quantum number $l > 0$ split up into a spin-up and a spin-down orbital with the total angular momentum numbers $j = l \pm 1/2$ and thus two different potentials are obtained. A weighted average potential

$$V_l(\mathbf{r}, \mathbf{r}') = \frac{1}{2l+1}\left[l V_{l-\frac{1}{2}}(\mathbf{r}, \mathbf{r}') + (l+1) V_{l+\frac{1}{2}}(\mathbf{r}, \mathbf{r}')\right] \quad (3)$$

was defined by Bachelet and Schlüter [8]. Then the spin-orbit (SO) coupling is given by the difference potential

$$\Delta V_l^{\mathrm{SO}}(\mathbf{r}, \mathbf{r}') = \frac{2}{2l+1}\left[V_{l+\frac{1}{2}}(\mathbf{r}, \mathbf{r}') - V_{l-\frac{1}{2}}(\mathbf{r}, \mathbf{r}')\right]. \quad (4)$$

of the two-spin components. In this way the total pseudopotential can be rewritten as a sum

$$V(\mathbf{r}, \mathbf{r}') = V_{\mathrm{loc}}(r)\, \delta(\mathbf{r} - \mathbf{r}') + \sum_l V_l(\mathbf{r}, \mathbf{r}')$$
$$+ \Delta V_l^{\mathrm{SO}}(\mathbf{r}, \mathbf{r}')\, \mathbf{L} \cdot \mathbf{S}, \quad (5)$$

of a scalar relativistic part and the difference potential $\Delta V_l^{\mathrm{SO}}(\mathbf{r}, \mathbf{r}')$. The last term of Eq. (5) is neglected and an average scalar relativistic pseudopotential is obtained which has the same analytic form as the nonrelativistic pseudopotential given by Eqs. (1) and (2).

Table 1 Goedecker, Teter and Hutter pseudopotential parameters optimized for BLYP

H	1	0.200000	−4.195961	0.730498		
He	2	0.200000	−9.147371	1.711978		
Li	3	0.400000	−14.116798	9.677248	−1.798865	0.086250
Be	4	0.325000	−24.089771	17.302757	−3.345610	0.166015
B	3	0.424072	−6.108908	0.985870		
		0.370860	6.343396			
C	4	0.338066	−9.136269	1.429260		
		0.302322	9.665512			
N	5	0.282871	−12.736467	1.951079		
		0.255234	13.678932			
O	6	0.243420	−16.991892	2.566142		
		0.220831	18.388851			
F	7	0.213840	−21.902415	3.275976		
		0.194590	23.796583			
Ne	8	0.190000	−28.619598	4.155495		
		0.178238	27.957849	0.833656		
				−1.076245		
		0.152764	0.331170			
Na	9	0.233965	−2.689483	−0.509478		
		0.149777	32.857159			
		0.123199	−13.999008			
Mg	10	0.200984	−19.330293	2.860058		
		0.141080	40.674730			
		0.104561	−10.736171			
Al	3	0.450000	−7.666832			
		0.497736	6.463032	−1.583870		
				2.044767		
		0.565458	1.818267			
Si	4	0.440000	−6.259587			
		0.444652	8.314609	−2.332779		
				3.011605		
		0.502792	2.332418			
P	5	0.430000	−5.929533			
		0.402869	10.414839	−3.131688		
				4.042991		
		0.452458	2.953583			
S	6	0.420000	−5.988800			
		0.369733	12.556485	−3.912905		
				5.051538		
		0.412876	3.587721			
Cl	7	0.410000	−6.357052			
		0.343119	14.681348	−4.640343		
				5.990657		
		0.381135	4.222924			
Ar	8	0.400000	−7.100000			
		0.321550	16.800999	−5.328711		
				6.879336		
		0.355444	4.877196			
K	9	0.400000	−2.880134	−1.211435		
		0.306347	17.510023	−5.610379		
				7.242968		
		0.321058	6.903211	−2.199258		
				2.602197		

3 Optimization of the GTH pseudopotential parameters

Firstly, the atomic all-electron wave functions for the actual electronic ground-state configurations were obtained from fully relativistic density functional calculations using a numerical atomic program. These all-electron wave functions were generated for each GGA functional and served as a reference for the optimization of the pseudo wavefunctions. The optimization of GTH pseudopotentials involves by definition

Table 2 Goedecker, Teter and Hutter pseudopotential parameters optimized for BLYP

Ca	10	0.390000	−4.035611	−1.612574
		0.289365	20.425660	−7.236748
				9.342602
		0.311779	7.531694	−2.085377
				2.467451
		0.691419	0.055223	
Sc	11	0.376875	9.840097	−1.165860
		0.359989	3.306103	2.547964
				−3.289408
		0.220994	−0.434882	6.464258
				−7.648614
		0.233380	−10.134039	
Ti	12	0.380000	8.711442	−0.700287
		0.337771	2.575264	3.692971
				−4.767605
		0.242531	−4.630541	8.870875
				−10.496161
		0.243317	−9.406653	
V	13	0.375000	7.095674	−0.322259
		0.329843	1.992040	4.739163
				−6.118233
		0.246213	−5.549745	8.764202
				−10.369943
		0.241153	−9.444362	
Cr	14	0.370000	5.814981	−0.675718
		0.316714	2.606983	5.067158
				−6.541672
		0.239613	−4.666682	7.572902
				−8.960379
		0.220929	−11.189892	
Mn	15	0.365000	6.178703	−0.444510
		0.297844	1.694336	6.390534
				−8.250144
		0.245825	−6.537424	7.845912
				−9.283408
		0.222447	−11.669616	
Fe	16	0.360000	7.011025	−0.222747
		0.276205	0.611496	7.992357
				−10.318089
		0.247130	−8.710556	8.684169
				−10.275248
		0.223534	−12.411504	
Co	17	0.355000	3.432978	0.614913
		0.275554	0.193629	9.181280
				−11.852982
		0.243128	−8.922049	9.232630
				−10.924196
		0.223625	−11.758783	
Ni	18	0.350000	4.076029	0.233128
		0.257147	0.098785	10.148642
				−13.101841
		0.249753	−8.348615	7.266771
				−8.598160
		0.212478	−13.672933	

Table 3 Goedecker, Teter and Hutter pseudopotential parameters optimized for BLYP

Cu	11	0.530000			
		0.430782	10.298526	−6.058370	1.700546
				10.587260	−4.390790
					3.485082
		0.550805	2.744587	−0.862955	
				1.021062	
		0.265586	−12.661582		
Zn	12	0.510000			
		0.398550	11.959460	−8.665221	2.808077
				15.754090	−7.250424
					5.754846
		0.545562	2.510500	−0.440325	
				0.520999	
		0.251685	−14.323098		
Ga	13	0.490000			
		0.414929	10.879160	−4.784493	0.608688
				7.166785	−1.571626
					1.247439
		0.567431	1.780264	0.277378	
				−0.328198	
		0.238927	−16.078668		
Ge	4	0.540000			
		0.427374	7.556515	−0.070902	−1.725963
				−2.715745	4.456418
					−3.537172
		0.574899	0.800563	0.713074	
				−0.843721	
		0.785473	0.218708		
As	5	0.520000			
		0.456983	5.579764	0.117773	−0.992439
				−1.766246	2.562466
					−2.033895
		0.554947	1.000977	0.683251	
				−0.808433	
		0.684981	0.348181		
Se	6	0.510000			
		0.433675	6.433699	−0.220640	−1.175453
				−1.627030	3.035007
					−2.408962
		0.472483	2.239703	0.401919	
				−0.475556	
		0.609118	0.494947		
Br	7	0.500000			
		0.436123	6.231283	0.218893	−1.124676
				−2.111875	2.903902
					−2.304901
		0.453793	2.465743	0.496368	
				−0.587311	
		0.533156	0.747241		
Kr	8	0.500000			
		0.423621	6.373829	0.498586	−1.419917
				−2.953167	3.666210
					−2.909964
		0.433913	2.632304	0.645177	
				−0.763384	
		0.513154	0.709545		

only a small set of parameters as it can be retrieved from Eqs. (1) and (2). The parameters are $r_{\text{loc}}^{\text{PP}}$ and C_i^{PP} for the local part and r_l and h_{ij}^l for the non-local part. The GTH pseudopotential parameter sets for the elements from H to Rn optimized for LDA are already available from [2]. These parameter sets provided a good initial guess for the optimization of the GGA parameter sets and the same pattern of nonzero parameters was used for the fit of the corresponding GGA parameter sets, whereas the weights for the penalty functions were adapted in

order to achieve an optimal fit for all pseudo wavefunctions. A stubborn but robust simplex-downhill procedure was used for the optimization. The typical difference between the optimized pseudo wavefunction and corresponding all-electron reference wavefunction in the valence region was usually less than 10^{-5} for the occupied valence orbitals and 10^{-3}–10^{-4}

Table 4 Goedecker, Teter and Hutter pseudopotential parameters optimized for BP

H	1	0.200000	−4.185769	0.726940		
He	2	0.200000	−9.130075	1.705475		
Li	3	0.400000	−14.060569	9.585899	−1.772485	0.084552
Be	4	0.325000	−24.051797	17.250016	−3.333976	0.165569
B	3	0.416891	−5.922294	0.924562		
		0.371077	6.295996			
C	4	0.336797	−8.868487	1.354476		
		0.302410	9.622712			
N	5	0.283092	−12.450889	1.875196		
		0.255290	13.636569			
O	6	0.244018	−16.705908	2.492927		
		0.220865	18.347594			
F	7	0.214489	−21.618322	3.205432		
		0.194610	23.757123			
Ne	8	0.190000	−27.056031	4.335635		
		0.176097	28.150757	0.833656		
				−1.076245		
		0.193497	−0.240663			
Na	1	0.754736	−2.139853			
		0.722073	2.089328	−0.338912		
				0.437533		
		0.875320	0.497225			
Na	9	0.210332	1.692589	0.503580		
		0.131731	40.129336			
		0.140673	−12.691904			
Mg	10	0.203445	−19.148633	2.823116		
		0.141013	40.615281			
		0.104856	−10.812360			
Al	3	0.450000	−7.517924			
		0.486266	6.977756	−1.915682		
				2.473135		
		0.561928	1.855842			
Si	4	0.440000	−6.317841			
		0.436036	8.904625	−2.694063		
				3.478020		
		0.498419	2.419375			
P	5	0.430000	−5.892296			
		0.396816	10.932888	−3.458033		
				4.464301		
		0.449121	3.030048			
S	6	0.420000	−6.033042			
		0.365460	13.051265	−4.217067		
				5.444211		
		0.410245	3.678229			
Cl	7	0.410000	−6.394602			
		0.340018	15.113473	−4.908115		
				6.336349		
		0.379141	4.306336			
Ar	8	0.400000	−7.100000			
		0.319226	17.158055	−5.553322		
				7.169309		
		0.353911	4.943474			
K	9	0.400000	−3.208037	−1.139580		
		0.305317	17.821132	−5.624592		
				7.261316		
		0.317286	7.270738	−2.458363		
				2.908774		

Table 5 Goedecker, Teter and Hutter pseudopotential parameters optimized for BP

Ca	10	0.390000	−5.150665	−1.276359
		0.291806	20.375018	−6.392254
				8.252364
		0.305851	8.086791	−2.351948
				2.782862
		0.690846	0.050575	
Sc	11	0.385000	8.151138	−0.545788
		0.364086	2.633743	3.011895
				−3.888340
		0.243373	−2.596433	7.977854
				−9.439525
		0.253163	−8.161687	
Ti	12	0.380000	8.752405	−0.720513
		0.337256	2.577937	3.671930
				−4.740441
		0.242447	−4.635718	8.847008
				−10.467920
		0.243277	−9.408158	
V	13	0.375000	7.151792	−0.343565
		0.329787	1.967060	4.726242
				−6.101552
		0.246174	−5.582364	8.796910
				−10.408644
		0.241159	−9.447430	
Cr	14	0.370000	5.658643	−0.680989
		0.314507	2.825352	5.001950
				−6.457490
		0.240791	−4.437221	7.252682
				−8.581489
		0.220357	−11.185498	
Mn	15	0.365000	6.086973	−0.457679
		0.296649	1.826416	6.373014
				−8.227525
		0.246911	−6.515553	7.910510
				−9.359842
		0.222358	−11.618284	
Fe	16	0.360000	6.766271	−0.229605
		0.278019	0.640923	7.903109
				−10.202870
		0.252111	−7.913426	7.666135
				−9.070693
		0.222865	−12.387749	
Co	17	0.355000	3.118708	0.609787
		0.273447	0.608700	9.059598
				−11.695891
		0.244865	−8.731942	9.194418
				−10.878983
		0.223214	−11.659403	
Ni	18	0.350000	1.980920	0.678735
		0.261517	0.640514	9.971298
				−12.872890
		0.222997	−11.035849	12.324159
				−14.582141
		0.215316	−12.607378	

for the unoccupied orbitals. Thus all optimizations were performed on a level corresponding to the LDA parameter sets.

In that way the parameters for the elements from H to Kr were optimized for the gradient-corrected exchange-correlation potentials of Becke, Lee, Yang, and Parr (BLYP) [9–11], Becke and Perdew (BP) [9,12], and Perdew, Burke and Ernzerhof (PBE) [13]. Only the semi-core versions of the pseudopotentials which include partially the core electrons were optimized, since the experience with the LDA pseudopotentials showed that only these pseudopotentials are very accurate in most cases.

The optimized parameter sets obtained for the BLYP, BP, and PBE functional are listed in the Tables 1–9.

The table entries refer to the following format:

Table 6 Goedecker, Teter and Hutter pseudopotential parameters optimized for BP

Cu	11	0.530000			
		0.428260	9.929973	−6.733781	2.061234
				12.045870	−5.322083
					4.224272
		0.561800	2.527065	−0.760266	
				0.899559	
		0.264818	−12.790290		
Zn	12	0.510000			
		0.398535	11.714302	−8.952715	3.103896
				16.606392	−8.014224
					6.361093
		0.542780	2.594550	−0.564109	
				0.667463	
		0.251199	−14.423696		
Ga	13	0.490000			
		0.414448	10.636900	−5.036262	0.717210
				7.668329	−1.851829
					1.469844
		0.570055	1.755905	0.262394	
				−0.310469	
		0.238636	−16.154283		
Ge	4	0.540000			
		0.426527	7.460088	−0.101485	−1.799778
				−2.796322	4.647007
					−3.688447
		0.570818	0.832322	0.672048	
				−0.795178	
		0.802293	0.201406		
As	5	0.520000			
		0.456157	5.518370	0.173127	−1.142209
				−2.081309	2.949170
					−2.340831
		0.556427	0.968716	0.692518	
				−0.819399	
		0.700852	0.313103		
Se	6	0.510000			
		0.433781	6.427602	−0.116660	−1.250925
				−1.884023	3.229876
					−2.563634
		0.472877	2.193509	0.463547	
				−0.548477	
		0.617793	0.457876		
Br	7	0.500000			
		0.438443	6.028091	0.369508	−1.265836
				−2.535916	3.268375
					−2.594192
		0.452653	2.454449	0.553264	
				−0.654631	
		0.572701	0.534532		
Kr	8	0.500000			
		0.422012	6.436401	0.554844	−1.490192
				−3.140099	3.847659
					−3.053985
		0.433814	2.587592	0.721291	
				−0.853443	
		0.547605	0.528788		

Table 7 Goedecker, Teter and Hutter pseudopotential parameters optimized for PBE

H	1	0.200000	−4.178900	0.724463		
He	2	0.200000	−9.122144	1.702708		
Li	3	0.400000	−14.081155	9.626220	−1.783616	0.085152
Be	4	0.325000	−24.067467	17.279022	−3.339106	0.165549
B	3	0.418991	−5.859462	0.903756		
		0.371320	6.297280			
C	4	0.338471	−8.803674	1.339211		
		0.302576	9.622487			
N	5	0.283791	−12.415226	1.868096		
		0.255405	13.630263			
O	6	0.244554	−16.667215	2.487311		
		0.220956	18.337458			
F	7	0.214930	−21.573028	3.199776		
		0.194684	23.743540			
Ne	8	0.190000	−27.120160	4.360450		
		0.176059	28.177371	0.833656		
				−1.076245		
		0.195475	−0.236294			
Na	9	0.236523	0.295105	−0.913885		
		0.143560	34.601492			
		0.129932	−14.277462			
Mg	10	0.192758	−20.575391	3.040167		
		0.141407	41.047292			
		0.102932	−9.985626			
Mg	2	0.576960	−2.690407			
		0.593924	3.503211	−0.716772		
				0.925348		
		0.707157	0.831158			
Al	3	0.450000	−7.554761			
		0.487435	6.959938	−1.888836		
				2.438477		
		0.562189	1.865299			
Si	4	0.440000	−6.269288			
		0.435634	8.951742	−2.706271		
				3.493781		
		0.497942	2.431277			
P	5	0.430000	−5.875943			
		0.396377	11.008862	−3.470356		
				4.480210		
		0.448298	3.056064			
S	6	0.420000	−5.986260			
		0.364820	13.143544	−4.241830		
				5.476180		
		0.409480	3.700891			
Cl	7	0.410000	−6.392082			
		0.339539	15.218990	−4.934523		
				6.370442		
		0.378474	4.338775			
Ar	8	0.400000	−7.100000			
		0.318815	17.252038	−5.585488		
				7.210834		
		0.353370	4.974216			
K	9	0.400000	−3.363552	−1.086530		
		0.305318	17.850623	−5.622649		
				7.258808		
		0.316484	7.333780	−2.460945		
				2.911829		

Legend (Table 6):

Element	Z_{eff}	r_{loc}	C_1	C_2	C_3	C_4
		r_0	$h^0_{1,1}$	$h^0_{1,2}$	$h^0_{1,3}$	
				$h^0_{2,2}$	$h^0_{2,3}$	
					$h^0_{3,3}$	
		r_1	$h^1_{1,1}$	$h^1_{1,2}$	$h^1_{1,3}$	
				$h^1_{2,2}$	$h^1_{2,3}$	
					$h^1_{3,3}$	

Legend (Table 7):

r_2	$h^2_{1,1}$	$h^2_{1,2}$	$h^2_{1,3}$
		$h^2_{2,2}$	$h^2_{2,3}$
			$h^2_{3,3}$

Only the parameters which were optimized are listed for each element. Hartwigsen et al. [2] derived the off-diagonal elements of the symmetric coefficient matrix $\mathbf{h}^l$ for the non-local projectors from the diagonal elements using a set of explicit

Table 8 Goedecker, Teter and Hutter pseudopotential parameters optimized for PBE

Ca	10	0.390000	−4.167072	−1.583798
		0.289356	20.531876	−7.129786
				9.204514
		0.327882	5.805605	−0.428753
				0.507308
		0.679617	0.058068	
Sc	11	0.385000	8.214900	−0.557059
		0.363611	2.646533	3.021084
				−3.900203
		0.243898	−2.634823	7.992137
				−9.456424
		0.253206	−8.165948	
Ti	12	0.380000	8.711442	−0.700287
		0.337771	2.575264	3.692971
				−4.767605
		0.242531	−4.630541	8.870875
				−10.496161
		0.243317	−9.406653	
V	13	0.375000	7.474704	−0.370264
		0.327795	1.940878	4.725688
				−6.100837
		0.244766	−5.978167	9.358639
				−11.073291
		0.241739	−9.499891	
Cr	14	0.370000	5.699658	−0.695486
		0.313934	2.869955	4.974456
				−6.421996
		0.240866	−4.476209	7.331414
				−8.674646
		0.220286	−11.197116	
Mn	15	0.365000	6.093046	−0.446469
		0.295686	1.887120	6.356837
				−8.206641
		0.245613	−6.570025	7.983360
				−9.446039
		0.222523	−11.612051	
Fe	16	0.360000	6.756789	−0.228833
		0.278263	0.629506	7.913132
				−10.215810
		0.251383	−7.932133	7.697079
				−9.107307
		0.222856	−12.385799	
Ni	18	0.350000	2.102166	0.648484
		0.261295	0.622658	9.970227
				−12.871507
		0.224253	−11.142708	12.429566
				−14.706861
		0.215348	−12.628146	

equations and thus they listed only the diagonal elements h_{ii}^l. In this work the coefficient matrix was orthonormalized using the matrix transformation

$$\mathbf{h}_d^l = \mathbf{U}\,\mathbf{h}^l\,\mathbf{U}^T \quad \text{with} \quad \mathbf{U}\,\mathbf{U}^T = \mathbf{1}\,, \tag{6}$$

where $\mathbf{h}_d^l$ is a diagonal matrix. In that way only the contributions of the diagonal elements h_{ii}^l have to be computed during the optimization. On the other hand, now the upper triangle including the diagonal elements of the coefficient matrix $\mathbf{h}^l$ has to be listed. The corresponding coefficient matrix for the SO term is not listed, but the parameters can be retrieved from the online database of the CP2K project [14], if an explicit calculation of the SO coupling is required and available.

Table 9 Goedecker, Teter and Hutter pseudopotential parameters optimized for PBE

Cu	11	0.530000			
		0.431355	9.693805	−6.470165	1.935952
				11.501774	−4.998607
					3.967521
		0.561392	2.545473	−0.784636	
				0.928394	
		0.264555	−12.828614		
Zn	12	0.510000			
		0.400316	11.530041	−8.791898	3.145086
				16.465775	−8.120578
					6.445509
		0.543182	2.597195	−0.594263	
				0.703141	
		0.250959	−14.466958		
Ga	13	0.490000			
		0.413962	10.592918	−5.152803	0.775294
				7.913255	−2.001799
					1.588879
		0.570154	1.759998	0.251224	
				−0.297253	
		0.238368	−16.211820		
Ge	4	0.540000			
		0.421865	7.510241	−0.588108	−1.447976
				−1.595888	3.738657
					−2.967467
		0.567529	0.913860	0.546875	
				−0.647072	
		0.813914	0.197177		
As	5	0.520000			
		0.455550	5.520673	0.035122	−1.061082
				−1.771193	2.739703
					−2.174572
		0.554606	1.021792	0.629208	
				−0.744489	
		0.703689	0.314795		
Se	6	0.510000			
		0.432460	6.518110	−0.222716	−1.196129
				−1.657978	3.088392
					−2.451335
		0.470492	2.281262	0.365335	
				−0.432271	
		0.625600	0.439799		
Br	7	0.500000			
		0.438039	6.078556	0.330498	−1.238382
				−2.440900	3.197489
					−2.537928
		0.453136	2.459304	0.522753	
				−0.618530	
		0.567714	0.559266		
Kr	8	0.500000			
		0.421657	6.465304	0.538660	−1.502601
				−3.139389	3.879700
					−3.079416
		0.433744	2.601165	0.705110	
				−0.834297	
		0.524691	0.635595		

4 Test calculations

The optimized GTH pseudopotentials were tested using a set of small molecules. The plane waves code CPMD (version 3.9.1) [15] was used to optimize the structure of these small molecules. To this end, each molecule was placed in a simple
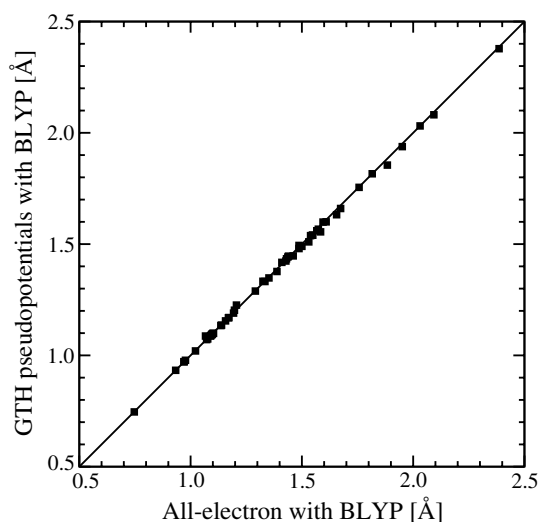
Fig. 1 Comparison of the bond distances calculated with CPMD [15] using the GTH pseudopotentials optimized for BLYP and the bond distances obtained by all-electron calculations with the 6-311++G(3df,3pd) basis set using the Gaussian 03 program [18] for the compounds of Tables 10 and 11 containing only the elements from H to Ar

cubic box of edge length 12 Å using the molecule option of CPMD, which allows to deal with isolated molecules, since the interaction with the periodic images becomes negligible. The convergence criterion for the atomic forces was set to 0.0001 a.u. for LDA and to 0.0005 a.u. for the GGA functionals. A wavefunction cutoff of 500 Ry for LDA and 1000 Ry for the GGA functionals was employed. Table 10 and 11 compare the structure data obtained with the new GTH pseudopotential parameter sets to the corresponding experimental data. The results for the GGA functionals show in most cases the typical bond elongation compared to the LDA data, whereas differences among the GGA functionals are rather small. The same trends are well-known from all-electron calculations. Molecules containing the elements from Sc to Ga were not included into the test set, since the requested convergence for the atomic forces could not be achieved because of the hardness of the semi-core pseudopotentials employed for these elements. However, these GTH pseudopotentials can be used with the Gaussian plane waves method as it is implemented in the QUICKSTEP code [5–7], which is part of the open source project CP2K [14]. QUICKSTEP is less affected by the hardness of these pseudopotentials, since the short-ranged integral terms of Eqs. (1) and (2) can be easily computed analytically over Gaussian functions (see Sect. 2). The development of Gaussian basis sets optimized for the use with the GTH pseudopotentials is in progress.

As a final test, the structures of the compounds of the Tables 10 and 11 were optimized at the all-electron level. The optimizations were performed with the Gaussian 03 program [18] employing the large standard Gaussian basis set 6-311++G(3df,3pd), which is only available for the elements from H to Ar. Thus just the compounds of the Tables 10 and 11 containing only the elements from H to Ar were consid-

Table 10 Structure data of small molecules optimized using the GTH pseudopotentials

Molecule	[Å,°]	LDA	BLYP	BP	PBE	Exp.	Ref.
H_2	r(HH)	0.766	0.746	0.750	0.751	0.741	[16]
LiH	r(LiH)	1.603	1.599	1.603	1.603	1.596	[16]
LiF	r(LiF)	1.550	1.555	1.579	1.575	1.564	[16]
LiCl	r(LiCl)	2.000	2.031	2.033	2.023	2.021	[16]
LiBr	r(LiBr)	2.150	2.183	2.183	2.177	2.170	[16]
BeF_2	r(BeF)	1.372	1.377	1.388	1.386	1.373	[17]
BH_3	r(BH)	1.198	1.190	1.196	1.196	1.190	[17]
BF_3	r(BF)	1.310	1.333	1.328	1.327	1.313	[17]
BCl_3	r(BCl)	1.727	1.755	1.748	1.746	1.742	[17]
BBr_3	r(BBr)	1.883	1.920	1.911	1.907	1.893	[17]
CH_4	r(CH)	1.096	1.093	1.095	1.095	1.087	[17]
C_2H_2	r(CC)	1.226	1.226	1.226	1.226	1.203	[17]
	r(CH)	1.087	1.087	1.087	1.087	1.063	
C_2H_4	r(CC)	1.321	1.332	1.333	1.332	1.330	[17]
	r(CH)	1.093	1.087	1.091	1.091	1.080	
	a(HCH)	116.7	116.5	116.6	116.6	117.1	
C_2H_6	r(CC)	1.508	1.538	1.532	1.527	1.522	[17]
	r(CH)	1.100	1.096	1.099	1.099	1.089	
	a(CCH)	111.7	111.4	111.4	111.5	111.2	
CH_3F	r(CH)	1.101	1.094	1.098	1.099	1.100	[17]
	r(CF)	1.376	1.418	1.403	1.401	1.383	
	a(HCH)	109.8	110.6	110.2	110.2	110.6	
CH_3Cl	r(CH)	1.096	1.089	1.093	1.094	1.087	[17]
	r(CCl)	1.760	1.816	1.794	1.787	1.776	
	a(HCH)	110.0	110.8	110.5	110.4	110.4	
CH_3OH	r(CH)	1.106	1.099	1.103	1.103	1.098	[17]
	r(CO)	1.406	1.446	1.433	1.430	1.429	
	r(OH)	0.971	0.971	0.970	0.969	0.975	
CO	r(CO)	1.125	1.134	1.135	1.135	1.128	[16]
CO_2	r(CO)	1.161	1.170	1.171	1.171	1.160	[17]
N_2	r(NN)	1.093	1.099	1.101	1.102	1.098	[16]
N_2O	r(NN)	1.129	1.136	1.137	1.137	1.127	[17]
	r(NO)	1.178	1.203	1.194	1.191	1.185	
NH_3	r(NH)	1.022	1.020	1.022	1.022	1.014	[17]
	a(HNH)	107.6	107.2	106.5	106.4	107.2	
HCN	r(CH)	1.078	1.071	1.073	1.074	1.065	[17]
	r(CN)	1.148	1.155	1.156	1.157	1.153	
H_2O	r(OH)	0.971	0.972	0.970	0.970	0.958	[17]
	a(HOH)	105.1	104.7	104.4	104.4	104.5	
H_2O_2	r(OO)	1.434	1.494	1.472	1.468	1.456	[17]
	r(OH)	0.978	0.978	0.977	0.976	0.967	
	a(OOH)	100.8	99.7	99.7	99.8	102.3	
	d(HOOH)	112.8	111.0	110.5	113.7	113.7	
F_2	r(FF)	1.388	1.434	1.417	1.415	1.412	[16]
HF	r(HF)	0.933	0.933	0.932	0.932	0.917	[16]
OF_2	r(OF)	1.394	1.442	1.425	1.422	1.405	[17]
	a(FOF)	104.2	104.3	104.4	104.4	103.1	

ered. A tight convergence criterion was applied for both the wavefunction and the structure optimizations and the use of any molecular symmetry was disabled. The exchange-correlation functional BLYP was employed using ultra-fine integration grids. The comparison of the all-electron and the GTH pseudopotential results is shown in Fig. 1.

The agreement between the all-electron and the GTH pseudopotential results is very satisfactory considering that Gaussian 03 and CPMD are based on quite different methods. Moreover, differences in the functional implementations may cause small deviations. The molecules LiF and NaH show the largest deviation with 0.029 Å, but most of the 56 bond distances differ only by less than 0.01 Å.

Table 11 Structure data of small molecules optimized using the GTH pseudopotentials

Molecule	[Å,°]	LDA	BLYP	BP	PBE	Exp.	Ref.
NaH	r(NaH)	1.866	1.855	1.901	1.903	1.887	[16]
NaF	r(NaF)	1.910	1.938	1.947	1.958	1.926	[16]
NaCl	r(NaCl)	2.332	2.378	2.379	2.382	2.361	[16]
NaBr	r(NaBr)	2.468	2.496	2.522	2.523	2.502	[16]
AlH	r(AlH)	1.670	1.660	1.669	1.677	1.648	[16]
AlF$_3$	r(AlF)	1.606	1.632	1.630	1.630	1.630	[17]
AlCl$_3$	r(AlCl)	2.050	2.081	2.075	2.074	2.068	[17]
SiH$_4$	r(SiH)	1.486	1.480	1.486	1.489	1.471	[17]
SiO	r(SiO)	1.497	1.510	1.515	1.517	1.510	[16]
PH$_3$	r(PH)	1.427	1.424	1.427	1.429	1.413	[17]
	a(HPH)	91.8	93.4	92.7	92.6	93.5	
HCP	r(CH)	1.082	1.074	1.079	1.080	1.066	[17]
	r(CP)	1.528	1.540	1.541	1.542	1.540	
PN	r(PN)	1.476	1.490	1.490	1.491	1.491	[16]
H$_2$S	r(SH)	1.351	1.348	1.349	1.350	1.336	[17]
	a(HSH)	91.2	92.1	91.7	91.6	87.8	
COS	r(CO)	1.159	1.169	1.169	1.169	1.154	[17]
	r(CS)	1.550	1.567	1.564	1.564	1.563	
CS	r(CS)	1.526	1.540	1.541	1.542	1.535	[16]
CS$_2$	r(CS)	1.545	1.560	1.558	1.558	1.553	[17]
SO$_2$	r(SO)	1.428	1.447	1.443	1.444	1.431	[17]
	a(OSO)	119.6	119.5	119.7	119.6	119.3	
SF$_6$	r(SF)	1.563	1.600	1.589	1.588	1.561	[17]
HCl	r(HCl)	1.289	1.289	1.288	1.288	1.275	[16]
KF	r(KF)	2.104	2.180	2.154	2.159	2.171	[16]
KCl	r(KCl)	2.598	2.684	2.665	2.659	2.667	[16]
KBr	r(KBr)	2.750	2.840	2.821	2.821	2.821	[16]
CaO	r(CaO)	1.781	1.822	1.810	1.812	1.822	[16]
CaS	r(CaS)	2.271	2.324	2.301	2.302	2.318	[16]
GeO	r(GeO)	1.592	1.623	1.620	1.631	1.625	[16]
GeH$_4$	r(GeH)	1.514	1.520	1.525	1.534	1.514	[17]
As$_4$	r(AsAs)	2.409	2.468	2.450	2.453	2.435	[17]
AsH$_3$	r(AsH)	1.521	1.528	1.529	1.535	1.528	[17]
	a(HAsH)	90.6	91.9	91.3	91.0	91.9	
H$_2$Se	r(SeH)	1.473	1.477	1.477	1.480	1.459	[17]
	a(HSeH)	90.0	90.7	90.4	90.3	91.0	
COSe	r(CO)	1.157	1.167	1.166	1.166	1.153	[17]
	r(CSe)	1.693	1.723	1.715	1.717	1.710	
CSe$_2$	r(CSe)	1.682	1.706	1.702	1.704	1.692	[17]
SeO$_2$	r(SeO)	1.608	1.635	1.630	1.633	1.608	[17]
	a(OSeO)	114.4	114.6	114.4	114.4	113.8	
HBr	r(HBr)	1.429	1.432	1.431	1.432	1.414	[16]
BrF	r(BrF)	1.758	1.771	1.789	1.788	1.759	[16]
BrCl	r(BrCl)	2.125	2.186	2.160	2.154	2.136	[16]
Br$_2$	r(BrBr)	2.274	2.338	2.311	2.306	2.281	[16]

5 Summary

Effective Gaussian-type pseudopotential parameter sets for the elements from H to Kr were presented. Parameter sets for the gradient-corrected exchange-correlation functionals BLYP, BP and PBE were optimized. Test calculation for small molecules were performed to show the accuracy and reliability of the presented pseudopotentials. All the GTH pseudopotential parameter sets for the presented exchange-correlation functionals including supplementary material are also available online [14]. The parameter sets are provided in different formats for a direct usage with the program packages CPMD and CP2K (QUICKSTEP).

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