RelatQvistQc separable dual-space Gaussian pseudopotentQals from H tW Rn

C. Hartwigsen, S. Goedecker, and J. Hutter
Max-Planck-Institut für FestkWrperforschung, D-70569 Stuttgart, Germany
~ReceQved 20 March 1998

We generalize the concept Wf separable dual-space Gaussian pseudopotentQals tW the relatQvistQc case. This allWws us tW construct this type Wf pseudopotential for the whole Periodic Table, and we present a complete

$$p_i^l \quad r^{l+2(i-1)} \exp\left(-\frac{r^2}{2 r_l^2}\right) \Big/ \; r_l^{l+(4i-1)/2} \sqrt{\Gamma\left(l+\frac{4i-1}{2}\right)} \qquad (3)$$

where G denotes the gamma functioV. The projectors satisfy the normalization coVditioV

E

A 2r

p r! 5

$$V(\mathbf{r},\mathbf{r}') = V_{\rm LW}(r) + \sum_l V_l(\mathbf{r},\mathbf{r}')\, P_l + \sum_l V_l^{\rm SO}(\mathbf{r},\mathbf{r}')\, \mathbf{L}\cdot\mathbf{S}, \tag{18}$$

where $V_{\rm LW}(r)$ and $V_l(\mathbf{r},\mathbf{r}')$ are now scalar relativistic quantities but with the same form (Eqs. (1) and (2)) as the nonrelativistic case. To express $V_l^{\rm SO}$), we also use Eq (2)

TABLE I.LDA pseudopotential parameters in atomic units. The meaning Wf the entries is given in the text.

H	1	0.200000	2 4.180237	0.725075
He2	0.200000		2 9.112023	1.698368
Li	1	0.787553	2 1.892612	0.286060
		0.6*6375	1.858811	
		1.079306		
		0.000019		

Li*sc*

9 0.246318 2 10.392083 7.545 1.12

0.141251 0.038386 3*.556987

Mg 2 0.651812 2 2.864297 0.1396*8

10.891113 0.556478 2.970957 1.329941

0.096277 0.677569 1.049881

0.005152

Mgsc 10 19.419008 0.210950 2.071331

141547 40.31*626

105469

TABLE I. ~*Continued*!.

TABLE I. ~*Continued*!.

2 0.009333 0.025291
0.408712 2 7.826456
0.002010
Ti^{sc} 12 0.380000 7.548789 2 0.588377
0.334235 6.925741 2 3.142005
0.242416 5.079086 2 6.284281
0.122395 0.057447
0.242947 2
0.005822
V 5 0.690000
0.514704 2.208670 1.896763 3.076377
0.743504 1.115751 0.286649
2 0.010973 0.030816
0.374890 2 5.841633
0.002717
V ^{sc} *13* *0.375000* *4.941291* *20.096443*
0.326651 *7.659390* 2 3.892229
0.246407 4.256232 2 5.941212
0.156408 0.008030
0.240792 2 8.828518
0.006548
Cr 6 0.660000
0.498578 2.400756 2.072337 2.952179
0.719768 1.145557 0.278236
2 0.013176 0.035625
0.354341 2 6.615878
0.003514
Cr sc 14 0.370000 5.113310 2 0.646819
0.306011 8.617835 2 4.137695
0.241090 3.161588 2 5.032906
0.169781 0.000411
0.219577 2 11.157868
0.009007
MV 7 0.640000
0.481246 2.799031 2.486101 2.565630
0.669304 1.368776 0.316763
2 0.013685 0.042938
0.327763 2 7.995418
0.004536
MV

^{sc} 15 0.365000 6.748683 2 0.576569
0.280753 9.379532 2 5.575280
0.254536 2 4.229057 0.071176
0.164188 2 0.039396
0.221422 2 12.115385
0.009590
Fe 8 0.610000
0.454482 3.016640 2.583038 3.257635
0.638903 [(01 . 499642) -4514 (0 . 3 2 6 3 0 . 4 3 0 6)]TJ/F3 1 Tf 7 . 9 3 2 -1 . 3 3 3 TD (2) Tj/F1 0 1 0 T f 0 . 8 3 3 0 TD [(
0.269268 10.193723 2 6.834982
0.247686 0.145613 2 5.234954
0.201450 2 0.075829
0.223021 2 12.026941
0.010322

TABLE I. ~*ContQnued.*

Co	9	0.580000			
		0.440457	3.334978	2.873150	3.091028
		0.610048	1.634005	0.356083	
			2 0.017521	0.058766	
		0.291661	2 10.358800		
			0.007137		

Co *sc*

TABLE I. ~*Continued*!.

			0.026949		0.031400			
		0.240803	2 15.795675					
			0.015503					
Ge	4	0.540000						
		0.493743	3.826891		1.100231	2		
							0.601064	1.362518
								0.043981
							0.788369	0.191205
				As	5	0.520000		
						0.456400	4.560761	1.692389

S

Br 7

0.903088

	10	0.480000	5.571455	2	1.079963			
					0.275441	9.995135		9.336679
					0.302243	3.169126		4.049231
						2	0.576265	0.990062

TABLE I. ~*Continued*!.

	Y	3	0.900000	2	0.343891			
			0.782457		1.520655		1.484368	2 0.189013
			0.949864		0.780950		0.368739	
		0.414360	2.522621	2	0.043336	2	4.363769	0.079989
		0.406442	2 0.569552	2	1.256930	2	3.020044	2 0.075368
			0.251526	2	0.009198	2	0.077005	2 0.011657
	Y^{sc}	11	0.475000	2	0.007507	13.217914		1.353178
Zr	4	0.750000	2 0.782611					
		0.649998	1.739877		2.388208		1.205349	
		0.874408	1.018294		0.528223			
			2 0.057486		0.104495			
		0.630668	2 1.173911		0.212179			
			0.009380	2	0.011973			
Zr								
	^{sc}	12	0.470000		15.782342		0.433648	

TABLE I.

TABLE I. ~*Continued*!.

			0.03+714	2 0.002009		
		1.240949	0.065412			
			0.003109			
Cd[sc]	12	0.550000	2.382713			
		0.491505	3.207932			
		0.598565	1.940150	1.515892		
			2 0.241409	0.376830		
		0.3+7874	2 4.190072	2 0.+70156		
			0.049329	2 0.058835		
IV	3	0.610000	2.865+77			
		0.+70602	1.256194	2 0.397255	2 0.278329	
		0.858132	0.494459	2 0.380789		
			0.066367	2 0.005563		
		1.088691	0.129208			
			0.004448			
[sc]IV	13	0.530000	2.395404			
		0.474081	3.554411	4.754135	1.565040	
		0.559819	2.223664	2.035278		
			2			
		0.360488	2 4.566414	2 033 TD73785		
			0.058765	2 0.073414		
SV	4	0.605000	4.610912			
		0.663544	1.648791	2 0.141974	2 0.576546	
		0.745865	0.+69355	2 0.445070		
			0.103931	0.005057		
		0.9444509 0.225115				
			0.007066			
Sb	5	0.590000	6.680228			
		0.597684	1.9514+7	0.03+537	2 0.786631	
		0.672122	0.970313	2 0.466731		
			0.139222	0.023513		
		0.856557				
			0.009432			
Te	6	0.575000	9.387085			
		0.556456	2.046890	2 0.029333	2 0.881119	
		0.615262	1.033478	2 0.481172		
			0.172997			
		0.805101	0.317411			
			0.010809			
I	70.560000	14.661825				
		0.552830	1.338054	2 0.834851	2 0.467438	
		0.562251	0.674496	2 0.57+787		
			0.2139670.093313			
		0.+94325	0.224345			
			0.010180			
Xe8	0.560000	12.734280				
		0.507371	2.236451	2 0.403551	2 1.132507	
		0.541024	1.130043	2 0.752764		
			0.236603	0.108473		
		0.+29821	0.280131			
			0.013362			
Cs	1	1.200000				
		1.224737	0.611527	0.239830	2 03294024	
		1.280478	0.227279			
			2 0.1076270.138132			
		1.107522	2 0.542163			
			0.003259			

TABLE I. ~*Continued*!.

			2 0.339955	1.359017	2 1.145883
		0.473709	2 0.429952		
			0.064044		
		0.291527	2 19.305057		
sc	16	0.523333	17.206792	2 0.532803	
		0.479677	1.723635	2 2.659367	
		0.490598	2 0.082403	2 1 Tf11009	0.000000
			2 0.240300	1.200867	2 1.054041
		0.470840	2 0.410630		
			0.063352		
		0.284040	2 19.984292		
			0.011924		
Eu *sc*	17	0. 20417	17.373516	2 0.648468	
		0.469043	1.763638	2 2.916932	

TABLE I. ~*Continued*!.

TABLE I. ~*Continued*!.

Re	+	0.693000	8.180816		
		0.509816	2.269379	3.528529	
		0.745839	0.496693	0.925829	
			2 0.370589	0.616765	
		0.500954	2 3.689630	2 1.894601	
			0.11155+	2 0.131595	
Re^{sc}	15	0.530000	5.592660	0.94395+	
		0.403252	2.760720	2 6.396415	0.868732
		0.440951	2 0.900546	2 2.511211	0.000000
			0.788715	2 0.489984	2 0.017012
		0.390395	0.875251	2 5.672543	
			0.209737	2 0.102862	
Os	8	0.667000	9.440459		
		0.510307	2.40236+	3.046706	
		0.717553	0.499523	1.053284	
			2 0.430746	0.701752	
		0.487586	2		

TABLE 1.

ward, solution Qs the explicit Qnclusion of the semicore electrons QntW the pseudopotential. In thQs work we decided on

TABLE III. Comparison of bond lengtPs of Uolecules calculated witP our pseudopotentials ~PSP! and GAUSSIAN 94 or NUMOL ~Ref. 21! ~ AE and tPe experimental data. All GAUSSIAN 94 calculationswere done with the 6-31G(3df,3pd) b

Li_2			1.44+	1.44+	1.40121
			5.100		
			, 2.929	3.029	3.01521Be2
BF			4.516	, 4.49+ 4.510	4.6322
H	r~CC!	2.263	2.072	2.072	2.05224C
	r~HC!	2.028	2.270	2.27423	
		2.030	2.002N		
			2.06+	2.0+0	2.07421NH
HCN			1.932	1.932	1.91223
	r~CN!		2.169	2.174	2.17925
	HC!	2.038	2.039	2.01325	
$_2$OO			1.836	1.834	1.80923CO
			2.622	2.613	2.66821HF
			CH		
			, 3.279	3.313	3.27121AlH
			SQH		
			3.54+	3.542	3.57821PH
			3.	3.609 [a]	
H_{CS}		2.882	2.897	2.90121	
CS					
			2.918	2.930	2.93423Cl
				[a]	
			, 2.969	2.303[a]	2.30+21CaH
			[sc], 3.187	4.126[a]	3.78321ScH
			[sc], 3.182	3.300[b]	
ScO			3.116[sc]		3.15221TiO
			, 2.845	2.959	3.00321CrO
			, 2.903		3.05221MnO
			[sc], 2.9912	[b]	3.11428FeO
				[b]	2.9+21CoO
					3.02429NQO
				[b]	
NQH			2.726		2.78721
			2.196	2.195	2.1922

TABLEL III. ~*Continued*!.

CuO	3.153[sc], 2.749	3.176	3.258	21
CuH	2.731[sc], 2.463	2.755	2.765	21
Cu_2	4.086[sc], 3.472	4.110[b]	4.195	21
ZnO	3.157[sc], 2.886	3.161[b]		
ZnH	3.010[sc], 2.858	3.025[b]	3.013	21

accuracy and necessary computational effort, aÄ shWuld be tested carefulTy. Therefore we Önstructed both types of pseudopotentials for most elements where semicore electrons caÄ play a significant role in electronic structure calculations.

V. MOLECULES

We tested Wur pseudopotentQals by the boÄ lengths of a large Vumber of molecules. In all .culations we used Wur scalar relativistic pseudopotentQals, neglecting the terms for spin-orbQt interaction. Whenever possible we tried tW determine values for the boÄd lengths, that are Önverged tW ' $10^{2\,3}$ bohr. TW obtain this high level of accuracy, extremelylarge boxes aÄd high plane-wave energycutoffs were needed, sW that for sWme molecules the accuracy of the calculations was Timited by our computational resWurces. The

$P^{1}_{1,3}\,5^{\,1}$

[29] T. C. DeVore and T. N. Gallaher, J. Chem. Phys. **71**, 474 ~1979!.
[30] J. Demaison *et al.*, in *AtomicJ.andJ.MolecularJ.Physics.J.Molecular Constants*