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Relativistic separable dual-space Gaussian pseudopotentials from H to Rn

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We generalize the concept of separable dual-space Gaussian pseudopotentials to the relativistic case. This allows us to construct this type of pseudopotential for the whole Periodic Table, and we present a complete table of pseudopotential parameters for all the elements from H to Rn. The relativistic version of this pseudopotential retains all the advantages of its nonrelativistic version. It is separable by construction, it is optimal for integration on a real-space grid, it is highly accurate, and, due to its analytic form, it can be specified by a very small number of parameters. The accuracy of the pseudopotential is illustrated by an extensive series of molecular calculations. [S0163-1829(98)05628-8]

I. INTRODUCTION

Pseudopotentials are a well-established tool in *ab initio* structure calculations of molecules and solids. First, by replacing the atom by a pseudoatom, the number of orbitals which have to be calculated is reduced, and, second, the size of the basis set can substantially be reduced because the pseudo-wave-functions are smoother than their all-electron counterparts. In addition, relativistic effects which are relevant for heavier elements can be included in the pseudopotential construction, so that a nonrelativistic calculation can reproduce these.

In 1982, Bachelet, Hamann, and Schlüter[1] published a list of pseudopotentials for all elements up to Pu, that has found widespread application. There have been many attempts since to improve the pseudopotential transferability and their numerical efficiency. One major advance was the introduction of a separable form by Kleinmann and Bylander,[2] that significantly reduces the computational effort for the calculation of the nonlocal part, especially when using a plane-wave basis set. Gonze, Stumpf, and Scheffler[3] investigated the Kleinmann-Bylander form carefully and computed a list[4] of pseudopotentials for many elements up to Xe. Goedecker, Teter, and Hutter proposed a dual-space Gaussian-type pseudopotential which is separable and satisfies an optimality criterion for the real-space integration of the nonlocal part. For large systems there is only a quadratic scaling with respect to the system size if the integration of the nonlocal part is performed on a real-space grid, compared to a cubic scaling if a Fourier space integration is used.[6] In contrast to most other pseudopotential construction methods, the authors of Ref. 5 also included unoccupied orbitals in their method, thereby generating highly transferable pseudopotentials. They gave the nonrelativistic pseudopotential parameters for the first two rows of the periodic system, and showed that their pseudopotentials give highly accurate results in molecular calculations. They obtained results which are much closer to the quasi-exact all-electron LDA (Refs. 7 and 8) (local-density approximation) value than what is obtained in all-electron calculations with a standard Gaussian 6-31G^* basis sets. In other words, the errors due to the pseudopotential approximation were much smaller than the errors in an all-electron calculation introduced by incomplete basis sets.

In this paper we give the parameters of dual-space Gaussian pseudopotentials for all elements from H to Rn. In contrast to Ref. 5, all pseudopotentials are now generated on the basis of a fully relativistic all-electron calculation, i.e., by solving the two-component Dirac equation. The generalization of the norm-conservation property to the relativistic case proposed by Bachelet and Schlüter[9] is used for the construction. We also introduced some slight modifications of the analytic form of the pseudopotential. The parameters are given in the context of the local-density approximation. Even though the parameters change only slightly if the pseudopotential is constructed within the framework of a generalized gradient approximation[10,11] (GGA) functional, we found that molecular properties are less accurately described if LDA pseudopotentials are inserted in a molecular calculation using GGA's. Since it is not possible to construct pseudopotential tables for all current GGA schemes, a program that can construct pseudopotentials for the most common GGA's can be obtained from the authors.

II. FORM OF THE PSEUDOPOTENTIAL

The local part of the pseudopotential is given by

$$V_{\mathrm{loc}}(r)=\frac{-Z_{\mathrm{ion}}}{r}\,\mathrm{erf}\left(\frac{r}{\sqrt{2}r_{\mathrm{loc}}}\right)+\exp\left[-\frac{1}{2}\left(\frac{r}{r_{\mathrm{loc}}}\right)^2\right]\times\left[C_1+C_2\left(\frac{r}{r_{\mathrm{loc}}}\right)^2+C_3\left(\frac{r}{r_{\mathrm{loc}}}\right)^4+C_4\left(\frac{r}{r_{\mathrm{loc}}}\right)^6\right], \quad (1)$$

where erf denotes the error function. Z_{ion} is the ionic charge of the atomic core, i.e., the total charge minus the charge of the valence electrons. The nonlocal contribution $V_l(\mathbf{r},\mathbf{r}')$ to the pseudopotential is a sum of separable terms

$$V_l(\mathbf{r},\mathbf{r}')=\sum_{i=1}^{3}\sum_{j=1}^{3}\sum_{m=-l}^{+l}Y_{l,m}(\hat{\mathbf{r}})p_i^l(r)h_{i,j}^l p_j^l(r')Y_{l,m}^*(\hat{\mathbf{r}}'), \quad (2)$$

where $Y_{l,m}$ are the spherical harmonics, and l the angular momentum quantum number. The projectors $p_i^l(r)$ are Gaussians of the form

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

where Γ denotes the gamma function. The projectors satisfy the normalization condition

$$\int_0^\infty p_i^l(r)p_i^l(r)r^2dr=1.\qquad(4)$$

It is a special property of our pseudopotential that it also has an analytical form if expressed in reciprocal space. The Fourier transform of the pseudopotential is given by

$$\begin{aligned}V_{\rm loc}(g)=&-\frac{4\pi Z_{\rm ion}}{\Omega g^2}e^{-(gr_{\rm loc})^2/2}+\sqrt{8\pi^3}\,\frac{r_{\rm loc}^{\;3}}{\Omega}e^{-(gr_{\rm loc})^2/2}\times\{C_1\\&+C_2(3-g^2r_{\rm loc}^{\;2})+C_3[15-10(gr_{\rm loc})^2+(gr_{\rm loc})^4]\\&+C_4[105-105(gr_{\rm loc})^2+21(gr_{\rm loc})^4-(gr_{\rm loc})^6]\}\end{aligned}\qquad(5)$$

for the local part, and

$$\begin{aligned}V_l(\mathbf{g},\mathbf{g}')=(-1)^l\sum_{i=1}^{3}\sum_{j=1}^{3}\sum_{m=-l}^{+l}Y_{l,m}(\hat{\mathbf{g}})p_i^l(g)h_{i,j}^lp_j^l(g')\\\times Y_{l,m}^*(\hat{\mathbf{g}}')\end{aligned}\qquad(6)$$

for the nonlocal part. The Fourier transform of the projectors $p_i^l(r)$ can be calculated analytically, and for the relevant cases one obtains

$$p_1^{l=0}(g)=\frac{4\sqrt{2r_0^{\,3}}\,\pi^{5/4}}{\sqrt{\Omega}\,\exp[\frac{1}{2}(gr_0)^2]},\qquad(7)$$

$$p_2^{l=0}(g)=\frac{\sqrt{8\dfrac{2r_0^{\,3}}{15}}\,\pi^{5/4}(3-g^2r_0^{\,2})}{\sqrt{\Omega}\,\exp[\frac{1}{2}(gr_0)^2]},\qquad(8)$$

$$p_3^{l=0}(g)=\frac{16\sqrt{\dfrac{2r_0^{\,3}}{105}}\,\pi^{5/4}(15-10g^2r_0^{\,2}+g^4r_0^{\,4})}{3\sqrt{\Omega}\,\exp[\frac{1}{2}(gr_0)^2]},\qquad(9)$$

$$p_1^{l=1}(g)=\frac{8\sqrt{\dfrac{r_1^{\,5}}{3}}\,\pi^{5/4}g}{\sqrt{\Omega}\,\exp[\frac{1}{2}(gr_1)^2]},\qquad(10)$$

$$p_2^{l=1}(g)=\frac{16\sqrt{\dfrac{r_1^{\,5}}{105}}\,\pi^{5/4}g(5-g^2r_1^{\,2})}{\sqrt{\Omega}\,\exp[\frac{1}{2}(gr_1)^2]},\qquad(11)$$

$$p_3^{l=1}(g)=\frac{32\sqrt{\dfrac{r_1^{\,5}}{1155}}\,\pi^{5/4}g(35-14g^2r_1^{\,2}+g^4r_1^{\,4})}{3\sqrt{\Omega}\,\exp[\frac{1}{2}(gr_1)^2]},\qquad(12)$$

$$p_1^{l=2}(g)=\frac{8\sqrt{\dfrac{2r_2^{\,7}}{15}}\,\pi^{5/4}g^2}{\sqrt{\Omega}\,\exp[\frac{1}{2}(gr_2)^2]},\qquad(13)$$

$$p_2^{l=2}(g)=\frac{16\sqrt{\dfrac{2r_2^{\,7}}{105}}\,\pi^{5/4}g^2(7-g^2r_2^{\,2})}{3\sqrt{\Omega}\,\exp[\frac{1}{2}(gr_2)^2]},\qquad(14)$$

$$p_1^{l=3}(g)=\frac{16\sqrt{\dfrac{r_3^{\,9}}{105}}\,\pi^{5/4}g^3}{\sqrt{\Omega}\,\exp[\frac{1}{2}(gr_3)^2]}.\qquad(15)$$

In both real and Fourier space, the projectors have the form of a Gaussian multiplied by a polynomial. Due to this property the dual-space Gaussian pseudopotential is the optimal compromise between good convergence properties in real and Fourier space. The multiplication of the wave function with the nonlocal pseudopotential arising from an atom can be limited to a small region around the atom as the radial projectors $p_i^l(r)$ asymptotically tend to zero outside the covalent radius of the atom. In addition, a very dense integration grid is not required, as the nonlocal pseudopotential is reasonably smooth because of its good decay properties in Fourier space.

The use of this form for the pseudopotential is also very advantageous if atom-centered basis functions are used instead of plane waves. Because of the separability all three-center integrals are products of two-center integrals, and so only these two-center integrals have to be calculated. If atom-centered Gaussian-type orbitals are used, these two-center integrals can easily be evaluated analytically.

In the relativistic case the spin orbit coupling splits up all orbitals with $l>0$ into spin-up and spin-down orbitals with an overall angular momentum $j=l\pm1/2$. So for each angular-momentum $l>0$, one spin-up orbital and one spin-down orbital with different wave functions and pseudopotentials exist. Following Bachelet and Schlüter,[9] we give a weighted average and difference potential of these potentials. The average pseudopotential is conveniently defined as

$$V_l(\mathbf{r},\mathbf{r}')=\frac{1}{2l+1}[lV_{l-1/2}(\mathbf{r},\mathbf{r}')+(l+1)V_{l+1/2}(\mathbf{r},\mathbf{r}')]\qquad(16)$$

weighted by the different j degeneracies of the $l\pm\frac{1}{2}$ orbitals. The difference potential describes the spin-orbit coupling, and is defined as

$$\Delta V_l^{\rm SO}(\mathbf{r},\mathbf{r}')=\frac{2}{2l+1}[V_{l+1/2}(\mathbf{r},\mathbf{r}')-V_{l-1/2}(\mathbf{r},\mathbf{r}')].\qquad(17)$$

The total pseudopotential is then given by

$$V(\mathbf{r},\mathbf{r}')=V_{\mathrm{loc}}(r)\,\delta(\mathbf{r}-\mathbf{r}')+\sum_{l}\;V_l(\mathbf{r},\mathbf{r}')+\Delta V_l^{\mathrm{SO}}(\mathbf{r},\mathbf{r}')\mathbf{L}\cdot\mathbf{S}, \tag{18}$$

where $V_{\mathrm{loc}}(r)$ 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 $\Delta V_l^{\mathrm{SO}}(\mathbf{r},\mathbf{r}')$, we also use Eq. (2) just replacing the $h_{i,j}^{l}$ by different parameters $k_{i,j}^{l}$, i.e.,

$$\Delta V_l^{\mathrm{SO}}(\mathbf{r},\mathbf{r}')=\sum_{i=1}^{3}\sum_{j=1}^{3}\sum_{m=-l}^{+l}Y_{l,m}(\hat{\mathbf{r}})p_i^l(r)k_{i,j}^l p_j^l(r')Y_{l,m}^{*}(\hat{\mathbf{r}}'). \tag{19}$$

Neglecting the contributions from $\Delta V_l^{\mathrm{SO}}(\mathbf{r},\mathbf{r}')$ in Eq. (18) gives an average potential that contains all scalar parts of the relativistic pseudopotential, whereas the total potential contains relativistic effects up to order α^2.

III. DETERMINATION OF THE PSEUDOPOTENTIAL PARAMETERS

The parameters of the pseudopotentials were found by minimizing the differences between the eigenvalues and the charges within an atomic sphere of the all-electron atom and the pseudoatom. In most cases the radius of the atomic sphere was taken to be the covalent radius of the atom. For consistency we always performed a fully relativistic calculation for the all-electron atom, even when relativistic effects are negligible. The exchange and correlation energy was calculated with the functional given in Ref. 5 This functional reproduces very well the Perdew-Wang[12] functional, but is much easier to compute. To ensure transferability of the pseudopotential, we also considered the next two or three higher unoccupied orbitals for each angular momentum, and the lowest orbital of the next two unoccupied angular momenta. However, in our calculations we never exceeded $l_{\max}=3$. The atom was put in an external parabolic confining potential to have well-defined unoccupied orbitals. The pseudopotential parameters given in Table I typically reproduce the eigenvalues of the occupied orbitals, with an error of less than 10^{-5} a.u., and for unoccupied orbitals to within 10^{-3} a.u. Pseudopotentials containing semicore electrons (Sec. IV) are an exception, as the errors for the semicore orbitals are usually larger than for the valence orbitals. In many cases we found it unnecessary to include all unoccupied orbitals in our fitting procedure. For most cases the inclusion of only the first unoccupied orbital for an angular momentum results in comparably good results for the following higher unoccupied orbitals. Nevertheless we always checked all-electron eigenvalues, and pseudoeigenvalues and charges of the unoccupied orbitals to verify this.

It was already discussed in Ref. 5 that our fitting procedure yields pseudopotentials that obey the norm-conservation[13] condition, and meets several additional conditions,[14–16] such as extended norm conservation and hardness, thereby leading to pseudopotentials of a very high quality. In Table II we give the transferability errors for several excited and ionized states for some elements.

The construction of our pseudopotential differs somehow from the usual method because we fit the pseudopotential parameters that give the best overall representation for the eigenvalues and charges of several orbitals, rather than producing pseudo-wave-functions that are identical to their all-electron counterparts beyond some cutoff radius. Therefore, the wave functions of the pseudoatom and the all-electron atom approach each other only exponentially. Nevertheless the difference is very small beyond the core region, as can been seen from Fig. 1. A second consequence of our fitting procedure is that, contrary to most other pseudopotential construction methods, the local part of our pseudopotential does not correspond to a certain wave function.

It is a special feature of our method that we fit our parameters directly against the all-electron eigenvalues and charges, rather than fitting analytical or numerical potentials that reproduce pseudo-wave-functions, which themselves are constructed from their all-electron counterparts. Therefore, our pseudopotentials require significantly fewer parameters than those tabulated by Bachelet, Hamann, and Schlüter.[1] During the generation of our pseudopotentials we found that there is in general no single minimal parameter set that gives the best overall pseudopotential for one atom. This finding is different to the former study of Ref. 5, where only the first two rows of the Periodic Table were considered. We always tried to use a minimum parameter set, which is sufficient to reproducing the desired accuracy of the fitted eigenvalues and charges. Identical parameter sets were used for comparable elements, i.e., the same parameter set was used for all $3d$ or $4d$ elements, respectively. The fitting of the pseudopotential parameters is numerically demanding, as many local minima exist, so that sometimes up to some 10^5 pseudopotential evaluations are necessary until one finds good parameter values. We used a slow Simplex-Downhill algorithm[17] for the optimization, that proved to be much more robust than more sophisticated methods. The pseudopotential parameter r_{loc} was set by hand, except for the first row, because this parameter is not easily accessible by our fitting procedure. For many elements we generated and tested pseudopotentials with different values of r_{loc}. After selection of the optimum pseudopotentials, the r_{loc} values for the elements in between were interpolated so that no discontinuities occur.

IV. SEMICORE ELECTRONS

For many atoms there is no unambiguous separation of the electronic system into a well-isolated core and valence shell. For example, it is well known the n-1 p levels of the heavy alkali atoms are relatively shallow in energy and extended in space. The $3d$ wave functions of the $3d$ elements are strongly localized, so that there is a significant overlap with the $3(s,p)$ wave functions, although the latter are much lower in energy than the $3d$ and $4(s,p)$ valence wave functions. The same is true for the $4d$ and $5d$ elements. Analogously, the $4f$ wave functions of the $4f$ elements are so localized that they overlap with the $5s$ and $5p$ wave functions. In all these cases, where a non-negligible overlap between valence and core wave functions exists, the frozen-core approximation underlying the construction of all pseudopotentials is not well satisfied. One way to overcome this problem is the inclusion of a nonlinear core correction[18] that considers the contribution of the core charge to the exchange-correlation potential. Another, more straightfor-

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

H	1	0.200000	−4.180237	0.725075		
He	2	0.200000	−9.112023	1.698368		
Li	1	0.787553	−1.892612	0.286060		
		0.666375	1.858811			
		1.079306	−0.005895			
			0.000019			
Li^{sc}	3	0.400000	−14.034868	9.553476	−1.766488	0.084370
Be	2	0.739009	−2.592951	0.354839		
		0.528797	3.061666			
		0.658153	0.092462			
			0.000129			
Be^{sc}	4	0.325000	−24.015041	17.204014	−3.326390	0.165419
B	3	0.433930	−5.578642	0.804251		
		0.373843	6.233928			
		0.360393	0.000000			
			0.000878			
C	4	0.348830	−8.513771	1.228432		
		0.304553	9.522842			
		0.232677	0.000000			
			0.004104			
N	5	0.289179	−12.234820	1.766407		
		0.256605	13.552243			
		0.270134	0.000000			
			0.003131			
O	6	0.247621	−16.580318	2.395701		
		0.221786	18.266917			
		0.256829	0.000000			
			0.004476			
F	7	0.218525	−21.307361	3.072869		
		0.195567	23.584942			
		0.174268	0.000000			
			0.015106			
Ne	8	0.190000	−27.692852	4.005906		
		0.179488	28.506098	−1.076245		
		0.214913	−0.000090			
			0.010336			
Na	1	0.885509	−1.238867			
		0.661104	1.847271	0.582004		
		0.857119	0.471133			
			0.002623			
Na^{sc}	9	0.246318	−7.545593	1.125997		
		0.141251	36.556987			
		0.139668	−10.392083			
			0.038386			
Mg	2	0.651812	−2.864297			
		0.556478	2.970957	1.329941		
		0.677569	1.049881			
			0.005152			
Mg^{sc}	10	0.210950	−19.419008	2.871331		
		0.141547	40.316626			
		0.105469	−10.891113			
			0.096277			
Al	3	0.450000	−8.491351			
		0.460104	5.088340	2.679700		
		0.536744	2.193438	0.000000		
			0.006154	0.003947		

TABLE I. (*Continued*).

Si	4	0.440000	−7.336103		
		0.422738	5.906928	3.258196	
		0.484278	2.727013	0.000000	
			0.000373	0.014437	
P	5	0.430000	−6.654220		
		0.389803	6.842136	3.856693	
		0.440796	3.282606	0.000000	
			0.002544	0.017895	
S	6	0.420000	−6.554492		
		0.361757	7.905303	4.471698	
		0.405285	3.866579	0.000000	
			0.005372	0.022062	
Cl	7	0.410000	−6.864754		
		0.338208	9.062240	5.065682	
		0.376137	4.465876	0.000000	
			0.010020	0.025784	
Ar	8	0.400000	−7.100000		
		0.317381	10.249487	5.602516	
		0.351619	4.978801	0.000000	
			0.016395	0.029171	
K	1	0.950000			
		0.955364	0.914612	0.287551	−0.300224
		1.086411	0.315462	0.068194	
			−0.004343	0.010261	
		0.720606	−1.529514		
			0.000354		
K^{sc}	9	0.400000	−4.989348	−0.756048	
		0.294826	11.238705	7.067779	
		0.322359	5.256702	0.938947	
			0.015795	0.048923	
Ca	2	0.800000			
		0.669737	1.645014	1.523491	0.295996
		0.946474	0.585479	0.126329	
			−0.003362	0.012779	
		0.526550	−3.032321		
			0.000814		
Ca^{sc}	10	0.390000	−4.928146	−1.232854	
		0.281909	12.352340	7.657455	
		0.310345	5.722423	0.923591	
			0.021701	0.056661	
		0.904330	0.016806		
			0.000371		
Sc	3	0.750000			
		0.597079	1.835768	1.734309	1.418483
		0.847994	0.784127	0.246733	
			−0.008463	0.020913	
		0.454653	−3.859241		
			0.001430		
Sc^{sc}	11	0.385000	7.425036	−0.489852	
		0.359707	6.119585	−2.563453	
		0.243234	6.376618	−6.016415	
			0.083053	0.093017	
		0.252945	−8.020892		
			0.004812		
Ti	4	0.720000			
		0.528411	1.866613	1.440233	3.658172
		0.791146	0.967916	0.260687	

TABLE I. (*Continued*).

			−0.009333	0.025291	
		0.408712	−4.826456		
			0.002010		
Ti^{sc}	12	0.380000	7.548789	−0.588377	
		0.334235	6.925740	−3.142005	
		0.242416	5.079086	−6.284281	
			0.122395	0.057447	
		0.242947	−9.125896		
			0.005822		
V	5	0.690000			
		0.514704	2.208670	1.896763	3.076377
		0.743504	1.115751	0.286649	
			−0.010973	0.030816	
		0.374890	−5.841633		
			0.002717		
V^{sc}	13	0.375000	4.941291	−0.096443	
		0.326651	7.659390	−3.892229	
		0.246407	4.256230	−5.941212	
			0.156408	0.008030	
		0.240792	−8.828518		
			0.006548		
Cr	6	0.660000			
		0.498578	2.400756	2.072337	2.952179
		0.719768	1.145557	0.278236	
			−0.013176	0.035625	
		0.354341	−6.615878		
			0.003514		
Cr^{sc}	14	0.370000	5.113362	−0.646819	
		0.306011	8.617835	−4.137695	
		0.241090	3.161588	−5.032906	
			0.169781	0.000411	
		0.219577	−11.157868		
			0.009007		
Mn	7	0.640000			
		0.481246	2.799031	2.486101	2.565630
		0.669304	1.368776	0.316763	
			−0.013685	0.042938	
		0.327763	−7.995418		
			0.004536		
Mn^{sc}	15	0.365000	6.748683	−0.576569	
		0.280753	9.379532	−5.575280	
		0.254536	0.371176	−4.229057	
			0.164188	−0.039396	
		0.221422	−12.115385		
			0.009590		
Fe	8	0.610000			
		0.454482	3.016640	2.583038	3.257635
		0.638903	1.499642	0.326874	
			−0.014909	0.049793	
		0.308732	−9.145354		
			0.005722		
Fe^{sc}	16	0.360000	5.392507	−0.030066	
		0.269268	10.193723	−6.834982	
		0.247686	0.145613	−5.234954	
			0.201450	−0.075829	
		0.223021	−12.026941		
			0.010322		

TABLE I. (*Continued*).

Co	9	0.580000			
		0.440457	3.334978	2.873150	3.091028
		0.610048	1.634005	0.356083	
			−0.017521	0.058766	
		0.291661	−10.358800		
			0.007137		
Co^{sc}	17	0.355000	3.418391	0.482078	
		0.259140	11.195226	−7.845825	
		0.251425	−0.551464	−4.639237	
			0.207915	−0.108249	
		0.221665	−12.075354		
			0.011475		
Ni	10	0.560000			
		0.425399	3.619651	3.088965	3.058598
		0.584081	1.742220	0.386341	
			−0.020384	0.068770	
		0.278113	−11.608428		
			0.008708		
Ni^{sc}	18	0.350000	3.610311	0.449638	
		0.245105	12.161131	−9.078929	
		0.234741	−0.820624	−6.029071	
			0.269572	−0.143442	
		0.214950	−13.395062		
			0.013538		
Cu	1	0.580000			
		0.843283	0.975787	−0.822070	−0.133237
		1.089543	0.024580	−0.249001	
			0.010792	−0.006734	
		1.291602	−0.065292		
			−0.000730		
Cu^{sc}	11	0.530000			
		0.423734	3.888050	3.276584	2.290091
		0.572177	1.751272	0.374943	
			−0.024067	0.076481	
		0.266143	−12.676957		
			0.010489		
Zn	2	0.570000			
		0.640712	2.088557	−0.218270	−0.941317
		0.967605	0.163546	−0.227086	
			0.012139	−0.004876	
		1.330352	0.010486		
			0.000225		
Zn^{sc}	12	0.510000			
		0.400866	4.278710	3.627342	2.849567
		0.539618	2.023884	0.431742	
			−0.025759	0.090915	
		0.252151	−14.338368		
			0.012767		
Ga	3	0.560000			
		0.610791	2.369325	−0.249015	−0.551796
		0.704596	0.746305	−0.513132	
			0.029607	−0.000873	
		0.982580	0.075437		
			0.001486		
Ga^{sc}	13	0.490000			
		0.384713	4.831779	4.238168	2.833238
		0.586130	1.940527	−0.299738	

TABLE I. (*Continued*).

			0.026949	0.031400	
		0.240803	−15.795675		
			0.015503		
Ge	4	0.540000			
		0.493743	3.826891	1.100231	−1.344218
		0.601064	1.362518	−0.627370	
			0.043981	0.009802	
		0.788369	0.191205		
			0.002918		
As	5	0.520000			
		0.456400	4.560761	1.692389	−1.373804
		0.550562	1.812247	−0.646727	
			0.052466	0.020562	
		0.685283	0.312373		
			0.004273		
Se	6	0.510000			
		0.432531	5.145131	2.052009	−1.369203
		0.472473	2.858806	−0.590671	
			0.062196	0.064907	
		0.613420	0.434829		
			0.005784		
Br	7	0.500000			
		0.428207	5.398837	1.820292	−1.323974
		0.455323	3.108823	−0.632202	
			0.074007	0.068787	
		0.557847	0.555903		
			0.007144		
Kr	8	0.500000			
		0.410759	5.911194	1.967372	−1.458069
		0.430256	3.524357	−0.691198	
			0.087011	0.086008	
		0.517120	0.629228		
			0.009267		
Rb	1	1.096207	0.847333	−0.748120	
		0.955699	0.887460	0.903088	−0.006750
		1.156681	0.461734	0.336113	
			−0.043443	0.057876	
		0.664323	−1.362938		
			0.003708		
Rb^{sc}	9	0.490000	4.504151	−0.741018	
		0.282301	9.536329	9.486634	
		0.301886	2.209592	5.475249	
			−0.867379	1.237532	
		0.514895	0.449376		
			0.008685		
Sr	2	1.010000	0.684749	−0.062125	
		0.837564	1.200395	0.926675	−0.315858
		1.174178	0.439983	0.018267	
			0.004022	0.022207	
		0.743175	−1.386990		
			0.002846		
Sr^{sc}	10	0.480000	5.571455	−1.079963	
		0.275441	9.995135	9.336679	
		0.302243	3.169126	4.049231	
			−0.576265	0.990062	
		0.502045	0.43728		
			0.008991		

TABLE I. (*Continued*).

Y	3	0.900000	−0.343891		
		0.782457	1.520655	1.484368	−0.189013
		0.949864	0.780950	0.368739	
			−0.043336	0.079989	
		0.653851	−1.256930	−0.075368	
			0.009198	−0.011657	
Y^{sc}	11	0.475000	13.217914	1.353178	
		0.414360	2.522621	−4.363769	
		0.406442	−0.569552	−3.020044	
			0.251526	−0.077005	
		0.513304	−1.571003	0.627616	
			0.012450	−0.007507	
Zr	4	0.750000	−0.782611		
		0.649998	1.739877	2.388208	1.205349
		0.874408	1.018294	0.528223	
			−0.057486	0.104495	
		0.630668	−1.173911	0.212179	
			0.009380	−0.011973	
Zr^{sc}	12	0.470000	15.782342	0.433648	
		0.396540	2.571767	−4.714509	
		0.388558	−0.794123	−3.172114	
			0.301247	−0.098654	
		0.520496	−1.548402	0.826127	
			0.013187	−0.010136	
Nb	5	0.724000	4.021058		
		0.699708	1.532651	1.428264	
		0.846672	0.609675	0.596788	
			−0.080816	0.125243	
		0.516072	−2.696830	−1.694967	
			0.025653	−0.031541	
Nb^{sc}	13	0.460000	13.505394	0.752434	
		0.393708	3.222025	−4.599342	
		0.403626	−0.822037	−2.247366	
			0.246821	−0.086659	
		0.513644	−1.489848	0.823817	
			0.014064	−0.012055	
Mo	6	0.699000	7.995868		
		0.678126	1.289607	0.998113	
		0.800771	0.301412	0.741615	
			−0.104124	0.153906	
		0.453384	−2.809708	−6.820946	
			0.068972	−0.075591	
Mo^{sc}	14	0.430000	16.237452	1.496536	
		0.376255	3.362426	−5.289276	
		0.361734	−0.379571	−4.067713	
			0.378681	−0.124561	
		0.525828	−1.543211	1.074388	
			0.014460	−0.014769	
Tc	7	0.673000	13.315381		
		0.677612	0.819218	0.348460	
		0.784275	0.028673	0.658363	
			−0.080760	0.140668	
		0.519890	−5.984224	0.721822	
			0.026025	−0.041776	

TABLE I. (*Continued*).

Tc^{sc}	15	0.430000	14.910011	1.046381	
		0.369721	3.917408	−5.268399	
		0.357772	−0.270000	−3.737771	
			0.340791	−0.065948	
		0.510487	−1.586709	1.132307	
			0.015790	−0.016485	
Ru	8	0.647214	8.687723		
		0.625656	1.637866	1.329335	
		0.746425	0.639012	0.650376	
			−0.095454	0.164257	
		0.440358	−4.883365	−3.063746	
			0.046652	−0.061808	
Ru^{sc}	16	0.430000	13.582571	0.596227	
		0.364084	4.480632	−5.268679	
		0.364053	−0.320372	−3.059714	
			0.337322	−0.103467	
		0.495850	−1.597870	1.165495	
			0.017773	−0.019725	
Rh	9	0.621429	5.397962		
		0.598079	2.242111	2.151597	
		0.709586	1.155278	0.704846	
			−0.114357	0.193923	
		0.369207	−1.053058	−10.923960	
			0.135036	−0.127750	
Rh^{sc}	17	0.420000	15.225012	0.415911	
		0.350052	4.715292	−5.805525	
		0.350253	−0.504694	−3.373040	
			0.389629	−0.122856	
		0.496950	−1.685594	1.387707	
			0.018875	−0.022837	
Pd	10	0.596000	5.209665		
		0.582204	2.411076	2.318920	
		0.688787	1.227253	0.758021	
			−0.136909	0.220805	
		0.442835	−4.377131	0.413271	
			0.033797	−0.047798	
Pd^{sc}	18	0.410000	15.720259	0.140765	
		0.342151	5.177686	−5.852819	
		0.343111	−0.372561	−3.258728	
			0.406984	−0.110764	
		0.494916	−1.608273	1.446609	
			0.020374	−0.026732	
Ag	1	0.650000	−2.376061		
		1.012705	0.897931	−0.748323	0.029787
		1.235842	0.130081	−0.277495	
			0.019692	−0.006821	
		1.016159	−0.038842		
			0.009455		
Ag^{sc}	11	0.570000	1.017053		
		0.498900	2.990284	3.912395	2.205847
		0.630009	1.813968	1.304450	
			−0.201869	0.319708	
		0.387660	−3.420076	−1.019949	
			0.045193	−0.051565	
Cd	2	0.625000	−1.796838		
		0.828465	1.485292	−0.424753	−0.407986
		0.972873	0.469208	−0.448111	

TABLE I. (*Continued*).

			0.037714	−0.002009	
		1.240949	0.065412		
			0.003109		
Cd^{sc}	12	0.550000	2.382713		
		0.491505	3.207932	4.140963	1.584234
		0.598565	1.940150	1.515892	
			−0.241409	0.376830	
		0.377874	−4.190072	−0.770156	
			0.049329	−0.058835	
In	3	0.610000	2.865777		
		0.770602	1.256194	−0.397255	−0.278329
		0.858132	0.494459	−0.380789	
			0.066367	−0.005563	
		1.088691	0.129208		
			0.004448		
In^{sc}	13	0.530000	2.395404		
		0.474081	3.554411	4.754135	1.565040
		0.559819	2.223664	2.035278	
			−0.306488	0.479435	
		0.360488	−4.566414	−0.773785	
			0.058765	−0.073414	
Sn	4	0.605000	4.610912		
		0.663544	1.648791	−0.141974	−0.576546
		0.745865	0.769355	−0.445070	
			0.103931	0.005057	
		0.944459	0.225115		
			0.007066		
Sb	5	0.590000	6.680228		
		0.597684	1.951477	0.037537	−0.786631
		0.672122	0.970313	−0.466731	
			0.139222	0.023513	
		0.856557	0.300103		
			0.009432		
Te	6	0.575000	9.387085		
		0.556456	2.046890	−0.029333	−0.881119
		0.615262	1.033478	−0.481172	
			0.172997	0.050641	
		0.805101	0.317411		
			0.010809		
I	7	0.560000	14.661825		
		0.552830	1.338054	−0.834851	−0.467438
		0.562251	0.674496	−0.577787	
			0.213967	0.093313	
		0.794325	0.224345		
			0.010180		
Xe	8	0.560000	12.734280		
		0.507371	2.236451	−0.403551	−1.132507
		0.541024	1.130043	−0.752764	
			0.236603	0.108473	
		0.729821	0.280131		
			0.013362		
Cs	1	1.200000			
		1.224737	0.611527	0.239830	−0.294024
		1.280478	0.244893	0.227279	
			−0.107627	0.138132	
		1.107522	−0.542163		
			0.003259		

TABLE I. (*Continued*).

Cs^{sc}	9	0.540000	35.234438	−3.318070	
		0.456821	−0.282378	−2.780956	
		0.362467	−2.696733	−2.290940	0.000000
			−2.748528	1.815069	1.204825
		0.761462	0.183754		
			0.010841		
		0.333507	−17.948259		
			0.004760		
Ba	2	1.200000			
		1.016187	0.922593	0.763495	−0.333465
		1.249880	0.447168	0.151081	
			−0.041017	0.088800	
		0.937158	−0.718934		
			0.005321		
Ba^{sc}	10	0.540000	24.478653	−2.500850	
		0.514776	1.046729	−0.977217	
		0.375190	−0.202439	0.680331	0.000000
			−0.415083	0.599763	0.927065
		0.665403	0.378419		
			0.017660		
		0.304920	−18.795208		
			0.006151		
La^{sc}	11	0.535000	19.909308	−1.474830	
		0.551775	1.293272	−1.121819	
		0.476308	1.172527	−0.828810	0.029857
			0.524623	−0.030901	0.142077
		0.626672	0.328377		
			0.020900		
		0.299310	−18.269439		
			0.007193		
Ce^{sc}	12	0.535000	18.847470	−0.765636	
		0.521790	1.321616	−1.700444	
		0.470324	0.972641	−1.451337	0.000000
			0.463710	0.090257	0.012566
		0.703593	0.074241		
			0.013265		
		0.306717	−17.214790		
			0.007568		
Pr^{sc}	13	0.532083	18.424739	−0.657669	
		0.526850	1.012621	−1.717982	
		0.458897	1.117060	−1.852109	0.000000
			0.314280	0.350982	−0.165254
		0.747610	0.017571		
			0.010905		
		0.300773	−17.897119		
			0.008547		
Nd^{sc}	14	0.529167	17.815030	−0.594798	
		0.503000	1.529110	−2.153732	
		0.467013	0.721553	−1.647499	0.000000
			−0.214396	1.100446	−0.832670
		0.325290	−0.543240		
			0.611413		
		0.294743	−18.520228		
			0.009598		
Pm^{sc}	15	0.526250	18.251723	−0.492107	
		0.489879	1.308978	−2.507751	
		0.472260	0.160512	−1.565305	0.000000

TABLE I. (*Continued*).

			−0.339955	1.359017	−1.145883
		0.473709	−0.429952		
			0.064044		
		0.291527	−19.305057		
			0.010619		
Sm^{sc}	16	0.523333	17.206792	−0.532803	
		0.479677	1.723635	−2.659367	
		0.490598	−0.082403	−1.111009	0.000000
			−0.240300	1.200867	−1.054041
		0.470840	−0.410630		
			0.063352		
		0.284040	−19.984292		
			0.011924		
Eu^{sc}	17	0.520417	17.373516	−0.648468	
		0.469043	1.763638	−2.916932	
		0.445907	0.518046	−2.135186	0.000000
			0.252258	0.584324	−0.480586
		0.490038	−0.426120		
			0.051028		
		0.278401	−20.946528		
			0.013267		
Gd^{sc}	18	0.517500	17.512556	−0.719534	
		0.462014	1.551856	−3.068703	
		0.456953	−0.058347	−1.697711	0.000000
			0.535540	0.022024	−0.054301
		0.482368	−0.562601		
			0.053128		
		0.273390	−21.923490		
			0.014666		
Tb^{sc}	19	0.514583	17.603616	−0.828080	
		0.448694	1.718481	−3.435239	
		0.424220	0.562400	−2.781827	0.000000
			−0.008725	1.144007	−0.860425
		0.482809	−0.625802		
			0.051754		
		0.268260	−22.911697		
			0.016197		
Dy^{sc}	20	0.511667	16.994331	−0.955298	
		0.440590	1.940320	−3.559798	
		0.434642	0.014315	−2.046238	0.000000
			−0.124371	1.327404	−1.092142
		0.467229	−0.668924		
			0.058286		
		0.261670	−23.922358		
			0.017938		
Ho^{sc}	21	0.508750	16.781570	−1.173514	
		0.432212	2.052797	−3.674534	
		0.420138	0.253295	−2.355289	0.000000
			0.895947	−0.275149	0.205729
		0.447131	−0.742863		
			0.069483		
		0.254992	−25.197211		
			0.019830		
Er^{sc}	22	0.505833	17.105293	−1.430953	
		0.419948	2.144503	−3.984203	
		0.414455	0.054087	−2.294477	0.000000
			1.255135	−0.891960	0.749717

TABLE I. (*Continued*).

		0.418385	−0.999006		
			0.091862		
		0.249126	−26.696809		
			0.021783		
Tm^{sc}	23	0.502917	17.247293	−1.627697	
		0.413373	1.947196	−4.121556	
		0.409923	−0.094493	−2.224087	0.000000
			2.045370	−2.347237	1.902736
		0.392870	−1.353308		
			0.119299		
		0.243917	−28.104159		
			0.023833		
Yb^{sc}	24	0.500000	17.357144	−1.773916	
		0.402309	2.120771	−4.802990	
		0.414358	−0.923212	−1.678540	0.000000
			−0.349470	2.074295	−1.814297
		0.444025	−0.889967		
			0.070076		
		0.238298	−29.932854		
			0.025718		
Lu^{sc}	25	0.497000	17.037053	−1.661610	
		0.391206	2.184678	−5.432346	
		0.393896	−0.719819	−2.723799	0.000000
			0.152450	1.395416	−1.238744
		0.436518	−1.173245		
			0.072130		
		0.232629	−31.852262		
			0.028006		
Hf^{sc}	12	0.560000	5.134801	0.529191	
		0.422810	2.564442	−6.013732	1.109760
		0.472681	−1.025275	−1.872548	0.000000
			0.607504	−0.331637	−0.121021
		0.426388	1.459363	−5.282764	
			0.222119	−0.121283	
Ta	5	0.744000	3.623116		
		0.581801	2.005338	3.027036	
		0.770646	0.518567	1.185378	
			−0.485635	0.695148	
		0.534370	−2.202200	−1.666675	
			0.086716	−0.094635	
Ta^{sc}	13	0.550000	4.546236	0.779422	
		0.421853	2.708136	−5.790959	0.947663
		0.461345	−0.724853	−2.215211	0.000000
			0.649992	−0.336371	−0.101322
		0.410994	1.348495	−5.386947	
			0.205344	−0.102353	
W	6	0.719000	4.058450		
		0.582463	2.161166	2.741500	
		0.742307	0.600973	1.299943	
			−0.509800	0.751739	
		0.534959	−2.517063	−0.789137	
			0.075772	−0.086193	
W^{sc}	14	0.540000	4.800251	0.901544	
		0.418570	2.692204	−6.022637	1.218316
		0.449555	−0.702084	−2.451680	0.000000
			0.715480	−0.385339	−0.077093
		0.399602	1.177436	−5.553621	
			0.205860	−0.100046	

TABLE I. (*Continued*).

Re	7	0.693000	8.180816		
		0.509816	2.269379	3.528529	
		0.745839	0.496693	0.925829	
			−0.370589	0.616765	
		0.500954	−3.689630	−1.894601	
			0.111557	−0.131595	
Re^{sc}	15	0.530000	5.592660	0.943957	
		0.403252	2.760720	−6.396415	0.868732
		0.440951	−0.900546	−2.511211	0.000000
			0.788715	−0.489984	−0.017012
		0.390395	0.875251	−5.672543	
			0.209737	−0.102862	
Os	8	0.667000	9.440459		
		0.510307	2.402367	3.046706	
		0.717553	0.499523	1.053284	
			−0.430746	0.701752	
		0.487586	−4.142035	−1.666100	
			0.116941	−0.139761	
Os^{sc}	16	0.520000	5.613073	0.921955	
		0.410578	2.785758	−6.692130	2.247034
		0.422395	−0.590006	−3.018323	0.000000
			0.870817	−0.412886	−0.139506
		0.380252	0.880133	−5.732892	
			0.216440	−0.103221	
Ir	9	0.641000	10.720016		
		0.509960	2.445999	2.811037	
		0.684971	0.461792	1.304726	
			−0.565347	0.859620	
		0.471745	−4.545484	−1.635428	
			0.127199	−0.151950	
Ir^{sc}	17	0.510000	4.904509	1.313786	
		0.404469	3.243278	−7.315509	2.956978
		0.411426	−0.380574	−3.504403	0.000000
			0.930121	−0.379865	−0.262716
		0.376428	0.754315	−5.875580	
			0.219517	−0.112145	
Pt	10	0.616000	11.027417		
		0.520132	2.447430	2.640360	
		0.658976	0.408453	1.647716	
			−0.763296	1.065883	
		0.451243	−4.552295	−2.102396	
			0.146912	−0.169306	
Pt^{sc}	18	0.500000	5.445832	1.156382	
		0.409942	2.994366	−7.448772	4.243095
		0.398652	−0.225181	−3.776974	0.000000
			1.017060	−0.348213	−0.331919
		0.367964	0.632067	−5.755431	
			0.226472	−0.114346	
Au	1	0.650000	−1.963712	−1.698123	
		0.919308	1.539599	−0.468779	−0.792039
		1.140351	0.471229	−0.497538	−0.209758
			0.039349	0.132970	−0.153427
Au^{sc}	11	0.590000	11.604428		
		0.521180	2.538614	2.701113	
		0.630613	0.394853	2.057831	
			−0.960055	1.296571	
		0.440706	−4.719070	−1.650429	

TABLE 1. (*Continued*).

			0.148484	−0.169493	
Hg	2	0.640000	−3.296329		
		0.812108	1.765041	−0.466127	−0.799941
		1.053714	0.474056	−0.531816	
			0.092330	−0.001118	
		1.100000	0.120638		
			0.020931		
Hg^{sc}	12	0.570000	2.134572		
		0.521802	3.293920	4.661001	
		0.621648	2.100960	1.689988	0.000000
			0.084989	0.072771	0.653348
		0.401894	−1.669886	−2.473265	
			0.155759	−0.122282	
Tl	3	0.630000	−1.235846		
		0.754005	1.875766	−0.303680	−0.781337
		0.903742	0.759668	−0.586721	
			0.168641	0.004459	
		1.063512	0.247614		
			0.022941		
Tl^{sc}	13	0.550000	7.301886		
		0.502423	3.326560	4.341390	
		0.572016	1.272807	2.992206	0.000000
			0.012233	0.031664	1.019164
		0.393185	−3.200652	−3.008296	
			0.186849	−0.170651	
Pb	4	0.617500	0.753143		
		0.705259	1.979927	−0.164960	−0.806060
		0.846641	0.864420	−0.540969	
			0.207711	0.012948	
		0.971939	0.374967		
			0.029256		
Bi	5	0.605000	6.679437		
		0.678858	1.377634	−0.513697	−0.471028
		0.798673	0.655578	−0.402932	
			0.305314	−0.023134	
		0.934683	0.378476		
			0.029217		
Po	6	0.592500	10.411731		
		0.647950	1.144203	−0.735851	−0.339386
		0.748947	0.594562	−0.353595	
			0.396354	−0.031462	
		0.880468	0.433232		
			0.033886		
At	7	0.580000	13.520411		
		0.627827	0.945557	−0.965903	−0.190429
		0.709823	0.527078	−0.318821	
			0.480774	−0.034954	
		0.838365	0.468948		
			0.037544		
Rn	8	0.570000	14.629185		
		0.615182	0.981832	−1.038963	−0.120456
		0.676697	0.612279	−0.344122	
			0.549896	−0.023760	
		0.788337	0.557746		
			0.045488		

TABLE II. Transferability errors.

Element	state	ΔE (Ha)	Error (Ha)
C	$2s^1 2p^3 3d^0$	0.3073	-0.40×10^{-3}
	$2s^2 2p^3 3d^0$	0.4294×10^{-1}	0.11×10^{-3}
	$2s^2 2p^1 3d^0$	0.3612	-0.44×10^{-3}
	$2s^2 2p^2 3d^1$	0.3882	0.95×10^{-4}
Si	$3s^1 3p^3 3d^0$	0.2529	-0.20×10^{-3}
	$3s^2 3p^3 3d^0$	-0.5293×10^{-2}	0.38×10^{-4}
	$3s^2 3p^1 3d^0$	0.2673	-0.28×10^{-3}
	$3s^2 3p^2 3d^1$	0.2462	0.43×10^{-4}
Ge	$4s^1 4p^3 4d^0$	0.2970	-0.48×10^{-3}
	$4s^2 4p^3 4d^0$	-0.1682×10^{-1}	0.58×10^{-4}
	$4s^2 4p^1 4d^0$	0.2681	-0.23×10^{-3}
	$4s^2 4p^2 4d^1$	0.1879	0.52×10^{-4}
Sn	$5s^1 5p^3 5d^0$	0.2605	-0.40×10^{-3}
	$5s^2 5p^3 5d^0$	-0.2482×10^{-1}	0.46×10^{-4}
	$5s^2 5p^1 5d^0$	0.2510	-0.35×10^{-3}
	$5s^2 5p^2 5d^1$	0.1084	0.34×10^{-4}
Pb	$6s^1 6p^3 6d^0$	0.3181	-0.35×10^{-3}
	$6s^2 6p^3 6d^0$	-0.3587×10^{-1}	-0.41×10^{-5}
	$6s^2 6p^1 6d^0$	0.2505	-0.46×10^{-3}
	$6s^2 6p^2 6d^1$	0.7216×10^{-1}	0.33×10^{-4}
Ti	$4s^1 4p^1 3d^2$	0.1198	-0.17×10^{-3}
	$4s^2 4p^0 3d^0$	0.1166×10^{1}	-0.47×10^{-1}
	$4s^0 4p^0 3d^0$	0.3258×10^{1}	-0.10
	$4s^2 4p^1 3d^2$	0.3593×10^{-1}	0.65×10^{-4}
Ti^{sc}	$4s^1 4p^1 3d^2$	0.1198	-0.37×10^{-4}
	$4s^2 4p^0 3d^0$	0.1166×10^{1}	-0.31×10^{-2}
	$4s^0 4p^0 3d^0$	0.3258×10^{1}	-0.28×10^{-2}
	$4s^2 4p^1 3d^2$	0.3593×10^{-1}	0.15×10^{-3}

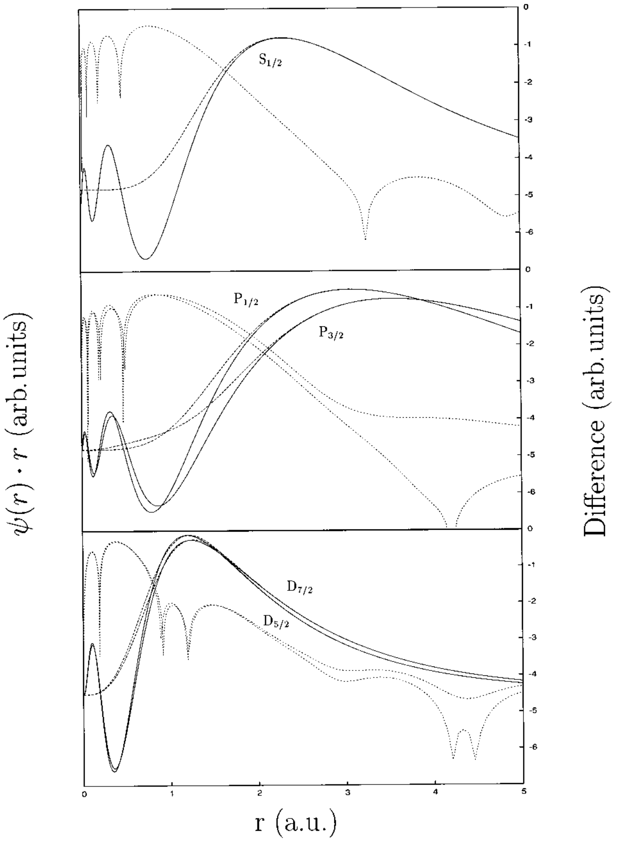

FIG. 1. Relativistic all-electron (solid line) wave function and pseudo-wave-function (dashed line) of the valence electrons of gold. The difference between them is shown by the dotted line on a logarithmic scale.

ward, solution is the explicit inclusion of the semicore electrons into the pseudopotential. In this work we decided on the second method. This ensures that our semicore pseudopotentials still can be used with programs where nonlinear corrections are not considered. In addition, the explicit inclusion of the semicore electrons ensures that our pseudopotentials still work well for systems where nonlinear core corrections fail. It is unnecessary that the eigenvalues and charge distribution of the semicore wave functions have the same accuracy as the valence wave functions of the pseudoatom. We always tried to generate semicore pseudopotentials with semicore pseudo-wave-functions that are as smooth as possible, but still yield accurate results for the valence wave functions. Therefore the error for the eigenvalues of semicore wave functions for our pseudopotentials is within 10^{-3}–10^{-2} a.u., which is about three orders of magnitude worse than the typical error for the valence wave functions.

The choice of which electrons are treated as semicore electrons also depends on the required accuracy. As we were interested in generating pseudopotentials that can be used together with plane-wave basis sets within a reasonable computational effort, we tried to include not too many semicore electrons into our pseudopotentials. Our semicore pseudopotentials for the group Ia and IIa elements, the transition metals of groups IIIb–VIIIb, and the lanthanides treat the $(n-1)$ s and the $(n-1)p$ electrons as semicore electrons. For the elements of groups Ib, IIb, and IIIa (except B and Al), all electrons of the completely filled nd shell are treated as semicore electrons.

For all elements mentioned above semicore wave functions improve the description of highly positive charged ions. In Table III the transferability error of two Ti pseudopotentials is listed for several states. For most states the calculated excitation energies are much closer to the all-electron values for the Ti semicore pseudopotential, including the $3s$ and $3p$ semicore electrons. This is most significant for the $4s^0 4p^0 3d^0$ state, which corresponds to a Ti^{4+} ion. For the $4e$ pseudopotential the error is 0.1 hartree, but only 0.28×10^{-2} hartree for the $12e$ semicore pseudopotential.

Pseudopotentials with semicore wave functions always require higher computational effort. They contain more electrons, and larger basis sets are necessary for a sufficient description of the localized semicore wave functions. In many applications like molecular structure calculations semicore pseudopotentials yield converged results with comparably small basis sets even if the calculated total energy is still far from its converged value. Therefore the inclusion of semicore electrons does not inevitably require the use of extremely large basis sets. In fact, in our molecular calculations the highest plane-wave energy cutoff was needed for calculations with the fluorine pseudopotential which has no semicore electrons at all.

In many cases it is not quite clear if semicore electrons play an important role or not. For most applications the need to use semicore pseudopotentials depends on the required

TABLE III. Comparison of bond lengths of molecules calculated with our pseudopotentials (PSP) and obtained with GAUSSIAN 94 or NUMOL (Ref. 21) (AE) and the experimental data. All GAUSSIAN 94 calculations were done with a $6-311++G(3df,3pd)$ basis set if not otherwise mentioned. Bond lengths are given in bohr.

Molecule		PSP	AE	Expt.	Ref.
H_2		1.447	1.447	1.401	21
Li_2		5.100^{sc}, 5.016	5.120	5.051	21
LiH		3.029^{sc}, 2.929	3.029	3.015	21
Be_2		4.516^{sc}, 4.497	4.510	4.63	22
BF_3		2.477	2.469	2.470	23
BH		2.363	2.371	2.373	21
CH_4		2.072	2.072	2.052	24
C_2H_2	r(CC)	2.263	2.270	2.274	23
	r(HC)	2.028	2.030	2.005	23
N_2		2.067	2.070	2.074	21
NH_3		1.932	1.932	1.912	23
HCN	r(CN)	2.169	2.174	2.179	25
	r(HC)	2.038	2.039	2.013	25
H_2O		1.836	1.834	1.809	23
CO		2.127	2.130	2.132	21
CO_2		2.196	2.195	2.192	23
F_2		2.622	2.613	2.668	21
HF		1.764	1.760	1.733	21
CH_3F	r(CF)	2.605	2.592	2.612	23
	r(HC)	2.082	2.082	2.069	23
Na_2		5.76	5.64	5.818	21
NaH		3.534^{sc}, 3.381	3.529	3.566	21
Mg_2		6.31	6.41	7.351	21
MgH		3.318^{sc}, 3.279	3.313	3.271	21
AlH		3.140	3.174	3.169	21
SiH_4		2.808	2.820	2.795	26
SiO		2.827	2.861	2.853	21
SiF_4		2.922	2.952	2.936	23
P_2		3.547	3.542	3.578	21
PH_3		2.696	2.704	2.671	27
PN		2.789	2.808	2.871	21
S_3		3.595	3.609[a]		
H_2S		2.553	2.558	2.524	23
CS		2.882	2.897	2.901	21
CS_2		2.918	2.930	2.934	23
Cl_2		3.725	3.742	3.756	21
HCl		2.436	2.440	2.409	21
CH_3Cl	r(CCl)	3.330	3.331	3.374	23
	r(CH)	2.072	2.072	2.060	23
K_2		6.936	7.358[a]	7.413	21
KH		2.200^{sc}, 2.969	2.303[a]	2.307	21
CaH		3.706^{sc}, 3.187	4.126[a]	3.783	21
ScH		3.304^{sc}, 3.182	3.300[b]		
ScO		3.116^{sc}	3.109[b]	3.152	21
TiO		3.018^{sc}, 2.840	3.020[b]	3.062	21
VO		2.943^{sc}, 2.845	2.959[b]	3.003	21
CrO		2.955^{sc}, 2.903	2.997[b]	3.052	21
MnO		2.996^{sc}, 2.991	3.032[b]	3.114	28
FeO		2.958	2.994[b]	2.97	21
CoO		2.932	3.037[b]	3.024	29
NiO		3.027	3.035[b]		
NiH		2.726		2.787	21

TABLEL III. (*Continued*).

CuO		3.153^{sc}, 2.749	3.176[b]	3.258	21
CuH		2.731^{sc}, 2.463	2.755[b]	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
GaH		3.176^{sc}, 3.095	3.173	3.143	21
GaO		3.167^{sc}, 3.022	3.173		
GaF		3.376^{sc}, 3.183	3.367	3.353	30
GeH_4		2.861	2.896	2.882	23
GeO		3.010	3.074	3.118	21
As_2		3.912	3.951	3.974	21
As_4		4.551	4.573	4.602	23
AsH_3		2.875	2.887	2.855	23
H_2Se		2.783	2.788	2.759	23
Se_2		4.089	4.097	4.076	21
Se_3 (C_{2v})		4.142	4.146		
SeO_2		3.041	3.045	3.038	30
Br_2		4.296	4.299	4.314	21
HBr		2.701	2.705	2.670	21
CH_3Br	r(CH)	2.069	2.063	2.052	23
r(CBr)		3.636	3.635	3.653	23
BrF		3.326	3.322	3.318	21
BrF_3	r_1(BrF)	3.437	3.434	3.420	23
	r_2(BrF)	3.289	3.285	3.252	
Rb_2		7.671^{sc}, 7.333		7.956	31
RbH		4.368^{sc}, 3.072		4.473	21
SrH		4.009^{sc}, 3.522		4.053	21
SrI2		5.560^{sc}, 5.327		5.69	23
SrO		3.591^{sc}		3.630	21
ZrO		3.235^{sc}, 2.848		3.234	21
RhC		3.027		3.049	21
PdH		2.865		2.889	
AgH		3.023^{sc}, 2.688		3.056	21
Ag_2		4.717^{sc}, 3.760		4.67	21
CdH		3.323^{sc}, 3.108		3.329	21
InH		3.504^{sc}, 3.394	3.512[c]	3.473	21
SnH		3.331		3.373	21
SnO		3.401		3.473	21
SnS		4.123		4.174	21
Sb_2		4.624		4.70	32
$SbCl_3$		4.414		4.411	33
Te_2		4.824		4.832	21
H_2Te		3.146	3.156[c]	3.133	23
HI		3.073	3.073[c]	3.031	21
I_2		5.029		5.039	21
Cs_2		8.479^{sc}, 7.976		8.783	34
CsH		4.630^{sc}, 3.171		4.713	21
BaH		4.176^{sc}, 3.403		4.217	21
IrC		3.324		3.180	21
PtH		2.872		2.888	21
PtC		3.612		3.371	21
AuH		2.898^{sc}, 2.424		2.879	21
HgH		3.278^{sc}, 3.067		3.284	21
TlH		3.600^{sc}, 3.440		3.534	21
TlCl		4.472		4.81	21
PbH		3.433		3.475	21

TABLE III (*Continued*).

PbS	4.237	4.526	22
$PbCl_2$	4.552	4.609	34
BiH	3.374	3.411	22

[a] GAUSSIAN 94 with $3-21G$ basis set.

[b] GAUSSIAN 94 with $6-311++G(3d,3pd)$ basis set.

[c] Reference 20.

accuracy and necessary computational effort, and should be tested carefully. Therefore we constructed both types of pseudopotentials for most elements where semicore electrons can play a significant role in electronic structure calculations.

V. MOLECULES

We tested our pseudopotentials by calculating the bond lengths of a large number of molecules. In all calculations we used our scalar relativistic pseudopotentials, neglecting the terms for spin-orbit interaction. Whenever possible we tried to determine values for the bond lengths, that are converged to $\approx 10^{-3}$ bohr. To obtain this high level of accuracy, extremely large boxes and high plane-wave energy cutoffs were needed, so that for some molecules the accuracy of the calculations was limited by our computational resources. The calculated bond lengths, together with their experimental values, are listed in Table III. As a reference for the quasi-exact LDA value, we also list the bond lengths calculated with GAUSSIAN 94 (Ref. 19) using a $6-311G++(3df,3pd)$ basis set (for the $3d$ elements, no f polarization functions have been used). With a few exceptions the values calculated with GAUSSIAN 94 agree within a few thousandths of a bohr, with the LDA results published by Dickson and Becke,[20] and therefore should be close to the LDA limit. For some molecules where no high precision basis sets are available, we took the all-electron results from Dickson and Becke. To estimate the error arising from the pseudopotential approximation, our calculated values should be compared with these LDA results rather than with the experimental bond lengths. Unfortunately exact LDA values for molecules containing heavier elements often are not available because of the lack of a sufficiently accurate basis set.

The bond lengths calculated with our pseudopotentials, including semicore electrons where necessary, agree very well with the all-electron values obtained with GAUSSIAN 94. The error of the pseudopotential approximation for first row atoms is nearly ten times smaller than the LDA error, and for the heavier elements at least comparable to the LDA error. In all cases except for the non-semicore pseudopotentials, the accuracy relative to the exact LDA value is, however, better than the results obtained with standard Gaussian $6-31G^*$ basis sets, and it is comparable to or better than the results obtained with other all-electron methods. It must be mentioned that our results especially for molecules with heavier elements are not exactly comparable to the values obtained with GAUSSIAN 94 or the values of Dickson and Becke, as our pseudopotentials also include relativistic effects.

For some non-semicore pseudopotentials, the error in the calculated bond lengths is quite large. Nevertheless these pseudopotentials may still be of interest for electronic structure calculations if no high precision is required, or if the computational resources are limited. These pseudopotentials require only small basis sets which is sometimes a necessity for the study of large systems.

Our calculated bond lengths containing only first or second row atoms also agree to within one or two thousandths of a bohr to those obtained with nonrelativistic versions of these pseudopotentials that have already been published[5] (differences in the case of HCN are due to the choice of a different simulation box). This clearly demonstrates that relativistic effects do not influence the bond lengths for these molecules on a relevant scale.

VI. PARAMETERS

In the following we list the parameters for all elements up to Rn. The entries in Table I have the following meaning:

$$\begin{array}{lllllll}
\text{Element} & Z_{\text{ion}} & r_{\text{loc}} & C_1 & C_2 & C_3 & C_4 \\
 & & r_0 & h^0_{1,1} & h^0_{2,2} & h^0_{3,3} & \\
 & & r_1 & h^1_{1,1} & h^1_{2,2} & h^1_{3,3} & \\
 & & & k^1_{1,1} & k^1_{2,2} & k^1_{3,3} & \\
 & & r_2 & h^2_{1,1} & h^2_{2,2} & h^2_{3,3} & \\
 & & & k^2_{1,1} & k^2_{2,2} & k^2_{3,3} & \\
 & & \vdots & & & & .
\end{array}$$

Only the nonzero parameters are shown in Table I. Parameters for elements marked with sc correspond to semicore pseudopotentials. In order to keep the table as small as possible, the coefficients $h^l_{i,j}$ and $k^l_{i,j}$ of the nonlocal projectors for $i \neq j$ are not listed. To obtain the full parameter set, the missing $h^l_{i,j}$ and $k^l_{i,j}$ have to be calculated from $h^l_{i,i}$ and $k^l_{i,i}$. The relevant equations for the $h^l_{i,j}$ are

$$h^0_{1,2} = -\frac{1}{2}\sqrt{\frac{3}{5}}h^0_{2,2}, \tag{20}$$

$$h^0_{1,3} = \frac{1}{2}\sqrt{\frac{5}{21}}h^0_{3,3}, \tag{21}$$

$$h^0_{2,3} = -\frac{1}{2}\sqrt{\frac{100}{63}}h^0_{3,3}, \tag{22}$$

$$h^1_{1,2} = -\frac{1}{2}\sqrt{\frac{5}{7}}h^1_{2,2}, \tag{23}$$

$$h^1_{1,3}=\frac{1}{6}\sqrt{\frac{35}{11}}h^1_{3,3}, \tag{24}$$

$$h^1_{2,3}=-\frac{1}{6}\frac{14}{\sqrt{11}}h^1_{3,3}, \tag{25}$$

$$h^2_{1,2}=-\frac{1}{2}\sqrt{\frac{7}{9}}h^2_{2,2}, \tag{26}$$

$$h^2_{1,3}=\frac{1}{2}\sqrt{\frac{63}{143}}h^2_{3,3}, \tag{27}$$

$$h^2_{2,3}=-\frac{1}{2}\frac{18}{\sqrt{143}}h^2_{3,3}, \tag{28}$$

$$h^l_{i,j}=h^l_{j,i}. \tag{29}$$

By this procedure we minimize linear dependencies of the $h^l_{i,j}$ during the fit. Replacing $h^1_{i,j}$ by $k^l_{i,j}$ in Eqs. (20)–(29) gives the equations for $k^l_{i,j}$. We found that the treating all $h^l_{i,j}$ for $i \neq j$ as independent pseudopotential parameters does not improve the results.

VII. SUMMARY

We developed a complete set of relativistic LDA pseudopotentials for the whole periodic system up to Rn. The pseudopotentials are easy to use as only a few parameters are necessary. All terms for both Fourier and real space are given analytically, and no tabulated functions are needed. The pseudopotentials are highly accurate and transferable, and have been tested in extensive atomic and molecular calculations.

Gaussian-type pseudopotentials for other exchange correlation functionals or gradient-corrected functionals can easily be constructed using our LDA parameter sets as an initial guess. The necessary programs are available from the authors upon request.

ACKNOWLEDGMENTS

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