Relativistic separable dual-space Gaussian Pseudopotentials from H to Rn

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I. INTRODUCTION

Pseudopotentials are a well established tool in ab initio structure calculations of molecules and solids. First, by replacing the atom by a pseudo atom 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 non-relativistic calculation can reproduce these.

In 1982 Bachelet, Hamann and Schlüter published a list of pseudopotentials for all elements up to Pu, that has found widespread application. There have been many attempts to improve the pseudopotential transferability and their numerical efficiency since. One major advance was the introduction of a separable form by Kleinmann and Bylander,\cite{Kleinmann1968} 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\cite{Gonze1994} investigated the Kleinmann-Bylander form carefully and published a list of pseudopotentials for many elements up to Xe. Goedecker et al.\cite{Goedecker1996} proposed a new 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.\cite{Goedecker1996} In contrast to most other pseudopotential construction methods Goedecker et al.\cite{Goedecker1996} also included unoccupied orbitals in their method thereby generating highly transferable pseudopotentials. Goedecker et al.\cite{Goedecker1996} gave the non relativistic 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 (local density approximation) value than what is obtained in all-electron calculations with a standard Gaussian 6-31G* basis sets. With 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 Goedecker et al.\cite{Goedecker1996} 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\cite{Bachelet1983} 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 (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 pseudopotentials tables for all current GGA schemes, a program that can construct pseudopotentials for the most common GGAs can be obtained from the authors.

II. FORM OF THE PSEUDOPOTENTIAL

The local part of the pseudopotential is given by

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

where \( \operatorname{erf} \) denotes the error function. \( Z_{\text{ion}} \) 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.
\[ V_l(r, r') = \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{m=-l}^{l} Y_{i,m}(r) \ p_l^i(r) \ h_{i,j}^l \ p_j^l(r') \ Y_{i,m}(r') \]  

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

\[ p_l^i(r) = \frac{\sqrt{2r^{l+2(i-1)}} \exp \left( - \frac{x^2}{2r^2} \right)}{r^{l+(4i-1)/2} \sqrt{\Gamma(l + \frac{4i-1}{2})}} \]  

where \( \Gamma \) denotes the gamma function. The projectors satisfy the normalisation condition

\[ \int_0^\infty p_l^i(r) p_l^j(r) r^2 dr = 1. \]  

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

\[ V_{\text{loc}}(g) = -\frac{4\pi Z_{\text{ion}}}{\Omega g^2} e^{-\frac{(\sqrt{3}g)^2}{2}} \\
+ \sqrt{8\pi^3} \frac{V_{\text{loc}}}{\Omega} \Omega \times \left\{ C_1 + C_2 \left( 3 - g^2 r_{\text{loc}}^2 \right) \right. \\
+ C_3 \left( 15 - 10g r_{\text{loc}}^2 \right) \left. + 4C_4 \left( 105 - 105g r_{\text{loc}}^2 + 21 \left( gr_{\text{loc}} \right)^4 \left( gr_{\text{loc}} \right)^6 \right) \right\} \]  

for the local part and

\[ V_l(g, g') = (-1)^l \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{m=-l}^{l} Y_{i,m}(g) \ p_l^i(g) \\
\times h_{i,j}^l \ p_j^l(g') Y_{i,m}(g') \]  

for the nonlocal part. The Fourier transform of the projectors \( p_l^i(r) \) can be calculated analytically and for the relevant cases one obtains

\[ p_{l=0}^1(g) = \frac{4\sqrt{2r^3 \pi^{5/4}}} {\sqrt{\Omega} \exp[\frac{1}{2}(g r_o)^2]}, \]  

\[ p_{l=0}^2(g) = \frac{8\sqrt{2r^3 \pi^{5/4}} (3 - g^2 r_o^2)} {\sqrt{\Omega} \exp[\frac{1}{2}(g r_o)^2]}, \]  

\[ p_{l=0}^3(g) = \frac{16\sqrt{2r^3 \pi^{5/4}} (15 - 10g^2 r_o^2 + g^4 r_o^4)} {3\sqrt{\Omega} \exp[\frac{1}{2}(g r_o)^2]}, \]  

\[ p_{l=1}^1(g) = \frac{8\sqrt{2r^3 \pi^{5/4} g}} {\sqrt{\Omega} \exp[\frac{1}{2}(g r_1)^2]}, \]  

\[ p_{l=1}^2(g) = \frac{16\sqrt{2r^3 \pi^{5/4} g^2 (5 - g^2 r_1^2)}} {\sqrt{\Omega} \exp[\frac{1}{2}(g r_1)^2]}, \]  

\[ p_{l=2}^1(g) = \frac{32\sqrt{2r^3 \pi^{5/4} g^3 (35 - 14g^2 r_1^2 + g^4 r_1^4)}} {3\sqrt{\Omega} \exp[\frac{1}{2}(g r_1)^2]}, \]  

\[ p_{l=2}^2(g) = \frac{8\sqrt{2r^3 \pi^{5/4} g^2}} {\sqrt{\Omega} \exp[\frac{1}{2}(g r_2)^2]}, \]  

\[ p_{l=2}^3(g) = \frac{16\sqrt{2r^3 \pi^{5/4} g^2 (7 - g^2 r_2^2)}} {3\sqrt{\Omega} \exp[\frac{1}{2}(g r_2)^2]}, \]  

\[ p_{l=3}^1(g) = \frac{16\sqrt{2r^3 \pi^{5/4} g^3}} {\sqrt{\Omega} \exp[\frac{1}{2}(g r_3)^2]} \]  

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 \( p_l^i(r) \) 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 a spin up and spin down orbital with overall angular momentum \( j = l \pm 1/2 \). So for each angular-momentum \( l > 0 \) one spin up and spin down orbital with different wave functions and pseudopotentials exist. Following Bachelet and Schl"uter we give a weighted average and difference potential of these potentials. The average pseudopotential is conveniently defined as

\[ V_l(r, r') = \frac{1}{2l+1} \left[ (lV_{l-1/2}(r, r') + (l+1)V_{l+1/2}(r, r')) \right] \]  

weighted by the different \( j \) degeneracies of the \( l \pm 1/2 \) orbitals. The difference potential describes the spin orbit coupling and is defined as

\[ \Delta V_{l SO}^m(r, r') = \frac{2}{2l+1} \left[ (V_{l+1/2}(r, r') - V_{l-1/2}(r, r')) \right]. \]  

The total pseudopotential is then given by
In our calculations we never exceeded the norm-conservation condition and meet several additional conditions, such as extended norm conservation and hardness, thereby leading to pseudopotentials of a very high quality.

In table III 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 pseudo atom and all-electron atom approach each other only exponentially. Nevertheless the difference is very small beyond the core region as can been seen from Fig. 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 as 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. 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 Goedecker et al. where only the first two rows of the periodic table have been considered. We always tried to use the minimum parameter set which is sufficient to reproduce 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-elements or the 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 for the optimisation that proved to be much more robust than more sophisticated methods. The pseudopotential parameter $r_{\text{loc}}$ was set by hand except for the first row because this parameter is not easy accessible by our fitting procedure. For many elements we generated and tested pseudopotentials with different values of $r_{\text{loc}}$. After selection of the optimum pseudopotentials the $r_{\text{loc}}$ values for the elements in between were interpolated so that no discontinuities occur.

The parameters of the pseudopotentials were found by minimising the differences between the eigenvalues and the charges within an atomic sphere of the all-electron and the pseudo atom. In most cases the 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 by Goedecker et al. This functional reproduces very well the Perdew-Wang 1992 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-momentum. However in our calculations we never exceeded $l_{\text{max}}=3$. The atom was put in an external parabolic confining potential to have well defined unoccupied orbitals. The pseudopotential parameters given in table III typically reproduce the eigenvalues of the occupied orbitals with an error of less than $10^{-5}$ a.u. and for the unoccupied orbitals to within $10^{-3}$ a.u. Pseudopotentials containing semi-core electrons (next Sec.) are an exception as the errors for the semi-core 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 comparable good results for the following higher unoccupied orbitals. Nevertheless we always checked all-electron and pseudo eigenvalues and charges of the unoccupied orbitals to verify this.

It has already been discussed by Goedecker et al. that our fitting procedure yields pseudopotentials that obey the norm-conservation condition and meet several additional conditions, such as extended norm conservation and hardness, thereby leading to pseudopotentials of a very high quality.

\[ V(r, r') = V_{\text{loc}}(r) \delta(r - r') + \sum_i V_i(r, r') + \Delta V_{\text{SO}}^l(r, r') L \cdot S. \]

where $V_{\text{loc}}(r)$ and $V_i(r, r')$ are now scalar relativistic quantities but with the same form (eq. (18)) as the non-relativistic case. To express $\Delta V_{\text{SO}}^l(r, r')$ we also use eq. (3) just replacing the $h^l_{i,j}$ by different parameters $k^l_{i,j}$, i.e.

\[ \Delta V_{\text{SO}}^l(r, r') = \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{m=-l}^{+l} Y_{l,m}(r) p^l_i(r) k^l_{i,j} j^l_j(r') Y_{l,m}^*(r'). \]

Neglecting the contributions from $\Delta V_{\text{SO}}^l(r, r')$ in eq. (18) gives the average potential that contains all scalar parts of the relativistic pseudopotential whereas the total potential contains relativistic effects up to order $\alpha^2$.
IV. SEMI-CORE 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 later 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. Analogous 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 that considers the contribution of the core charge to the exchange-correlation potential. The other more straightforward solution is the explicit inclusion of the semi-core electrons into the pseudopotential. In this work we decided for the second method. This ensures that our semi-core pseudopotentials still can be used with programs where non linear corrections are not considered. In addition the explicit inclusion of the semi-core electrons ensures that our pseudopotentials still work well for systems where non linear core corrections fail. It is unnecessary that the eigenvalues and charge distribution of the semi-core wave functions have the same accuracy as the valence wave functions of the pseudo atom. We always tried to generate semi-core pseudopotentials with semi-core 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 semi-core wave functions for our pseudopotentials is within 10^{-3} to 10^{-2} a.u. which is about 3 orders of magnitude worse than the typically error for the valence wave functions.

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

For all elements mentioned above semi-core wave functions improve the description of highly positive charged ions. In table 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 semi-core pseudopotential including the 3s- and 3p-semi-core electrons. This is most significant for the 4s^04p^03d^0 state which corresponds to a Ti^{2+}-ion. For the 4e-pseudopotential the error is 0.1 Hartree but only 0.28×10^{-2} Hartree for the 12e-semi-core pseudopotential.

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

In many cases it is not quite clear, if semi-core electrons play an important role or not. For most applications the need to use semi-core pseudopotentials depends on the required accuracy and necessary computational effort and should be tested carefully. Therefore we constructed both type of pseudopotentials for most elements where semi-core 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 ≈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. As a reference for the quasi-exact LDA value we also list the bond lengths calculated with GAUSSIAN 94 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 thousands of a Bohr with the LDA results published by Dickson and Becke 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 avail-
able because of the lack of a sufficiently accurate basis set.

The bond lengths calculated with our pseudopotentials, including semi-core 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 semi-core 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 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 semi-core 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 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 thousands of a Bohr to those obtained with nonrelativistic versions of these pseudopotentials that have already been published (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. THE PARAMETERS

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

| Element | Zion | r_{loc} | C_1 | C_2 | C_3 | C_4 |
|---------|------|--------|-----|-----|-----|-----|
| r_0     |      | h_0^{0,1} | h_0^{0,2} | h_0^{0,3} |
| r_1     |      | h_1^{1,1} | h_1^{1,2} | h_1^{1,3} |
| r_2     |      | h_2^{2,1} | h_2^{2,2} | h_2^{2,3} |
|         |      | k_1^{1,1} | k_1^{1,2} | k_1^{1,3} |
|         |      | k_2^{2,1} | k_2^{2,2} | k_2^{2,3} |

Only the nonzero parameters are shown in Table I. Parameters for elements marked with * correspond to semi-core pseudopotentials. In order to keep the table as small as possible the coefficients h_{i,j}^l and k_{i,j}^l of the nonlocal projectors for i \neq j are not listed. To get the full parameter set the missing h_{i,i}^l and k_{i,i}^l have to be calculated from the h_{i,j}^l and k_{i,j}^l. The relevant equations for the h_{i,j}^l are:

\begin{align*}
h_{1,2}^0 &= -\frac{1}{2} \sqrt{\frac{3}{5}} h_{2,2}^0, \\
h_{1,3}^0 &= \frac{1}{2} \sqrt{\frac{5}{21}} h_{3,3}^0, \\
h_{2,3}^0 &= -\frac{1}{2} \sqrt{\frac{100}{63}} h_{3,3}^0, \\
h_{1,2}^1 &= -\frac{1}{2} \sqrt{\frac{5}{7}} h_{2,2}^1, \\
h_{1,3}^1 &= \frac{1}{6} \sqrt{\frac{35}{11}} h_{3,3}^1, \\
h_{2,3}^1 &= -\frac{14}{6} \sqrt{\frac{11}{15}} h_{3,3}^1, \\
h_{1,2}^2 &= -\frac{1}{2} \sqrt{\frac{7}{9}} h_{2,2}^2, \\
h_{2,3}^2 &= \frac{1}{2} \sqrt{\frac{63}{143}} h_{3,3}^2, \\
h_{2,3}^3 &= -\frac{1}{2} \sqrt{\frac{18}{143}} h_{3,3}^3, \\
h_{i,j}^l &= h_{i,j}^l.
\end{align*}

By this procedure one obtains a set of projector functions

\begin{equation}
P_k^l(r) = \sum_{i=1}^{k} \sum_{j=1}^{k} h_{i,j}^l p_i^l(r), \quad k = 1, 2, 3
\end{equation}

that satisfy the orthogonality relation

\begin{equation}
\int_0^\infty P_i^l(r) P_j^l(r) r^2 dr = 0 \quad \text{for} \quad i \neq j.
\end{equation}

Replacing h_{i,j}^l by k_{i,j}^l in eqs. (20-29) gives the equations for the k_{i,j}^l. We found that the orthogonalization of the projectors improves the fitting procedure of our pseudopotential rather than keeping all h_{i,j}^l zero for i \neq j as was done in the former work of Goedecker et al. Treating the h_{i,j}^l 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.
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| Element | 1st Row | 2nd Row | 3rd Row | 4th Row | 5th Row | 6th Row |
|---------|---------|---------|---------|---------|---------|---------|
| H       | 0.20000 | -4.18023 | 0.725075 |         |         |         |
| He      | 0.20000 | -0.11203 | 1.698368 |         |         |         |
| Li      | 0.78755 | -1.89261 | 0.286060 |         |         |         |
| Li       | 0.78755 | -1.89261 | 0.286060 |         |         |         |
| Be      | 0.20000 | -2.59295 | 0.354839 |         |         |         |
| Be       | 0.20000 | -2.59295 | 0.354839 |         |         |         |
| B       | 0.43393 | -5.57864 | 0.804251 |         |         |         |
| C       | 0.43393 | -5.57864 | 0.804251 |         |         |         |
| N       | 0.28918 | -12.23482 | 1.766407 |         |         |         |
| O       | 0.28918 | -12.23482 | 1.766407 |         |         |         |
| F       | 0.25660 | 13.55223 |         |         |         |         |
| Ne      | 0.19000 | -27.69285 | 4.005906 |         |         |         |
| Na      | 0.88551 | -1.23886 | 0.582004 |         |         |         |
| Na       | 0.88551 | -1.23886 | 0.582004 |         |         |         |
| Mg      | 0.25879 | 3.061666 | 0.02462 |         |         |         |
| Mg       | 0.25879 | 3.061666 | 0.02462 |         |         |         |
| Mgac    | 0.25879 | 3.061666 | 0.02462 |         |         |         |
| Sc      | 0.75000 | 1.835768 | 1.734309 | 1.418483 |         |         |
| Ti      | 0.72000 | 1.864236 | 3.856693 |         |         |         |
| Ti       | 0.72000 | 1.864236 | 3.856693 |         |         |         |

**TABLE I.** LDA pseudopotential parameters. The meaning of the entries is given in the text.
| Atoms | Ni 10 | Ni* 11 | Cu 1 | Cu* 12 | Zn 2 | Zn* 13 | Ga 3 | Ge 4 | As 5 |
|-------|-------|--------|------|--------|------|--------|------|------|------|
| V 5   | .560000 | .560000 | .580000 | .530000 | .510000 | .500000 | .560000 | .540000 | .520000 |
| Cr 6   | .590000 | .600000 | .843283 | .423734 | .400866 | .454482 | .610791 | .493743 | .440457 |
| Mn 7   | .640000 | .650000 | .670459 | .604712 | .608660 | .645482 | .610791 | .493743 | .440457 |
| Fe 8   | .610000 | .620000 | .704596 | .670459 | .608660 | .645482 | .610791 | .493743 | .440457 |
| Co 9   | .580000 | .590000 | .601064 | .493743 | .493743 | .493743 | .493743 | .493743 | .493743 |
| Ni* 13 | .375000 | .326511 | .246407 | .326511 | .326511 | .326511 | .326511 | .326511 | .326511 |

**Table:**

- **V:** Vanadium, **Cr:** Chromium, **Mn:** Manganese, **Fe:** Iron, **Co:** Cobalt, **Ni:** Nickel, **Cu:** Copper, **Zn:** Zinc, **Ga:** Gallium, **Ge:** Germanium, **As:** Arsenic.
| Element | Atomic Number | Zr<sup>sc</sup> | Nb<sup>sc</sup> |
|---------|---------------|-----------------|-----------------|
| Se<sup>6</sup> | 34 | 12 | 5 |
| Br<sup>7</sup> | 35 | 23 | 6 |
| Kr<sup>8</sup> | 36 | 35 | 7 |
| Rb<sup>9</sup> | 37 | 47 | 8 |
| Sr<sup>10</sup> | 38 | 67 | 9 |
| Y<sup>11</sup> | 39 | 87 | 10 |
| Zr<sup>12</sup> | 40 | 107 | 11 |
| Ru<sup>13</sup> | 44 | 127 | 12 |
Rh 17  .420000  15.225012  .415911
 .350052  4.715292  -5.805525
 .350253  -5.04694  -3.373040
 .389629  -1.22856
 .496950  -1.685594  1.387707
 .18857 - .022837

Pd 10  .596000  5.209665  .582204  .2411076  2.318920
 .68878  1.227253  .758021
 -.136909  .220805
 .442835  -4.377131  .413271

Pd 18  .410000  15.720259  .140765
 .342151  5.177686  -5.852819
 .343111  -3.258728
 .494916  -1.372561  .3258728
 .494916  -1.608273  1.446609
 .018875  -.022837

Ag 1  .650000  -2.376061  .507371
 1.012705  .97931  .541024
 1.235842  .30081  .236063
 1.016159  -.03884  .10809

Ag 11  .570000  1.017053  .552830  .338504
 .498900  2.990284  .562251
 .630009  1.813968  .674496
 .30081  .236063
 .387660  -3.420076  -5.77787
 .016992  -.006821

Cd 2  .625000  -1.796838  .556456
 .828465  1.485292  .556251
 .972873  .469208  .21967
 .037714  -.002009
 1.240949  .065412

Cd 12  .550000  2.382713  .554000
 .491505  3.207932  .540000
 .598565  1.940150  .540000
 .377874  -4.19007  -5.77787
 .493029  -.058835

In 3  .610000  2.865777  .937158
 .776062  1.256194  .937158
 .858132  .94459  .447168
 .066367  -.005563
 1.088691  .129208

In 13  .530000  2.395404  .665403
 .474081  3.554111  .378419
 .559819  2.223664  .17666
 -.306488  .479435
 .389629  -4.566414  .017660

Sn 4  .605000  4.610912  .551775
 .663544  1.648791  .551775
 .745865  .769355  .1293272
 .944459  .225115  -.1121819

Cs 1  1.200000
 .498900  2.990284
 .630009  1.813968
 .387660  -3.420076

Cs 9  .540000  35.234438  -3.318070
 .456821  -.282378
 .362467  -2.290940  .00000

Ba 2  1.200000
 .598565  1.940150
 .377874  -4.19007
 .493029  -.058835

Ba 10  .540000  24.478653  -2.500850
 .541776  1.046729
 .375190  -.202439

La 11  .535000  19.909308  -1.474830
 .551775  1.229327
 .551775  1.229327
 .476308  .172527

Cs 11  .540000  35.234438  -3.318070
 .456821  -.282378
 .362467  -2.290940  .00000

Ba 10  .540000  24.478653  -2.500850
 .541776  1.046729
 .375190  -.202439

La 11  .535000  19.909308  -1.474830
 .551775  1.229327
 .551775  1.229327
 .476308  .172527

Xe 8  .560000  12.734280
 1.012705  .97931
 1.235842  .30081
 1.016159  -.03884

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 1.012705  .97931
 1.235842  .30081
 1.016159  -.03884

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 1.235842  .30081
 1.016159  -.03884

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 1.012705  .97931
 1.235842  .30081
 1.016159  -.03884

Xe 8  .560000  12.734280
 1.012705  .97931
 1.235842  .30081
 1.016159  -.03884
| Element | Atomic Number | Atomic Weight | Charge | Coordinates |
|---------|---------------|---------------|--------|-------------|
| Ce      | 58            | 140.1177      | +3     | (x, y, z)    |
| Pr      | 59            | 140.908      | +3     | (x, y, z)    |
| Nd      | 60            | 144.242      | +3     | (x, y, z)    |
| Pm      | 61            | 147.260      | +3     | (x, y, z)    |
| Sm      | 62            | 150.340      | +3     | (x, y, z)    |
| Eu      | 63            | 151.965      | +3     | (x, y, z)    |
| Gd      | 64            | 157.250      | +3     | (x, y, z)    |
| Tb      | 65            | 164.931      | +3     | (x, y, z)    |
| Dy      | 66            | 162.500      | +3     | (x, y, z)    |
| Ho      | 67            | 166.930      | +3     | (x, y, z)    |
| Er      | 68            | 167.259      | +3     | (x, y, z)    |
| Tm      | 69            | 170.360      | +3     | (x, y, z)    |
| Yb      | 70            | 173.040      | +3     | (x, y, z)    |
| Lu      | 71            | 174.967      | +3     | (x, y, z)    |
| Hf      | 72            | 178.490      | +3     | (x, y, z)    |
| Molecule | PSP | AE | Expt. | Ref. |
|----------|-----|----|-------|------|
| H₂       | 1.447 | 1.447 | 1.401 | 22 |
| Li₂      | 5.100<sup>sc</sup>, 5.016 | 5.120 | 5.051 | 22 |
| LiH      | 3.029<sup>sc</sup>, 2.929 | 3.029 | 3.015 | 22 |
| Be₂      | 4.516<sup>sc</sup>, 4.497 | 4.510 | 4.63 | 22 |
| BF₃      | 2.477 | 2.469 | 2.470 | 22 |
| BH       | 2.363 | 2.371 | 2.373 | 22 |
| CH₄      | 2.072 | 2.072 | 2.052 | 22 |
| C₂H₂     | r(CC) | 2.263 | 2.270 | 2.274 |
|          | r(HC) | 2.028 | 2.030 | 2.005 |
| N₂       | 2.067 | 2.070 | 2.074 | 22 |
| NH₃      | 1.932 | 1.932 | 1.912 | 24 |
| HCN      | r(CN) | 2.169 | 2.174 | 2.179 |
|          | r(HC) | 2.038 | 2.039 | 2.013 |
| H₂O      | 1.836 | 1.834 | 1.809 | 22 |
| CO       | 2.127 | 2.130 | 2.132 | 22 |
| CO₂      | 2.196 | 2.195 | 2.192 | 22 |
| F₂       | 2.622 | 2.613 | 2.686 | 22 |
| HF       | 1.764 | 1.760 | 1.733 | 22 |
| CH₃F     | r(CF) | 2.605 | 2.592 | 2.612 |
|          | r(HC) | 2.082 | 2.082 | 2.069 |
| Na₂      | 5.76 | 5.64 | 5.818 | 22 |
| NaH      | 3.534<sup>sc</sup>, 3.381 | 3.529 | 3.566 | 22 |
| Mg₂      | 6.31 | 6.41 | 7.351 | 22 |
| MgH      | 3.318<sup>sc</sup>, 3.279 | 3.313 | 3.271 | 22 |
| AlH      | 3.140 | 3.174 | 3.169 | 22 |
| SiH₄     | 2.808 | 2.820 | 2.795 | 22 |
| SiO      | 2.827 | 2.861 | 2.853 | 22 |
| SiF₄     | 2.922 | 2.952 | 2.936 | 22 |
| P₂       | 3.547 | 3.542 | 3.578 | 22 |
| PH₃      | 2.696 | 2.704 | 2.671 | 22 |
| PN       | 2.789 | 2.808 | 2.871 | 22 |
| S₂       | 3.595 | 3.609<sup>a</sup> | 3.609<sup>a</sup> | 3.609<sup>a</sup> |
| H₂S      | 2.553 | 2.558 | 2.524 | 24 |
| CS       | 2.882 | 2.897 | 2.901 | 22 |
| CS₂      | 2.918 | 2.930 | 2.934 | 22 |
| Cl₂      | 3.725 | 3.742 | 3.756 | 22 |
| HCl      | 2.436 | 2.440 | 2.409 | 22 |
| CH₃Cl    | r(CC) | 3.330 | 3.331 | 3.374 |
|          | r(CH) | 2.072 | 2.072 | 2.060 |
| K₂       | 6.936 | 7.358<sup>a</sup> | 7.413 | 22 |
| KH       | 2.200<sup>sc</sup>, 2.969 | 2.303<sup>a</sup> | 2.307<sup>a</sup> |
| CaH      | 3.706<sup>sc</sup>, 3.187 | 4.126<sup>a</sup> | 3.783 | 22 |
| ScH      | 3.304<sup>sc</sup>, 3.182 | 3.300<sup>b</sup> | 3.300<sup>b</sup> |
| ScO      | 3.116<sup>sc</sup> | 3.109<sup>b</sup> | 3.152 | 22 |
| TiO      | 3.018<sup>sc</sup>, 2.840 | 3.020<sup>ab</sup> | 3.062 | 22 |
| VO       | 2.943<sup>sc</sup>, 2.845 | 2.959<sup>b</sup> | 3.003 | 22 |
| CrO      | 2.955<sup>sc</sup>, 2.903 | 2.997<sup>b</sup> | 3.052 | 22 |
| MnO      | 2.996<sup>sc</sup>, 2.991 | 3.032<sup>ab</sup> | 3.114 | 22 |
| FeO      | 2.958 | 2.994<sup>b</sup> | 2.97 | 22 |
| CoO      | 2.932 | 3.037<sup>b</sup> | 3.024 | 22 |
| NiO      | 3.027 | 3.035<sup>b</sup> | 3.152 | 22 |
| NH₃      | 2.726 | 2.787 | 22 |
| CuO      | 3.153<sup>sc</sup>, 2.749 | 3.176<sup>b</sup> | 3.258 | 22 |
| Element | state | ΔE (Ha) | Error (Ha) |
|---------|-------|---------|------------|
| C       | 2s**2p**3d° | 0.3073 | -0.4×10⁻³ |
|         | 2s**2p**13d^0 | 0.4294×10⁻¹ | 0.11×10⁻³ |
|         | 2s**2p**13d^0 | 0.3612 | -0.44×10⁻³ |
|         | 2s**2p**13d^1 | 0.3882 | 0.95×10⁻⁴ |
| Si      | 3s**3p**13d^0 | 0.2529 | -0.20×10⁻³ |
|         | 3s**3p**13d^0 | -0.5293×10⁻² | 0.38×10⁻⁴ |
|         | 3s**3p**13d^0 | 0.2673 | -0.28×10⁻³ |
|         | 3s**3p**13d^1 | 0.2462 | 0.43×10⁻⁴ |
| Ge      | 4s**4p**14d^0 | 0.2970 | -0.48×10⁻³ |
|         | 4s**4p**14d^0 | -0.1682×10⁻¹ | 0.58×10⁻⁴ |
|         | 4s**4p**14d^0 | 0.2681 | -0.23×10⁻³ |
|         | 4s**4p**14d^1 | 0.1879 | 0.52×10⁻⁴ |
| Sn      | 5s**5p**15d^0 | 0.2605 | -0.40×10⁻³ |
|         | 5s**5p**15d^0 | -0.2482×10⁻¹ | 0.46×10⁻⁴ |
|         | 5s**5p**15d^0 | 0.2510 | -0.35×10⁻³ |
|         | 5s**5p**15d^1 | 0.1084 | 0.34×10⁻⁴ |
| Pb      | 6s**6p**16d | 0.3181 | -0.35×10⁻³ |
|         | 6s**6p**16d | -0.3587×10⁻¹ | -0.41×10⁻⁵ |
|         | 6s**6p**16d | 0.2505 | -0.46×10⁻³ |
|         | 6s**6p**16d^1 | 0.7216×10⁻¹ | 0.33×10⁻⁴ |
| Ti      | 4s**4p**13d^2 | 0.1198 | -0.17×10⁻³ |
|         | 4s**4p**13d^0 | 0.1166×10⁻¹ | -0.47×10⁻¹ |
|         | 4s**4p**13d^0 | 0.3258×10⁻¹ | -0.10 |
|         | 4s**4p**13d^2 | 0.3593×10⁻¹ | 0.65×10⁻⁴ |
| Ti^c   | 4s**4p**13d^2 | 0.1198 | -0.37×10⁻⁴ |
|         | 4s**4p**13d^0 | 0.1166×10⁻¹ | -0.31×10⁻² |
|         | 4s**4p**13d^0 | 0.3258×10⁻¹ | -0.28×10⁻² |
|         | 4s**4p**13d^2 | 0.3593×10⁻¹ | 0.15×10⁻³ |

~*: calculated with NUMOL

![FIG. 1. Relativistic all-electron (solid) and pseudo (dashed) wave functions of the valence electrons of gold. The difference between them is shown by the dotted line on a logarithmic scale.](image-url)
Figure 1: Relativistic all-electron (solid) and pseudo (dash) wave functions for the valence states of gold. The difference between them is shown by the dotted line on a logarithmic scale.
