Separable Dual Space Gaussian Pseudo-potentials

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PACS: 31.10.+z and 71.10.+x

Abstract

We present pseudo-potential coefficients for the first two rows of the periodic table. The pseudo potential is of a novel analytic form, that gives optimal efficiency in numerical calculations using plane waves as basis set. At most 7 coefficients are necessary to specify its analytic form. It is separable and has optimal decay properties in both real and Fourier space. Because of this property, the application of the nonlocal part of the pseudo-potential to a wave-function can be done in an efficient way on a grid in real space. Real space integration is much faster for large systems than ordinary multiplication in Fourier space since it shows only quadratic scaling with respect to the size of the system. We systematically verify the high accuracy of these pseudo-potentials by extensive atomic and molecular test calculations.
1 Introduction

Pseudo-potentials are an essential ingredient for efficient electronic structure calculations. First, by eliminating the core electrons the number of orbitals that has to be calculated is reduced. Second, the pseudo-wave-functions are much smoother in the core region than the all-electron wave-functions and the number of basis functions can therefore be reduced. Especially if plane waves are used as basis set this reduction of the size of the basis set is essential. The introduction of the norm-conserving property\(^1\) made pseudo-potentials an easy to handle and popular tool for electronic structure calculations. Many attempts have since then been made to construct norm-conserving pseudo-potentials, which are numerically more efficient than the original ones. The introduction of the separable form\(^2\) of the norm-conserving pseudo-potentials was a major advance. In spite of all these improvements there is still cubic scaling with respect to the size of the system. For large systems this part arising from the nonlocal pseudo-potential takes most of the computer time. It has been recognized for a long time in different contexts\(^3\), that the cubic scaling of the nonlocal pseudo-potential part can be circumvented by doing the integration on a grid in real space and proposals have been made to construct pseudo-potentials with good properties for real space integration by modifying existing pseudo-potentials of the Kleinman-Bylander type\(^4\). The Kleinman-Bylander form was initially not intended for real space use and therefore does not satisfy any optimality condition for real space integration. In contrast to previous work we therefore start out with an analytical form, which has all of the optimality properties with respect to real space integration build in. A small number of parameters is then adjusted in such a way as to reflect the properties of different atoms. In contrast to most implementations of separable Kleinman-Bylander forms, it is thus not necessary to store the projectors in numerical form on dense radial grids requiring very large files. Instead the whole information on the first two rows of the periodic table can be condensed in a small table on less than a page. This method thus puts real space integration of the nonlocal pseudo-potential terms for the first time on a systematic basis. It is at the same time extremely easy to implement in a plane wave program because all the matrix elements can be calculated analytically. The chosen analytical form gives nevertheless enough freedom to impose all the well established pseudo-potential conditions and the pseudo-potential is therefore highly accurate.

2 Form of the pseudo potential

The local part \(V_{\text{loc}}(r)\) of this novel pseudo-potential is given by

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

(1)
where \( \text{erf} \) denotes the error function. \( Z_{\text{ion}} \) is the ionic charge (i.e. charge of the nucleus minus charge of the core electrons), and \( r_{\text{loc}} \) gives the range of the Gaussian ionic charge distribution leading to the \( \text{erf} \) potential.

The nonlocal part of the Hamiltonian \( H(\vec{r}, \vec{r}') \) is a sum of separable terms

\[
H(\vec{r}, \vec{r}') = 2 \sum_{i=1}^{\infty} \sum_{m} Y_{s,m}(\hat{r}) p_{s}^i(r) h_{s}^* p_{s}^i(r') Y_{s,m}^*(\hat{r}') 
\]

\[
+ \sum_{m} Y_{p,m}(\hat{r}) p_{p}^i(r) h_{p}^* p_{p}^i(r') Y_{p,m}^*(\hat{r}') ,
\]

where \( Y_{l,m} \) denotes a Spherical Harmonic. The radial projectors \( p_{l}^i(r) \) are Gaussians, where \( l \) takes on the values 0, 1 or alternatively \( s, p \).

\[
p_{1}^l(r) = \sqrt{2} \frac{r^l e^{-\frac{1}{2}(\pi r)^2}}{\Gamma(l + \frac{3}{2})}
\]

\[
p_{2}^l(r) = \sqrt{2} \frac{r^{l+2} e^{-\frac{1}{2}(\pi r)^2}}{\Gamma(l + \frac{7}{2})} .
\]

They are normalized such that

\[
\int_{0}^{\infty} p_{l}^i(r) p_{l}^i(r) r^2 dr = 1 ,
\]

where \( \Gamma \) denotes the Gamma function. The nonlocal potential tends rapidly to zero outside the core region.

The pseudo-potential can easily be transformed in Fourier space. Calculating the matrix elements for plane waves normalized within a volume \( \Omega \), \( \frac{1}{\sqrt{\Omega}} e^{i \vec{K} \vec{r}} \) we obtain for the local part

\[
V_{\text{loc}}(K) = -4\pi \frac{Z_{\text{ion}} e^{-\frac{1}{2}(K r_{\text{loc}})^2}}{K^2} + \sqrt{\frac{(2\pi)^3}{\Omega}} \frac{r_{\text{loc}}^3}{\Omega} e^{-\frac{1}{2}(r_{\text{loc}} K)^2} \left( C_1 + C_2 (3 - (r_{\text{loc}} K)^2) + C_3 (15 - 10 (r_{\text{loc}} K)^2 + (r_{\text{loc}} K)^4) + C_4 (105 - 105 (r_{\text{loc}} K)^2 + 21 (r_{\text{loc}} K)^4 - (r_{\text{loc}} K)^6) \right)
\]

For the nonlocal part we obtain

\[
H(\vec{K}, \vec{K}') = \sum_{i=1}^{\infty} \sum_{m} Y_{s,m}(\hat{K}) p_{s}^i(K) h_{s}^* p_{s}^i(K') Y_{s,m}^*(\hat{K}') 
\]

\[
- \sum_{m} Y_{p,m}(\hat{K}) p_{p}^i(K) h_{p}^* p_{p}^i(K') Y_{p,m}^*(\hat{K}) .
\]

The projectors \( p_{l}^i(K) \) can be calculated analytically and the result involves degenerate hyper-geometric functions. For the relevant cases the result is

\[
p_{1}^s(K) = \frac{1}{\sqrt{\Omega}} \frac{1}{4r_s \sqrt{2r_s} \pi^\frac{3}{2} e^{-\frac{1}{2}(K r_s)^2}} .
\]
\[
p_2^s(K) = \frac{1}{\sqrt[4]{\Omega}} 8r_s^4 \sqrt{\frac{2r_s}{15}} \pi^\frac{4}{3} e^{-\frac{3}{2} (K r_s)^2} (3 - (K r_s)^2) \tag{10}
\]
\[
p_1^p(K) = \frac{1}{\sqrt[4]{\Omega}} 8r_p^2 \sqrt{\frac{r_p}{3}} \pi^\frac{2}{3} e^{-\frac{1}{2} (K r_p)^2} K \tag{11}
\]

We see the projectors have the same form in real and Fourier space, a Gaussian multiplied by a polynomial. As is well known, the minimum uncertainty wave-packet is a Gaussian. This new pseudo-potential has therefore optimal decay properties both in real and Fourier space. Both properties are of utmost importance for the construction of a numerically efficient pseudo-potential. If the multiplication of the wave-function with the nonlocal pseudo-potential arising from an atom is done on a grid in real space, we want the nonlocal potential to be localized in a small region around the atom. We can then restrict the real space integration to this small region around the atom. In addition, we do not want to use a very dense integration grid in this region, i.e. we want the nonlocal pseudo-potential to be reasonably smooth. The first requirement is related to the decay properties of the pseudo-potential in real space, the second to its decay properties in Fourier space. The optimal compromise between both requirements is a dual space Gaussian pseudo-potential.

Even though this pseudo-potential was primarily developed for use in combination with plane waves as basis set, it can also easily be implemented with Gaussians as basis functions. All the matrix elements can be calculated analytically and with O(N) scaling.

3 Numerical method used for finding the pseudo-potential parameters

The pseudo-potential parameters were found by a least square fitting procedure. The penalty function involved the differences of the eigenvalues and charges within an atomic sphere of the all-electron and pseudo atom. These two conditions are equivalent to the condition for a norm-conserving pseudo-potential if they are applied to the occupied states. In addition we also included these differences for the first two or three unoccupied states within each angular momentum and for the lowest state of the first two unoccupied angular momentums. In order to have well defined excited states the atom was put in an additional parabolic confining potential. The inclusion of these excited states guarantees, that the energy versus logarithmic derivative curve of the pseudo atom reproduces the corresponding all-electron curve over a wide energy range of typically half a Hartree. The sets of pseudo potential parameters which we give in Table 5 and 6 typically reproduce the eigenvalues and charges of the occupied states to within 10^{-6} atomic units and of the unoccupied ones to within 10^{-3} atomic units. It turns out, that this fitting procedure also ensures, that additional requirements that are generally considered\textsuperscript{5,6} to lead to pseudo-potentials of very high quality such as extended norm-conservation and hardness are automatically satisfied as will be discussed later.
Figure 1: The pseudo-potential coefficients (Table 5) exhibit clear trends along the periodic table. On this figure the decay constants \( r_{\text{loc}} \) and \( r_s \) are shown by the solid line going with the right axis and the coefficients \( C_1 \), \( C_2 \) and \( h_1^s \) by the three dotted lines going with the left axis. All these parameters were found by the least square fitting program.

4 Discussion of the pseudo-potential parameters

We found that exactly one projector is necessary per orthogonalization constraint. For first row atoms there is therefore only one projector for the s-electrons, for second row atoms there are two for the s-channel and one for the p-channel. For the alkaline and earth alkaline atoms (Li,Be,Na,Mg) we included the outermost shell of core electrons as valence electrons, since these core levels are very shallow in energy and extended in space. Since the set of PSP parameters in table 1 are quasi minimal, they exhibit the trends across the periodic table in the same way as other physically meaningful quantities do (Fig.1).

The parameters \( r_{\text{loc}}, r_s \) and \( r_p \) are not comparable with the parameter \( r_c \) from other pseudo-potentials. For many pseudo-potentials the wave-function of the pseudo and all-electron atom agree outside \( r_c \). In our case they approach each other exponentially without ever strictly coinciding. The rate at which they approach is of course related to these parameters. In Fig. 2 and 3 the wave-functions for C and Si are shown.

There are two factors, that determine the convergence of all the relevant quantities with respect to the plane wave energy cutoff. The first factor is the location of the peak of the pseudo-wave-function. In order to get a just qualitatively reasonable result, the the minimal wave-length representable by the plane wave basis set has to be equal to roughly 4 times the radius of this maximum. Once this criterium is satisfied systematic convergence starts. If the wave-function is analytic, the convergence will be exponential. Because in this pseudo-potential both the local and nonlocal potentials are analytic, the wave-function is analytic as well and one has therefore optimal asymptotic convergence.
Figure 2: The wave-functions (full line) and pseudo-wave-functions (dashed line) for Carbon. The difference between them is shown by the dotted line on a logarithmic scale

Figure 3: The wave-functions (full line) and pseudo-wave-functions (dashed line) for Silicon. The difference between them is shown by the dotted line on a logarithmic scale
The only thing, that would allow to make the pseudo-potential softer would therefore be to shift the maximum of the pseudo-wave-functions outward. This leads however to a very fast deterioration of the physical properties of the pseudo potential. In the construction of these pseudo-potentials we did therefore not trade accuracy for extreme softness. We also found, that by taking a harder and accurate pseudo-potential with a relatively low energy cutoff, one obtains results that are of comparable quality as the ones obtained with a softer and less accurate pseudo-potential at the same energy cutoff. In the second case it is just much more difficult to realize that the results are inaccurate. In Fig. 4 we show some examples of the convergence of the energy and bond length with respect to the plane wave energy cutoff. The fact, that the convergence curve is a nearly perfect straight line on logarithmic scale shows that the asymptotic convergence sets in very early.

As can be seen from table 5 and 6, the length scales of the pseudo-potential are typically a third to a forth of the covalent radius of the atom. In a real space implementation, the integration volume of the projectors can therefore typically be restricted to within a sphere whose radius is slightly larger than the covalent radius. This means, that the integration spheres do not appreciably overlap, and the real space method is therefore already faster for system of very small size.

Figure 4: The three dotted lines show the convergence of the total energy for Si, C and O (in the order of increasing hardness). The dashed line going with the left hand axis shows the convergence of the total energy for the CO molecule, the solid line going with the right axis the convergence of the bond length in the same molecule. Not surprising, the total energy convergence in the molecule is determined and nearly identical to the one of the harder Oxygen.
5 Accuracy

We performed many atomic and molecular calculations to test the accuracy of this pseudo-potential. We found that the predictive power of widely used pseudo-potential tests such as plots of the energy vs logarithmic derivative curve and transferability tests of excited and ionized atoms is rather limited with respect to the target molecular calculations. We will therefore just mention that the pseudo-potentials of Table 5 and 6 satisfy these tests very well and give some examples for C and Si. In table 1 we give the transferability errors for several for several excited and ionized states. The reference state is the neutral atom in its spherically symmetrized ground state.

Table 1: Transferability errors:

|          | $s^1$ $p^1$ $d^0$ | $s^2$ $p^1$ $d^0$ | $s^2$ $p^1$ $d^0$ | $s^2$ $p^2$ $d^1$ |
|----------|------------------|------------------|------------------|------------------|
| Carbon   | .3071E+00        | .4272E-01        | .3618E+00        | .3881E+00        |
| Silicon  | .36E-03          | .22E-04          | .31E-03          | .19E-04          |

|          | $s^1$ $p^1$ $d^0$ | $s^2$ $p^1$ $d^0$ | $s^2$ $p^1$ $d^0$ | $s^2$ $p^2$ $d^1$ |
|----------|------------------|------------------|------------------|------------------|
| Carbon   | .2509E+00        | -.5638E-02       | .2680E+00        | .1707E+00        |
| Silicon  | .19E-03          | -.58E-04         | -.22E-03         | .11E-03          |

In Table 2 we compare the hardness\(^6\) of the all-electron and pseudo atom. The hardness is the second derivative of the total energy with respect to the occupation numbers, $\frac{\partial^2 E}{\partial n_1 \partial n_2}$, where $n_1$ is the occupation of the s-state and $n_2$ the occupation of the p-state. It is thus a symmetric 2 by 2 matrix.

Table 2: Comparison of hardness of atom and pseudo-atom

|          | All-electron atom | Pseudo atom       |
|----------|------------------|------------------|
| Carbon   | .4288E+00        | .4160E+00        |
|          | .4160E+00        | .4160E+00        |
| Silicon  | .3129E+00        | .2850E+00        |
|          | .2850E+00        | .2846E+00        |
The ultimate test for any pseudo-potential are molecular calculations. We therefore calculated the bond lengths for a large number of molecules and compared them with the quasi exact LDA limit as given by Dickson and Becke\textsuperscript{7}. The test molecules were chosen in such a way that they contain not only single bonds, but as well multiple bonds, which typically are shorter than single bonds and therefore more difficult to describe with a pseudo-potential. Also molecules whose constituent atoms have large differences in electro-negativity were preferably chosen. In these cases, the inert region\textsuperscript{8} shrinks considerably, since the atom with the larger electro-negativity imposes its electronic structure up into regions very close to the nucleus of the less electro-negative atom. They are thus the most difficult molecules for treatment with pseudo-potentials. In these molecules the bond length deviate also very much from what one would obtain by adding the covalent radii.

The results are shown in table 3. We see, that the errors for compounds containing the first row atoms B,C,N,O and F as well as H are extremely small. These errors arising from the pseudo-potential approximation are of the order of a few thousands of a Bohr and thus nearly ten times smaller than the errors arising from the LDA approximation. The errors for compounds containing the second row atoms are larger and comparable to the LDA errors. These relatively large errors can be traced back to the relatively shallow outermost core shells of these second row atoms. The errors are therefore largest for Al and smallest for Cl. We could see no improvement of the situation by adding nonlinear core correction terms\textsuperscript{14}. The errors of molecules containing Li, Be, Na and Mg are also very small, since the outermost core levels were included as valence states. It was however very difficult to calculate highly precise bond lengths for these molecules with our plane wave program. Because these atoms are very extended, huge boxes are necessary in addition to high plane wave energy cutoffs resulting in many millions of plane waves. This large basis set results in a high numerical noise level and we give the bond length therefore in some cases only to within 2 digits. Also Dickson and Becke quote some of these molecules only with 2 digits of precision in the bond length. In addition we also realized that Gaussian 94 using a 6-311G++(3df,3pd) basis set does not agree to within a few thousands of a Bohr with Dicksons results as is the case for the other molecules. In the paper by Dickson and Becke there are no results for the 2 molecules with some of the largest differences in electro-negativity, namely $SiF_4$ and $BF_3$. We compare them therefore with the results obtained from Gaussian94\textsuperscript{16} in Table 4. Assuming that these results are correct to within a few thousands of an Bohr, the errors are then indeed at the upper end of the typical limit for errors for first and second row atoms. In summary, we can say that we obtain for molecules with only first row atoms an accuracy that is nearly equal to the accuracy obtained with an all-electron calculation using a very good Gaussian basis set. For molecules involving second row atoms the accuracy is clearly inferior. In all cases the accuracy is however much better than what is obtained with standard Gaussian 6-31G* basis sets\textsuperscript{7,9} or also some other all-electron methods\textsuperscript{10}. The molecular calculations of Table 3 and 4 were done within a Fourier space framework. We duplicated however some calculations in real space and obtained indistinguishable results.
Table 3: Comparison of the bond lengths for several small molecules as obtained with this pseudopotential with the quasi exact LDA result and the experimental data. In the last column we give the error of the LDA result compared to experiment. The experimental bond lengths were also taken from reference 7.

| Molecule   | PSP Bond length (a.u.) | Diff. PSP LDA | Diff. PSP EXP | Diff. LDA, EXP |
|------------|------------------------|---------------|---------------|---------------|
| H2:        | 1.447                  | .001          | .046          | .045          |
| Li2:       | 5.099                  | -.021         | .048          | .069          |
| LiH:       | 3.029                  | .000          | .014          | .014          |
| Be2:       | 4.515                  | -.006         | -.115         | -.109         |
| BH:        | 2.363                  | -.010         | .034          | .044          |
| CH4:       | 2.072                  | .000          | .020          | .020          |
| C2H2(CC):  | 2.263                  | -.006         | -.011         | -.005         |
| C2H2(CH):  | 2.028                  | -.002         | .023          | .025          |
| N2:        | 2.067                  | -.001         | -.007         | -.006         |
| NH3:       | 1.931                  | .001          | .019          | .018          |
| HCN(CN):   | 2.171                  | -.003         | -.008         | -.005         |
| HCN(HC):   | 2.046                  | .007          | .033          | .026          |
| H2O:       | 1.835                  | .002          | .026          | .024          |
| CO:        | 2.127                  | -.002         | -.005         | -.003         |
| CO2:       | 2.196                  | .001          | .004          | .003          |
| F2:        | 2.622                  | .007          | -.046         | -.053         |
| FH:        | 1.764                  | .003          | .031          | .028          |
| CH3F(CF):  | 2.605                  | .012          | -.007         | -.019         |
| CH3F(CH):  | 2.081                  | -.001         | .012          | .013          |
| Na2:       | 5.67                   | -.00          | -.15          | -.15          |
| Mg2:       | 6.46                   | .01           | -.89          | -.90          |
| AlH:       | 3.146                  | -.023         | .032          | .055          |
| SiH4:      | 2.810                  | -.011         | .015          | .026          |
| SiO:       | 2.831                  | -.028         | -.022         | -.006         |
| P2:        | 3.547                  | -.025         | -.031         | -.006         |
| PH3:       | 2.695                  | -.009         | .024          | .033          |
| PN:        | 2.790                  | -.017         | -.027         | -.010         |
| S3:        | 3.587                  | -.022         |               |               |
| H2S:       | 2.551                  | -.005         | .027          | .032          |
| CS:        | 2.884                  | -.012         | -.017         | -.005         |
| CS2:       | 2.917                  | -.010         | -.017         | -.007         |
| HCl:       | 2.435                  | -.004         | .026          | .030          |
| CH3Cl(CC): | 3.328                  | -.001         | -.032         | -.031         |
| CH3Cl(CH): | 2.072                  | .000          | .022          | .022          |

Table 4: Comparison of the bond lengths for two particular difficult molecules as obtained with this pseudo-potential and with Gaussian94 using a 6-31G++(3df,3pd) basis set.

| Molecule   | PSP Bond length (a.u.) | Diff. to Gaussian94 LDA b.l. |
|------------|------------------------|------------------------------|
| BF3:       | 2.477                  | .011                         |
| SiF4:      | 2.926                  | -.023                        |
6 The parameters

In the following we list the parameters we found. We constructed them both for the LDA approximation and one gradient corrected scheme, namely the BLYP scheme. Gradient corrected schemes have been examined in detail. In generally they do not significantly improve bond lengths but they allow to treat hydrogen bonding which is important in many systems containing first row atoms. In the case of the LDA approximation, we used a new parameterization of the results of Ceperley and Alder described in Appendix 1. Since this parameterization does not have any discontinuities in its derivatives, it results in less numerical noise, which was very helpful in the minimization procedure. In addition it can also be calculated much faster numerically. Nevertheless, one can use these pseudo-potential parameters with any other LDA parameterization, without changing the results on a relevant scale. The entries in table 5 and 6 have the following meaning with the notation of the previous sections:

| Element | $Z_{\text{nuc}}$ | $Z_{\text{ion}}$ |
|---------|----------------|----------------|
| $r_{\text{loc}}$ | $C_1$ | $C_2$ | $C_3$ | $C_4$ |
| $r_s$ | $h_1$ | $h_2$ |
| $r_p$ | $h_3$ | $h_4$ |
| H     | 1                | 1        |
|-------|------------------|----------|
| Li    | -14.0093922      | 9.5099073| -1.7532723 | .0834586 |
| Be    | -23.9909934      | 17.1717632| -3.3189599 | .1650828 |
| B     | -5.6004798       | 6.2352212| .8062843   |
| C     | -8.5753285       | 9.5341929| 1.2341279 |
| N     | -12.2046419      | 13.5228129| 1.7558249 |
| O     | -16.4822284      | 18.1996387| 2.3701353 |
| F     | -21.408490       | 23.5641867| 3.0763646 |
| Na    | -22.5984025      | 30.5987103| 3.2558639 |
| Mg    | -27.2076704      | 36.6930557| 3.9727355 |
| Al    | -6.8340578       | 1.9160118| 1.9395165 |
| Si    | -6.9136286       | 3.2081318| 2.5888808 |
| P     | -6.6409658       | 3.2859445| 3.1506638 |
| S     | -6.5960716       | 4.2228399| 3.6696625 |
| Cl    | -6.8903645       | 4.9069762| 4.1601818 |
### Table 6: BLYP pseudo-potential parameters

| Element | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     |
|---------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| H       | 20.00 | -4.11 | .692 | 3     |
| Li      | 4.00  | -14.10 | 9.65 | -1.79 | .085 |
| Be      | 3.25  | -24.06 | 17.25 | -3.33 | .165 |
| B       | 4.24  | -6.08 | 6.32 | 3     |
| C       | 3.37  | -9.12 | 9.65 | 1.42 | 4     |
| N       | 2.82  | -12.75 | 1.95 | 1.26 | 5     |
| O       | 2.42  | -17.01 | 2.56 | 2.56 | 6     |
| F       | 2.13  | -21.93 | 3.26 | 3.26 | 7     |
| Na      | 2.47  | -22.46 | 3.27 | 3.27 | 9     |
| Mg      | 2.34  | -26.51 | 3.94 | 3.94 | 10    |
| Al      | 4.50  | -5.55 | 3.02 | 1.06 | 3     |
| Si      | 4.49  | -5.98 | 2.88 | 1.88 | 4     |
| P       | 4.31  | -5.87 | 2.94 | 2.54 | 5     |
| S       | 4.20  | -6.01 | 4.37 | 3.19 | 6     |
| Cl      | 4.10  | -6.39 | 4.98 | 3.79 | 7     |

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7 Conclusions

We have presented a novel pseudo-potential. It is extremely easy to implement both in real and Fourier space since all terms are given analytically and not numerically. Its optimality property resulting from its dual space Gaussian form guarantees optimal efficiency when it is used in real space. It is highly accurate and even in the worst case of compounds containing Al, Si and P the errors of this pseudo-potential do not dominate the errors arising from density functional theory. In all the molecular calculations we did, we could not find a single molecule, where the error in the bond length due to the pseudo-potential approximation was larger than one percent.

8 Acknowledgments

We thank the Cornell Theory Center for the access to its SP2, where all the heavy computations were done. S. G. thanks Doug Allan and Pietro Ballone for interesting discussions as well as M. Parrinello for useful remarks on the manuscript.

9 Appendix

In this work we used the following parameterization of the exchange correlation energy functional:

\[ \epsilon_{xc} = \frac{a_0 + r_s(a_1 + r_s(a_2 + r_s(a_3))}{r_s(b_1 + r_s(b_2 + r_s(b_3 + r_s(b_4)))}, \]

where

\[
\begin{align*}
a_0 &= .4581652932831429, \\
a_1 &= 2.217058676663745, \\
a_2 &= 0.740551735357053, \\
a_3 &= 0.0196822787861798, \\
b_1 &= 1.0, \\
b_2 &= 4.504130959426697, \\
b_3 &= 1.110667363742916, \\
b_4 &= 0.02359291751427506.
\end{align*}
\]

The exchange correlation energy in atomic units of Hartree is then given by

\[ E_{xc} = \int \rho(r) \epsilon_{xc}(\rho(r))dr \]

where the \( r_s \) parameter is related to the density \( \rho \) by \( \frac{4\pi}{3}r_s^3 = \frac{1}{\rho} \). This parameterization was obtained by a fit to what is considered to be the most precise results for the exchange correlation energy\textsuperscript{12,13}. In Table 7 we give the best available energy as well as the differences
to the widely used parameterization of Perdew and Zunger$^{13}$ and to our Pade approximation. As can be seen the accuracy of both parameterizations is very similar. However the Pade form of the exchange correlation energy and its derivative (the exchange correlation potential) can be evaluated 6 times faster (on a IBM RS6000 workstation) and it leads to less noise since it does not have any discontinuities in higher derivatives at $r_s=1$. Since the two approximations are so similar, we could not find any significant difference in physical observables such as bond lengths for the two parameterizations.

Table 7: Comparison of the accuracy of the approximation by Perdew Zunger and our Pade approximation with the best available results obtained by quantum Monte Carlo methods.

| $r_s$ | best (Ha) | Pade - best | PZ - best |
|------|-----------|-------------|-----------|
| 0.01 | -.46E+02  | -.4E-01     | -.3E-04   |
| 0.10 | -.47E+01  | -.4E-03     | -.4E-04   |
| 0.50 | -.99E+00  | .8E-03      | -.2E-04   |
| 1.00 | -.52E+00  | -.2E-03     | .5E-03    |
| 2.00 | -.27E+00  | -.6E-03     | .2E-03    |
| 3.00 | -.19E+00  | -.2E-03     | .3E-03    |
| 4.00 | -.15E+00  | -.6E-04     | .3E-03    |
| 5.00 | -.12E+00  | -.2E-04     | .2E-03    |
| 6.00 | -.10E+00  | .1E-03      | .3E-03    |
| 10.00| -.65E-01  | -.2E-03     | -.6E-04   |
| 20.00| -.34E-01  | .1E-03      | .2E-03    |
| 50.00| -.15E-01  | -.2E-03     | -.2E-03   |
| 100.00| -.79E-02 | -.1E-03     | -.1E-03   |
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