Smooth relativistic Hartree-Fock pseudopotentials for H to Ba and Lu to Hg

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We report smooth relativistic Hartree-Fock pseudopotentials (also known as averaged relativistic effective potentials or AREPs) and spin-orbit operators for the atoms H to Ba and Lu to Hg. We remove the unphysical extremely non-local behaviour resulting from the exchange interaction in a controlled manner, and represent the resulting pseudopotentials in an analytic form suitable for use within standard quantum chemistry codes. These pseudopotentials are suitable for use within Hartree-Fock and correlated wave function methods, including diffusion quantum Monte Carlo calculations.

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Pseudopotentials or effective core potentials (ECPs) are commonly used within electronic structure calculations to replace the chemically inert core electrons. The influence of the core on the valence electrons is then described by an angular-momentum-dependent effective potential, leading to greatly improved computational efficiency in ab initio calculations for heavy atoms. The use of pseudopotentials is well established within Hartree-Fock (HF) and Density Functional Theory (DFT), and in correlated wave function calculations.

Our main interest is in diffusion quantum Monte Carlo (DMC) calculations. This technique provides an accurate solution of the interacting electron problem for which the computational effort scales with the number of electrons, \( N \), as approximately \( N^3 \), which is better than other correlated wave function approaches. Unfortunately, scaling with atomic number, \( Z \), is approximately \( Z^{5-6} \). The use of a pseudopotential reduces the effective value of \( Z \), making DMC calculations feasible for heavy atoms.

There is evidence that HF pseudopotentials give better results within DMC than DFT pseudopotentials. It appears that the complete neglect of core-valence correlation within HF theory leads to better pseudopotentials than the description of core-valence correlation provided by DFT. Moreover, core-valence correlation can be included within correlated wave function calculations performed with HF pseudopotentials by using core polarization potentials. Core polarization potentials mimic the effects of dynamical polarization of the core by the valence electrons, as well as static polarization effects due to the other ions. We would therefore like to use HF pseudopotentials in our DMC calculations, preferably constructed from Dirac-Fock (DF) theory in order to include the relativistic effects which are significant for heavy atoms.

Standard quantum chemistry packages are convenient for generating the “guiding wave functions” required in DMC calculations. We would therefore like our pseudopotentials to be available in the standard parameterized form of a sum of Gaussian functions multiplied by powers of the electron-nucleus separation.

Extensive sets of parameterized pseudopotentials are available in the literature, but they have generally been constructed with different goals to ours. Relativistic pseudopotentials generated within DFT and the local density approximation have been available for some time, but, as mentioned above, it appears that HF pseudopotentials are superior for our purposes.

Pseudopotentials defined within HF theory have been published by Hay and Wadt for much of the periodic table, and Christiansen and coworkers have generated similar HF pseudopotentials from DF atomic calculations, thereby including relativistic effects. “Energy consistent” HF pseudopotentials including relativistic effects have also been developed by the Stuttgart and Bonn groups, and are also publicly available. There is considerable freedom in constructing pseudopotentials, and many of those available in the quantum chemistry literature diverge at the nucleus, normally as \( 1/r^3 \) or \( 1/r \). This singular behaviour leads to large “time-step” errors and even instabilities in DMC calculations. Moreover, we cannot imagine that this singular behaviour is advantageous in quantum chemistry methods, as it leads to pseudo wave functions with behaviour at small \( r \) which cannot be described within a Gaussian basis set. All of the HF pseudopotentials discussed above possess such singularities at the nuclear site.

Greeff and Lester and Ovcharenko et al. have generated non-singular HF pseudopotentials for the atoms B-Ne and Al-Ar, which are available in a suitable parameterized form. These are constructed explicitly for use in DMC calculations, and satisfy some of our criteria. Unfortunately these pseudopotentials cover only a small part of the periodic table, do not have \( d \) angular momentum channels, do not include relativistic effects, and are not particularly smooth even though they are non-singular at the origin.

In this paper we report the generation of a library of accurate HF pseudopotentials which are non-singular at the origin, include relativistic effects, are parameterized in a form appropriate for quantum chemistry packages, and are smooth to aid transferability. We also require our pseudopotentials to be well-localized (by which we mean non-local only in a small region around the nucleus), as the evaluation of the non-local energy within DMC is
expensive.

We also seek to quantify the errors present in our pseudopotentials. Transferability errors are expected to be the most significant, but errors due to other sources are also assessed. These errors result from the approximations required to construct HF pseudopotentials from all-electron (AE) DF data, from the removal of the unphysical long ranged non-local behaviour discussed by Trail and Needs, and from the parameterisation of the pseudopotentials.

The rest of this paper is organized as follows. In section II we describe the form of the relativistic pseudopotentials obtained from AE DF orbitals by inversion of the HF equations. In section III we present and analyse pseudopotentials obtained from AE DF orbitals by inversion of Eqs. (1,2) for valence orbitals. In IV we present and analyse pseudopotentials generated parameterized spin-orbit (SO) pseudopotentials.

Atomic units are used throughout, unless otherwise indicated.

I. FORM OF THE PSEUDOPOTENTIALS

The coupled radial DF equations\textsuperscript{18,19} are

\begin{equation}
\frac{dG_i}{dr} + \frac{k_i}{r} G_i - \left[ \frac{2}{\alpha} - \alpha V_i^{\text{eff,F}} \right] F_i = \alpha \epsilon_i F_i \label{eq:1}
\end{equation}

\begin{equation}
\frac{dF_i}{dr} - \frac{k_i}{r} F_i - \alpha V_i^{\text{eff,G}} G_i = - \alpha \epsilon_i G_i \label{eq:2},
\end{equation}

where $\alpha = 1/c$ is the fine structure constant, $i$ is the state index, and $G_i$ and $F_i$ are the radial components of the major and minor (or large and small) parts of the Dirac orbitals. The $i$ index is unique to each orbital, and hence the non-zero integer quantum number $k_i$ can be associated with each $i$,

\begin{equation}
k_i = \begin{cases} l_i = j_i + \frac{1}{2} & k_i > 0 \smallskip \hline -(l_i + 1) = -(j_i + \frac{1}{2}) & k_i < 0. \end{cases} \label{eq:3}
\end{equation}

The orbital dependent effective potentials, $V_i^{\text{eff,G}}$ and $V_i^{\text{eff,F}}$, are functionals of the set $\{G,F\}$.

In what follows we also consider the standard approximation to Eqs. (12) for valence orbitals.\textsuperscript{18,19} Taking $\epsilon_i$ and $V_i^{\text{eff,F}}$ to be small in Eqs. (12), as is the case for the valence orbitals outside of the core region (this can be taken as one of the criteria for the core-valence partition), leads to

\begin{equation}
\left[ - \frac{1}{2} \frac{d^2}{dr^2} + \frac{k_i (k_i + 1)}{2 r^2} + V_i^{\text{eff,G}} \right] G_i = \epsilon_i G_i \label{eq:4},
\end{equation}

\begin{equation}
\frac{\alpha}{2} \left( \frac{dG_i}{dr} + \frac{k_i}{r} G_i \right) = F_i \label{eq:5}.
\end{equation}

Equations (1) and (5) are equivalent to Eqs. (12) up to, but not including, terms of order $\alpha^2$, and it should be noted that a self-consistent eigenstate of Eqs. (12) does not satisfy Eqs. (13) exactly in any region of space. The effective potential in Eqs. (2) and (4) is given by

\begin{equation}
V_i^{\text{eff,G}} = - \frac{Z}{r} + V_h[\rho] + \frac{\hat{V}_G^{\text{AE}}[\{G,F\},k_i]}{G_i} \label{eq:6},
\end{equation}

where the first term arises from the nuclear charge and the second is the Hartree potential due to the total electron density, $\rho$. The third term is the effective exchange potential acting on the major part of the radial Dirac orbital. Both the Hartree and exchange terms are functionals of $\{G,F\}$, and the effective exchange potential is different for each orbital (the cancelling self-interaction has been included in the exchange and Hartree terms).

To generate a non-relativistic HF pseudopotential from the AE DF solutions of Eqs. (12) we follow the procedure described by Kleinman.\textsuperscript{22} The AE DF atomic solutions are partitioned into core states whose influence is represented by the pseudopotential, and valence states which are represented by the pseudo-orbitals. We then construct non-relativistic pseudo-orbitals which preserve desired properties of the original AE DF valence orbitals.

The pseudo-orbitals are chosen to satisfy the Schrödinger-like equation

\begin{equation}
\left[ - \frac{1}{2} \frac{d^2}{dr^2} + \frac{k_i (k_i + 1)}{2 r^2} + V_i^{\text{eff,F}} \right] \phi_i = \epsilon_i \phi_i \label{eq:7},
\end{equation}

where the pseudo-orbital, $\phi_i$, is a scalar orbital and the corresponding eigenvalue $\epsilon_i$ is equal to that of Eqs. (12) for the AE orbital $i$. We may relate Eq. (7) to the Dirac-Fock equation by taking the limit $\alpha \to 0$ in Eqs. (13), which leads to a scalar Schrödinger equation.

The effective potential, $V_i^{\text{eff}}$ for state $i$ is then given by

\begin{equation}
V_i^{\text{eff}} = V_i(r) + V_h[\rho^{\text{pseudo}}] + \frac{\hat{V}_G^{\text{AE}}[\phi,0]}{\phi_i} \label{eq:8},
\end{equation}

where $\rho^{\text{pseudo}}$ is the charge density obtained from the occupied pseudo states. This defines the pseudopotential for orbital $i$, $V_i(r)$, in terms of the pseudo-orbital $\phi_i$. Given $\phi_i$ and $\epsilon_i$, $V_i(r)$ may be obtained by direct inversion of Eqs. (7) and (8).

In the non-relativistic case we would construct valence pseudo-orbitals, $\phi_i$, which are equal to the equivalent AE orbitals outside of a 'core radius', $r_c$. In the relativistic case this procedure must be modified, since the DF orbitals consist of two components. We could simply take
\( \phi_i = G_i \) for \( r > r_{ci} \), but this is unsatisfactory because it implies that charge has been removed from the system. Instead we take the form
\[
\phi_i(r) = \begin{cases} f_i(r) & r < r_{ci} \\ \left[ G_i(r)^2 + F_i(r)^2 \right]^{1/2} & r \geq r_{ci} , \end{cases} \tag{9}
\]
which preserves the valence charge density outside of the core region. Inside \( r_{ci} \) the orbitals are given by the, as yet, unspecified function \( f_i \). This function is generally chosen such that \( \phi_i \) is node-less, smooth at \( r_{ci} \) to a certain order of differentiation, and that it satisfies the norm-conservation condition, that is, the total charge inside of \( r_{ci} \) is the same as for the AE orbital.

The pseudopotentials \( V_i \) are not quite appropriate for use in non-relativistic calculations as they provide different pseudopotentials for the same \( l \) values. However, the valence states chosen to construct the pseudopotential have unique \( k \) numbers, and therefore the index \( k \) is interchangeable with the pseudo-atom orbital index, \( i \). Taking the average of the pseudopotentials with the same \( l \) quantum numbers weighted by the different \( j \) degeneracies, we obtain the averaged relativistic effective potential (AREP)\(^{20,21}\)
\[
V_i^P = \frac{1}{2l+1} [V_{k_i,l} + (l+1)V_{k_i,-l-1}] . \tag{10}
\]
This includes all of the Dirac relativistic effects except the SO coupling. The SO operator, \( V_i^{so} \), may be expressed in terms of a SO pseudopotential, \( V_i^{so} \), and angular momentum operators,
\[
\hat{V}_i^{so} = V_i^{so} \hat{L} \cdot \hat{S} \tag{11}
\]
\[
= \frac{2}{2l+2} \left[ V_{k_i,-l-1} - V_{k_i,l} \right] \hat{L} \cdot \hat{S} . \tag{12}
\]
To use the pseudopotential in a calculation for a molecule or solid it is expressed in terms of projection operators, and separated into local and non-local parts,
\[
\hat{V}_\text{pseudo} = V_i^P \langle l \rangle_{l_{\text{max}}} \left( \sum_l \sum_{m=-l}^{l} |Y_{lm}(r)| (V_i^P(r) - V_{l \text{local}}(r)) |Y_{lm}| \right) . \tag{13}
\]
Orbitals with \( l > l_{\text{max}} \) feel the local potential, \( V_i^P \text{local} \).

II. GENERATION OF THE PSEUDOPOTENTIALS

We take the core states to be the ‘noble core’ (for example, for Si we take 1s2s2p as core states and 3s3p as valence states) or noble core plus a filled \( d \) shell. We generate pseudopotentials for the \( s,p \) and \( d \) channels. We use the atomic ground state configurations to obtain channels for which the corresponding AE valence orbitals are bound. For channels which have no corresponding AE valence orbitals in the ground state we use the excited state configurations of Bachelet et al.\(^{19}\), which provide an appropriate bound state. Fischer’s interpretation of fractional occupation numbers within HF and DF theory\(^{21}\) is used. In most cases we choose the core radii, \( r_{ci} \), to be 0.9 of the distance from the outermost node to the outermost maximum, although for some cases we choose smaller radii.

To define our pseudo-orbitals we use the Troullier-Martins scheme\(^{22}\) where the pseudo-orbitals within the core region are given by
\[
f_i(r) = r^{l_i+1} \exp \left[ \sum_{m=0}^{6} c_{2m} r^{2m} \right] , \tag{14}
\]
and the coefficients \( c_{2m} \) are to be determined. The factor \( r^{l_i+1} \) ensures that no \( 1/r^2 \) singularity occurs in the effective potential (and resulting pseudopotential), and \( c_1 = 0 \) ensures that no \( 1/r \) singularity is present. All of the \( c_{2m+1} \) terms have been excluded to prevent the appearance of a cusp of any order in the pseudopotentials at the origin, so improving the asymptotic behaviour of the pseudo-orbitals and pseudopotentials in momentum space. The seven coefficients in Eq. (14) are determined by the conditions of:

1. norm-conservation within \( r_{ci} \),
\[
\int_0^{r_{ci}} \phi_i(r)^2 dr = \int_0^{r_{ci}} [G_i(r)^2 + F_i(r)^2] dr ; \tag{15}
\]

2. continuity of \( \phi_i(r) \) and its first four derivatives at \( r_{ci} \);

3. zero curvature of the screened potential at the origin,
\[
\frac{d^2 V_{\text{eff}}}{dr^2} \bigg|_{r=0} = 0 . \tag{16}
\]

In the core region we obtain \( V_{\text{eff}} \) by inversion of Eq. (10), and obtain \( V_i \) by ‘unscreening’ \( V_{\text{eff}} \) using the pseudo-orbitals.

Outside of the core region we could in principle apply the same inversion procedure, but this would involve taking numerical differences of small quantities, which is prone to errors. Instead we note that the eigenvalues of the AE DF and pseudo valence states are equal, and that we expect Eqs. (16) to be an extremely good approximation for valence states in the region outside of the core. We may then use Eqs. (1), (6), (7), and (8) to obtain
\[
\begin{align*}
V_i &= -\frac{Z}{r} + V_i [\rho - \rho^{\text{pseudo}}] + \\
&\quad \hat{V}_x^G \{\langle G, F \rangle, k_i \} G_i - \hat{V}_x^G \{\langle \phi, 0 \rangle, k_i \} \phi_i - \\
&\quad \frac{1}{2} \left( G'' - \frac{G''}{\phi} \right) , \tag{17}
\end{align*}
\]
for \( r > r_{ci} \). The final term in this expression arises from the kinetic energy, and we neglect this, which introduces an error of order \( \alpha^2 \). This approximation may seem unnecessary, but errors of this order are already present if we assume that the pseudo-valence electrons may be treated as scalar relativistic, and it has the advantage that the valence charge density outside of the core region is preserved. We also found that this error, when detectable, is smaller than that due to the fact that Eq. (14) is already an approximation, even outside of the core region. Some authors have chosen \( \phi_i = \lambda G_i \) outside of the core, so that the kinetic terms in Eq. (17) are zero. The \( \lambda \) constant may be chosen to ensure that \( \phi_i \) is normalized. This would cause a negligible (in most cases undetectable) change in the pseudopotentials generated here.

All DF and HF calculations were carried out using fine radial grids and therefore do not suffer from basis set errors. We used the DF code of Anokhin et al.\(^\text{23}\) for the AE DF calculations, the HF code of Fischer\(^\text{24}\) for the AE HF calculations, and the pseudopotential HF calculations were performed using our own code. Grid and convergence parameters were chosen so as to achieve 10-digit accuracy in the total energy, and the ground state energies were checked against those of Visscher and Dyall\(^\text{25}\), and Librelon and Jorge.\(^\text{26}\) The above procedure provides us with relativistic screened pseudopotentials for each of the valence states considered and, from Eq. (17), the \( V_i \). We then use Eq. (10) and (12) to obtain the AREP and SO potentials.

### A. Non-local asymptotic behaviour

In a previous paper,\(^\text{17}\) we examined pseudopotentials constructed within HF theory using this inversion procedure, and found them to be non-local over all space, the deviation from the ionic Coulomb potential remaining finite as \( r \to \infty \). As the presence of this ‘extreme non-locality’ is a consequence of the non-locality of the exchange interaction in HF theory, and the DF exchange interaction is of essentially the same form, this effect also occurs for the pseudopotentials defined here.

The presence of this long-ranged non-locality leads to a loss of transferability and problems in defining a total energy for extended systems. Here we remove the ‘extreme non-locality’ using the method presented in our previous paper,\(^\text{17}\), which we briefly summarize here.

In order to generate a new version of the pseudopotential, \( V_{p,loc}^i(r) \), which is non-local only close to the atomic core, the original pseudopotential is transformed using

\[
 V_{p,loc}^i(r) = \begin{cases} 
  \gamma_l(r) + V_p^i(r) & r < r_c \\
  e^{-\eta (r-r_c)} \times \left( \gamma_l(r) + V_p^i(r) - V_h[\rho_{core}] + \frac{Z}{r} \right) & r \geq r_c 
\end{cases}
\]

where \( V_h[\rho_{core}] - Z/r \) is the ionic potential and \( \eta^{-\frac{1}{2}} = \max_j [r_{dJ}/16] \) is a parameter which specifies the length scale over which the transformed pseudopotential becomes local outside of the core region. The function \( \gamma_l \) is given by

\[
 \gamma_l(r) = \begin{cases} 
  q_l + p_l r^4 \left( 1 - \frac{2}{3\gamma^2} r^2 \right) & r < r_c \\
  q_l + p_l r^4 & r \geq r_c 
\end{cases}
\]

where the parameters \( q_l \) and \( p_l \) are chosen such that the HF eigenvalues of the original pseudopotential are preserved, and that the logarithmic derivatives of the original pseudo-orbitals at \( r_{ci} \) are preserved to high accuracy.\(^\text{17}\) Although the norm of the original pseudopotential is not exactly preserved this was not found to significantly affect transferability.

### B. Expansion in a Gaussian basis

For applications within quantum chemistry codes it is normally necessary to have the pseudopotentials available as an expansion in Gaussian functions. The pseudopotentials described so far are tabulated on a radial grid, and in this section we develop a Gaussian fitting procedure which is both accurate and reliable.

Our aim is to find an expansion of the localized AREP \( V_{l,loc}^i \) in a standard Gaussian form,

\[
 V_{l,loc}^p = \sum_{q,l} A_{ql} n_{ql} r^{-a_{ql}} e^{-a_{ql} r^2} = Z_{val}/r + V_{l,local}^p \quad l = \text{local} \\
 V_{l,loc}^p - V_{l,local}^p \quad l \neq \text{local} 
\]

where \( Z_{val} \) is the number of valence electrons in the neutral atom. A set of \( n_{ql} \) is chosen such that the pseudopotential can be represented accurately by the expansion, with no singularity present at the origin. Once we have this expansion it may be applied in the same projector form as Eq. (13). It is important to note that we expand the localized tabulated pseudopotential in terms of Gaussian functions. This is desirable since the removal of the long-ranged non-local tail significantly improves the accuracy and stability of any fitting procedure using localized basis functions, such as the Gaussian expansion.

In order arrive at an algorithm to generate our expansion we must decide what properties a ‘good’ Gaussian expansion must have. We require a good expansion to reproduce both the eigenvalues and orbitals of the tabulated pseudopotential to high accuracy, and so reproduce the scattering properties of the tabulated pseudopotential. We require a good expansion to be close to the tabulated pseudopotentials in the least-squares sense, because such deviations tend to make the fitted ones less smooth and reduce the transferability. We also require the parameterized pseudopotentials to be non-local only in a region near the core, although this criterion is partly included in the previous two, together with the use of the localized tabulated pseudopotentials. These are stringent
requirements and we therefore require a rather larger expansion than has been used in earlier work. Finally we require an expansion which is compatible with quantum chemistry codes, and we have successfully tested our parameterized form in both the CRYS
tal and GAUSSIAN codes.

We chose the local part of the pseudopotential to be \( l = 2 \) for all atoms, and to obtain an accurate (in the least squares sense) representation of the pseudopotential we chose \( q_{\text{max}} = 8 \), with \( n_{ql} = -1, 0, 1, 2 \) for the local part and \( n_{ql} = 0, 1, 2 \) for the non-local parts. This gives 16 parameters for each channel. It is helpful to reduce this number by imposing constraints on the functional form of the pseudopotential. We require that \( V_p^l \) is finite and has zero derivative at the nucleus, as did Greeff and Lester. In addition we require the second derivative of \( V_p^l \) to be zero at the nucleus and that \( \tilde{V}_p^l(0) = V_p^{l,\text{loc}}(0) \). The latter two conditions make \( V_p^l \) smoother because they force it to be closer to the original tabulated pseudopotential. These conditions are imposed by reducing the number of free \( A_{ql} \) parameters.

Since Eq. (20) is linear in the \( \{A_{ql}\} \) it is also possible to use Singular Value Decomposition (SVD) to define the remaining \( A_{ql} \) parameters as those which give the minimum least squares deviation from the original tabulated pseudopotential.

A further (nonlinear) least squares minimization with respect to the remaining free parameters \( \{a_{ql}\} \) provides a ‘good fit’ to the tabulated pseudopotential, but does not provide an expansion which accurately reproduces the eigenstates of the original pseudopotential. We take the \( \{a_{ql}\} \) parameters obtained from this least squares procedure as a starting point for a second stage of optimization. Here we employ a generalization of an algorithm developed by Barthelat et al.\(^{25}\)

To progress further we perform a HF atomic calculation with LS coupling and using the tabulated pseudopotential \( V_p^{l,\text{loc}} \), yielding the pseudo-states \( \{\tilde{\phi}_l^p, \tilde{\epsilon}_l^p\} \). For a given set of parameters for each channel, we also perform a similar HF atomic calculation using the parameterized pseudopotential \( \tilde{V}_p^l \), to give the pseudo-states \( \{\tilde{\phi}_l^p, \tilde{\epsilon}_l^p\} \). We then define a functional of the pseudo-states of both the tabulated and parameterized pseudopotentials,

\[
\Sigma = \sum_l \langle \tilde{\phi}_l^p | \tilde{O}_l^p | \tilde{\phi}_l^p \rangle ,
\]

where

\[
\tilde{O}_l = \tilde{\epsilon}_l^p | \tilde{\phi}_l^p \rangle \langle \tilde{\phi}_l^p | - \epsilon_l^p | \tilde{\phi}_l^p \rangle \langle \phi_l^p | ,
\]

which is a function of the \( \{a_{ql}\} \) for all \( l \) which correspond to valence states in the atomic configuration considered. We vary the available \( a_{ql} \) of the parameterized pseudopotential to search for a minimum of \( \Sigma \) where the overlap \( \langle \tilde{\phi}_l^p | \phi_l^p \rangle \) is maximized and the error in the eigenvalue \( |\tilde{\epsilon}_l^p - \epsilon_l^p| \) is minimized separately for each available \( l \). In the original formulation of Barthelat et al.\(^{25}\) no sum over states was present in Eq. (21), and each channel was optimized separately. We found that optimizing each channel separately did not allow convergence to be achieved to a high enough accuracy for the majority of atoms, whereas optimization over all states provided reliable convergence.

A standard quasi-Newton minimization algorithm was used in the optimization, and we found that the stability and efficiency could be improved by introducing

\[
a'_{ql} = \ln a_{ql} ,
\]

and minimizing with respect to the \( \{a'_{ql}\} \).

We considered the optimization to be successful when the pseudo-states of the parameterized pseudopotentials satisfied the conditions

\[
1 - \frac{\langle \phi_l^p | \tilde{\phi}_l^p \rangle}{\tilde{\epsilon}_l^p - \epsilon_l^p} < 10^{-6},
\]

\[
|\tilde{\epsilon}_l^p - \epsilon_l^p| < 10^{-5} \text{ a.u.} ,
\]

for the \( s \) and \( p \) block atoms, and

\[
1 - \frac{\langle \phi_l^p | \tilde{\phi}_l^p \rangle}{\tilde{\epsilon}_l^p - \epsilon_l^p} < 10^{-5},
\]

\[
|\tilde{\epsilon}_l^p - \epsilon_l^p| < 10^{-4} \text{ a.u.} ,
\]

for the transition metal atoms.

On implementation it became apparent that, for most atoms, the final values of the parameters are surprisingly sensitive to their initial values, suggesting that \( \Sigma \) has many minima. We also found that, without the SVD definition of the \( A_{ql} \) parameters, the rescaling of Eq. (23) or the concomitant optimization implied by the sum in Eq. (21), this procedure did not converge for many atoms, suggesting that these aspects of the algorithm are necessary to provide a functional with minima which are distinct and well defined. The presence of many locally optimum parameter sets is also an advantage, as when a set of optimized parameters does not satisfy our criteria a new contender may easily be obtained by making a small change to the initial parameter set.

As an example we consider C, for which our parameterized pseudopotential is shown in Fig. 1. The \( s \) and \( p \) channels were obtained from the neutral ground state, while the \( d \) channel was obtained from an excited ionic state \((1s^22s^22p^2)^{1s0}2p[1.00\text{ a.u.}] \)), taken from Bachelet et al.\(^{10}\) Inset in the same figure is the difference between the parameterized pseudopotential and the original TM (extremely non-local) pseudopotential. This figure demonstrates that our parameterisation accurately reproduces the original pseudopotential, with the greatest difference occurring at small \( r \). Most of this difference is not due to the fitting procedure - it is due to the change in the pseudopotential required to enforce locality outside of a small radius (in this case \( r_{\text{loc}} = 1.2 \text{ a.u.} \)) while preserving the eigenvalues and logarithmic derivatives of the original pseudo-states.

In Fig. 2 the \( s \) and \( p \) components of our C pseudopotential are compared with the non-singular (non-relativistic) pseudopotential published by Ovcharenko et al.\(^{26}\) Fig. 2 shows that our C pseudopotential is smoother than that.
of Ovcharenko et al., and we found this to be the case for all of their pseudopotentials. This is probably due to the extra constraints we apply in our construction of the pseudo-orbitals.

Fig. 3 shows the $s$ pseudo-orbitals resulting from our C pseudopotential, together with those from the pseudopotentials of Ovcharenko et al.\textsuperscript{16} (OAL), Christiansen et al.\textsuperscript{13} (PC), and those of the Stuttgart group\textsuperscript{49} (ISP). The $+1/r^2$ divergence of the PC pseudopotential forces the $s$ pseudo-orbital to go rapidly to zero at the nucleus, while the $−1/r$ divergence of the ISP pseudopotential forces the $s$ pseudo-orbital to have a cusp at the nucleus. Our pseudopotential gives the smoothest pseudo-orbital of those plotted.

We have generated pseudopotentials using the scheme described above for the atoms H to Ba and Lu to Hg. We include H and He even though they have no core electrons because the smoothness of the resulting pseudopotentials may make them useful in some circumstances.

To provide a quantitative measure of the errors introduced by the various approximations used in the construction of the pseudopotentials we investigated how well the pseudopotentials reproduce the AE atomic results at the various levels of approximation. Atomic \textit{LS} and \textit{jj} coupled HF calculations were performed with the pseudopotentials using our own code. Here we report detailed results for the Li, Be, C, Si, Ti, Cr, Fe, Br, Mo, Ag, and Sb atoms, which are representative of the general accuracy achieved. Note that we have deliberately chosen several transition metal atoms as they generally exhibit the largest errors.

If there were no approximations in our pseudopotential construction procedure, then a HF pseudopotential calculation with the exchange interaction defined using \textit{jj} coupling should exactly reproduce the AE DF eigenvalues of the occupied levels of the ground state. In practice, however, this is not achieved, and the pseudopotential generation method we use may be viewed as introducing four types of error. These are shown in Table I together with the separate averages over the \textit{jj} channels of the parameterized pseudopotential. For both the errors and the eigenvalues themselves we take an average over values corresponding to the same \textit{l} weighted by the different \textit{j}-degeneracies, just as we did to construct the AREP.

The first type of error, $\Delta \epsilon_1$, is introduced by the fact that the pseudo-orbital is not an exact solution of Eq. (4) outside of the core region. The second error, $\Delta \epsilon_2$, is introduced by the \textit{j}-averaging of the pseudopotential. This error results from the exclusion of SO coupling from the pseudopotential, and is due to the higher order effects of SO coupling. The third error $\Delta \epsilon_3$ is introduced by the localization of the pseudopotential (by construction this error would be zero for \textit{LS} coupling). Finally, the fourth error, $\Delta \epsilon_4$, is introduced by the imperfect parameterisation. These four errors are shown in Table I and are defined such that their sum is the total error of the (averaged) eigenvalues resulting from the parameterized pseudopotential. Results are given for the atoms listed above, together with the separate averages over the $s$, $p$ and $d$ block atoms considered in this paper.

The total error is small for all atoms, it is negligible for the $s$-block atoms and is largest for the heaviest transition metal atoms. Generally, the largest total errors are dominated by the error due to the removal of SO coupling, this error increasing rapidly with increasing atomic number (compare $\Delta \epsilon_2$ for Mo and Ag). $\Delta \epsilon_1 + \Delta \epsilon_3 + \Delta \epsilon_4$
remains below $10^{-4}$ a.u., with the exception of a few heavy transition metal atoms such as Mo. Errors due to the approximation of the Dirac equation as a Schrödinger equation in the valence region remain consistently small, and errors due to localization and parameterization are largest for the transition metal atoms.

In Table III we compare the $j$-averaged eigenvalues resulting from HF calculations using our soft parameterized pseudopotentials, and eigenvalues resulting from the singular PC pseudopotentials. For all comparisons with PC pseudopotentials we choose those constructed using the same core partition as our own. The $j$-averaged valence eigenvalues of the original AE DF atom are well reproduced by both the soft and singular pseudopotentials, with our soft pseudopotentials performing slightly better. We conclude that our pseudopotentials have been parameterized successfully.

III. TESTING OF THE PSEUDOPOTENTIALS

The analysis in the previous section demonstrates that our pseudopotentials have been parameterized accurately. Of course this does not demonstrate their transferability, and it is this issue which is addressed in this section.

Although designed to reproduce $jj$ coupling results, our pseudopotentials are intended for use within $LS$ coupling calculations, and therefore we have calculated HF excitation energies and ionization energies within $LS$ coupling for both our pseudopotentials and those of Christiansen et al.\textsuperscript{15} (PC). Both of these types of pseudopotential contain relativistic effects at the DF level, and therefore we compare these results with AE HF results in which scalar relativistic effects are incorporated perturbatively. The calculations were performed using Fischer’s code with the Breit-Pauli scalar relativistic correction added to the total energy, correct to order $\alpha^2$. This order of correction would not be particularly accurate for AE calculations on the heavier atoms, but these errors arise largely from the deep core electrons and do not contribute significantly to the energy differences between the low-lying excited states considered here.

In Table III we compare excitation energies for the same atoms considered in Tables II and IV. Excitation energies obtained for the AE atoms are compared with those from our soft AREP parameterized pseudopotentials and the singular PC pseudopotentials. We find that our pseudopotentials reproduce the excitation energies to the same accuracy as those of PC.

We also consider the errors for our full set of pseudopotentials in reproducing the AE DF excitation energies. It is apparent that the excitation energies are reproduced most accurately for the $s$-block atoms with an average absolute error of 0.00084 a.u. (0.022 eV), that they are less well reproduced for $p$-block atoms with an average absolute error of 0.00344 a.u. (0.090 eV), and that the largest errors occur for the transition metal atoms, with an average absolute error of 0.01204 a.u. (0.32 eV). The large error value for the transition metals is mainly due to the $5d$ transitions - the average absolute errors are 0.00687 a.u. (0.18 eV), 0.00754 a.u. (0.20 eV), and 0.02116 a.u. (0.55 eV) for the $3d$, $4d$, and $5d$ transition metals respectively. Further examination of the results reveals that these errors are inherent in the pseudopotentials themselves, and not due to the errors examined in the previous section. Our pseudopotentials and the PC pseudopotentials also appear to produce very similar errors, providing support for this interpretation. For the transition metal atoms it should be possible to reduce these errors by including the $3s$ and $3p$ electrons as valence states, giving “small core” pseudopotentials.\textsuperscript{32}

In Table V we compare the first ionization potentials calculated for the atoms considered in the previous tables. The results are of similar quality to those for the excitation energies given in Table III and show a similar trend that the errors tend to increase with $Z$. The PC pseudopotentials perform slightly better for the ionization potentials than our soft pseudopotentials, but the difference does not appear to be significant considering the number of atoms studied.

Our pseudopotential generation procedure also provides a description of SO splitting in terms of the SO pseudopotential, $V_{i}^{so}$ defined in Eq. (22). We may define a Gaussian parameterisation of this as

$$V_{i}^{so} = \sum_{q} B_{q} r_{i} e^{-b_{q} r_{i}^{2}},$$

where $V_{i}^{so}$ is the fitted potential and the $B_{q}$ and $b_{q}$
play the same role as the $A_{ql}$ and $a_{ql}$ in the AREP. No Coulomb potential terms are required, and no local potential term is required since $V_{l}^{so} = 0$ for $l > l_{\text{max}}$ is a physically reasonable approximation. In addition we require $B_{ql} = 0$ for $l = 0$, since $V_{l}^{so} = 0$ for $l = 0$.

It would be possible to follow the same route of localization and parameterisation used for the AREP. This would require $jj$ coupled HF calculations to be used in the localization and fitting procedures of section [11] (as opposed to $LS$ coupled HF), so we could seek a $V_{l}^{so}$ which reproduces the SO splitting of the original AE DF calculation. Here we use a simpler procedure and apply least squares fitting with respect to $\{B_{ql}, b_{ql}\}$, with the initial $\{b_{ql}\}$ taken as the values of the equivalent AREP parameters.

We considered the selection of atoms and ions shown in Table [V]. The SO splitting is defined as the difference between the energies of states where $J$ differs by one due to the transfer of an electron between orbitals of the same $l$, but different $j$ quantum number. The difference in energy of the states due to the SO interaction was obtained from AE DF calculations (not including further relativistic corrections), and from $jj$-coupled HF calculations with the parameterized pseudopotentials. For the pseudopotential calculations $V_{l}^{p}$ and $V_{l}^{so}$ are used to construct a Relativistic Effective Potential (REP) that depends on $j$ - the parameterized equivalent of $V_{l}$ in section [11] - and this REP provides the external potential. Since the SO splitting is not obtained perturbatively any differences between AE and AREP+SO results are solely due to the REP.

We calculated energy differences between $2P_{1/2}$ and $2P_{3/2}$ states for $s$ and $p$-block atoms, and between $2D_{3/2}$ and $2D_{5/2}$ states for $d$-block atoms. In Table [V] we compare the SO splitting energies obtained from AE DF calculations, those obtained using our parameterisation of $V_{l}^{d}$ and $V_{l}^{so}$, and those obtained using the (singular) parameterized SO pseudopotentials published by Pacios and Christiansen. Our AE results differ somewhat from those reported by Christiansen et al., who used the code of Desclaux. These discrepancies appear to be due to the finer radial grids and higher tolerances used in our calculations. We have also found discrepancies between our results and Christiansen's et al., using their REPs, which we believe is due to the same effect. We also note that our code reproduces the accurate ground state energies of Visscher and Dyall, but the code of Desclaux does not.

We find that in most cases our pseudopotentials reproduce the DF splitting energies more accurately than those of PC, with an average absolute percentage error of 4.8% compared to 8.2% for PC. The largest percentage error is for Li (27%, compared with 34% from PC), where the splitting is small. For the rest of the atoms considered, the errors are < 11%, compared with < 24% for PC.

Parameter values for our pseudopotentials and SO pseudopotentials are provided as supplementary material, and are given to the same numerical precision used to generate the results in this paper.

**IV. CONCLUSIONS**

We have developed smooth HF pseudopotentials which emulate the influence of relativistic core electrons for the atoms H to Ba and Lu to Hg. These are the Averaged Relativistic Effective Potentials and SO pseudopotentials of Kleinman and Bachelet and Schlüter. We use the Troullier-Martins scheme to generate smooth pseudopotentials, and remove the unphysical extremely non-local behaviour which results from the exact exchange in a controlled manner.

The resulting (tabulated) pseudopotentials are then represented in a convenient analytic form suitable for use in standard quantum chemistry codes, using a fitting procedure based on the method first described by Barthelat et al. The version of this scheme employed here increases the efficiency and accuracy of the fitting procedure, and preserves the smoothness of the Troullier-Martins pseudopotentials.

An analysis of the performance of our parameterized pseudopotentials for a number of test cases reveals that they reproduce the original AE atomic results well in most cases, and perform well in comparison with pseudopotentials published by previous authors which possess singularities at the nuclei.

The pseudopotentials we have generated are finite at the nucleus and are smoother than other HF based pseudopotentials, which should aid the convergence of methods employing Gaussian basis sets. These pseudopotentials are appropriate for use within non-relativistic theories of the valence electrons, such as HF theory or correlated wave function methods, including DMC.

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See EPAPS Document No. E-JCPSA6-122-304518 for the parameters of our pseudopotentials and SO pseudopotentials. A direct link to this document may be found in the online article’s HTML reference section. The document may also be reached via the EPAPS homepage [http://www.aip.org/pubservs/epaps.html] or from ftp.aip.org in the directory /epaps. See the EPAPS homepage for more information.

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| Atom | l  | $\epsilon_i^{AE}$ | $\epsilon_i^{jj}$ | $\Delta\epsilon_1$ | $\Delta\epsilon_2$ | $\Delta\epsilon_3$ | $\Delta\epsilon_4$ | $\Delta\epsilon_{tot}$ | $\times 10^{-5}$ |
|------|----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Li   | s  | -0.19634        | -0.19634        | 0.0             | 0.0             | 0.0             | 0.0             | 0.0             | 0.0             |
| Be   | s  | -0.30932        | -0.30933        | -0.1            | 0.0             | 0.0             | -0.4            | -0.4            | 0.0             |
| C    | s  | -0.71212        | -0.71213        | -0.9            | 0.0             | 0.0             | 0.4             | -0.5            | 0.0             |
|      | p  | -0.40867        | -0.40869        | 0.3             | 0.1             | -2.2            | -0.5            | -2.3            | 0.0             |
| Si   | s  | -0.54522        | -0.54522        | -0.2            | 0.0             | 0.1             | 0.3             | 0.2             | 0.0             |
|      | p  | -0.27967        | -0.27968        | 0.0             | 0.3             | -1.1            | -0.6            | -1.3            | 0.0             |
| Ti   | s  | -0.22369        | -0.22357        | -0.5            | 0.0             | 1.5             | 10.7            | 11.7            | 0.0             |
|      | d  | -0.39560        | -0.39542        | 5.3             | 0.1             | 6.0             | 6.1             | 17.6            | 0.0             |
| Cr   | s  | -0.21104        | -0.21127        | -1.4            | 0.1             | -13.5           | -7.9            | -22.7           | 0.0             |
|      | d  | -0.31518        | -0.31494        | 2.8             | 0.6             | 17.4            | 2.8             | 23.6            | 0.0             |
| Fe   | s  | -0.26375        | -0.26375        | -1.5            | 0.1             | 1.1             | 0.7             | 0.4             | 0.0             |
|      | d  | -0.59311        | -0.59295        | 8.7             | 1.1             | 3.3             | 3.1             | 16.3            | 0.0             |
| Br   | s  | -1.02099        | -1.02101        | -0.8            | 0.0             | 0.3             | -1.9            | 0.0             | 0.0             |
|      | p  | -0.45616        | -0.45600        | -0.1            | 0.0             | -0.1            | 0.0             | 0.0             | 0.0             |
| Mo   | s  | -0.21217        | -0.21270        | -0.5            | 1.2             | -41.2           | -11.9           | -52.4           | 0.0             |
|      | d  | -0.29622        | -0.29585        | -0.5            | 5.5             | 36.8            | 5.5             | 37.3            | 0.0             |
| Ag   | s  | -0.23716        | -0.23712        | -1.0            | 3.9             | 0.0             | 1.6             | 4.5             | 0.0             |
|      | d  | -0.51128        | -0.51108        | 0.8             | 21.1            | 0.0             | -2.8            | 19.2            | 0.0             |
| Sb   | s  | -0.62683        | -0.62689        | -0.3            | -1.2            | 0.0             | -5.3            | 0.5             | -6.4            |
|      | p  | -0.30062        | -0.29996        | 0.0             | 54.7            | 13.4            | -2.3            | 65.8            | 0.0             |

| Block | $\Delta\epsilon$ | $\Delta\epsilon_{block}$ |
|-------|------------------|-----------------------------|
| s     | 0.1              | 0.0                         |
| p     | 0.8              | 9.4                         |
| d     | 1.9              | 19.7                        |

Mean $|\Delta\epsilon|$ = $P_i \Delta\epsilon_i$ = $\sum_i \Delta\epsilon_i$ is the total error.

**TABLE I**: Eigenvalues (a.u.) for the neutral ground states of selected atoms. Eigenvalues obtained from HF pseudopotential calculations with $jj$ coupling are compared with AE DF eigenvalues. All eigenvalues shown are j-weighted averages. Errors are due to:

- $\Delta\epsilon_1$ - transforming the Dirac equation to a Schrödinger equation in the valence region.
- $\Delta\epsilon_2$ - higher order effects due to excluding SO coupling.
- $\Delta\epsilon_3$ - localization.
- $\Delta\epsilon_4$ - parameterisation.

$\Delta\epsilon_{tot} = \epsilon_i^{jj} - \epsilon_i^{AE} = \sum_i \Delta\epsilon_i$ is the total error.
| Atom | Orbital | AE DF | Our | PC |
|------|---------|-------|-----|-----|
| Li   | s       | -0.19634 | -0.19634 | -0.19646 |
| Be   | s       | -0.30932 | -0.30933 | -0.30955 |
| C    | s       | -0.71212 | -0.71213 | -0.71406 |
|      | p       | -0.40867 | -0.40869 | -0.40916 |
| Si   | s       | -0.54522 | -0.54522 | -0.54653 |
|      | p       | -0.27967 | -0.27968 | -0.27885 |
| Ti   | s       | -0.22369 | -0.22357 | -0.22365 |
|      | d       | -0.39560 | -0.39542 | -0.39546 |
| Cr   | s       | -0.21104 | -0.21127 | -0.21109 |
|      | d       | -0.31518 | -0.31494 | -0.31513 |
| Fe   | s       | -0.26375 | -0.26375 | -0.26374 |
|      | d       | -0.59311 | -0.59295 | -0.59314 |
| Br   | s       | -1.02099 | -1.02101 | -1.02111 |
|      | p       | -0.45616 | -0.45600 | -0.45660 |
| Mo   | s       | -0.21217 | -0.21270 | -0.21602 |
|      | d       | -0.29622 | -0.29585 | -0.28839 |
| Ag   | s       | -0.23716 | -0.23712 | -0.23623 |
|      | d       | -0.51128 | -0.51108 | -0.51140 |
| Sb   | s       | -0.62683 | -0.62689 | -0.62690 |
|      | p       | -0.30062 | -0.29996 | -0.29950 |

Mean error 0.00006 0.00011
Mean absolute error 0.00015 0.00098

TABLE II: Eigenvalues (a.u.) for the neutral ground states of selected atoms. The eigenvalues obtained from AE DF calculations are compared with those from HF pseudopotential calculations with \( jj \) coupling using our soft parameterized pseudopotentials, and with those from the singular parameterized pseudopotentials of Pacios and Christiansen.\(^{12,13}\) (PC). All eigenvalues shown are \( j \)-weighted averages.
| Atom | Configuration | AE HF with RC | Our PC | 
|------|---------------|--------------|--------|
| Li   | 2s\(^2\)S    | 0.00000      | 0.00000| 0.00000|
|      | 2p\(^2\)P    | 0.06767      | 0.06769| 0.06782|
|      | 3d\(^4\)D    | 0.14076      | 0.14078| 0.14089|
| Be   | 2s\(^2\)S    | 0.00000      | 0.00000| 0.00000|
|      | 2s\(^1\)2p\(^3\)P | 0.06157   | 0.05951| 0.06076|
|      | 2s\(^1\)3d\(^3\)D | 0.23892 | 0.23910| 0.23942|
| C    | 2s\(^2\)2p\(^3\)P | 0.00000     | 0.00000| 0.00000|
|      | 2s\(^1\)2p\(^3\)S | 0.08982   | 0.08461| 0.08663|
|      | 2s\(^2\)2p\(^3\)d\(^3\)F | 0.34003 | 0.34060| 0.34102|
| Si   | 3s\(^3\)p\(^3\)P | 0.00000     | 0.00000| 0.00000|
|      | 3s\(^3\)p\(^3\)S | 0.09313   | 0.09076| 0.09243|
|      | 3s\(^2\)3p\(^3\)d\(^3\)F | 0.21425 | 0.21458| 0.21390|
| Ti   | 3d\(^2\)4s\(^3\)F | 0.00000     | 0.00000| 0.00000|
|      | 3d\(^3\)4s\(^5\)F | 0.02505   | 0.02945| 0.02957|
|      | 3d\(^4\)5D   | 0.16459      | 0.18113| 0.18015|
| Cr   | 3d\(^3\)4s\(^7\)S | 0.00000     | 0.00000| 0.00000|
|      | 3d\(^5\)4s\(^5\)D | 0.26201   | 0.27226| 0.26986|
| Fe   | 3d\(^5\)4s\(^5\)D | 0.00000     | 0.00000| 0.00000|
|      | 3d\(^6\)4s\(^5\)F | 0.07555   | 0.07984| 0.08006|
|      | 3d\(^8\)5F   | 0.28933      | 0.30548| 0.30477|
| Br   | 4s\(^2\)4p\(^3\)P | 0.00000     | 0.00000| 0.00000|
|      | 4s\(^1\)4p\(^3\)S | 0.55464   | 0.55820| 0.55803|
|      | 4s\(^2\)4p\(^4\)d\(^4\)F | 0.33407 | 0.33376| 0.33440|
| Mo   | 4d\(^5\)5s\(^1\)S | 0.00000     | 0.00000| 0.00000|
|      | 4d\(^4\)5s\(^5\)D | 0.08763   | 0.10114| 0.09298|
|      | 4d\(^6\)5D   | 0.15962      | 0.17646| 0.18216|
| Ag   | 4d\(^10\)5s\(^1\)S | 0.00000     | 0.00000| 0.00000|
|      | 4d\(^9\)5s\(^3\)D | 0.14411   | 0.14888| 0.15060|
|      | 4d\(^10\)5p\(^3\)P | 0.11066   | 0.10873| 0.11195|
| Sb   | 5s\(^2\)5p\(^3\)S | 0.00000     | 0.00000| 0.00000|
|      | 5s\(^1\)5p\(^5\)P | 0.27820   | 0.28326| 0.28370|
|      | 5p\(^3\)P     | 0.76145      | 0.78007| 0.78147|

**Mean error** 0.00513 0.00539
**Mean absolute error** 0.00621 0.00585

**TABLE III:** Excitation energies (a.u.) for selected atoms. Excitation energies obtained from AE HF calculations with relativistic corrections (RC), are compared with those from HF pseudopotential calculations with LS coupling. Results are shown for both our soft parameterized pseudopotentials, and for the singular parameterized pseudopotentials of Pacios and Christiansen.\(^{12,13}\) (PC).
| Atom | $E_{\text{AE}}$ | $E_{\text{ion}}$ | $E_{\text{PC}}$ |
|------|----------------|----------------|----------------|
| Li   | 0.19632        | 0.19634        | 0.19646        |
| Be   | 0.29566        | 0.29584        | 0.29618        |
| C    | 0.39625        | 0.40032        | 0.39724        |
| Si   | 0.28083        | 0.28743        | 0.28083        |
| Ti   | 0.20374        | 0.20044        | 0.20115        |
| Cr   | 0.22054        | 0.22849        | 0.22757        |
| Fe   | 0.23288        | 0.22623        | 0.22792        |
| Br   | 0.39481        | 0.39473        | 0.39530        |
| Mo   | 0.22801        | 0.24066        | 0.24459        |
| Ag   | 0.23088        | 0.23353        | 0.23274        |
| Sb   | 0.31787        | 0.31923        | 0.31852        |

Mean error | 0.00231 | 0.00188
Mean absolute error | 0.00414 | 0.00325

**TABLE IV:** Comparison of first ionization potentials obtained from AE calculations ($E_{\text{AE}}$), from HF calculations using our soft parameterized pseudopotentials ($E_{\text{ion}}$), and for the singular parameterized pseudopotentials of Pacios and Christiansen12,13 ($E_{\text{PC}}$) (LS coupling is used throughout).

| Atom | Configuration | AE | DF | Our | PC |
|------|---------------|----|----|-----|----|
| Li   | $p^1$         | 0.6| 0.8| 0.9 |
| Be$^+$| $p^1$         | 8.9| 8.5| 9.3 |
| B    | $p^1$         | 20.6| 20.0| 21.8 |
| C$^+$| $p^1$         | 79.3| 75.8| 84.5 |
| N$^2^+$| $p^1$        | 209.8| 197.9| 219.9 |
| O$^3^+$| $p^1$        | 452.3| 454.4| 498.9 |
| F    | $p^5$         | 410.5| 402.4| 438.9 |
| Ne$^+$| $p^5$        | 815.4| 820.5| 892.0 |
| Al   | $p^1$         | 120.0| 116.1| 114.8 |
| Si$^+$| $p^1$        | 308.7| 293.9| 292.2 |
| P$^{2^+}$| $p^1$      | 599.3| 556.1| 553.9 |
| S$^{2^+}$| $p^1$      | 1019.4| 1020.0| 1013.5 |
| Cl   | $p^5$         | 920.6| 903.9| 910.3 |
| Ar$^+$| $p^5$        | 1494.1| 1472.6| 1487.4 |
| Sc   | $d^5$         | 165.7| 169.2| 191.0 |
| Ti$^+$| $d^5$        | 370.1| 410.7| 458.4 |
| Ti$^{2^+}$| $d^5$     | 405.4| 440.6| 487.3 |
| Cu   | $d^9$         | 2122.9| 2110.5| 2292.9 |
| Zn$^+$| $d^9$        | 2820.0| 2814.1| 3036.3 |
| Ga   | $p^1$         | 811.8| 756.6| 772.0 |
| Ge$^+$| $p^1$        | 1764.0| 1681.9| 1710.4 |
| Br   | $p^5$         | 3744.5| 3777.9| 3867.3 |
| Kr$^+$| $p^5$       | 5458.8| 5944.1| 5431.0 |

Mean % error | 0.4 | 5.7
Mean absolute % error | 4.8 | 8.2

**TABLE V:** Spin-orbit splitting (cm$^{-1}$) for selected atoms. Splitting obtained from all-electron DF calculations (with no relativistic correction) are compared with those resulting from $jj$-coupled HF calculations using parameterized AREP and SO pseudopotentials. Results are given for both our soft parameterized AREP and SO pseudopotentials, and those of Christiansen et al.12,13,34 (PC).