Norm-conserving Hartree-Fock pseudopotentials and their asymptotic behaviour

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(Dated: October, 2004)

We investigate the properties of norm-conserving pseudopotentials (effective core potentials) generated by inversion of the Hartree-Fock equations. In particular we investigate the asymptotic behaviour as $r \to \infty$ and find that such pseudopotentials are non-local over all space, apart from a few special special cases such as H and He. Such extreme non-locality leads to a lack of transferability and, within periodic boundary conditions, an undefined total energy. The extreme non-locality must therefore be removed, and we argue that the best way to accomplish this is a minor relaxation of the norm-conservation condition. This is implemented, and pseudopotentials for the atoms H–Ar are constructed and tested.

PACS numbers: 71.15.Dx, 21.60.Jz, 02.70.Ss

The pseudopotential approximation is a vital part of the practical application of \textit{ab initio} methods to problems in quantum chemistry and condensed matter physics. In the pseudopotential approach the tightly bound core electrons are removed and their influence on the rest of the system is represented by an effective potential. This reduces the number of electrons that must be considered and yields a smoother potential. These properties significantly reduce the computational effort required for complex systems.

Over the past few years ultra-soft\textsuperscript{8,9,10,11,12} pseudopotentials and separable norm-conserving Kleinman-Bylander\textsuperscript{3} pseudopotentials have come to dominate within plane-wave Density Functional Theory (DFT) technology. Within the quantum chemistry community it is more usual to use non-separated norm-conserving pseudopotentials, which are the kind we deal with here. Such pseudopotentials can, however, be converted to the separable Kleinman-Bylander form.

Our main interest is in diffusion quantum Monte Carlo (DMC) calculations\textsuperscript{4}. Norm-conserving pseudopotentials are routinely used within DMC calculations\textsuperscript{5,6}, and there is evidence to show that Hartree-Fock (HF) theory provides better pseudopotentials for this purpose than DFT\textsuperscript{7}. HF pseudopotentials have been used in various correlated valence quantum chemistry calculations, and we suggest they would be suitable for use in perturbation theories such as the GW scheme, which has been applied to a number of condensed matter systems\textsuperscript{8}.

It turns out that most of the HF pseudopotentials available in the quantum chemistry literature diverge at the origin, normally like $1/r^2$ or $1/r$, which makes them unsuitable for use in DMC calculations\textsuperscript{9,10,11,12}. Recently Ovcharenko \textit{et al.}\textsuperscript{13} developed HF pseudopotentials for Be-Ne and Al-Ar which are finite at the origin, and we will compare the pseudopotentials generated here with these. We would like our pseudopotentials to be as smooth as possible, since lack of smoothness can reduce the transferability of a pseudopotential. In addition we wish to generate HF orbitals using a variety of basis sets, including plane waves, for which a smooth pseudopotential reduces the computational cost.

It is advantageous to make the region over which the pseudopotential is non-local as small as possible as the evaluation of the non-local energy within DMC is expensive. Having a small region of non-locality also tends to promote transferability, but tends to make the pseudopotential less smooth.

An important issue arises in generating HF pseudopotentials by inversion of the HF equations. It has long been understood that if the norm is not conserved the Hartree potential due to the pseudo-ion does not decay as $-Z_{\text{val}}/r$ at large $r$ (where $Z_{\text{val}}$ is the ionic charge)\textsuperscript{14}. It has also been appreciated that the exchange interaction gives a long range tail to the pseudopotential which should be removed\textsuperscript{11,14}. We find that even if norm-conservation is enforced the exchange interaction results in a “non-Coulombic tail” that decays more slowly than the Coulomb part of the pseudopotential, persists far from the atom, and is non-local. Non-Coulombic tails in HF pseudopotentials have been reported before in the literature, but the form that we derive here is different from that described by Kahn \textit{et al.}\textsuperscript{15} and Hay \textit{et al.}\textsuperscript{16}, who suggest that the deviation from $-Z_{\text{val}}/r$ decays faster than $1/r$.

These non-Coulombic tails increase the cost of calculations, lead to unphysical results and, in the case of periodic boundary conditions, leave the total energy undefined. Consequently the tail must be removed for practical applications. Although past workers have constructed HF pseudopotentials with this long range non-local tail removed, we are not aware of a detailed discussion in the literature of the form and magnitude of this tail. Understanding this long ranged effect is important when considering how to remove it.

In what follows we investigate the general properties of norm-conserving\textsuperscript{12} HF pseudopotentials, with particular emphasis on their non-locality and asymptotic behaviour. We present a method to localise the potential such that it is non-local only within a relatively small region surrounding the nucleus, and enforce the desired asymptotic behaviour.

In section\textsuperscript{11} we discuss pseudopotentials obtained from inversion of the HF equations, in section\textsuperscript{11} we derive
the asymptotic behaviour of these pseudopotentials, and report detailed results for Ne. In section \[\text{III}\] we present and analyse results for the atoms H-Ar. We draw our conclusions in section \[\text{IV}\]. Atomic units are used throughout, unless otherwise indicated.

I. PSEUDOPOTENTIALS FROM INVERSION OF THE HF EQUATIONS

The pseudopotential generation procedure we apply is similar to that used by others, such as Hay and Wadt, or Troullier and Martins. In this section we provide a brief summary of the procedure for generating norm-conserving pseudopotentials, primarily to define the notation and context.

For an isolated atom a HF orbital, $\psi_{i}$, may be labelled by the quantum numbers $i$, $l_{i}$ and $m_{i}$. Separating the angular and radial coordinates leads to

$$
\psi_{i,l_{i},m_{i}}(r) = \frac{\phi_{i}(r)}{r} Y_{l_{i},m_{i}}(\Omega). \tag{1}
$$

The radial part of the orbital, $\phi_{i}(r)$, satisfies

$$
\left[ -\frac{1}{2} \frac{d^{2}}{dr^{2}} + \frac{l_{i}(l_{i}+1)}{2r^{2}} + V_{i}^{\text{eff}} \right] \phi_{i} = \epsilon_{i} \phi_{i}, \tag{2}
$$

where the effective potential for orbital $i$ is

$$
V_{i}^{\text{eff}} = -\frac{Z}{r} + V_{h}[\rho] + \frac{\hat{V}_{x}([\phi], l_{i} \phi_{i})}{\phi_{i}}. \tag{3}
$$

The first term arises from the nuclear charge and the second is the Hartree potential due to the total electron density. The third term is the effective exchange potential, which is different for each orbital. For convenience in what follows we have included the (cancelling) self-interaction in the second and third terms.

To construct a pseudopotential we first partition the atomic orbitals into core orbitals, whose influence will be represented by the pseudopotential, and valence orbitals, which will be represented by the pseudo-orbitals. The eigenvalues of the pseudo-orbitals are constrained to equal the equivalent all-electron (AE) eigenvalues, and the pseudo-orbitals themselves are constrained to equal the equivalent AE orbitals outside of a “core radius”, $r_{ci}$. Inside $r_{ci}$ the orbitals are given by an as-yet unspecified function $f_{i}$, so that

$$
\tilde{\phi}_{i}(r) = \begin{cases} f_{i}(r) & r < r_{ci}, \\ \phi_{i}(r) & r \geq r_{ci}. \end{cases} \tag{4}
$$

$f_{i}(r)$ is chosen such that $\tilde{\phi}_{i}(r)$ is nodeless, smooth up to a certain order of differentiation at $r = r_{ci}$, and that its norm is equal to that of $\phi_{i}(r)$.

The pseudo-orbital for state $i$ satisfies

$$
\left[ -\frac{1}{2} \frac{d^{2}}{dr^{2}} + \frac{l_{i}(l_{i}+1)}{2r^{2}} + \tilde{V}_{i}^{\text{eff}} \right] \tilde{\phi}_{i} = \epsilon_{i} \tilde{\phi}_{i}, \tag{5}
$$

and hence the effective potential, $\tilde{V}_{i}^{\text{eff}}$, can be obtained by inverting Eq. (5). The pseudopotential for state $i$, $\tilde{V}_{i}(r)$, is then defined by the pseudo-atom equivalent of Eq. (3):

$$
\tilde{V}_{i}^{\text{eff}} = \tilde{V}_{i}(r) + V_{h}[\tilde{\rho}] + \frac{\hat{V}_{x}([\tilde{\phi}], l_{i} \tilde{\phi}_{i})}{\tilde{\phi}_{i}}. \tag{6}
$$

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,

$$
\tilde{V}_{\text{pseudo}} = \tilde{V}_{\text{local}}(r) + \sum_{l_{max}}^{l_{max}} \sum_{m=-l_{max}}^{l_{max}} |Y_{lm}(\tilde{V}_{i}(r) - \tilde{V}_{\text{local}}(r))/Y_{lm}|. \tag{7}
$$

The orbitals with $l > l_{max}$ feel the local potential, $\tilde{V}_{\text{local}}$. Here the index $l$ is interchangeable with the pseudo-atom orbital index, $i$, since the valence states chosen to construct the pseudopotential must have unique $l$ quantum numbers.

II. EXTREME NON-LOCALITY OF HF PSEUDOPOTENTIALS

In this section we address the question of the locality of the pseudopotentials defined above. We define a pseudopotential to be local within a radius $r_{loc}$ if, for all $i$ and $j$,

$$
|\tilde{V}_{i}(r) - \tilde{V}_{j}(r)| \leq \delta \quad \text{for } r > r_{loc}, \tag{8}
$$

for some $r_{loc}$ and small $\delta$.

By definition $\tilde{\phi}_{i} = \phi_{i}$ for $r > r_{ci}$ and hence $\tilde{V}_{i}^{\text{eff}} = V_{i}^{\text{eff}}$ for $r > r_{ci}$. This equality, together with Eqs. (3) and (6) gives

$$
\tilde{V}_{i}(r) = -\frac{Z}{r} + V_{h}[\rho - \tilde{\rho}] + \frac{\hat{V}_{x}([\phi], l_{i} \phi_{i})}{\phi_{i}} - \frac{\hat{V}_{x}([\tilde{\phi}], l_{i} \tilde{\phi}_{i})}{\tilde{\phi}_{i}}, \quad r > r_{ci}. \tag{9}
$$

The first two terms are independent of the orbital and, since $\rho$ and $\tilde{\rho}$ differ by the exponentially decaying core contribution, the sum of these terms approaches $-Z_{val}/r$ as $r \to \infty$. However, since the HF exchange potential is non-local there is no reason to expect the final two terms to cancel, or to approach zero faster than $1/r$ as $r \to \infty$.

To obtain the asymptotic form of $\tilde{V}_{x}([\phi], l_{i} \phi_{i})$, we start from the asymptotic behaviour of the atomic HF orbitals. Handy et al. have shown that the asymptotic form of the atomic HF orbitals as $r \to \infty$ is dominated by an exponential decay with exponent $\alpha = (-2\epsilon_{HO})^{1/2}$,
where $HO$ denotes the highest occupied orbital. Handler et al. derived the full asymptotic form,

$$\phi_i(r) \sim r^{l_i+1}(a_i + b_i r^{-1} + \ldots) e^{-\alpha r},$$  \hspace{1cm} (10)

where we use $\sim$ to denote “asymptotically approaches as $r \to \infty$”. They found expressions for $\beta_i$ which can be summarised as

\[
\begin{array}{ccc}
  i & l_i & \beta_i \\
  \hline
  = HO & = l_{HO} & \beta \\
  \neq HO & \neq l_{HO} & \beta - |l_i - l_{HO}| - 1 \\
  \neq HO & = l_{HO} & 0 \\
  \neq HO & = l_{HO} & 0 - 2(l_{min} + 1)
\end{array}
\]

where $\beta = (Z - (2N - 1) - \alpha)/\alpha$, there are $2N$ electrons in the atomic configuration, and $l_{min}$ is the lowest non-zero $l$ value in the configuration.

In Eq. (11) and the rest of this section we limit our analysis to closed shell atoms to aid clarity. The generalisation to open shell atoms using spin averaging or eigenfunctions of the total angular momentum is straightforward but algebraically complex, and does not change our conclusions.

Eqs. (10) and (11) do not apply to $s$-electron-only atoms. In this case the exponent for each orbital is different and is given by $\alpha_i = (-2\epsilon_i)^{1/2}$, and it is straightforward to demonstrate that the sum of the exchange terms in Eq. (10) approaches zero exponentially as $r$ increases. We do not consider these pure-$s$ atoms in what follows.

Expressing the HF exchange potential in spherical polar co-ordinates and taking the limit as $r \to \infty$ gives

$$\tilde{V}_i[\{\phi\}, l_i]\phi_i(r) \sim - \sum_j \sum_l (2l_j + 1)w_j \left( \begin{array}{ccc} l_j & l & l_i \\
 0 & 0 & 0 \end{array} \right) \frac{1}{l_{w+1}} \int_0^\infty r^{2l} \phi_j \phi_i dr,$$ \hspace{1cm} (12)

where the Wigner $3j$ notation has been used for triple integrals over spherical harmonics. The occupation of shell $j$ is denoted by $w_j$, where $w_j = 1$ for a full shell.

We define the effective exchange potential for orbital $i$ as

$$V_i^\star(r) = \frac{\tilde{V}_i[\{\phi\}, l_i]\phi_i(r)}{\phi_i(r)}.$$ \hspace{1cm} (13)

Next we explicitly separate the exchange interaction between electrons within shell $i$ from the remaining exchange, and use the asymptotic forms for the orbitals of Eq. (10), to obtain

$$V_i^\star(r) \sim - \frac{1}{r} - \sum_{k=1}^{l_i} (2l_i + 1)w_i \left( \begin{array}{ccc} l_i & 2k & l_i \\
 0 & 0 & 0 \end{array} \right) \frac{1}{l_{w+1}} \int_0^\infty r^{2k} \phi_i dr$$

$$- \sum_{j \neq i} \sum_l (2l_j + 1)w_j \left( \begin{array}{ccc} l_j & l & l_i \\
 0 & 0 & 0 \end{array} \right) \frac{1}{l_{w+1}} \int_0^\infty r^{n_{ij}} (a_{ij} + b_{ij} r^{-1} + \ldots) \int_0^\infty r^l \phi_j \phi_i dr,$$ \hspace{1cm} (14)

where $n_{ij} = \beta_j - \beta_i - l - 1$. The first term in Eq. (14) is always present and is a part of the self-interaction correction (SIC) which is the same for all orbitals. The second term is part SIC and part exchange interaction, and is non-zero only for $l_i > 0$. If present this introduces terms $\propto 1/r^{2k+1}$ for $k = 1, \ldots, l_i$ which are different for each orbital.

The third term is the remainder of the exchange interaction, and we consider the maximum power $n_{ij}$ that appears in this expression with a non-zero coefficient. Given that the Wigner $3j$ symbol is non-zero only for $|l_i - l_j| \leq l \leq l_i + l_j$ and $l_i + l_j + l$ even, and that the integral is zero for $l = 0$, we find that the maximum $n_{ij} = n_i$ takes the values

\[
\begin{array}{cccc}
  i & l_i & n_i & l \\
  \hline
  = HO & = l_{HO} & -(2m + 2) & m \\
  \neq HO & \neq l_{HO} & 0 & |l_i - l_{HO}| \\
  \neq HO & = l_{HO} & 0 & 2 \\
  \neq HO & = l_{HO} & 0 & l_{min}
\end{array}
\]

where $m = \min\{l_i, l_{HO}\}$, $|l_i - l_{HO}|$ and $l_{min}$ is as defined for Eq. (11).

Using Eq. (15) we may write the effective exchange potential in the limit $r \to \infty$ as

$$V_i^\star(r) \sim - \frac{1}{r} - \sum_{\{ij\}, n_{ij}=0} w_j (a_{ij} + b_{ij} r^{-1}) \int_0^\infty r^l \phi_j \phi_i dr$$

$$- \sum_{\{ij\}, n_{ij}=-1} w_j a_{ij} r^{-1} \int_0^\infty r^l \phi_j \phi_i dr + O(r^{-2}),$$ \hspace{1cm} (16)
where the Wigner 3j and its pre-factor in Eq. (14) have been subsumed into the parameters \( a_{ijl} \) and \( b_{ijl} \), and the sums are taken over the \( l \) and \( j \) that give \( n_{ij} = 0 \) and \( n_{ij} = -1 \). For \( i = \text{HO} \), only the SIC term appears since \( a_{ijl} = b_{ijl} = 0 \). Note that for \( i \neq \text{HO} \), \( V_{l}^{\text{eff}}(\infty) \) is non-zero and the effective exchange potential contains a \( r^{-1} \) term in addition to the SIC.

Using the same line of argument, the pseudo-atom effective exchange potential at large distances is given by

\[
\tilde{V}_{i}^{\text{eff}}(r) \sim -\frac{1}{r} - \sum_{\{ij\} | n_{ij} = 0} \tilde{w}_{ij} (a_{ijl} + b_{ijl} r^{-1}) \int_{0}^{\infty} r l \tilde{\phi}_{j} \tilde{\phi}_{i} dr \\
- \sum_{\{ij\} | n_{ij} = -1} \tilde{w}_{ij} a_{ijl} r^{-1} \int_{0}^{\infty} r l \tilde{\phi}_{j} \tilde{\phi}_{i} dr + O(r^{-2}),
\]  

(17)

again with \( a_{ijl} = b_{ijl} = 0 \) for \( i = \text{HO} \). The sum over \( l, j \) is as before, and a similar non-zero limit and \( r^{-1} \) term appear. The occupation of pseudo-shell \( j \), \( \tilde{w}_{ij} \), is defined as for the AE atom, but is zero for core states. Since the integrals in Eq. (16) and Eq. (17) are not in general equal, the limits for the AE and pseudo-atom effective exchange potentials are not equal and do not cancel in Eq. (19). In addition, exchange terms due to core-valence interactions will not cancel as no core orbitals are present in the pseudo-atom.

The asymptotic behaviour of the pseudopotential can be obtained to \( O(r^{-2}) \) from the explicit forms of the external, Hartree, and exchange potentials. Starting with the AE effective potential, Eq. (3) can be expressed as

\[
V_{i}^{\text{eff}} \sim -(Z - (2N - 1)) r^{-1} - \sum_{\{ij\} | n_{ij} = 0} w_{ij} (a_{ijl} + b_{ijl} r^{-1}) \int_{0}^{\infty} r l \phi_{j} \phi_{i} dr \\
- \sum_{\{ij\} | n_{ij} = -1} w_{ij} a_{ijl} r^{-1} \int_{0}^{\infty} r l \phi_{j} \phi_{i} dr + O(r^{-2}).
\]  

(18)

If we write the asymptotic form of the pseudopotential as

\[
\tilde{V}_{i} \sim s_{i} - (Z_{\text{val}} + g_{i}) r^{-1} + O(r^{-2}),
\]  

(19)

where \( s_{i} \) and \( g_{i} \) are constants then the equivalent expression for the pseudo-atom effective potential is

\[
\tilde{V}_{i}^{\text{eff}} \sim s_{i} - (Z_{\text{val}} - (2N_{\text{val}} - 1) + g_{i}) r^{-1} - \sum_{\{ij\} | n_{ij} = 0} \tilde{w}_{ij} (a_{ijl} + b_{ijl} r^{-1}) \int_{0}^{\infty} r l \tilde{\phi}_{j} \tilde{\phi}_{i} dr \\
- \sum_{\{ij\} | n_{ij} = -1} \tilde{w}_{ij} a_{ijl} r^{-1} \int_{0}^{\infty} r l \tilde{\phi}_{j} \tilde{\phi}_{i} dr + O(r^{-2}),
\]  

(20)

where there are \( 2N_{\text{val}} \) valence electrons. Since \( V_{i}^{\text{eff}} = \tilde{V}_{i}^{\text{eff}} \) for \( r > r_{ci} \) we may equate the coefficients of \( r^{-1} \) and \( r^{0} \) to give

\[
s_{i} = \begin{cases} 
0 & i = \text{HO} \\
\sum_{\{ij\} | n_{ij} = 0} a_{ijl} \left[ \tilde{w}_{ij} \int_{0}^{\infty} r l \tilde{\phi}_{j} \tilde{\phi}_{i} dr - w_{ij} \int_{0}^{\infty} r l \phi_{j} \phi_{i} dr \right] & i \neq \text{HO},
\end{cases}
\]  

(21)

and, assuming that the charge of the AE and pseudo-atoms are equal \( (Z - 2N = Z_{\text{val}} - 2N_{\text{val}}) \),

\[
g_{i} = \begin{cases} 
0 & i = \text{HO} \\
- \sum_{\{ij\} | n_{ij} = 0} b_{ijl} \left[ \tilde{w}_{ij} \int_{0}^{\infty} r l \tilde{\phi}_{j} \tilde{\phi}_{i} dr - w_{ij} \int_{0}^{\infty} r l \phi_{j} \phi_{i} dr \right] + \sum_{\{ij\} | n_{ij} = -1} a_{ijl} \left[ \tilde{w}_{ij} \int_{0}^{\infty} r l \tilde{\phi}_{j} \tilde{\phi}_{i} dr - w_{ij} \int_{0}^{\infty} r l \phi_{j} \phi_{i} dr \right] & i \neq \text{HO}.
\end{cases}
\]  

(22)

For \( i \neq \text{HO} \), \( s_{i} \) and \( g_{i} \) are generally non-zero since the AE and pseudo-orbitals differ in the core region. In addition, terms due to exchange between state \( i \) and core states have no counterpart in the pseudo-atom to cancel with, as \( w_{ij} = 1 \) and \( \tilde{w}_{ij} = 0 \) for the core states. This orbital dependent “offset potential” and “ghost charge” result from a remnant of the AE exchange interaction remaining in the pseudopotential as it is not completely removed by the exchange interaction in the pseudo-atom, and is generally due to both valence-valence and valence-core exchange. Because these terms are orbital dependent the pseudopotential itself is non-local over all space and does not satisfy the locality criteria of Eq. (3) for any \( r_{loc} \). It should be stressed that this extreme non-locality is necessary if we require our HF pseudopotential to be both norm conserving and to reproduce the AE valence eigenvalues and orbitals outside of the core region.

To illustrate the physical consequences of this behaviour we consider the total energy of a collection of identical pseudo-atoms. The total energy should tend
towards the total energy of the isolated pseudo-atoms as they are separated further apart. This is true if each channel of the pseudopotential approaches $-Z_{\text{val}}/r$ for large $r$. For the extreme non-local behaviour found here this is not the case, and an unphysical interaction persists at large distances. For extended systems this is catastrophic because the total energy is undefined.

Extreme non-locality may be avoided in the construction of a pseudopotential by using a different configuration to construct each channel, such that the configuration used to construct channel $l$ has $l = l_{\text{HO}}$. Although this is practical for H and He, for heavier atoms this requires the construction of pseudopotentials from electronic configurations far from those we wish to use them for. It would not be reasonable to expect the resulting pseudopotentials to be transferable to systems of interest, and they would not reproduce the valence states of the neutral isolated atom.

### A. The Kleinman-Bylander form

The Kleinman-Bylander form is expressed in terms of operators that project the orbitals onto a set of basis functions, and takes the general form

$$\tilde{V}^{KB} = \tilde{V}_{\text{local}}(r) + \sum_{ij} |\tilde{\psi}_i\rangle D_{ij} \langle \tilde{\psi}_j|,$$  

(23)

for some $\{\tilde{\psi}\}$. The pseudopotentials discussed in section 1 may be expressed in this form if we define

$$D_{ij} = \langle \tilde{\psi}_i|\tilde{V}_j - \tilde{V}_{\text{local}}|\tilde{\psi}_j\rangle,$$  

(24)

where the $\tilde{\psi}_i$ are the eigenstates of the pseudo-atom. If a complete set of $\tilde{\psi}_i$ is included in the sum in Eq. (23), this form would be exactly equal to Eq. (7). In practice a more useful approach is to use a small number of localised, bound, atomic states (such as those used to construct the original pseudopotential) with $\tilde{V}_{\text{local}}(r)$ chosen such that $\tilde{V}_{\text{local}} \rightarrow -Z_{\text{val}}/r$ as $r \rightarrow \infty$. For this choice of localised bound states, $\tilde{V}^{KB}$ is well-behaved at large $r$, since the subspace covered by the projection does not include this asymptotic region - the non-local part of the pseudopotential has been localised by representing it within a localised subspace.

We conclude that converting a norm-conserving HF pseudopotential to Kleinman-Bylander form removes the long ranged non-locality, and so allows these potentials to be implemented computationally in a manner which avoids the unphysical behaviour described previously. It should be noted that the “frozen remnant” of the atomic exchange interaction which makes up the non-Coulombic tail is still present (although limited to a subspace represented by the pseudo-orbitals), and it may still lead to significant errors.

### B. DFT pseudopotentials

Extreme non-locality does not occur for pseudopotentials constructed within Kohn-Sham DFT because the effective potential that represents the electron-electron interaction is the same for all electrons (i.e., it is local). More explicitly, in DFT the local exchange-correlation potential takes the place of the exchange potential in Eq. (10) and hence the equivalent expression for the pseudopotential is

$$\tilde{V}_i(r) = -\frac{Z}{r} + V_h[\rho - \bar{\rho}] + V_{xc}[\rho] - V_{xc}[\bar{\rho}], \quad r > r_c.$$  

(25)

For $r > r_c$, where $r_c = \max[r_{ci}]$, all $\tilde{V}_i(r)$ are the same, so the pseudopotential is local outside of the core region.

Within the Optimised Potential Method (OPM)\textsuperscript{22,23} the exchange-correlation energy functional is replaced by an “exact” exchange energy functional (possibly with an added approximate correlation functional) defined explicitely in terms of the Kohn-Sham orbitals and implicitly in terms of the charge density. This exact exchange (EXX) functional takes the form of the Fock term of HF, but is evaluated using the KS orbitals and hence the calculation remains KS-DFT\textsuperscript{24} and the OPM exchange energy does not equal the HF exchange energy. Norm-conserving pseudopotentials have been defined within this theoretical picture by Engel et al. and others, and “spurious long range structure”\textsuperscript{25,26,27} consistently appears in these pseudopotentials.

Given the highly non-local nature of the Fock term it seems reasonable that the exchange potential is also an extremely non-local functional of the density. We also expect the exchange potential to approach zero as $r \rightarrow \infty$, since this behaviour is part of the definition of the EXX potential itself\textsuperscript{22}. These two observations, together with Eq. (25), explain the existence of the structure found by Engel et al.\textsuperscript{22} They found that pseudopotentials constructed by removing this long range structure resulted in improved bond distances and energies for simple dimers and bulk Al. Note that the OPM case is in some regards similar to that found in the HF case, but it is essentially different in that the potential is local for $r > r_c$ and approaches $-Z_{\text{val}}/r$ faster than $1/r$.

For local (e.g., the local density approximation or LDA) or semi-local (e.g., the generalised gradient approximation or GGA) exchange-correlation functionals we note that $\rho$ and $\bar{\rho}$ differ by the exponentially decaying core contribution and obtain the relation

$$\lim_{r \rightarrow \infty} \tilde{V}_i(r) = -\frac{Z_{\text{val}}}{r} + \mathcal{O}(e^{-\alpha r}).$$  

(26)

The absence of an offset or ghost charge is a consequence of the locality of the approximate exchange-correlation functional. It is clear that there is no DFT analogue of the extreme non-locality present in HF pseudopotentials.
III. Results

A. Size of the extreme non-local terms

To construct a pseudopotential from an AE atomic HF calculation we must define a form for the pseudo-orbitals inside the core radius, \( f_i \). We chose the Troullier-Martins form

\[
f_i(r) = r^{j+1} \exp \left[ \sum_{m=0}^{6} c_m r^{2m} \right],
\]

which is based on the observation that the pseudo-orbitals are smoother if the odd derivatives of the screened pseudopotential at the nucleus are set to zero. The coefficients are determined by requiring norm-conservation of the charge in the core region, continuity of \( \phi_i \) and its first four derivatives at \( r_{ci} \), and the requirement that \( \tilde{V}_i(r) \) has zero curvature at the origin.

As an example we consider Ne (1s\(^2\)2s\(^2\)2p\(^6\)) and perform a numerical HF calculation and construct \( \tilde{\phi} \) for the 2s and 2p orbitals. We then obtain s and p pseudopotentials as described in section II. We also calculate the \( r^{-3} \) and \( r^0 \) contributions to the asymptotic behaviour directly from the pseudo-orbitals.

First we note that, for Ne, the highest occupied orbital is \( i = 2p \). From Eqs. (14) and Eq. (15) it follows that the \( p \) part of the pseudopotential approaches \( Z_{val}/r \) as \( r^{-3} \) due to the \( 2p - 2p \) exchange interaction.

For the \( s \) part, the exchange interaction contributes the \( 2s - 2p \) term, which is the only interaction appearing in Eqs. (18) and (20). To obtain values for \( s_{2s} \) and \( g_{2s} \), we first obtained the asymptotic behaviour of the effective potential \( \tilde{V}_i^{eff}(r) \) by direct substitution of the asymptotic form of the orbital into Eq. (2). Equating powers of \( r \) leads to

\[
(e_{2s} - e_{2p}) = -a_{2p,2s,1} \int_0^\infty r \phi_{2p} \phi_{2s} dr,
\]

and

\[
2\sqrt{2}|\epsilon_{2p}|^{1/2} = b_{2p,2s,1} \int_0^\infty r \phi_{2p} \phi_{2s} dr.
\]

Using the numerical values of the integrals and eigenvalues we obtain the values of \( a_{2p,2s,1} \) and \( b_{2p,2s,1} \), and by using Eqs. (21) and (22) we obtain \( s_{2s} = 0.0095 \) a.u. (0.26 eV) and \( g_{2s} = 0.023 \) e, that is, a positive offset to the potential and a positive ghost charge.

The difference between the \( s \) part of the Ne pseudopotential and the Coulomb potential, \( V_s + Z_{val}/r \) is shown in Fig. 1. It is clear that the pseudopotential does not approach the Coulomb potential for large \( r \). The calculated asymptotic form, \( s_{2s} + g_{2s}/r \), is also shown. The difference between the pseudopotential and the calculated asymptotic form at large \( r \) arises mainly from a \( 1/r^4 \) term which was not included in the asymptotic form.

B. Localising the pseudopotential

Here we consider several methods for removing the non-Coulombic tails of the pseudopotentials in order to localise them within some radius \( r_{loc} \). In what follows we define the localisation radius, \( r_{loc} \), as in Eq. (3), with \( \delta = 5 \times 10^{-6} \) a.u.

Previous workers (for example, Gref and Lester) have expanded pseudopotentials in a Gaussian basis, a standard form for quantum chemistry applications. Due to the functional form of this expansion the parameterised pseudopotential is non-local in a finite region surrounding the nucleus, and approaches the Coulombic form as \( r \to \infty \), hence the expansion may be used as a localisation procedure. Generally this expansion is obtained numerically by requiring the parameterised pseudopotential to reproduce the pseudo-states of the original pseudopotential to within a given accuracy. Although this method can work well it is difficult to control the smoothness and the localisation radius, \( r_{loc} \), since the error in the expanded pseudopotential (and accompanying pseudo-states) must compensate for the absence of...
the long range behaviour present in the original pseudopotential. We prefer to control the localisation of the original pseudopotential and then, if desired, expand the resulting potential in a Gaussian basis. Gaussian expansions are not considered further in this paper, but we will present parameterised pseudopotentials obtained in this way in a separate paper.\(^{29}\)

We have freedom in our choice of \(r_{ci}\) and \(f_i(r)\), and by varying these quantities we might be able to localise the pseudopotential in the sense of Eq. (5), since variations in these quantities will alter the integrals in Eqs. (21) and (22). For Ne (and for most atoms) the first term in Eqs. (21) and (22) is larger than the second because the AE orbitals possess radial intervals where they are negative, while the pseudo-orbitals are positive for all \(r\). In order to decrease the value of this integral, causing \(s_{2s}\) and \(\phi_{2s}\), to become closer to zero, \(f_i(r)\) might be chosen such that, on average, the electron is closer to the nucleus. This might be achieved by increasing \(r_{ci}\), allowing the maximum of \(\phi_{2s}\) to be closer to the nucleus. Also, the form of \(f_i(r)\) may be altered (a convenient way of achieving this is to relax the continuity of the 3\(^{rd}\) and/or 4\(^{th}\) derivatives). Calculations suggest that neither of these approaches is useful - for a good cancellation of the integrals in Eqs. (21)(22) \(r_{ci}\) must be very large, or \(f_i(r)\) must take a form such that the corresponding pseudopotential is far from smooth.

Next we consider an elegant procedure described by Engel et al.\(^{27}\) and used by them to remove the (local) intermediate range structure present in OPM pseudopotentials. This approach employs a self-consistent modification of the pseudo-orbitals over all space, while conserving the norm. The same method may be applied to localise HF pseudopotentials.

The pseudopotential at iteration \(n\) is denoted by \(\hat{V}_{i;n}\), and the associated pseudo-orbitals are \(\{\hat{\phi}_i\}_n\). The pseudopotentials calculated in section 4 correspond to \(n=1\). We construct an effective potential which is not yet self-consistent,

\[
\hat{V}_{i;n} = -\frac{Z}{r} + V_h[\rho_{\text{core}}] + V_h[\rho_{\text{loc}}] + \frac{\hat{V}_{i}[\hat{\phi}_i;n]}{\hat{\phi}_i;n},
\]

where \(-\frac{Z}{r} + V_h[\rho_{\text{core}}]\) is the Coulomb+Hartree potential due to the ionic core. Equation (30) is the external potential we desire outside of the core radius together with the effective interaction potential of the pseudo-orbitals \(\{\hat{\phi}_i\}_n\). Taking the correct asymptotic form for the orbitals, we integrate in from \(\infty\) to \(r_{ci}\) at energy \(\epsilon_i\) to obtain the new orbitals \(\{\hat{\phi}_i\}_{n+1}\) in this region, and these are normalised by requiring that the norm of the newly generated and original pseudo-orbitals outside of \(r_{ci}\) are equal. In the core region the new orbital is constructed by using the Troullier-Martins form and criteria described at the beginning of this section. Taking \(\{\hat{\phi}_i\}_{n+1}\), we invert the HF equations as described in section 4 to find the new external potential that results in these orbitals \(\{\hat{\phi}_i\}_{n+1}\) on solution of the HF equations, \(\hat{V}_{i;n+1}\).

The new set of orbitals are then used in Eq. (30) to generate the effective potential \(\hat{V}_{i;n+1}\), and the entire process repeated until self-consistency is achieved - we use \(|\hat{V}_{i;n+1} - \hat{V}_{i;n}| < 10^{-6}\) a.u. for all \(r\). At self-consistency \(\hat{V}_{i;n}\) is the pseudopotential we require. This method finds the HF orbitals that take the Troullier-Martins form in the core region, result from a local ionic potential outside of the core region, and have the same eigenvalues and norm as the original AE atom valence states.

A number of difficulties presented themselves with this method. We found that for atoms with few valence electrons it was not possible to achieve self-consistency. This appeared to be because the analytic form used for the orbitals in the core region was not general enough to give a self-consistent solution. Furthermore, although Engel’s approach conserves the norm of the original AE states, it does not conserve the magnitude or the radial derivative of the orbitals at \(r_{ci}\). Consequently the new pseudopotential does not conserve the logarithmic derivative or its energy derivative, and does not reproduce the scattering properties of the AE atom. For example, for the \(s\)-channel of Ne the new pseudopotentials result in a \(-0.24\%\) change in the magnitude of the orbital at the core radius, a \(+3.9\%\) change in the logarithmic derivative, and a \(+0.40\%\) change in the energy derivative of the logarithmic derivative. These errors may be acceptable, although the error in the logarithmic derivative might be problematic.

By introducing an interface region between the core region and the valence region (where the pseudopotential is ionic) it is in principle possible to modify Engel’s method such that the magnitude of the orbital, the logarithmic derivative and the energy derivative of the logarithmic derivative are all conserved at the core radius. This was attempted using the Troullier-Martins form together with additional criteria. We found that either self-consistency could not be achieved or that the resulting pseudopotentials were far from smooth.

The method we chose to use is to apply a transformation to the original pseudopotential such that deviations from the Hartree-Coulombic ionic core potential are removed beyond a certain radius but desirable properties of the original potentials are preserved. We investigated the transformation

\[
\hat{V}_{i;loc} = \begin{cases} 
\gamma_i(r) + \hat{V}_i(r) & r < R_i \\
 e^{-\alpha(r-R_i)^2} \times \left( \gamma_i(r) + \hat{V}_i(r) - V_h[\rho_{\text{core}}] + \frac{\hat{\phi}_i}{\hat{\phi}_i} \right) + V_h[\rho_{\text{core}}] - \frac{\hat{\phi}_i}{\hat{\phi}_i} & r \geq R_i
\end{cases}
\]

where \(-\frac{Z}{r} + V_h[\rho_{\text{core}}]\) is the ionic potential. The Gaussian decay of the non-Coulombic part of the potential occurs over a distance \(\sim 1/\alpha^{-\frac{1}{2}}\), and the zeroth and first derivatives of \(\hat{V}_{i;loc}\) are continuous at \(R_i\). The precise value of \(\alpha\) has very little influence on the final result - the cutoff radius, \(R_i\), governs the quality of the pseudopotential.
For the simple cutoff function corresponding to $\gamma_i = 0$ and $\alpha^{-\frac{2}{3}} = 0.15$ a.u. we chose $R_i$ as the minimum value for which the $|\epsilon_i - \bar{\epsilon}_i^{\text{loc}}| \leq 10^{-5}$ a.u., where the $\bar{\epsilon}_i^{\text{loc}}$ are the eigenvalues of the new pseudopotential. For Ne this new pseudopotential is local (in the sense of Eq. (5)) outside of a radius of $r_{\text{loc}} = 3.35$ a.u. Although this is large in comparison with the core radii of the orbitals themselves, it may be acceptable, although it would be expensive for DMC. Moreover, this approach enforces a Gaussian decay on a monotonically increasing function, essentially creating a (smoothed) step-like behaviour in the pseudopotential, and it seems likely that this would introduce transferability problems. Note that if we seek to remove this step-like behaviour by decreasing $\alpha$ then $r_{\text{loc}}$ rapidly becomes impractically large.

A more successful approach is to choose $R_i = r_{\text{ci}}$ and $\alpha^{-\frac{2}{3}} = r_{\text{ci}}/\alpha$ (as before, the final result is insensitive to the choice of this parameter) so that the pseudopotential is non-local in a small region and no step-like behaviour occurs. In order to reproduce the eigenvalues of the original pseudopotential, $\gamma_i$ must be non-zero, and we use

$$\gamma_i(r) = \begin{cases} q_i + p_i r^4 \left(1 - \frac{2}{3R_i^2} r^2\right) & r < R_i \\ q_i + p_i R_i^4 \alpha & r \geq R_i \end{cases}, \quad (32)$$

where $\alpha$ is chosen as before and $q_i$ and $p_i$ are orbital dependent parameters. This function is continuous and smooth at $r = R_i$, and the second derivative is zero at $r = 0$ (see the discussion following Eq. (27)). Our goal is to search for values of these parameters such that the localised pseudopotential preserves certain desirable features of the original pseudopotential. We require that the conditions

$$\left[ \frac{\partial}{\partial r} \ln \bar{\phi}_i^{\text{loc}} - \frac{\partial}{\partial r} \ln \bar{\phi}_i \right]_{R_i} = 0 , \quad \bar{\epsilon}_i^{\text{loc}} - \epsilon_i = 0 , \quad (33)$$

are satisfied in order to reproduce the original eigenvalues and aid transferability. Conservation of these two quantities takes precedence over norm conservation and we do not require the norm of $\bar{\phi}_i^{\text{loc}}$ to be equal to the norm of $\bar{\phi}_i$ as we could not find a reliable method to achieve this and give a smooth pseudopotential.

Conservation of the logarithmic derivative of each pseudo-orbital at $R_i$ may be achieved exactly, but a simpler and more convenient approximation is used here. Starting with the equations for the original pseudo-orbital and the pseudo-orbital resulting from the localised pseudopotential we may follow a similar derivation to that used to arrive at the standard norm-conservation condition to obtain

$$\frac{1}{2} \left[ \frac{\partial}{\partial r} \ln \bar{\phi}_i^{\text{loc}} - \frac{\partial}{\partial r} \ln \bar{\phi}_i \right]_{R_i} = \int_0^{R_i} \bar{\phi}_i^{\text{loc}} \Delta V \frac{\partial \bar{\phi}_i}{\partial r} dr - (\bar{\epsilon}_i^{\text{loc}} - \epsilon_i) \int_0^{R_i} \bar{\phi}_i^{\text{loc}} \bar{\phi}_i dr , \quad (34)$$

where the eigenvalues are not yet constrained to be equal and $\Delta V = \hat{V}_i^{\text{eff,loc}} - \hat{V}_i^{\text{eff}}$ is the difference between the effective potentials for calculations carried out with the original and localised pseudopotentials (for the configuration used to construct the pseudopotentials). Our approximation is to take $\Delta V$ to be close to the difference between the external potentials, $\Delta V \approx \hat{V}_i^{\text{loc}} - \hat{V}_i = \gamma_i$, for $r < R_i$.

We start by using simple iteration. For a fixed $q_i$ we take an initial value of $p_i = 0$ and solve for the resulting pseudo-orbitals. We then update $p_i$ by solving $\int_0^{R_i} \bar{\phi}_i^{\text{loc}} \frac{\partial \bar{\phi}_i}{\partial r} dr = 0$ for $p_i$ and continue until self-consistency is achieved. This is repeated for different values of $q_i$ and the condition $\bar{\epsilon}_i^{\text{loc}} - \epsilon_i = 0$ is enforced by straightforward bisection. This process is repeated to obtain self-consistency across all channels, and we obtain eigenvalues which differ by $< 10^{-7}$ a.u., and $\int_0^{R_i} \bar{\phi}_i^{\text{loc}} \frac{\partial \bar{\phi}_i}{\partial r} dr = 0$ to numerical precision. Note that as we have not taken into account the change in the effective potential due to changes in the exchange and Hartree potentials, the LHS of Eq. (34) is not zero, and there will be a small change in the logarithmic derivative.

Localised pseudopotentials for Ne are shown in Fig. 2. The $s$ and $p$ channels were obtained from the neutral ground state, while the $d$ part was obtained from an excited ionic state $(1s^22s^12p^27s^3d^0)$. All excited state configurations used to obtain pseudopotential channels not bound in the ground state configuration are taken from Bachelet et al. Inset in the same figure is the difference between the localised pseudopotential and the original numerically exact pseudopotential. This figure demonstrates that our localisation procedure deforms the pseudopotentials by a small amount, mostly within the core region.

For all atoms considered we found that this process
results in a localised pseudopotential which modifies the form of the associated orbitals over all space, but by a very small amount - about 0.1% of each electron is removed from a region around the core radius and redistributed into two regions, one closer to and one further from the nucleus. The removal of offset and ghost charge (and higher order terms) results from a small change in the asymptotic behaviour of the orbital at large $r$. Normalisation must be preserved, and hence the orbitals are also changed slightly at small $r$. This effect is illustrated in Fig. 3 which shows the difference between the radial charge density of Ne resulting from the localised pseudopotential and the radial charge density resulting from the original pseudopotential.

The transformed Ne pseudopotential is local (in the sense of Eq. (33)) outside of a radius of $r_{loc} = 0.74$ a.u. A similarly localised pseudopotential constructed by applying Eq. (34) with $\gamma_i = 0$ (using the same $\alpha$ and $R_i$ values) results in a large error in the 2s eigenvalue of $-1.2 \times 10^{-2}$ a.u.

As the localised version of the pseudopotential is not equal to the original pseudopotential it is not exactly norm conserving, and does not preserve the form of orbitals outside the core region or at the core radius. To illustrate the magnitude of these effects we return to Ne, specifically the s channel as this is the major source of the extreme non-locality present in the original pseudopotential. The localisation process results in a $-0.27\%$ change in the magnitude of the orbital at the core radius, a $-0.05\%$ change in the logarithmic derivative (due to assuming that the exchange and Hartree terms to do not contribute in Eq. (34)), and a $+0.80\%$ change in the energy derivative of the logarithmic derivative.

The minor relaxation of norm-conservation that accompanies the localisation may influence the transferability of the pseudopotential. However, the familiar conservation of the first order change in the radial logarithmic derivative with respect to energy is only valid when the potential inside the core region is fixed. For both the HF and DFT this is not the case even for an isolated atom, since $\frac{\partial V^{\text{eff}}}{\partial \epsilon_{ij}}$ is a functional of $\{\phi\}$ and each $\phi_i$ is a function of $\{\epsilon\}$, and we have shown (from Eq. (34)) that the norm-conservation relation is replaced by

$$\frac{\partial}{\partial \epsilon_j} \frac{\partial}{\partial r} \ln |\phi_i|_{r_{ci}} = -\delta_{ij} \frac{2}{|\phi_i(r_{ci})|^2} \int_0^{r_{ci}} |\phi_i|^2 dr + \frac{2}{|\phi_i(r_{ci})|^2} \int_0^{r_{ci}} |\phi_i|^2 \frac{\partial V^{\text{eff}}}{\partial \epsilon_j} dr.$$  

(35)

This applies to both the AE and pseudo-atoms. Given that Eq. (35) tells us that first order changes in the radial logarithmic derivative depend on the variation of the effective potential with $\epsilon_i$ as well as the norm, and that norm-conserving pseudopotentials have been successful in the past, it is likely that the very small relaxation of norm-conservation is not significant.

As a further test of the approach described above we have generated localised pseudopotentials for H-Ar. The core radii and localisation radii of these pseudopotentials are given in Table I. Useful pseudopotentials are required to be transferable, that is, to accurately reproduce the behaviour of the AE atom in other environments. In Table II we compare excitation energies of the atoms H-Ar resulting from AE, original pseudopotentials, and localised pseudopotential calculations. Excitation energies are calculated for each atom as the difference between the total

| Atom | $r_{ca}$ | $r_{cp}$ | $r_{cd}$ | $r_{loc}$ |
|------|---------|---------|---------|---------|
| H    | 0.50    | 0.50    | 0.50    | 0.49    |
| He   | 0.60    | 0.60    | 0.60    | 0.59    |
| Li   | 2.19    | 2.37    | 2.37    | 2.71    |
| Be   | 1.88    | 1.96    | 1.96    | 2.20    |
| B    | 1.41    | 1.41    | 1.41    | 1.63    |
| C    | 1.10    | 1.10    | 1.10    | 1.29    |
| N    | 0.94    | 0.88    | 0.84    | 1.09    |
| O    | 0.80    | 0.75    | 0.99    | 1.13    |
| F    | 0.70    | 0.64    | 0.89    | 1.02    |
| Ne   | 0.63    | 0.57    | 0.63    | 0.74    |
| Na   | 2.70    | 2.85    | 2.85    | 3.25    |
| Mg   | 2.38    | 2.38    | 2.38    | 2.71    |
| Al   | 1.94    | 2.28    | 2.28    | 2.64    |
| Si   | 1.67    | 2.01    | 2.06    | 2.36    |
| P    | 1.48    | 1.71    | 1.71    | 1.98    |
| S    | 1.33    | 1.50    | 1.50    | 1.74    |
| Cl   | 1.19    | 1.34    | 1.34    | 1.55    |
| Ar   | 1.09    | 1.20    | 1.31    | 1.54    |

TABLE I: Core radii and localisation radii (a.u.).
energies of the excited and ground states for each type of calculation.

We compare our pseudopotentials with the HF pseudopotentials of Ovcharenko et al.\textsuperscript{13}. This is the most appropriate comparison as both sets of pseudopotentials are soft (in the sense of possessing no singularity at the origin). The pseudopotentials of Ovcharenko et al.\textsuperscript{13} are, however, parameterised, and we note that some of the differences in accuracy will correspond to errors in the parameterisation rather than differences in the methods of generation.

In Table III we compare the ionisation potentials resulting from the AE, the original pseudopotentials, the localised pseudopotentials, and the pseudopotentials published by Ovcharenko et al.\textsuperscript{13} in the same manner as Table I. Ionisation potentials are defined for each atom as the difference between the total energies of the ionised and ground states for each type of calculation.

From Table I and III it is apparent that the differences between the energies resulting from the localised and original pseudopotentials is negligible in comparison to the differences between the energies obtained from the AE and pseudopotential calculations. This suggests that the localisation procedure has been successful, and that the transferability is unlikely to be improved by requiring a more exact reproduction of the original pseudo-orbitals.

Our localised pseudopotentials reproduce the AE excitation energies well, suggesting that our pseudopotentials are transferable, and that the small relaxation of the norm-conservation criterion has no significant effect. Our pseudopotentials also appear to reproduce the excitation energies rather better than those of Ovcharenko et al. In a few cases this appears to be due to the lack of a $d$ channel in the pseudopotentials of Ovcharenko et al. (e.g. P), but for most atoms considered this is not significant (e.g. Al).

In addition to this our pseudopotentials are softer than those of Ovcharenko et al., see Fig. 4 for a comparison of the Si pseudopotentials.

IV. CONCLUSIONS

We have shown that in general a non-local norm-conserving pseudopotential constructed within HF theory will be non-local over all space, resulting in a long range interaction between atoms that is incorrect and not present in the equivalent AE calculation. In particular it is apparent that the total-energy cannot be defined for extended systems. Although our analysis of extreme non-locality was for closed shell atoms within HF theory, it is apparent that the same non-locality persists for open shell atoms and for Dirac-Fock theory, since the nature of the exchange interaction remains the same (although the explicit equations become more complex) - it is represented by a non-local functional of all states which is different for each state.

This extreme non-locality is of particular relevance to the application of pseudopotentials within the DMC method. HF pseudopotentials have been shown to give good results within DMC calculations, but computational efficiency requires the region of non-locality to be as small as possible. In light of this we have implemented a localisation procedure which generates a new pseudopotential that is non-local in a small region surrounding each nucleus. Localisation together with reproduction of the atomic eigenvalues and logarithmic derivatives is achieved at the cost of a small relaxation of the norm-conservation condition, due to an alteration of the asymptotic form of the pseudo-orbital.

We have calculated localised pseudopotentials for H-Ar, and tests for these atoms demonstrate the reliability of our approach. We have also demonstrated their transferability by presenting calculations of excited states for these atoms. This suggests that the approach given here provides accurate, well localised, smooth, HF pseudopotentials suitable for use in ab initio methods such as DMC, GW, and quantum chemistry techniques.

In a future paper we will further generalise our approach to relativistic HF pseudopotentials (relativistic effective potentials), parameterise these pseudopotential in terms of a Gaussian basis set for use in quantum chemistry codes, and present a library of pseudopotentials for $Z = 1 - 56$ and $71 - 80$.

Acknowledgments

Financial support was provided by the Engineering and Physical Sciences Research Council (EPSRC), UK.
DFT is only strictly valid for local external potentials, hence for a non-local pseudopotential there is formally no one-to-one correspondence between the charge density and the (now non-local) effective potential. However, it is common practice to choose a particular correspondence in order to implement KS-DFT with non-local pseudopotentials. In standard KS-DFT we define the effective potential as the sum of the non-local pseudopotential and the same explicit functional of density used in the local external potential case. For the OPM method we define the effective potential as the sum of the non-local pseudopotential and the same implicit functional of density used in the local external potential case.
| Atom | Configuration | $E_{\text{exc}}$ | $E_{\text{exc}}^{\text{AE}}$ | $E_{\text{exc}}^{\text{OAL}}$ |
|------|---------------|-----------------|-----------------|-----------------|
| H    | 1$s^{1}[2S]$ | 0.0000          | 0.0000          | 0.0000          |
|      | 2$p^{1}[2P]$ | 0.3750          | 0.3750          | 0.3750          |
|      | 3$d^{1}[2D]$ | 0.4444          | 0.4444          | 0.4444          |
| He   | 1$s^{2}[2S]$ | 0.0000          | 0.0000          | 0.0000          |
|      | 1$s^{2}2p^{1}[3P]$ | 0.7302    | 0.7308          | 0.7308          |
|      | 1$s^{2}3d^{1}[3D]$ | 0.8061    | 0.8067          | 0.8067          |
| Li   | 2$s^{1}[2S]$ | 0.0000          | 0.0000          | 0.0000          |
|      | 2$p^{1}[2P]$ | 0.0677          | 0.0677          | 0.0677          |
|      | 3$d^{1}[2D]$ | 0.1407          | 0.1408          | 0.1408          |
| Be   | 2$s^{2}[2S]$ | 0.0000          | 0.0000          | 0.0000          |
|      | 2$s^{2}p^{1}[3P]$ | 0.0615    | 0.0595          | 0.0595          |
|      | 2$s^{2}3d^{1}[3D]$ | 0.2389    | 0.2390          | 0.2390          |
| B    | 2$s^{2}2p^{1}[2P]$ | 0.0000    | 0.0000          | 0.0000          |
|      | 2$s^{2}2p^{3}[4P]$ | 0.0784    | 0.0764          | 0.0765          |
|      | 2$s^{2}3d^{1}[3D]$ | 0.2355    | 0.2358          | 0.2358          |
| C    | 2$s^{2}2p^{4}[3P]$ | 0.0000    | 0.0000          | 0.0000          |
|      | 2$s^{2}p^{1}[3S]$ | 0.0894    | 0.0840          | 0.0841          |
|      | 2$s^{2}2p^{3}3d^{1}[3F]$ | 0.3402    | 0.3408          | 0.3407          |
| N    | 2$s^{2}p^{3}[4S]$ | 0.0000    | 0.0000          | 0.0000          |
|      | 2$s^{2}p^{4}[4P]$ | 0.4126    | 0.4097          | 0.4095          |
|      | 2$s^{2}2p^{3}3d^{1}[4F]$ | 0.4565    | 0.4571          | 0.4570          |
| O    | 2$s^{2}2p^{3}[3P]$ | 0.0000    | 0.0000          | 0.0000          |
|      | 2$s^{2}2p^{3}3d^{1}[3D]$ | 0.3809    | 0.3808          | 0.3808          |
|      | 2$s^{2}2p^{5}[3P]$ | 0.6255    | 0.6257          | 0.6256          |
| F    | 2$s^{2}2p^{4}[2P]$ | 0.0000    | 0.0000          | 0.0000          |
|      | 2$s^{2}2p^{3}3d^{1}[4F]$ | 0.5220    | 0.5223          | 0.5222          |
|      | 2$s^{2}2p^{6}[3S]$ | 0.8781    | 0.8832          | 0.8830          |
| Ne   | 2$s^{2}2p^{6}[1S]$ | 0.0000    | 0.0000          | 0.0000          |
|      | 2$s^{2}2p^{6}3d^{1}[3F]$ | 0.6734    | 0.6740          | 0.6738          |
|      | 2$s^{2}2p^{6}3d^{3}[3D]$ | 1.7565    | 1.7613          | 1.7610          |
| Na   | 3$s^{1}[2S]$ | 0.0000          | 0.0000          | 0.0000          |
|      | 3$p^{1}[3P]$ | 0.0725          | 0.0727          | 0.0727          |
|      | 3$d^{1}[2D]$ | 0.1263          | 0.1264          | 0.1264          |
| Mg   | 3$s^{2}[2S]$ | 0.0000          | 0.0000          | 0.0000          |
|      | 3$s^{2}p^{1}[3P]$ | 0.0679    | 0.0672          | 0.0671          |
|      | 3$s^{2}3d^{1}[3D]$ | 0.1843    | 0.1845          | 0.1845          |
| Al   | 3$s^{2}3p^{1}[2P]$ | 0.0000    | 0.0000          | 0.0000          |
|      | 3$s^{2}3p^{3}[4P]$ | 0.0858    | 0.0850          | 0.0851          |
|      | 3$s^{2}3d^{2}[2D]$ | 0.1441    | 0.1443          | 0.1443          |
| Si   | 3$s^{2}3p^{3}[3P]$ | 0.0000    | 0.0000          | 0.0000          |
|      | 3$s^{2}3p^{3}[3S]$ | 0.0913    | 0.0890          | 0.0891          |
|      | 3$s^{2}3p^{3}3d^{1}[3F]$ | 0.2146    | 0.2147          | 0.2147          |
| P    | 3$s^{2}3p^{5}[3S]$ | 0.0000    | 0.0000          | 0.0000          |
|      | 3$s^{2}3p^{3}3d^{1}[4F]$ | 0.3066    | 0.3010          | 0.3009          |
|      | 3$s^{2}3p^{4}[4P]$ | 0.3023    | 0.3030          | 0.3030          |
| S    | 3$s^{2}3p^{5}[3P]$ | 0.0000    | 0.0000          | 0.0000          |
|      | 3$s^{2}3p^{3}3d^{1}[5D]$ | 0.2671    | 0.2658          | 0.2657          |
|      | 3$s^{2}3p^{3}[3P]$ | 0.4260    | 0.4269          | 0.4269          |
| Cl   | 3$s^{2}3p^{5}[2P]$ | 0.0000    | 0.0000          | 0.0000          |
|      | 3$s^{2}3p^{3}3d^{1}[4F]$ | 0.3733    | 0.3735          | 0.3734          |
|      | 3$s^{2}3p^{5}[2S]$ | 0.5653    | 0.5671          | 0.5671          |
| Ar   | 3$s^{2}3p^{6}[1S]$ | 0.0000    | 0.0000          | 0.0000          |
|      | 3$s^{2}3p^{6}3d^{1}[3F]$ | 0.4824    | 0.4838          | 0.4837          |
|      | 3$s^{2}3p^{6}3d^{3}[3D]$ | 1.1597    | 1.1623          | 1.1621          |

Average error: $+1 \times 10^{-4} +7 \times 10^{-5} +9 \times 10^{-4}$

Maximum error: $-5 \times 10^{-3} -5 \times 10^{-3} -1 \times 10^{-2}$

**TABLE II:** Comparison of excitation energies obtained from AE calculations ($E_{\text{exc}}^{\text{AE}}$), from calculations using the extremely non-local and localised pseudopotentials generated within this paper ($E_{\text{exc}}$ and $E_{\text{exc}}^{\text{OAL}}$ respectively), and from calculations using the pseudopotentials generated by Ovcharenko et al. ($E_{\text{exc}}^{\text{OAL}}$) (a.u.).
| Atom | \(E_{\text{ion}}^{AE}\) | \(E_{\text{ion}}^{\text{loc}}\) | \(E_{\text{ion}}^{\text{OAL}}\) |
|------|----------------|-----------------|----------------|
| H    | 0.50000        | 0.50000         | -              |
| He   | 0.86168        | 0.86230         | -              |
| Li   | 0.19631        | 0.19632         | 0.19632        |
| Be   | 0.29563        | 0.29578         | 0.29578        |
| B    | 0.29149        | 0.29199         | 0.29196        | 0.29173 |
| C    | 0.39640        | 0.39702         | 0.39693        | 0.39696 |
| N    | 0.51293        | 0.51357         | 0.51352        | 0.51378 |
| O    | 0.43679        | 0.43672         | 0.43680        | 0.43679 |
| F    | 0.57763        | 0.57790         | 0.57794        | 0.57672 |
| Ne   | 0.72928        | 0.72982         | 0.72982        | 0.73124 |
| Na   | 0.18195        | 0.18210         | 0.18210        | -      |
| Mg   | 0.24283        | 0.24299         | 0.24303        | -      |
| Al   | 0.20204        | 0.20227         | 0.20227        | 0.20531 |
| Si   | 0.28123        | 0.28175         | 0.28172        | 0.28164 |
| P    | 0.36901        | 0.36984         | 0.36977        | 0.36957 |
| S    | 0.33171        | 0.33061         | 0.33060        | 0.33130 |
| Cl   | 0.43348        | 0.43372         | 0.43366        | 0.43339 |
| Ar   | 0.54298        | 0.54444         | 0.54433        | 0.54395 |

Average error \(3 \times 10^{-4}\) \(3 \times 10^{-4}\) \(6 \times 10^{-4}\)

Maximum error \(1 \times 10^{-3}\) \(1 \times 10^{-3}\) \(-3 \times 10^{-3}\)

TABLE III: Comparison of ionisation potentials obtained from AE calculations \(E_{\text{ion}}^{AE}\), from calculations using the extremely non-local and localised pseudopotentials generated within this paper \(E_{\text{ion}}^{\text{loc}}\) and \(E_{\text{ion}}^{\text{OAL}}\) respectively, and from calculations using the pseudopotentials generated by Ovcharenko et al. \(E_{\text{ion}}^{\text{OAL}}\) (a.u.).