Multi-radius Soler-Williams Augmented Plane Waves (SAPWMR), Multi-Radius Soler-Williams Linearized Augmented Plane Waves (SLAPWMR) and extensions

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In this work we present a new basis set for electronic structures (Density Functional Theory (DFT)) calculations. This basis set extends Soler Williams Linearized Augmented Plane Wave (SLAPW) basis sets by allowing variable Muffin Tin (MT) sphere radii for the different angular momentum channels and for different magnitude wave vectors of the augmented plane waves. With the correct choice of MT radius, this allows us to match additional derivatives of the wave function at the MT radius without having to resort to additional higher derivative terms as part of the wave function expansion inside the MT sphere. This should lead to low wave vector basis set and low linearization energy errors, arguably as good as APW basis set size and LAPW basis linearization errors. We call these basis sets SAPWMR and SLAPWMR depending on the number of derivative like wave functions kept inside the MT radii. Similarly local orbital (LO and lo basis wave functions depending on the number of derivative terms in the MT radius) are suggested with a variable radius. that reduces the number of derivative like terms needed to make them continuous or continuously differentiable. As such semi-core states can also be well handled by our methods. Furthermore in the appendix Full Potential Hamiltonian calculations (FLAPW) are extended to FSLAPWMR full potential calculations for Hamiltonian matrix elements. In the Appendix we introduce some further ideas to improve the speed of DFT calculations which are relevant to the basis sets presented here and to other basis sets such as the LAPW basis set.

I. INTRODUCTION

In the modern environment where high throughput calculations are becoming more and more practical and common place there is naturally significant interest in mathematical modeling and computational methods for modern real materials [1–5]. Ab-initio, first principles, simulations with Density Functional Theory (DFT) both in the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA) are becoming more and more commonplace and useful [1-4]. In order to attain predictive (rather then postdictive) power for electronic structure calculations and do systematic materials searches [1, 2] it is imperative to increase the speed of DFT electronic structures calculations. Many programming improvements have been made, in particular introducing parallelizable matrix diagonalization and working on clusters of easily as many as fifty cores or more [1–3] that speed up calculations significantly. In this work we would like to focus not on algorithmic improvements in computational speed but on structural ones (ones associated with the specifics of DFT) which are still compatible with the many programming improvements such as parallelization.

Within these approximations (LDA and GGA), currently, there are two main approaches to studying DFT plane wave basis sets and pseudo potentials and all electron calculations with augmented basis sets, most commonly Linearized Muffin Tin Orbitals (LMTO) [6–11] and Linearized Augmented Plane Wave (LAPW) basis sets [6, 7, 12–15]. Both methods strive to overcome the difficulty of finding an efficient basis set near the atomic nucleus. Near an atomic nucleus the Khon Sham (KS) potential is rapidly varying and requires high wave vectors to accurately describe it, this leads to impractically large sized secular equations for modern computers to handle efficiently. In the pseudopotential approach the high wave vector physical KS potential is replaced with a slowly varying one that gives the same logarithmic derivative of the wave function at the atomic sphere radius (roughly the radius of the atom) - that is the same boundary condition or scattering phase shift, whereby the problem is mapped onto a more easily solvable one. Because of the form of modern numerical Schridoinger equation diagonalization codes, it is more efficient to use pseudopotential methods rather then work directly with boundary conditions. In the Augmented wave function (all electron) approach the potential is assumed to be slowly varying in the interstitial (between the nuclei) so plane waves (or Bessel functions multiplied by spherical harmonics) are used there while near the nucleus (inside the MT sphere) the wavefunction is augmented. In the Muffin Tin (MT) sphere pieces (near the nuclei), the exact solution to the radially averaged KS potential times a spherical harmonic is used as the basis wavefunctions. The two pieces of the wave function are then glued together with some boundary conditions, usually by matching the wavefunction and some of its derivatives on the boundary. One of the main difficulties to overcome in these all electron methods is to find what energy to use for the solution of the radially averaged KS potential. In the Augmented Plane Wave (APW) methods of Slater [16] and Koringa-Khon-Rostoker (KKR) [17, 18] the energy is found self consistently, which requires the solution of the radially averaged KS potential at all energies which increases computational costs by easily an order of magnitude [1–3, 6, 8, 19], making them often impractical. In many cases it pays to linearize the problem, say with LAPW basis sets, and focus on the solution at some linearization energy (often in the middle of the valence

band) and study the wave function at that energy as well as its derivative with respect to energy as a basis for the whole energy range. This leads to manageable linearization errors and a significant speedup of calculations. Furthermore it is possible to write down the Full Potential Hamiltonian for this basis set, e.g. FLAPW and compute overlap and Hamiltonian matrix elements for the KS secular self consistency equations [10, 11, 20–24]. In some cases the valence band is not the only partially occupied band near the Fermi energy, and as such of interest, in some cases semi-core states which are neither completely localized nor completely extended are essential. In this case it is advantageous to add localized orbitals (LO and lo basis sets depending on the exact number of wave functions kept in the MT sphere) to represent (have good overlap with) some of these semi-core states [1, 19, 26].

In this work we will focus on all electron LAPW like basis sets. These are often employed as basis sets for transition metal 3d and 4d compounds and a variety of other crystalline solids [1]. Here we extend the Soler-Williams version of the LAPW basis set [14, 15] to include the possibility that the MT radius depends on the angular momentum channel and the magnitude of the plane wave wave vector considered in the interstitial. This allows us to match an additional derivative of the wave function at the MT sphere radius without having to resort to higher derivative wave functions $\dot{u}_l = \frac{\partial}{\partial E} u_l$ or $\ddot{u}_l = \frac{\partial^2}{\partial E^2} u_l$ etc (here u_l is the solution to the spherically symmetrized Khon Sham (KS) Hamiltonian). This feature (the ability to match many derivatives so as to lower linearization error) and the ability not to use higher derivative terms (the basis sets become very stiff in the presence of higher derivative terms as the wave function becomes more and more Bessel function like in the MT sphere) leads to a pleasant combination of features of low basis set sizes and low linearization errors. We will also show how to extend LO and lo to these situations where semicore states are important. In an Appendix we show how to extend FLAPW to FSLAPWMR for these basis sets. In another Appendix we present further ideas on how to improve computational speed for solid state DFT like calculations for these basis sets and many other related ones in particular the LAPW basis set by adjusting basis set size during iterative self consistency loops.

II. SAPWMR

A. Main idea

Suppose you have a material with multiple atoms per unit cell. The more correlated the atomic orbital of an atom the more important it is to make the MT sphere of the atom it is attached to as big as possible. However it is important that these MT spheres do not overlap limiting the size of a possible MT sphere. Here we show how to overcome this difficulty and optimize basis set size. This is done both by allowing overlaps for correlated atoms and correlated angular momentum channels and by lowering the number of derivative terms needed inside the MT sphere. The key formula we will need is [25]:

$$\frac{1}{\sqrt{V}}\exp\left(i\left(\mathbf{k}+\mathbf{K}\right)\cdot\mathbf{r}\right) = \exp\left(i\left(\mathbf{k}+\mathbf{K}\right)\cdot\mathbf{r}_{\mu}\right)\frac{1}{\sqrt{V}}4\pi\sum_{l,m}Y_{lm}^{*}\left(\widehat{\mathbf{k}+\mathbf{K}}\right)Y_{lm}\left(\widehat{\mathbf{r}-\mathbf{r}_{\mu}}\right)i^{l}J_{l}\left(|\mathbf{k}+\mathbf{K}||\mathbf{r}-\mathbf{r}_{\mu}|\right)$$
(1)

Here \mathbf{r}_{μ} is the center of the μ 'th MT sphere and \mathbf{k} is a wave vector in the first Brilluoin zone while \mathbf{K} is a wave vector in the reciprocal lattice and V is the volume of the unit cell in the direct lattice. This is a decomposition of plane waves into Bessel functions times spherical harmonics and shows that plane waves are just a sum of Bessel functions multiplied by spherical harmonics with appropriate coefficients inside the MT spheres. Consider the following wave functions [14, 15]:

$$\begin{aligned} \breve{\chi}_{\mathbf{K}}^{\mathbf{k}}\left(\mathbf{r};\mathbf{r}_{\mu,1},...,\mathbf{r}_{\mu,M}\right) &= \frac{1}{\sqrt{V}}\exp\left(i\left(\mathbf{k}+\mathbf{K}\right)\cdot\mathbf{r}\right) + \\ &+ \sum_{\mu=1}^{M}\sum_{l,m}Y_{lm}\left(\widehat{\mathbf{r}-\mathbf{r}_{\mu}}\right)\left[A_{lm}^{\mu}u_{l\mu}^{E}\left(\mathbf{r}-\mathbf{r}_{\mu}\right) - \frac{1}{\sqrt{V}}4\pi i^{l}J_{l}\left(|\mathbf{k}+\mathbf{K}||\mathbf{r}-\mathbf{r}_{\mu}|\right)Y_{lm}^{*}\left(\widehat{\mathbf{k}+\mathbf{K}}\right)\exp\left(i\left(\mathbf{k}+\mathbf{K}\right)\cdot\mathbf{r}_{\mu}\right)\right] \times \\ &\times\Theta\left(|\mathbf{r}-\mathbf{r}_{\mu}|-S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)\right) \end{aligned}$$
(2)

Here we have subtracted out the part of the plane wave inside the MT sphere in the second term of the second line of Eq. (2) that is decomposed it as in Eq. (1) into Bessel functions times spherical harmonics and subtracted them piece by piece from the solutions of the exact radially symmetric KS equations. Indeed here:

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + \bar{V}_{KS}(r)\right] r u^E_{l\mu}(r) = E r u^E_{l\mu}(r) \quad (3)$$

and $\bar{V}_{KS}(r)$ is the spherically average Khon Sham (KS) potential. Here M is the total number of atoms per unit

cell and Θ is the heavy-side function. Now the MT sphere radius can depend on l and the wave function is well defined even when the MT spheres overlap. We also choose the coefficients A_{lm} such that the wave function is continuous as S_{μ}^{l} , whereby we must have that:

$$A_{lm}^{\mu} = \frac{\frac{1}{\sqrt{V}} 4\pi i^{l} J_{l} \left(|\mathbf{k} + \mathbf{K}| |\mathbf{r} - \mathbf{r}_{\mu}| \right) Y_{lm}^{*} \left(\widehat{\mathbf{k} + \mathbf{K}} \right)}{u_{l\mu}^{E} \left(S_{\mu}^{l} \left(|\mathbf{k} + \mathbf{K}| \right) \right)} \times \exp\left(i \left(\mathbf{k} + \mathbf{K} \right) \cdot \mathbf{r}_{\mu} \right)$$
(4)

Now we choose S^l_{μ} such that the wave function is also

continuously differentiable at S^l_{μ} , so that the linearization error goes as $\sim (\epsilon - E_l)^4$ [1, 2] despite having APW basis set that is no terms proportional to $\dot{u}^E_{l\mu}$.

B. Practical methods to find $S^l_{\mu}(|\mathbf{k} + \mathbf{K}|)$: root finding using Newton's method

We want to have that the discontinuity of the wave function's logarithmic derivative which scales with:

$$F\left(S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)\right) \equiv J_{l}\left(|\mathbf{k}+\mathbf{K}|S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)\right)\frac{d}{dr}u_{l\mu}^{E}\left(S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)\right) - u_{l\mu}^{E}\left(S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)\right)\frac{d}{dr}J_{l}\left(|\mathbf{k}+\mathbf{K}|S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)\right) = 0$$

$$\tag{5}$$

vanish. Here we have chosen logarithmic derivatives rather then usual ones as there is a free coefficient A_{lm}^{μ} that is scaled out by the logarithmic derivative and need not be considered for this calculation. Now the derivative of this expression $F\left(S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)\right)$ with respect to $S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)$ is given by:

$$\frac{\partial F\left(S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)\right)}{\partial S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)} = J_{l}\left(|\mathbf{k}+\mathbf{K}|S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)\right)\frac{d^{2}}{dr^{2}}u_{l\mu}^{E}\left(S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)\right) - \frac{d^{2}}{dr^{2}}J_{l}\left(|\mathbf{k}+\mathbf{K}|S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)\right)u_{l\mu}^{E}\left(S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)\right)$$

$$(6)$$

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Now we apply Newtons method iteratively by writing:

$$S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)_{j+1} = S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)_{j} - \frac{F\left(S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)_{j}\right)}{\frac{\partial F\left(S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)_{j}\right)}{\partial S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)_{j}}}$$
(7)

to converge to the point where the discontinuity is zero by Newton's root finding algorithm (here j is the j'th solution and j + 1 is the j + 1'st solution and we iterate till sufficient convergence). Now to speed things along we can subdivide the range of $|\mathbf{k} + \mathbf{K}|$ into a large number of points in order and use the solution of the k'th point as the starting value of the k+1'st iteration of Newton's method, thereby already starting close to an exact solution.

C. Argument why the convergent basis set will be small

We notice that the LAPW method is based on the idea that we may well expand many wave functions in the *l*'th angular momentum channel inside the μ 'th MT sphere in the basis of $u_{l\mu}^{E}(r)$ and $\dot{u}_{l\mu}^{E}(r)$ and write:

$$\psi_{l\mu}(r) = \left\langle u_{l\mu}^{E} \mid \psi_{l\mu} \right\rangle u_{l\mu}^{E}(r) + \left\langle \dot{u}_{l\mu}^{E} \mid \psi_{l\mu} \right\rangle \dot{u}_{l\mu}^{E}(r) + \dots (8)$$

Now for practical coding purposes we do not wish to compute overlaps but instead we note that any solution of the exact KS Hamiltonian must be smooth everywhere including at the MT sphere radius and replace the overlap condition with the condition the basis wave functions are continuous and continuously differentiable on the MT boundary. In the multi-radius case we still maintain the same expansion as in Eq. (8) except we choose the radius for our expansion such that $\langle \dot{u}_{l\mu}^E | \psi_{l\mu} \rangle \cong 0$ that is the wave function is continuous and continuously differentiable at the MT radius $S_{\mu}^l (|\mathbf{k} + \mathbf{K}|)$ but has only the $u_{l\mu}^E(r)$ component are needed to maintain the continuity of the wave function and its derivative. This leads to a combination of the LAPW features of small linearization error and the APW feature of small basis sets.

D. lo basis extensions

We would like to consider the case where there are semi-core states (that is states that are near but below the Fermi energy but not in the valence band). One option for these states is multi-window basis sets [1]where a second or more linearization energy is chosen and the basis is doubled or more. A more efficient method is the localized orbitals lo basis set [1, 19, 26] where specific angular momentum channels associated with these semicore states are chosen and augmented with additional degrees of freedom. Here we can also do a variation on lo states (say lowr states) where we choose

$$\chi_{\tilde{lo}}^{lm,\mu}\left(\mathbf{r}\right) = \begin{cases} 0 & |\mathbf{r} - \mathbf{r}_{\mu}| \ge S_{\mu}^{\tilde{lo},i} \\ Y_{lm}\left(\mathbf{r} - \mathbf{r}_{\mu}\right) A_{lm}^{\mu} u_{l}^{E_{l}^{1}}\left(\mathbf{r},\mathbf{r}_{\mu}\right) & |\mathbf{r} - \mathbf{r}_{\mu}| < S_{\mu}^{\tilde{lo},i} \end{cases}$$
(9)

Where we choose the radius $S_{\mu}^{\tilde{l}o,l}$ so that $u_l^{E_l^1}\left(S_{\mu}^{\tilde{l}o,l}\right) = 0$ so that we have very good wave functions near the core and still some matching near the MT surface. This leads to improved conversion as the wave function exactly solves the spherically averaged KS Hamiltonian inside the MT sphere and does not depend on any derivative terms, which increase basis set size.

III. SLAPWMR

A. Setup

The ideas associated with SLAPWMR are similar to those of SAPWMR except we keep more derivative terms inside the MT sphere thereby lowering linearization errors further. Now let us introduce the following wave functions:

$$\begin{split} \check{\chi}_{\mathbf{K}}^{\mathbf{k}}\left(\mathbf{r};\mathbf{r}_{\mu,1},...,\mathbf{r}_{\mu,M}\right) &= \frac{1}{\sqrt{V}}\exp\left(i\left(\mathbf{k}+\mathbf{K}\right)\cdot\mathbf{r}\right) + \\ &+ \sum_{\mu=1}^{M}\sum_{l,m}Y_{lm}\left(\widehat{\mathbf{r}-\mathbf{r}_{\mu}}\right)\left[A_{lm}^{\mu}u_{l}^{E}\left(\mathbf{r}-\mathbf{r}_{\mu}\right) + B_{lm}^{\mu}\dot{u^{E}}_{l}\left(\mathbf{r}-\mathbf{r}_{\mu}\right) - \frac{1}{\sqrt{V}}4\pi i^{l}J_{l}\left(|\mathbf{k}+\mathbf{K}||\mathbf{r}-\mathbf{r}_{\mu}|\right)Y_{lm}^{*}\left(\widehat{\mathbf{k}+\mathbf{K}}\right)\exp\left(i\left(\mathbf{k}+\mathbf{K}\right)\cdot\mathbf{r}_{\mu}\right)\right] \times \\ &\times\Theta\left(|\mathbf{r}-\mathbf{r}_{\mu}| - S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)\right) \end{split}$$
(10)

Here M is the total number of atoms per unit cell and Θ is the heavy-side function. Now the MT sphere radius can depend on l and the wave function is well defined even when the MT spheres overlap). We also demand that:

$$\begin{pmatrix}
A_{lm}^{\mu} \\
B_{lm}^{\mu}
\end{pmatrix} = \frac{4\pi i^{l}}{\left[S_{\mu}^{l}\right]^{2}\sqrt{V}}Y_{lm}^{*}\left(\widehat{\mathbf{k}+\mathbf{K}}\right)\left(\frac{\dot{u}_{l}\left(S_{\mu}^{l}\right)\frac{d}{dr}J_{l}\left(|\mathbf{k}+\mathbf{K}|S_{\mu}^{l}\right) - \frac{d}{\partial r}\dot{u}_{l}\left(S_{\mu}\right)J_{l}\left(|\mathbf{k}+\mathbf{K}|S_{\mu}^{l}\right)}{\frac{d}{dr}J_{l}\left(|\mathbf{k}+\mathbf{K}|S_{\mu}^{l}\right) - u_{l}\left(S_{\mu}\right)\frac{d}{dr}J_{l}\left(|\mathbf{k}+\mathbf{K}|S_{\mu}^{l}\right)}\right)\exp\left(i\left(\mathbf{k}+\mathbf{K}\right)\cdot\mathbf{r}_{\mu}\right)$$
(11)

so that the wave functions and its first derivatives are everywhere continuous. We now also demand that the second derivative is continuous leading to a linearization error of $\sim (\epsilon - E_l)^6$ [1, 2].

B. Practical methods to find $S^l_{\mu}(|\mathbf{k} + \mathbf{K}|)$: root finding using Newton's method

We will use Newton's method to compute the MT radius $S^l_{\mu}(|\mathbf{k} + \mathbf{K}|)$. We want:

$$F\left(S_{\mu}^{l}\right) \equiv \left(\frac{d^{2}}{dr^{2}}u_{l}\left(S_{\mu}^{l}\right) \quad \frac{d^{2}}{dr^{2}}\dot{u}_{l}\left(S_{\mu}^{l}\right)\right) \left(\frac{\dot{u}_{l}\left(S_{\mu}^{l}\right)\frac{d}{dr}J_{l}\left(\left|\mathbf{k}+\mathbf{K}\right|S_{\mu}^{l}\right) - \frac{d}{dr}\dot{u}_{l}\left(S_{\mu}\right)J_{l}\left(\left|\mathbf{k}+\mathbf{K}\right|S_{\mu}^{l}\right)}{\frac{d}{dr}u_{l}\left(S_{\mu}^{l}\right)J_{l}\left(\left|\mathbf{k}+\mathbf{K}\right|S_{\mu}^{l}\right) - u_{l}\left(S_{\mu}\right)\frac{d}{dr}J_{l}\left(\left|\mathbf{k}+\mathbf{K}\right|S_{\mu}^{l}\right)\right) - \left[S_{\mu}^{l}\right]^{2}\frac{d^{2}}{dr^{2}}J_{l}\left(\left|\mathbf{k}+\mathbf{K}\right|S_{\mu}^{l}\right) = 0$$

$$\tag{12}$$

Now the derivative of

$$\frac{\partial F\left(S_{\mu}^{l}\right)}{\partial S_{\mu}^{l}} = \left(\frac{d^{3}}{dr^{3}}u_{l}\left(S_{\mu}^{l}\right) \frac{d^{3}}{dr^{3}}\dot{u}_{l}\left(S_{\mu}^{l}\right) \right) \left(\frac{\dot{u}_{l}\left(S_{\mu}^{l}\right)\frac{\partial}{\partial r}J_{l}\left(\left|\mathbf{k}+\mathbf{K}\right|S_{\mu}^{l}\right) - \frac{\partial}{\partial r}\dot{u}_{l}\left(S_{\mu}\right)J_{l}\left(\left|\mathbf{k}+\mathbf{K}\right|S_{\mu}^{l}\right)}{\partial_{r}u_{l}\left(S_{\mu}^{l}\right)J_{l}\left(\left|\mathbf{k}+\mathbf{K}\right|S_{\mu}^{l}\right) - u_{l}\left(S_{\mu}\right)\frac{\partial}{\partial r}J_{l}\left(\left|\mathbf{k}+\mathbf{K}\right|S_{\mu}^{l}\right)}{\partial_{r}^{2}u_{l}\left(S_{\mu}^{l}\right)\frac{d^{2}}{\partial r^{2}}J_{l}\left(\left|\mathbf{k}+\mathbf{K}\right|S_{\mu}^{l}\right) - u_{l}\left(S_{\mu}\right)\frac{\partial}{\partial r}J_{l}\left(\left|\mathbf{k}+\mathbf{K}\right|S_{\mu}^{l}\right)}{dr^{2}}\right) \right) \\ + \left(\frac{d^{2}}{dr^{2}}u_{l}\left(S_{\mu}^{l}\right) \frac{d^{2}}{dr^{2}}\dot{u}_{l}\left(S_{\mu}^{l}\right) \right) \left(\frac{\dot{u}_{l}\left(S_{\mu}^{l}\right)\frac{d^{2}}{\partial r^{2}}J_{l}\left(\left|\mathbf{k}+\mathbf{K}\right|S_{\mu}^{l}\right) - \frac{d^{2}}{dr^{2}}\dot{u}_{l}\left(S_{\mu}\right)J_{l}\left(\left|\mathbf{k}+\mathbf{K}\right|S_{\mu}^{l}\right)}{u_{l}\left(S_{\mu}^{l}\right)J_{l}\left(\left|\mathbf{k}+\mathbf{K}\right|S_{\mu}^{l}\right) - u_{l}\left(S_{\mu}\right)\frac{d^{2}}{dr^{2}}J_{l}\left(\left|\mathbf{k}+\mathbf{K}\right|S_{\mu}^{l}\right)}{dr^{2}}\right) - 2S_{\mu}^{l}\frac{d^{2}}{dr^{2}}J_{l}\left(\left|\mathbf{k}+\mathbf{K}\right|S_{\mu}^{l}\right) - \left[S_{\mu}^{l}\right]^{2}\frac{d^{3}}{dr^{3}}J_{l}\left(\left|\mathbf{k}+\mathbf{K}\right|S_{\mu}^{l}\right)\right)$$
(13)

Now we apply Newtons method iteratively by writing:

$$S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)_{j+1} = S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)_{j} - \frac{F\left(S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)_{j}\right)}{\frac{\partial F\left(S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)_{j}\right)}{\partial S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)_{j}}}$$
(14)

Here j is the j'th solution and j + 1 is the j + 1'st solution and we iterate till sufficient convergence. Now to speed things along we can subdivide the range of $|\mathbf{k} + \mathbf{K}|$ into a large number of points and use the solution of the k'th point as the starting value of the k+1'st iteration of Newton's method much like in SAPWMR.

C. Key advantage

By an argument very similar to section II C we see that these wave functions combine the advantages of Higher Derivative Local Orbital (HDLO) linearization energies

D. LO basis extensions

The LO basis wave functions we may be simplified:

$$\chi_{LO}^{lm,\mu}(\mathbf{r}) = \begin{cases} 0 & |\mathbf{r} - \mathbf{r}_{\mu}| \ge S_{\mu}^{LO,l} \\ Y_{lm}(\mathbf{r} - \mathbf{r}_{\mu}) \left[A_{lm}^{\mu} u_{l}^{E_{l}^{1}}(\mathbf{r}, \mathbf{r}_{\mu}) + B_{lm}^{\mu} \dot{u}_{l}^{E_{l}^{1}}(\mathbf{r}, \mathbf{r}_{\mu}) \right] & |\mathbf{r} - \mathbf{r}_{\mu}| < S_{\mu}^{LO,l} \end{cases}$$
(15)

Where both the wave function and its first derivative are continuous everywhere (we note that $S_{\mu}^{LO,l}$ is an additional parameter needed for this to be possible).

IV. CONCLUSIONS

In this work we have modified the APW and LAPW basis wave functions to allow for multiple radii for the MT spheres at the same location (with the radius depending on the angular momentum channel and the magnitude of the wave vector). This additional degree of freedom allowed us to match more derivatives at the MT boundary without having to add additional higher derivative wave function terms. We believe that this will allow for LAPW basis accuracy with APW basis set size and HDLO basis accuracy with LAPW basis set size and so forth (See appendix A). LO and lo extensions have also been proposed allowing for the study of semi-core states. In the appendix we have extended FLAPW to FSAPWMR and FSLAPWMR allowing for full potential calculations of the Hamiltonian and overlap matrices. In the Appendix we also give some additional methods to increase computational speed for DFT type calculations by adjusting basis set size during iteration loops. In the future it would be of interest to do numerical tests of the efficiency of these basis sets.

Appendix A: HDLOMR: wave functions

It is possible to play this trick one more time that is pick wave functions of the form 12 [12], 13 [13]:

$$\begin{aligned} &\check{\chi}_{\mathbf{K}}^{\mathbf{k}}\left(\mathbf{r};\mathbf{r}_{\mu,1},...,\mathbf{r}_{\mu,M}\right) \\ &= \frac{1}{\sqrt{V}}\exp\left(i\left(\mathbf{k}+\mathbf{K}\right)\cdot\mathbf{r}\right) + \\ &+ \sum_{\mu=1}^{M}\sum_{l,m}Y_{lm}\left(\widehat{\mathbf{r}-\mathbf{r}_{\mu}}\right)\left[A_{lm}^{\mu}u_{l}\left(\mathbf{r}-\mathbf{r}_{\mu}\right) + B_{lm}^{\mu}\dot{u}_{l}\left(\mathbf{r}-\mathbf{r}_{\mu}\right) + C_{lm}^{\mu}\ddot{u}_{l}\left(\mathbf{r}-\mathbf{r}_{\mu}\right) - \\ &- \frac{1}{\sqrt{V}}4\pi i^{l}J_{l}\left(|\mathbf{k}+\mathbf{K}||\mathbf{r}-\mathbf{r}_{\mu}|\right)Y_{lm}^{*}\left(\widehat{\mathbf{k}+\mathbf{K}}\right)\exp\left(i\left(\mathbf{k}+\mathbf{K}\right)\cdot\mathbf{r}_{\mu}\right)\right] \times\Theta\left(|\mathbf{r}-\mathbf{r}_{\mu}| - S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)\right) \end{aligned}$$
(A1)

Then pick $S^l_{\mu}(|\mathbf{k} + \mathbf{K}|)$ such that the wave function, its first, second and third derivative are continuous in the entire volume. This greatly reduces the linearization error in the energies to $O(\epsilon - E_l)^8$ but greatly slows down the calculation to speeds comparable to HDLO calculations. It is also possible to invent new forms of LO based on

this idea.

1. LO basis extensions

The LO basis wave functions we may be simplified:

$$\chi_{LO}^{lm,\mu}\left(\mathbf{r}\right) = \begin{cases} 0 & |\mathbf{r} - \mathbf{r}_{\mu}| \ge S_{\mu}^{LO,l} \\ Y_{lm}\left(\mathbf{r} - \mathbf{r}_{\mu}\right) \left[A_{lm}^{\mu} u_{l}^{E_{l}^{1}}\left(\mathbf{r}, \mathbf{r}_{\mu}\right) + B_{lm}^{\mu} \dot{u}_{l}^{E_{l}^{1}}\left(\mathbf{r}, \mathbf{r}_{\mu}\right) + C_{lm}^{\mu} \dot{u}_{l}^{E_{l}^{2}}\left(\mathbf{r}, \mathbf{r}_{\mu}\right) \right] & |\mathbf{r} - \mathbf{r}_{\mu}| < S_{\mu}^{LO,l} \end{cases}$$
(A2)

Where both the wave function, its first and second

derivative are continuous everywhere (we note that $S^{LO,l}_{\mu}$

is an additional parameter needed for this to be possible).

Appendix B: FSAPWMR

For simplicity we will assume that the various multiradius MT spheres do not overlap.

1. Definition of Hamiltonian

First we will assume continuity of wave-functions and derivatives:

$$\Psi_{I}(\mathbf{r}) = \Psi_{II}(\mathbf{r})$$
$$\nabla\Psi_{I}(\mathbf{r}) \cdot d\mathbf{S}_{\mu} = \nabla\Psi_{II}(\mathbf{r}) \cdot d\mathbf{S}_{\mu}$$
(B1)

Here $d\mathbf{S}_{\mu}$ is the outward pointing normal of the sphere and *I* means inside the MT sphere while *II* means outside it (interstitial). In this case we have that the Hamiltonian matrix elements are given by:

Where at stationarity $J = V_{KS}$ the Khon-Sham potential. We will use the two symbols interchangeably as the stress calculations need only be done once the system is converged, that is at stationarity.

2. Wave functions

Recall that the SAPW functions now with noncollinear spin order are given by Eq. (2). Here the wavefunctions satisfies the usual radial Schrödinger equation:

$$\left[-\frac{\partial^2}{\partial\rho^2} + \frac{l\left(l+1\right)}{\rho^2} + \bar{J}_{\alpha}\left(\rho\right) - \mu\right]\rho u_l^{\alpha}\left(\rho\right) = E\rho u_l^{\alpha}\left(\rho\right)$$
(B3)

for some appropriately chosen energy E and $\rho = |\mathbf{r} - \mathbf{r}_{\mu}|$ and we have suppressed for clarity the positions index \mathbf{r}_{μ} . Where

$$\bar{J}_{\alpha}\left(\rho\right) = \frac{1}{4\pi} \int d\hat{\Omega} \left[J \left(\mathbf{r}_{\mu} + \rho \hat{\Omega}\right) + \vec{J} \left(\mathbf{r}_{\mu} + \rho \hat{\Omega}\right) \cdot \vec{\sigma}_{\alpha\alpha} \right]$$
(B4)

3. Interstitial

We now pick $N \gg \mathcal{N}_{\mu}$, where \mathcal{N}_{μ} is the total number of angular momentum channels which are not Bessel functions in μ 'th MT sphere. Now let us pick \mathbf{K}_1 and \mathbf{K}_2 , Now let us order the $2\mathcal{N}_{\mu}$ radii by at each μ .

$$S^{l_1}_{\mu}\left(|\mathbf{k} + \mathbf{K}_i|\right) \le S^{l_2}_{\mu}\left(|\mathbf{k} + \mathbf{K}_j|\right) \le \dots \le S^{l_{2N_{\mu}}}_{\mu}\left(|\mathbf{k} + \mathbf{K}_m|\right)$$
(B5)

Now let us call the interstitial region by

$$\bigcap_{\mu} |\mathbf{r} - \mathbf{r}_{\mu}| \ge S_{\mu}^{l_{2\mathcal{N}\mu}} \left(|\mathbf{k} + \mathbf{K}_{m}| \right) \tag{B6}$$

Now for $l \leq N$ we have that:

$$u_{l}^{\alpha}\left(\mathbf{r}-\mathbf{r}_{\mu}\right) = \begin{cases} u_{l}^{\alpha}\left(\mathbf{r}-\mathbf{r}_{\mu}\right) & |\mathbf{r}-\mathbf{r}_{\mu}| < S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right) \\ \frac{J_{l}\left(|\mathbf{k}+\mathbf{K}||\mathbf{r}-\mathbf{r}_{\mu}|\right)}{\frac{J_{l}\left(|\mathbf{k}+\mathbf{K}|S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)\right)}{u_{l}^{\alpha}\left(S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)\right)}} & |\mathbf{r}-\mathbf{r}_{\mu}| \ge S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right) \end{cases}$$
(B7)

Now for l > N we define

$$u_l^{\alpha} \left(\mathbf{r} - \mathbf{r}_{\mu} \right) = J_l \left(|\mathbf{k} + \mathbf{K}| |\mathbf{r} - \mathbf{r}_{\mu}| \right)$$
$$A_{lm}^{\mu\alpha} \left(\mathbf{k} + \mathbf{K} \right) = \frac{1}{\sqrt{V}} 4\pi i^l Y_{lm}^* \left(\widehat{\mathbf{k} + \mathbf{K}} \right) \tag{B8}$$

We write:

$$J(\mathbf{r}) = \begin{cases} \sum_{\mathbf{K}} J_I^{\mathbf{K}} \exp\left(i\mathbf{K} \cdot \mathbf{r}\right) & Interstitial\\ \sum_{l,m} J_{l,m}\left(|\mathbf{r}|\right) Y_{l,m}\left(\hat{\mathbf{r}}\right) & MT \end{cases}$$
(B9)

$$\vec{J}(\mathbf{r}) = \begin{cases} \sum_{\mathbf{K}} \vec{J}_{I}^{\mathbf{K}} \exp\left(i\mathbf{K}\cdot\mathbf{r}\right) & Interstitial\\ \sum_{l,m} \vec{J}_{l,m}\left(|\mathbf{r}|\right) Y_{l,m}\left(\hat{\mathbf{r}}\right) & MT \end{cases} (B10)$$

an similarly for the vectorized quantities. Then we have that:

$$\begin{bmatrix} \bar{O}_{\mathbf{k}} \end{bmatrix}_{\mathbf{K},\mathbf{K}'}^{\alpha\beta} = \begin{bmatrix} \bar{O}_{\mathbf{k}} \end{bmatrix}_{\mathbf{K},\mathbf{K}'}^{I\alpha\beta} + \begin{bmatrix} \bar{O}_{\mathbf{k}} \end{bmatrix}_{\mathbf{K},\mathbf{K}'}^{MT\alpha\beta} \\ \begin{bmatrix} -\bar{\Delta}^{\mathbf{k}} + \bar{J}^{\mathbf{k}} + \bar{J}^{\mathbf{k}} \cdot \vec{\sigma} \end{bmatrix}_{\mathbf{K},\mathbf{K}'}^{\alpha\beta} = \begin{bmatrix} -\bar{\Delta}^{\mathbf{k}} + \bar{J}^{\mathbf{k}} + \bar{J}^{\mathbf{k}} \cdot \vec{\sigma} \end{bmatrix}_{\mathbf{K},\mathbf{K}'}^{I\alpha\beta} + \begin{bmatrix} -\bar{\Delta}^{\mathbf{k}} + \bar{J}^{\mathbf{k}} + \bar{J}^{\mathbf{k}} \cdot \vec{\sigma} \end{bmatrix}_{\mathbf{K},\mathbf{K}'}^{MT\alpha\beta}$$
(B11)

Now in the interstitial we have that

$$\begin{bmatrix} \bar{O}_{\mathbf{k}} \end{bmatrix}_{\mathbf{K},\mathbf{K}'}^{I\alpha\beta} = \Theta_{\mathbf{K}-\mathbf{K}'}\delta_{\alpha\beta}$$
$$\begin{bmatrix} -\bar{\Delta}^{\mathbf{k}} + \bar{J}^{\mathbf{k}} + \bar{\bar{J}}^{\mathbf{k}} \cdot \vec{\sigma} \end{bmatrix}_{\mathbf{K},\mathbf{K}'}^{I\alpha\beta} = \begin{bmatrix} \left(J_{KS} + \vec{J}_{KS} \cdot \vec{\sigma} \right)^{\alpha\beta} \Theta \end{bmatrix}_{\mathbf{K}-\mathbf{K}'} + \frac{1}{2m} \left[\mathbf{k} + \mathbf{K}' \right]^2 \Theta_{\mathbf{K}-\mathbf{K}'}\delta_{\alpha\beta}$$
(B12)

Where

$$[F\Theta]_{\mathbf{K}} = \sum_{\mathbf{K}'} [F]_{\mathbf{K}'} \Theta_{\mathbf{K}-\mathbf{K}'}$$
(B13)

and

$$\Theta_{\mathbf{K}} = \left(\delta_{\mathbf{K},0} - \sum_{\mu} \exp\left(-i\mathbf{K} \cdot \mathbf{r}_{\mu}\right) \frac{\left(4\pi S_{\mu}^{l_{2\mathcal{N}_{\mu}}}\left(|\mathbf{k} + \mathbf{K}_{m}|\right)\right)^{3}}{V} \cdot \frac{j_{1}\left(|\mathbf{K}| S_{\mu}^{l_{2\mathcal{N}_{\mu}}}\left(|\mathbf{k} + \mathbf{K}_{m}|\right)\right)}{|\mathbf{K}| S_{\mu}^{l_{2\mathcal{N}_{\mu}}}\left(|\mathbf{k} + \mathbf{K}_{m}|\right)}\right)$$
(B14)

Γ

4. MT pieces

We write:

$$\begin{bmatrix} -\bar{\Delta}^{\mathbf{k}} + \bar{J}^{\mathbf{k}} + \bar{J}^{\mathbf{k}} \cdot \vec{\sigma} \end{bmatrix}_{\mathbf{K},\mathbf{K}'}^{MT\alpha\beta}$$
$$= \sum_{\mu} \sum_{l,m} \sum_{l'm'} A_{lm}^{\alpha} \left(\mathbf{k} + \mathbf{K}\right)^{*} \cdot t_{lm,l'm'}^{\mu,\phi,\phi\alpha\beta} \cdot A_{l'm'}^{\beta} \left(\mathbf{k} + \mathbf{K}'\right)$$
(B15)

Where there no sum over repeated indices and

$$t_{lm,l'm'}^{\mu,\phi,\phi\alpha\beta} = \sum_{l''} I_{l'll''}^{\mu\alpha\beta} G_{l'll''}^{m'mm''}$$
(B16)

and:

$$G_{l,l',l''}^{m,m',m''} = \int Y_{l,m}^* Y_{l',m'} Y_{l'',m''} d\Omega,$$

$$I_{l,l',l''}^{\mu\alpha\beta} = \int u_{l\alpha}^*(r) \left[J_{l''}^{\mu}(r) + \bar{J}_{l''}^{\mu} \cdot \vec{\sigma} \right] u_{l'\beta}(r) r^2 dr$$
(B17)

Appendix C: FSLAPWMR

For simplicity we will assume that the various multiradius MT spheres do not overlap.

1. Definition of Hamiltonian

This is similar to Section B1 and will not be repeated.

2. Wave functions

This is similar to Section B 2 and will not be repeated.

3. Interstitial

We note that $N \gg \mathcal{N}_{\mu}$. Now let us pick \mathbf{K}_1 and \mathbf{K}_2 , Now let us order the $2\mathcal{N}_{\mu}$ radii by at each μ .

$$S^{l_1}_{\mu}\left(|\mathbf{k} + \mathbf{K}_i|\right) \le S^{l_2}_{\mu}\left(|\mathbf{k} + \mathbf{K}_j|\right) \le \dots \le S^{l_{2N_{\mu}}}_{\mu}\left(|\mathbf{k} + \mathbf{K}_m|\right)$$
(C1)

Now let us call the interstitial region by

$$\bigcap_{\mu} |\mathbf{r} - \mathbf{r}_{\mu}| \ge S_{\mu}^{l_{2N\mu}} \left(|\mathbf{k} + \mathbf{K}_{m}| \right)$$
(C2)

Now for $l \leq N$ we have that:

$$u_{l}^{\alpha}\left(\mathbf{r}-\mathbf{r}_{\mu}\right) = \begin{cases} u_{l}^{\alpha}\left(\mathbf{r}-\mathbf{r}_{\mu}\right) & |\mathbf{r}-\mathbf{r}_{\mu}| < S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right) \\ \frac{J_{l}\left(|\mathbf{k}+\mathbf{K}||\mathbf{r}-\mathbf{r}_{\mu}|\right)}{\frac{J_{l}\left(|\mathbf{k}+\mathbf{K}|S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)\right)}{u_{l}^{\alpha}\left(S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right)\right)}} & |\mathbf{r}-\mathbf{r}_{\mu}| \ge S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right) \end{cases}$$

$$(C3)$$

Where furthermore

$$\dot{u}_{l}^{\alpha}\left(\mathbf{r}-\mathbf{r}_{\mu}\right) = \begin{cases} \dot{u}_{l}^{\alpha}\left(\mathbf{r}-\mathbf{r}_{\mu}\right) & |\mathbf{r}-\mathbf{r}_{\mu}| < S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right) \\ 0 & |\mathbf{r}-\mathbf{r}_{\mu}| \ge S_{\mu}^{l}\left(|\mathbf{k}+\mathbf{K}|\right) \end{cases}$$
(C4)

Now for l > N we define

$$u_l^{\alpha} \left(\mathbf{r} - \mathbf{r}_{\mu} \right) = J_l \left(|\mathbf{k} + \mathbf{K}| |\mathbf{r} - \mathbf{r}_{\mu}| \right)$$
$$A_{lm}^{\mu\alpha} \left(\mathbf{k} + \mathbf{K} \right) = \frac{1}{\sqrt{V}} 4\pi i^l Y_{lm}^* \left(\widehat{\mathbf{k} + \mathbf{K}} \right)$$
$$B_{lm}^{\mu\alpha} \left(\mathbf{k} + \mathbf{K} \right) = 0 \tag{C5}$$

a. Main setup

This is identical to Section B3a and will not be repeated.

4. MT piece

We write:

$$\left[\bar{O}_{\mathbf{k}}\right]_{\mathbf{K},\mathbf{K}'}^{MT\alpha\beta} = \sum_{\mu} \sum_{l,m} \left[A_{lm}^{\alpha} \left(\mathbf{k} + \mathbf{K}\right)^{*} A_{lm}^{\beta} \left(\mathbf{k} + \mathbf{K}'\right) \delta_{\alpha\beta} + B_{lm}^{\alpha} \left(\mathbf{k} + \mathbf{K}\right)^{*} B_{lm}^{\beta} \left(\mathbf{k} + \mathbf{K}'\right) \left\langle \dot{u}_{l}^{\alpha} \mid \dot{u}_{l}^{\beta} \right\rangle \right]$$
(C6)

And:

$$\begin{bmatrix} -\bar{\Delta}^{\mathbf{k}} + \bar{J}^{\mathbf{k}} + \bar{J}^{\mathbf{k}} \cdot \vec{\sigma} \end{bmatrix}_{\mathbf{K},\mathbf{K}'}^{MT\alpha\beta} = \sum_{\mu} \sum_{l,m} \sum_{l'm'} \begin{bmatrix} A_{lm}^{\alpha} (\mathbf{k} + \mathbf{K})^{*} \cdot t_{lm,l'm'}^{\mu,\phi,\phi\alpha\beta} \cdot A_{l'm'}^{\beta} (\mathbf{k} + \mathbf{K}') + B_{lm}^{\alpha} (\mathbf{k} + \mathbf{K})^{*} \cdot t_{lm,l'm'}^{\mu,\phi,\dot{\phi}\alpha\beta} \cdot B_{l'm'}^{\beta} (\mathbf{k} + \mathbf{K}') + B_{lm}^{\alpha} (\mathbf{k} + \mathbf{K})^{*} \cdot t_{lm,l'm'}^{\mu,\phi,\phi\alpha\beta} \cdot A_{l'm'}^{\beta} (\mathbf{k} + \mathbf{K}') + B_{lm}^{\alpha} (\mathbf{k} + \mathbf{K})^{*} \cdot t_{lm,l'm'}^{\mu,\phi,\phi\alpha\beta} \cdot A_{l'm'} (\mathbf{k} + \mathbf{K}') \end{bmatrix}$$

$$(C7)$$

Where there no sum over repeated indices and

$$t_{lm,l'm'}^{\mu,\phi,\phi\alpha\beta} = \sum_{l'} I_{l'll'}^{\mu\alpha\beta} G_{l'll''}^{m'mm''}$$

$$t_{lm,l'm'}^{\mu,\phi,\dot{\phi}\alpha\beta} = \sum_{l'} J_{l'll''}^{\mu\alpha\beta} G_{l'll''}^{m'mm''}$$

$$t_{lm,l'm'}^{\mu,\dot{\phi},\phi\alpha\beta} = \sum_{l''} K_{l'll''}^{\mu\alpha\beta} G_{l'll''}^{m'mm''}$$

$$t_{lm,l'm'}^{\mu,\dot{\phi},\dot{\phi}\alpha\beta} = \sum_{l''} L_{l'll''}^{\mu\alpha\beta} G_{l'll''}^{m'mm''}$$
(C8)

$$\begin{aligned} G_{l,l',l''}^{m,m',m''} &= \int Y_{l,m}^* Y_{l',m'} Y_{l'',m''} d\Omega, \\ I_{l,l',l''}^{\mu\alpha\beta} &= \int u_{l\alpha}^* \left(r \right) \left[J_{l''}^{\mu} \left(r \right) + \vec{J}_{l''}^{\mu} \cdot \vec{\sigma} \right] u_{l'\beta} \left(r \right) r^2 dr \\ J_{l,l',l''}^{\mu\alpha\beta} &= \int u_{l\alpha}^* \left(r \right) \left[J_{l''}^{\mu} \left(r \right) + \vec{J}_{l''}^{\mu} \cdot \vec{\sigma} \right] \dot{u}_{l'\beta} \left(r \right) r^2 dr \\ K_{l,l',l''}^{\mu\alpha\beta} &= \int \dot{u}_{l}^* \left(r \right) \left[J_{l''}^{\mu} \left(r \right) + \vec{J}_{l''}^{\mu} \cdot \vec{\sigma} \right] u_{l'} \left(r \right) r^2 dr \\ L_{l,l',l''}^{\mu\alpha\beta} &= \int \dot{u}_{l}^* \left(r \right) \left[J_{l''}^{\mu} \left(r \right) + \vec{J}_{l''}^{\mu} \cdot \vec{\sigma} \right] \dot{u}_{l'} \left(r \right) r^2 dr \end{aligned}$$
(C9)

Appendix D: Lagrange Function, basis set and running cutoff (additional ideas to improve speed)

The results presented in this appendix are relevant to almost any basis set, so we will phrase it with great generality. For a practical calculation it is important to introduce a finite basis $|\lambda\rangle$ to compute $-\frac{1}{\beta} \ln [Tr [\exp(-\beta H_{KS})]]$ - the Helmholtz free energy of the KS Hamiltonian. We now introduce the overlap and KS Hamiltonian matrices:

$$O^{\lambda\lambda'} = \langle \lambda \mid \lambda' \rangle$$

$$H_{KS}^{\lambda\lambda'} = \int d^{d}\mathbf{r}\lambda^{*}\left(\mathbf{r}\right) \left[-\frac{\nabla^{2}}{2m} + J\left(\mathbf{r}\right) - \mu\right]\lambda'\left(\mathbf{r}\right) \quad (D1)$$

We now introduce the secular equation

$$\sum_{\lambda'} H_{KS}^{\lambda\lambda'} V_n^{\lambda'} = \varepsilon_n \sum_{\lambda'} O^{\lambda\lambda'} V_n^{\lambda'}$$
(D2)

In which case we have that

$$F_{LDA}\left(D\left(\mathbf{r}\right), J\left(\mathbf{r}\right), \mu\right) = -\frac{1}{\beta} \sum_{n} \frac{1}{1 + \exp\left(-\beta\varepsilon_{n}\right)} + \frac{e^{2}}{2} \int d^{d}\mathbf{r} d^{d}\mathbf{r}' \frac{D\left(\mathbf{r}\right) D\left(\mathbf{r}'\right)}{|\mathbf{r} - \mathbf{r}'|} + \int d^{d}\mathbf{r} D\left(\mathbf{r}\right) \varepsilon_{LDA}^{\beta}\left(D\left(\mathbf{r}\right)\right) - \int d^{d}\mathbf{r} J\left(\mathbf{r}\right) D\left(\mathbf{r}\right) + \mu N$$
(D3)

The Helmholtz free energy Lagrange function is then extremized with respect to $D(\mathbf{r})$, $J(\mathbf{r})$ and μ by an iterative solution of the self consistency equations till convergence. Here $D(\mathbf{r})$ is the electron density and $J(\mathbf{r})$ and μ are Lagrange multipliers. For simplicity we have focused on LDA (which is not essential).

For a practical calculation for 3D solids it is important to introduce a basis set often indexed by $\mathbf{k} + \mathbf{K}$ with \mathbf{k} in the first Brillouin zone and **K** in the reciprocal lattice and for practical reasons is limited to $\mathbf{K} < \mathbf{K}_{max}$. In many DFT calculations the dominant contribution to computational time is solving Eq. (D2) for a total of \mathcal{N} times till convergence with each run taking $\sim \mathbf{K}_{max}^9$ time for a total of $\sim \mathcal{N}\mathbf{K}_{max}^9$ computations. At each step from numerical simulations it is known that the error from an exact solution of the extermination of the Helmholtz Lagrange function is given by [1]:

$$\Delta \varepsilon \sim \varepsilon_0 \left[\exp\left(-A\mathfrak{n}^{\alpha} \right) + \exp\left(-B\mathbf{K}_{max}^{\zeta} \right) \right]$$
(D4)

where we are in the \mathfrak{n} 'th iteration. Here we propose to introduce a $\mathbf{K}_{max}(\mathfrak{n})$ where

$$B\mathbf{K}_{max}^{\zeta}\left(\mathfrak{n}\right) = A\mathfrak{n}^{\alpha} \Rightarrow \mathbf{K}_{max}\left(\mathfrak{n}\right) = \left(\frac{A}{B}\right)^{1/\zeta} \mathfrak{n}^{\alpha/\zeta} \quad (D5)$$

As such computational time will then scale as

$$T \sim \int_{-\infty}^{0} dt \mathbf{K}_{max}^{9} \exp\left(9\frac{\alpha}{\zeta}t\right) \Rightarrow \mathbf{K}_{max}^{9} \left[\frac{\zeta}{9\alpha} + 1\right]$$
(D6)

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Where we have estimated the last iteration loop more carefully as it is often dominant. This leads to a computational improvement of the scale of $\sim \frac{N}{1+\frac{\zeta}{9\alpha}}$ on top of those described in the main text.

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