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Chirp-wave expansion of the electron wavefunctions in atoms

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ABSTRACT

The description of the electron wavefunctions in atoms is generalized to the fractional Fourier series. This method introduces a continuous and infinite number of chirp basis sets with linear variation of the frequency to expand the wavefunctions, in which plane-waves are a special case. The chirp characteristics of each basis set can be adjusted through a single parameter. Thus, the basis set cutoff can be optimized variationally. The approach is tested with the expansion of the electron wavefunctions in atoms, and it is shown that chirp basis sets substantially improve the convergence in the description of the electron density. We have found that the natural oscillations of the electron core states are efficiently described in chirp-waves.

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1. Introduction

The electrons in periodic potentials are described by Bloch waves [1], which are in general expanded on an auxiliary set of basis functions. Plane-waves are in particular convenient because they are periodic and conform a complete orthonormal basis set, therefore they do not suffer of basis set superposition error. However, plane-waves are inefficient in describing the radial nodes of the wavefunctions. In particular, the kinetic energy of valence electrons is substantially increased due to the orthogonality of their wavefunctions inside the atomic core region. In order to minimize this inconvenience, methods to decouple the core and valence states have been developed. Slater [2] used radial solutions inside spheres surrounding the atoms, reducing the number of plane-waves to only the necessary to describe the valence electrons in between the spheres. Herring further developed the concept by orthogonalizing each valence plane-wave function to all core wavefunctions [3], and later formalized as a pseudopotential theory by Phillips and Kleinman [4].

The number of auxiliary basis function directly impacts the computational cost of the electronic structure calculations, and ultimately restricts the systems that can be efficiently modeled. This has motivated the expansion of Bloch waves on alternative basis functions [5]. In particular, Gygi has recently reformulated the plane-wave approach in curvilinear coordinates in which the adaptive Riemannian metric and plane-wave cutoff are treated variationally [6]. However, until now plane-waves in combination with pseudopotentials have been the most widely adopted approach, to reduce the computational complexity of the Schrödinger equation for electrons in periodic potentials. Nevertheless, basis sets that can more efficiently describe the electron wavefunctions may foster the capabilities of electronic structure calculations.

In this article, we present the formalism for the expansion of the electron wavefunctions in atoms using chirp-wave (ChW) basis sets. The method is based on a set of orthonormal linear chirp functions, associated to plane-waves by

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the fractional Fourier transform (FrFT) [7,8]. The resulting chirp basis functions are analogous to perform a local gauge transformation to a set of plane-waves. The approach is analog to Gygi’s generalized plane-wave method, however, in our framework the transformation is performed in the momentum coordinates.

2. Chirp basis sets

The continuous fractional Fourier transform (FrFT) [7,8] operator \mathcal{F}_α as defined in [9] can be expressed as

$$\mathcal{F}_\alpha[f(u)] = K_\alpha \int f(u) e^{i\pi \frac{(u^2+x^2) \cos \alpha - 2ux}{\sin \alpha}} du, \tag{1}$$

where $\alpha = a\pi/2$ is the fractional order for $0 < |a| < 2$. In particular for $a = 1$ correspond the standard Fourier transform. The coefficient K_α is given by

$$K_\alpha = \frac{e^{i(s(\alpha)\pi/4 - \alpha/2)}}{\sqrt{|\sin \alpha|}}, \tag{2}$$

with $s(\alpha) = \text{sgn}(\sin \alpha)$. Subsequently, an orthonormal set of chirp functions can be derived through the FrFT [10]. Let $\delta_{m\tau}(u) = \delta(u - m\tau)$ be a Dirac delta distribution in the FrFT domain, with m an integer number. Evaluating the \mathcal{F}_α of $\delta_{m\tau}$ we get

$$\mathcal{F}_{-\alpha}[\delta_{m\tau}](x) = K_{-\alpha} e^{-i\pi \frac{(m^2\tau^2+x^2) \cos \alpha - 2m\tau x}{\sin \alpha}}. \tag{3}$$

For non-integer values of a , we obtain chirp functions with instantaneous frequency that varies linearly with the position at the chirp rate $k = \pi \cot \alpha$. Based on the above result, we can define a set of linear chirp functions determined by

$$\text{ChW}_{m\tau;\alpha}(x) = K_{-\alpha} e^{-i[\eta + (kx - G)x]}, \tag{4}$$

with constant phase $\eta = \pi m^2 \tau^2 \cot \alpha$ and starting frequency $G = (2\pi m\tau) / \sin \alpha$. For $\tau = 1/L$ and $a = 1$ the functions are plane-waves with lattice vector L , and G the respective vectors of the reciprocal lattice.

Using the relation $\mathcal{F}_\alpha[\text{ChW}_{m\tau;\alpha}(x)] = \delta_{m\tau}$ and the unitary property of the \mathcal{F}_α operator, for a non-integer a , we can straightforward prove their orthogonality as follows

$$\begin{aligned} \langle \text{ChW}_{m\tau;\alpha} | \text{ChW}_{m'\tau;\alpha} \rangle &= \langle \mathcal{F}_{-\alpha} \delta_{m\tau} | \mathcal{F}_{-\alpha} \delta_{m'\tau} \rangle \\ &= \langle \delta_{m\tau} | \mathcal{F}_{-\alpha}^\dagger \mathcal{F}_{-\alpha} \delta_{m'\tau} \rangle \\ &= \langle \delta_{m\tau} | \delta_{m'\tau} \rangle. \end{aligned} \tag{5}$$

Therefore, the ChW functions form an orthonormal and complete basis set that continuously depends on a , here after called the ChW_a basis set.

Our approach can be rationalized as a local gauge transformation of the first class [11], in which the chirp functions are related to plane-waves through a gauge transformation of the following form,

$$e^{iGx} \rightarrow e^{i\phi(x)} e^{iGx} = e^{-i(\eta + kx^2)} e^{iGx}. \tag{6}$$

Consequently, plane-waves are the special case when the local phase $\phi(x) = 0$. This happens when $a = 1$. Thus, we can describe the electron wavefunctions in chirp-waves using the following expansion

$$\varphi(x) = \sum_{m=-\infty}^{\infty} C_{m;\alpha} \text{ChW}_{m\tau;\alpha}(x). \tag{7}$$

The expansion coefficients for a given function $\varphi(x)$ can be efficiently obtained through a single discrete fractional Fourier transform ($\mathcal{D}r \mathcal{F}_\alpha$) of the sampled function $\varphi(x_m)$, as follows

$$C_{m;\alpha} = \frac{e^{i(s(\alpha)\pi/4 - \alpha/2)}}{\sqrt{|\sin \alpha|}} f_\alpha(u_m), \tag{8}$$

with $f_\alpha(u_m) = \mathcal{D}r \mathcal{F}_\alpha[\varphi(x_m)]$. The linear chirps are non-periodic functions, therefore the chirp basis constructed using the above approach can only be used to expand aperiodic functions in the finite interval $[-L/2, L/2]$. However, the electron density is gauge invariant, so it is possible to expand wavefunctions in chirp-waves series. This in general implies

$$\rho(x) = |\varphi_\alpha(x)|^2 = |\varphi_{\alpha=\pi/2}(x)|^2, \tag{9}$$

which is all what is, in principle, required in density functional theory (DFT) to solve the Kohn–Sham equations [12]. The theoretical sampling rate to perfectly reconstruct a function in chirp-waves, using its FrFT spectrum, is $\eta = \sin \alpha / L$ [10]. Nevertheless, in electronic structure calculations a more important quantity is the energy convergence criteria. On the other hand, the contribution of the spectra of a function with compact support become less important as the coefficient index m increases. Therefore, in practice, a perfect reconstruction may not be strictly necessary.

In order to compare the performance of ChW and PW basis sets, we have considered the expansion in series of three φ_{ns} orbitals of the Krypton atom. The orbitals were computed within the DFT using the local density approximation (LDA)

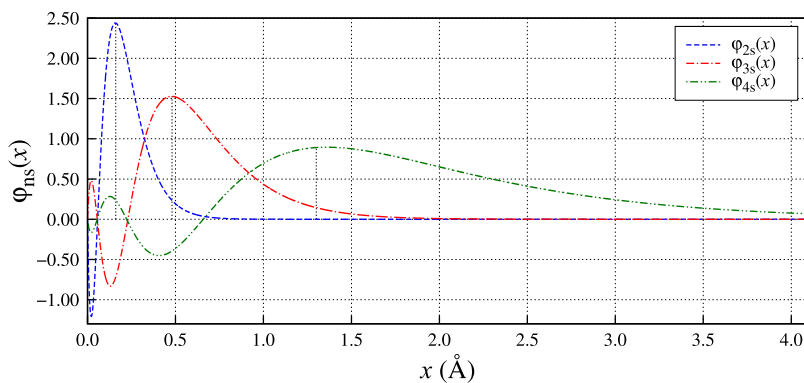


Fig. 1. Radial wavefunctions of the Krypton atom. The vertical dotted lines indicate the core radius.

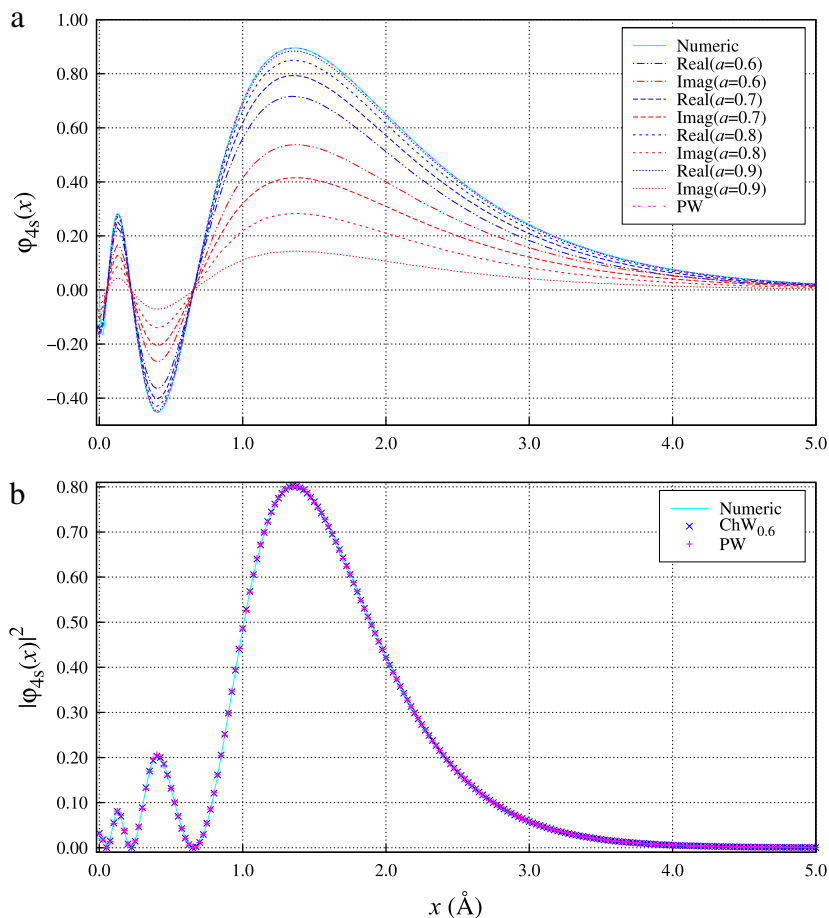


Fig. 2. (a) The numeric, ChW_a , and PWs represented φ_{4s} orbital. (b) The probability density distribution. All the ChW_a series overlap, but only the $\text{ChW}_{0.6}$ is shown.

exchange and the Vosko, Wilk, and Nusair correlation functional (VWN) [13] using our numerical non-relativistic DFT code for atoms. The radial cutoff distance of 10 Å was used in all the calculations.

We have selected the radial part of φ_{2s} , φ_{3s} and φ_{4s} orbitals (see Fig. 1). This set of orbitals spans the conventional partition of the electron states in atoms, i.e., the core, semicore and valence states. The sampled functions, $\varphi_{ns}(x_m)$, will serve to verify the performance of the ChW basis sets for each instance. We computed the fast Fourier transform (FFT) and the discrete FrFT ($a = 0.1, 0.2, \dots, 0.9$) for each φ_{ns} orbital using 900 equally spaced samples. Only half of the coefficients are necessary because the spectrum is symmetric around the origin for pair functions.

The chirped characteristics of the functions in the ChW_a basis set is adjusted through the a parameter. As a demonstration, we have reconstructed the φ_{4s} orbital using 450 basis functions of the ChW_a and PW series. Fig. 2 shows the reconstructed

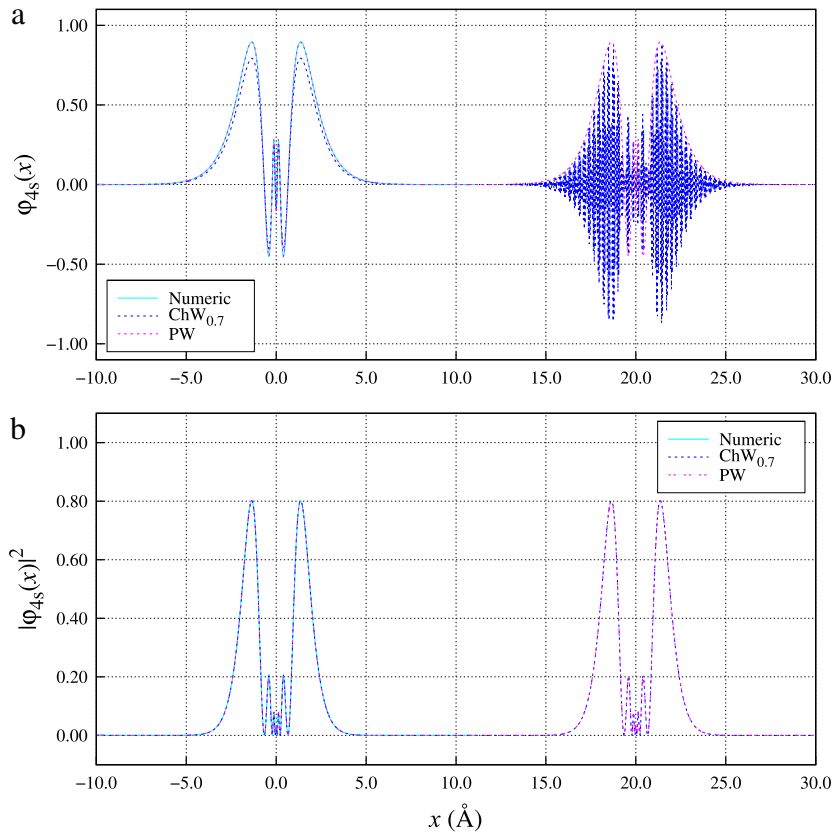


Fig. 3. (a) The numeric, real component of the $\text{ChW}_{0.7}$ and PW φ_{4s} orbital. (b) The electron density in ChWs and PWs are periodic functions.

φ_{4s} orbital for the different series. The sampled function and the PWs reconstructed orbital, as expected, are overlapped. On the other hand, the ChW reconstructed functions, according with the definition of chirp series of Eq. (7), are in general complex, and their real and imaginary components vary with the a parameter. Therefore, the real valued wavefunction might not be reconstructed using ChWs. However, as seen in Fig. 2(b), because the electron density is gauge invariant, the electron densities are almost identical regardless of the value of a .

Fig. 3 shows the reconstructed φ_{4s} function and its next nearest image on the right side. The plotted real part of the $\text{ChW}_{0.7}$ reconstructed orbital is aperiodic, however, the electron density is correctly a periodic function. This result is also independent of the chosen ChW_a basis set.

In principle, if we know the electron density of a system, the energy can be computed within the DFT. For this reason, we have expanded the orbitals using ChW_a and the standard PW series employing from 10 to 450 basis functions, using a step of 10. We have evaluated the mean absolute error (MAE), to determine the accuracy in the description of the electron density, using the following expression

$$\text{MAE}[ns] = \frac{1}{p} \sum_{m=1}^p |\varphi_{ns}^{\text{num}}(x_m)|^2 - |\varphi_{ns}^{\alpha}(x_m)|^2, \quad (10)$$

where φ^{num} is the numerical computed orbital, and φ^{α} is the sampled function of the ChW or PW reconstructed orbitals, and p is the number of samples. In order to assess the description of the electron density separately, Eq. (10) was independently evaluated for the core and valence regions, using the following core radii, $r_{2s} = 0.156 \text{ \AA}$, $r_{3s} = 0.489 \text{ \AA}$, and $r_{4s} = 1.373 \text{ \AA}$, as illustrated in Fig. 1. The evaluated MAEs for the core and valence regions as a function of the number of basis functions are shown in Figs. 4 and 5, respectively.

3. Results and discussion

In general, the MAEs evaluated in the core regions are relatively larger than in the valence regions, up to two order of magnitude. However, from Fig. 4, it is clear that the convergence of the core regions in ChW_a series can be achieved with considerably less terms than with PW series. This indicates that chirp-waves are more suitable functions to describe this region. Furthermore, a very large cutoff may be necessary for the PW series to reach the same convergence as some of the

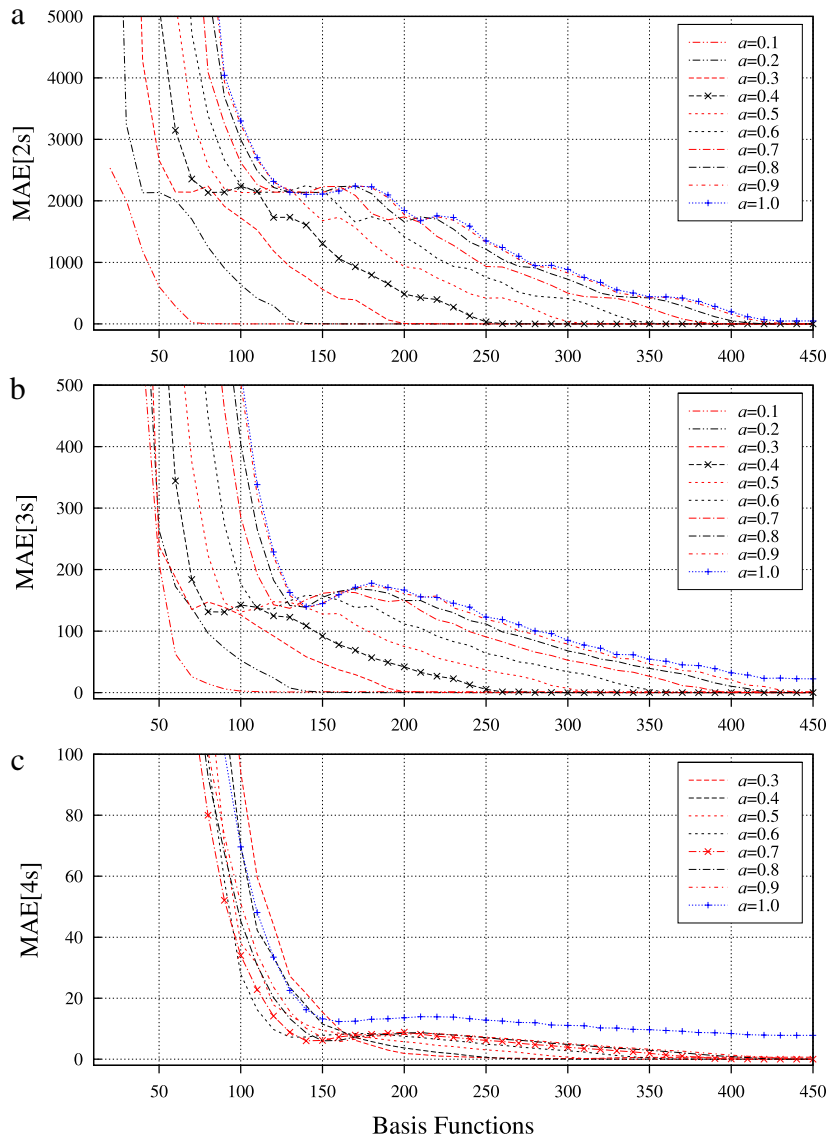


Fig. 4. MAE (in arb. units) of the electron density distribution for the core region. The ChW_a basis set is indicated by a , for $a = 1$ is the standard PW basis set.

ChWs series. On the other hand, the MAEs for the valence regions are more even, as can be observed in Fig. 5, and only the core orbital φ_{1s} requires a substantially larger cutoff to converge. Nevertheless, the ChW_a expansions converge prior to the PWs in all the cases.

Figs. 4 and 5 show that for particular values of a , the ChW_a series require a considerable lower cutoff in order to correctly represent the electron density as compared to PWs. Note that this trend becomes more important for core electrons. In fact, the remarkably small cutoff for values of $0.1 \leq a < 0.4$ suggests a strong chirp-like nature of the core states, indicating that these are better approximated by ChWs. In contrast, we found that small values of a were not suitable for the valence region and resulted in very large MAEs, and therefore, were not included in Fig. 5. In order to accurately describe the valence region, values of $a \geq 0.4$ were necessary. In this sense, a suitable a may be used in order to correctly describe the core and valence regions simultaneously. In Figs. 4 and 5, we have highlighted with the symbol \times the curves with our suggested best values of a for each orbital.

The convergence for a particular ChW_a basis set relies on a and the characteristic of the orbital, with more favorable small values of a for the core region than for the valence region. This characteristic makes the ChWs very attractive, because a can be treated as a variational parameter to search for the optimum ChW_a basis sets that require the lower cutoff.

The chirp-wave series, as defined in Eq. (7), are not suitable for the representation of the real valued wavefunction due to the gauge field, however, the electron density is gauge invariant and can be accurately reconstructed. ChWs share similar

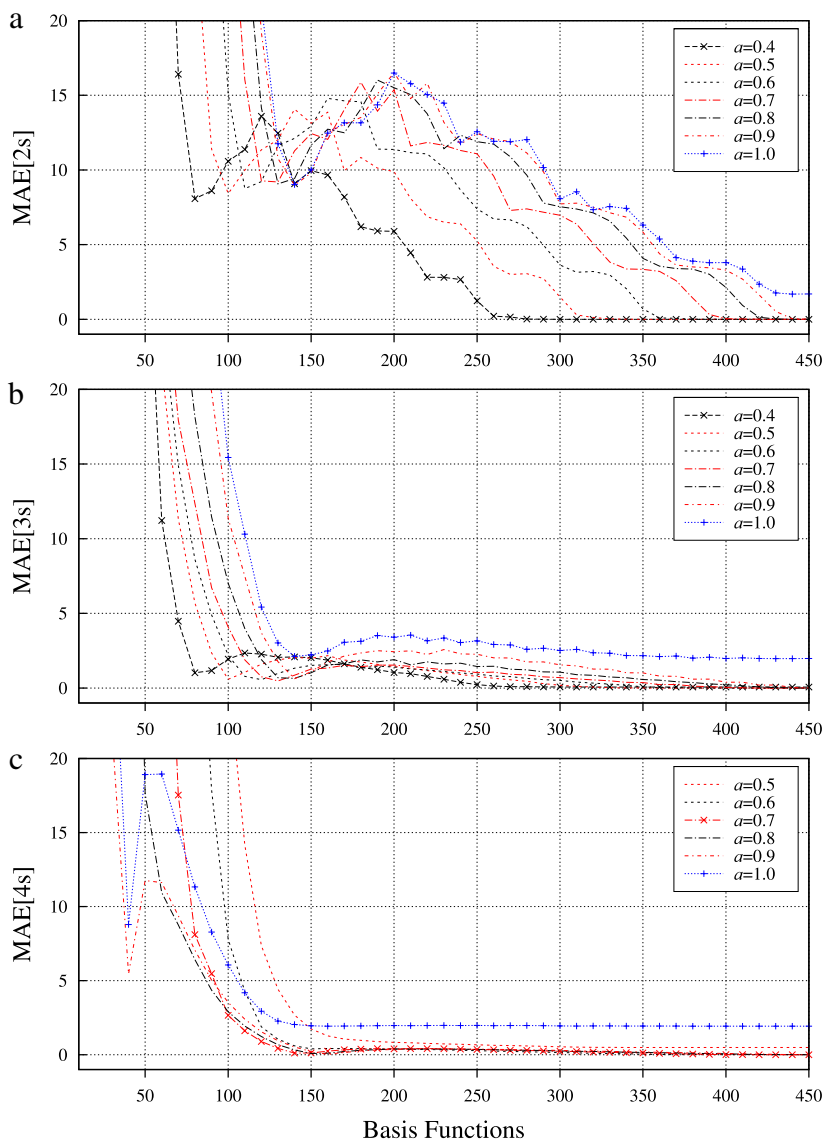


Fig. 5. MAE (in arb. units) of the electron density distribution for the valence region. The ChW_a basis set is indicated by a , for $a = 1$ is the standard PW basis set.

advantages as conventional approaches, because chrip-waves span a continuous range in the momentum coordinates, and are not fully localized as plane-waves. In particular, we have found that the natural oscillations of the core states are resembled by linear chrip functions. This explains why chrip-waves are capable of describing the electron density in the core region with a much more efficiency than plane-waves.

4. Conclusions

Our results suggest that the chrip-wave basis sets provide particular characteristics that allow for the efficient representation of the electron wavefunctions. In some aspects, chrip-waves may open the bridge for the inclusion of semicore states at a low computational cost, eliminating the drawback of approximations. Moreover, the explicit inclusion of core states for accurately relativistic and other core effects, is very important in studies including heavy atoms, allowing the modeling of properties of atomic systems in which semicore and core states are critically necessary.

As chrip-waves can more efficiently represent the wavefunctions in the core region, chrip-waves can also take great advantage of pseudopotentials. For instance, ChW s can be used in combination with hard pseudopotentials to extend their transferability to a wide range of chemical environments.

We have described some advantages of the chirp-wave basis sets in the expansion of *a priori* calculated electron wave functions. However, in most practical applications the electron wavefunctions are unknown. In that case, the coefficients of the chirp expansion in Eq. (7) can be obtained using matrix diagonalization or iterative minimization techniques [14]. We are currently implementing and testing a DFT/ChW code for atomic clusters in the position coordinates. Future development will be focused on the solution in the FrFT domains. The formulation of the Schrödinger equation within the framework of the density functional theory for supercell and band calculations in FrFT position–momentum domains is the work in progress.

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