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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.

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 variational [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 $\mathcal{F}_\alpha$ 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 $s(\alpha) = \operatorname{sgn}(\sin\alpha)$. 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 $\mathcal{F}_\alpha$ 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

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

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

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

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,

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

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

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

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)