Journal of Physics: Conference Series

PAPER • OPEN ACCESS

Fitting continuum wave functions with complex Gaussians

To cite this article: A Ammar *et al* 2020 *J. Phys.: Conf. Ser.* **1412** 152079

Fitting continuum wave functions with complex Gaussians

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Synopsis One particle atomic and molecular bound functions can be easily fitted with a set of real Gaussian type orbitals (r-GTOs). Here we explore how continuum wave functions such as Bessel, Coulomb or generalized Sturmian functions can be represented by a set of real or complex Gaussian type orbitals (c-GTOs) that can, ultimately, enter a molecular scattering calculation.

The well known r-GTOs are largely used in quantum chemistry and molecular physics due to remarkable mathematical properties, including the Gaussian product theorem that greatly facilitates a number of integral calculations. A set of N r-GTOs can also be used to represent atomic and molecular one particle bound functions like, for example, Slater orbitals [1]. Representing scattering states is much more delicate because of their oscillating nature. Some studies have shown, though, that it is feasible [2, 3], but with a large number N of nodeless r-GTOs (logically, N increases as the energy of the continuum state increases). An alternative approach is to consider c-GTOs (Gaussians with complex exponents) that have an intrinsic oscillating behavior making them, a priori, more suitable to represent continuum functions.

In this contribution, we wish to explore the representation of spherical Bessel, Coulomb and generalized Sturmian functions [4] by a set of c-GTOs, and compare the efficiency with respect to using r-GTOs. As an example, here, we consider a set of 9 sample Coulomb functions $F_l(Z,k,r)$ for $l = 0, 1, ..., 8$, with energy $\frac{k^2}{2} = 2$ a.u. and a charge $Z = 1$. We have fitted them with either N r-GTOs or N c-GTOs

$$F_l(Z,k,r) = \sum_{i=1}^{N} c_{i,l} \exp(-\alpha_i r^2) \qquad (1)$$

by applying the approach of Nestmann and Peyerimhoff [2] in a range $r \in [0, 12]$ a.u. and using a quadratic approximation method [5]. Figure 1 shows the fitting of the $l = 0$ Coulomb function taking $N = 12$ in both expansions. It is easy to clearly appreciate the superiority of c-GTOs.

We are now in the process of applying c-GTOs representations of continuum states in scattering problems such as photoionization of small molecules.

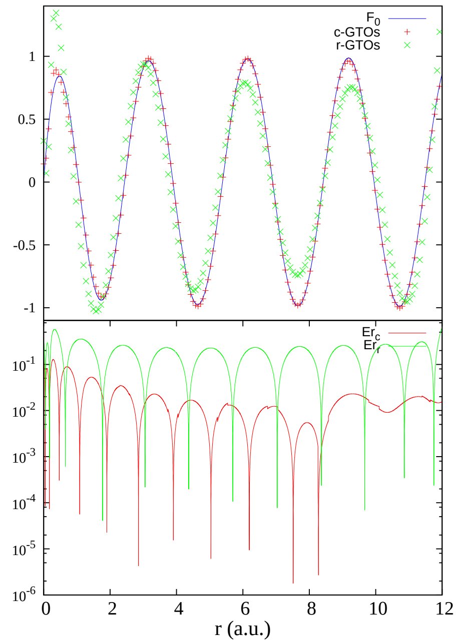

Figure 1. Upper panel: the coulomb function for $l = 0$ (blue), with its fitting by 12 c-GTOs (red dots) and by 12 r-GTOs (green dots). Bottom panel: the respective absolute error.

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