

Towards the Study of Heavy-Element Containing Solids with the CRYSTAL Program: Developments and Applications

Jacques K. Desmarais,^{a,b,c} C. Ravoux,^{a,d} K.E. El-Kelany,^{a,e} R. Dovesi^a and A. Erba^a

^a*Univ. di Torino, Dip. di Chimica, Torino – Italy*

^b*Univ. of Saskatchewan, Dep. of Geological Sciences, Saskatoon – Canada*

^c*Univ. of Saskatchewan, Dep. of Physics and Engineering Physics, Saskatoon – Canada*

^d*Laboratoire Structures Proprietes et Modelisation des Solides, Gif-surYvette – France*

^e*Univ. of Minia, Dep. of Chemistry, Minia – Egypt*

e-mail: presenting jkd788@mail.usask.ca

The CRYSTAL¹ code for quantum-mechanical simulations of periodic systems is based on a linear-combination of atomic-orbitals (LCAO) framework. Crystalline orbitals are expressed as a linear-combination of Bloch functions that are in turn defined using a basis-set of solid-spherical Gaussian-type functions (SGTF). In its initial version, the CRYSTAL code described the wavefunction as a linear-combination of s-, p- and d- type SGTF. The code was generalized to f-type functions in 2003. Here we generalize the code to g-type SGTF, which represents the first step towards a better description of systems containing heavy-elements. Among them are lanthanides and actinides, which have occupied 4f and 5f bands and the g-type functions represent the first polarisation shell. We develop new small-core pseudopotential basis sets of the form (11sp7d8f2g)/[4sp2d3f2g] for the lanthanide and actinide series in the solid state.

The new code and basis sets are applied to the strongly-correlated lanthanide sesquioxides Ln₂O₃ series (Ln=La,Ce,Pr,Nd). We provide a detailed description of their geometric, electronic and magnetic structures using global-hybrid functionals. The critical role of the fraction of Fock exchange is addressed. In particular, a new theoretical approach based on a self-consistent definition - through the material's dielectric response - of the optimal fraction of exchange in hybrid functionals² is applied for the first time to strongly correlated materials. Our description of Ce₂O₃ is in agreement with the existing copious literature on this system, which suggest that our description of the other members of the series is reliable, for which very little has been published before.

1. R. Dovesi, A. Erba, C.M. Zicovich-Wilson, B. Civalleri, L. Maschio, M. Rerat, S. Casassa, J. Baima, S. Salustro, B. Kirtman, *WIRES Comput. Mol. Sci.* **2018**, 8, e1360-e1396
2. A. Erba, *J. Phys. Condens. Matt.* **2017**, 314001-314006