Algebraic search for cooperative-rotational rigid-unit modes

Branton J. Campbell, Tyler Averett, Chrisopher Yost, Shae Machlus, Harold T. Stokes
Dept. of Physics & Astronomy, Brigham Young University, Provo, Utah 84602, USA

Thomas A. Whittle, Siegbert Schmid
School of Chemistry, The University of Sydney, Sydney, NSW, 2006, Australia

Christopher J. Howard
School of Engineering, University of Newcastle, Callaghan, NSW, 2308, Australia

Crystalline solids consisting of three-dimensional networks of interconnected polyhedra or other rigid units are ubiquitous amongst functional materials. In many cases, application-critical properties are sensitive to the rotations of individual rigid units. But the shared atoms that connect the rigid units together impose severe constraints on any rotational degrees of freedom, which must then be cooperative throughout the entire network. Successful efforts to identify cooperative-rotational rigid-unit modes (RUMs) in crystals have employed split-atom harmonic potentials, exhaustive testing of the rotational symmetry modes allowed by group representation theory, and even simple geometric considerations. Here, we present a purely algebraic approach to RUM identification wherein the constraints of interconnectedness are applied to a linear system of equations. The new approach appears to be fully general and quite straightforward to implement.