Treatment of Vibronic Properties in Infinite Periodic Systems

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There are many important spectroscopic properties that are determined either entirely, or in large part, by the electronic response to nuclear displacements. Some examples are Raman intensities, static and dynamic (i.e. nonlinear optical) vibrational hyperpolarizabilities, and vibrational circular dichroism. The practical calculation of vibronic properties for infinite periodic systems, or systems that may be modeled as infinite and periodic, typically requires special considerations. We will focus here primarily on static and dynamic vibrational hyperpolarizabilities that have recently been obtained, for the first time, by the finite field nuclear relaxation (FF-NR) method. The successful implementation of this computational scheme in the CRYSTAL computer code, which utilizes Gaussian-type basis sets, will be described. B3LYP results, in particular for BN nanotubes, indicate that vibrational contributions can be as important, or much more important, than pure electronic contributions depending on the property, tensor component, optical frequency, and nanotube radius. Application of the FF-NR treatment, as well as extensions of this approach, to other systems will be discussed along with computational methods for other properties.