

First principles calculation of vibrational spectra in solids: From fingerprinting defects in diamond to the impact of water in molecular crystals.

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The atomic scale structural characterization of solids is a task often involving spectroscopic techniques. Although the spectroscopic data provides direct information of the system, its translation into suitable structure information is indirect as a theoretical structural model is required. In this work, we investigate the influence of defects on the vibrational spectrum of the host material by means of first principles quantum mechanical calculations. We discuss the role of the Brillouin zone and present a quantitative measure which allows for the isolation of the vibrational spectrum of a defect.

Vibrational spectra of large systems

The calculation of the vibrational spectrum of a large molecule or a solid remain computationally challenging when performed at the quantum mechanical level. This originates from the large number of atoms involved in the full system in both cases. In contrast, the feature of interest often involves only a small number of atoms. Within the context of (bio)molecular systems, a large number of methods have been developed to make reduce the computational cost, for example, by simplifying the parts of the system one is not interested in, or even ignoring it entirely (*e.g.*, fragment methods).

In case of a solid, idealized as infinite periodic crystal, one can limit oneself to a single unit cell. The single point spectrum in reciprocal space and the infinity of the system is then converted into a small finite system and a spectrum in each point of a finite size (continuous) Brillouin zone in reciprocal space. This unfortunately ignores the fact that significant Coulomb interactions can be larger in range than the unit cell size.

Water in Molecular crystals and Eu doping of diamond

Water molecules in alpha-lactose crystals are responsible for the typical fingerprint of these molecular crystals in the low THz regime. Simulation of the vibrational spectrum over the first Brillouin zone shows long ranged Coulombic interactions to be present leading to imaginary modes outside the Brillouin zone center. We show that these modes are not a sign of a structural

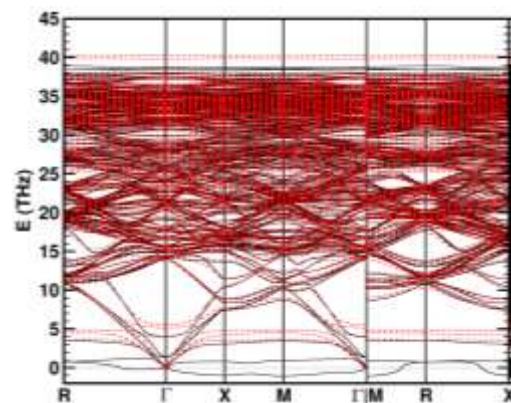


Figure 1: Phonon band structure of Eu doped diamond.

instability of the system, and can be removed through the use of supercell systems. In contrast, for substitutionally Eu-doped diamond, we show that the ground state structure is the result of a strain stabilized Jahn-teller distortion, which presents itself as a clearly identifiable imaginary modes (*cf.*, Figure 1).[1]

Isolating vibrational spectra of defects

Because many defects are very localized in nature, one may expect the vibrational spectrum to be linked to only a small subset of atoms in the system. To this date, a standard strategy of determining the contribution atoms is rather ad hoc, by selecting an increasing number of atoms only considering their relative position with regard to the defect. Using the atom projected vibrational spectrum of a system, we present a quantitative method for determining the defect character of each atom in the system, allowing for a rational incremental improvement of the defect spectrum. We show the qualitative picture to be independent of the system size, allowing one to use small unit cells to determine the relevant defect atoms, which can then be selected for construction of the spectrum in much larger supercells, at much reduced computational cost.[2]

References

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- [2] D. E. P. Vanpoucke, “Fingerprinting defects in diamond:Partitioning the vibrational spectrum,” Submitted, 2019.