

Anharmonic Frequencies: Good, Fast, Cheap - Pick Three

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Abstract

Quartic force fields (QFFs) computed using coupled cluster theory are an invaluable tool in the generation of highly accurate anharmonic theoretical vibrational, rotational, and rovibrational spectra. Despite their broad success, the levels of theory required to achieve reasonable accuracy are too costly to apply QFFs to large molecules like polycyclic aromatic hydrocarbons (PAHs). Since the early 1980s, PAHs have been hypothesized to be the carriers of the unidentified infrared bands (UIRs), which are a set of ubiquitous infrared spectral features found in virtually all kinds of astronomical environments. Their ubiquity makes them very appealing targets for investigation here on Earth since any insight into their spectra can shed light on chemical and physical conditions in the environments where they are observed in space. However, their tendency to aggregate into soot makes them very difficult to isolate experimentally, and their great size makes them impossible to study with high-level theoretical methods like the aforementioned coupled cluster QFFs.

Previous theoretical work has thus turned to density functionals such as B3LYP and small basis sets like 4-31G to compute harmonic frequencies that are then scaled to approximate fundamental frequencies. QFFs with semi-empirical methods offer an even faster alternative to density functional theory combined with explicit handling of anharmonicity effects, but the accuracy decreases concomitantly with the speed increase. One way around this issue is to take advantage of the exposure of the semi-empirical parameters in these methods by optimizing them to minimize the difference between semi-empirical energies and ab initio energies. Training semi-empirical methods in this way on a test set of small molecules for which high-level ab initio QFFs are available should yield methods that are cheaper still than the present standard of B3LYP/4-31G, while also capturing the accuracy of coupled cluster QFFs. Such a method can then be applied to predict the spectra of large PAHs in an effort to elucidate the carriers of the UIRs.