Vibrational effects on electric and magnetic properties of large molecules

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We will present results for zero-point vibrational corrections to a number of different electric and magnetic properties for polyatomic molecules. These results have been obtained using a variation-perturbation approach in which the vibrational wave function is expanded around an effective geometry. At this effective geometry, the leading anharmonic corrections to the vibrational wave function vanishes, and a harmonic oscillator approximation suffices for describing the vibrational wave functions. It can also be shown that higher-order corrections to the vibrational wave function are smaller than if the expansion is carried out around the equilibrium geometry.

The approach has been implemented with the purpose of being applicable to large molecules in a routine manner. This strategy has enabled us to study vibrational corrections to molecular properties of a large number of fairly large molecules, enabling us discover some trends and general observations about the importance and magnitude of vibrational corrections.

We will present the results of several recent investigations of zero-point vibrational corrections to molecular properties such as nuclear shielding constants, magnetizabilities, rotational g tensors, polarizabilities and quadrupole moments. In particular, we will show that the zero-point vibrational corrections to proton shieldings are transferable from one molecule to another, depending only on the functional group to which the the proton is attached. Isotope effects and temperature effects calculated using this approach will also be presented.