Molecular Vibrational Frequencies and the Diagonal Born-Oppenheimer Correction within the Nuclear-Electronic Orbital Framework

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Multicomponent quantum chemical methods, where more than one type of particle is treated quantum mechanically, are employed to investigate nuclear quantum effects. The nuclear-electronic orbital (NEO) method treats select nuclei, typically protons, quantum mechanically on the same level as the electrons [1]. A variety of multicomponent density functional theory and wavefunction based methods have been developed within the NEO framework.

A challenge within the NEO framework is the calculation of molecular vibrational frequencies that include motions of both classical and quantum nuclei for comparison to experimental spectra. To compute such vibrational frequencies, an extended NEO Hessian that depends on the expectation values of the quantum nuclei as well as the coordinates of the classical nuclei is constructed and diagonalized [2]. This extended Hessian is constructed from quantities related to vibrational excitations calculated with multicomponent time-dependent density functional theory. The resulting vibrational frequencies for a series of molecular systems, including those with multiple quantum protons, demonstrate that this method includes the significant anharmonicity in the quantum proton stretching modes.

Another issue that arises within the NEO framework is the validity of the Born-Oppenheimer separation between the quantum protons and the other nuclei. The diagonal Born-Oppenheimer correction (DBOC) in the NEO framework has been derived and applied to a series of molecular systems. The effect of including the DBOC in the NEO potential energy surface for a series of molecules has been found to be negligible, with equilibrium geometries changing on the order of 10^{-4} Å and heavy atom stretching frequencies changing by ~1–2 cm^{-1} per quantum proton that is bonded to a heavy nucleus participating in the vibrational mode. These results suggest that inclusion of the DBOC does not significantly impact the potential energy surface.

References

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2. Y. Yang, P. E. Schneider, T. Culpitt, F. Pavošević, and S. Hammes-Schiffer, *J. Phys. Chem. Lett.* **10**, 1167 (2019).