Size-consistent vibrational many-body methods

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Any many-body method should be designed to give extensive ground state energy (grows linearly with the system size) and intensive transition energies (independent of the system size) to be applicable to large systems. Harmonic approximation for vibrations satisfies these criteria, and can be attributed as a size-consistent method; however it cannot describe phonon coupling, high temperature heat capacity, thermal expansion and conductivity, even qualitatively. Vibrational many-body methods that incorporate anharmonicity have been well established for small molecules, but these methods are not directly applicable to larger systems since they are not designed to be size-consistent. Analogues to the crystal-orbital methods in electronic structure theory, we generalized the formalism of the vibrational self-consistent field (VSCF), vibrational Møller–Plesset perturbation (VMP), and vibrational coupled-cluster (VCC) methods on the basis of a quartic force field (QFF) in normal coordinates. Consequently, numerous terms that have nonphysical size dependence are identified algebraically and eliminated, leading to compact and strictly size-extensive equations for the ground state energy. We recently implemented the size-consistent VSCF (XVSCF) method for finite systems. XVSCF requires only quartic force constants of the \( F_{ijij} \) type, which reduces the scaling from quartic to quadratic, spontaneously. Moreover, the effective (mean-field) potential of XVSCF felt by each mode is revealed to be harmonic, making the XVSCF equations subject to a self-consistent analytical solution without matrix diagonalization or a basis-set expansion, which are necessary in VSCF. Accordingly, XVSCF is nearly three orders of magnitude faster than VSCF implemented with the reduced set of force constants. Yet, XVSCF and VSCF are expected to yield comparable results for larger molecules, implying the inclusion of unnecessary, nonphysical terms in VSCF. This is shown numerically by a toy model of a linear chain. Its efficiency, and size-consistent design allows XVSCF to be applicable for perfectly periodic systems like polymers and solids as well as very large systems such as biomolecules and proteins. Despite of its size-consistent design and efficiency with respect to the VSCF method, XVSCF still lacks accuracy due to the mean-field treatment. Post-XVSCF methods are necessary to include the missing vibrational correlation, and implementations of these methods are currently underway in our laboratory. Recent advances in this respect will also be presented.