

Quantum Chemistry for Solids — Vibrational Many-Body Methods

There are various software packages available to perform ab initio calculations for electronic and vibrational properties of molecules, however when solids are considered, DFT for the electronic and harmonic approximation for the vibrational structure are generally the only choices. Our grand objective is building a software designed for extended systems such as polymers, slabs, and solids with similar capabilities to the programs existing for molecules.

For the electronic structure, our group is working on two different yet complimentary approaches which are basically classified as localized and delocalized methods.¹

For the vibrational structure, which is my research area, we aim to go beyond the harmonic approximation which is incapable of explaining phonon coupling, high temperature heat capacity, thermal expansion and conductivity, even qualitatively. There are two challenges in that regard, first is building up the necessary size-extensive many-body theories and second is implementing them in a cost-efficient fashion.

We established the formalism of the size-extensive vibrational many-body methods for extended systems by generalizing 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.^{2,3} Numerous terms in the formalism of VSCF that have nonphysical size dependence are eliminated, leading to compact and strictly size-extensive equations for the ground state energy. We recently implemented the size-extensive VSCF (XVSCF) method for finite systems.⁴ Apart from being the only size-extensive variational mean-field method, XVSCF also reduces the scaling of the calculation from quartic to quadratic, since it only requires certain type of force constants. 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. The codes for these methods are built into a software package called MaVi and will be ultimately available to the academic community.

1. S. Hirata, O. Sode, M. Keçeli, and T. Shimazaki, "Electron correlation in solids: Delocalized and localized orbital approaches," a chapter in *Accurate Condensed-Phase Quantum Chemistry* edited by F. Manby, p.129--161 (CRC Press, Boca Raton, 2010).

2. S. Hirata, M. Keçeli, and K. Yagi, *The Journal of Chemical Physics* 133, 034109 (2010), "First-principles theories for anharmonic lattice vibrations."

3. M. Keçeli, S. Hirata, and K. Yagi, *The Journal of Chemical Physics* 133, 034110 (2010), "First-principles calculations on anharmonic vibrational frequencies of polyethylene and polyacetylene in the δ approximation."

4. M. Keçeli and S. Hirata, *The Journal of Chemical Physics* 135, 134108 (2011), "Size-extensive vibrational self-consistent field (XVSCF) method."