

## 結晶の量子多体理論

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### Quantum Many-Body Theories for Crystals

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Three of more of the following topics will be covered in my talk:

(1) **Thermodynamic limit.** Why is energy extensive and is application of thermodynamics to chemistry valid? It has taken 40 years for the finest mathematicians to complete the proof of the extensivity of energy or, equivalently, the existence of thermodynamic (infinite-volume) limit of energy density. I will offer an alternative, more accessible explanation (if not a rigorous proof) of the extensivity of energy for electrically neutral, metallic and nonmetallic crystals by establishing the same for its individual energy components.

(2) **Size-consistency theorems.** On the basis of the findings described in (1), I will present the design guidelines of size-consistent electronic and vibrational many-body methods. They are as follows: The significance of the distinct use of the intermediate and standard normalization for extensive and intensive operator amplitudes, respectively; The extensive and intensive diagram theorems, which serve as the unambiguous diagrammatic-topological criteria for determining size consistency; The extensive-intensive operator consistency theorem, which stipulates the balance between the extensive and intensive operators. Charge-consistent redefinitions of integrals are also given on this basis. (With Dr. Yu-ya Ohnishi.)

(3) **Size-extensive vibrational self-consistent field method.** I will introduce diagrammatically size-extensive vibrational self-consistent field (XVSCF) methods. XVSCF requires only even-order force constants of certain types for anharmonic frequencies and additionally odd-order force constants of some types when zero-point averaged geometries are desired. Its mean-field potential felt by each mode is shown to be quadratic, rendering the effective one-mode Schrödinger equations be solved analytically without a basis set expansion or matrix diagonalization. XVSCF is many orders of magnitude faster than VSCF, while the latter is shown to reduce to the former in the bulk limit. (With Dr. Murat Keçeli and Matthew Hermes.)

(4) **Vibrational second-order Dyson methods.** I will introduce diagrammatic vibrational second-order perturbation methods based on XVSCF references, namely, the Møller–Plesset partitioning of the Hamiltonian. I will show that the diagonal Dyson self-energies in the second order perturbation theory are accurate estimates of the anharmonic vibrational corrections to XVSCF zero-point energies and transition frequencies. The results obtained from self-consistent solutions of the Dyson equation resist divergence in the presence of strong Fermi resonance, which is typical of state-to-state applications of vibrational perturbation theory. A set of diagrammatic rules for the vibrational diagrams will be proposed. (With Matthew Hermes.)

(5) **Finite-temperature many-body perturbation theory.** Kohn and Luttinger showed that the conventional finite-temperature extension of many-body perturbation theory had the incorrect zero-temperature limit in metals and, on this basis, argued that the theory was incorrect. I will show that this inconsistency arises from the non-inclusion of temperature effects in the energies of the zeroth-order eigenstates of perturbation theory, which causes not only the Kohn–Luttinger conundrum but also another inconsistency, namely, different rates of divergence of correlation energy in metals between the zero- and nonzero-temperature formalisms. I will propose a new, renormalized many-body perturbation theory, which is shown to have the correct zero-temperature limit and the same rate of divergence in metals as the well-established zero-temperature counterpart and is, therefore, argued to be the correct theory. With this theory implemented for one-dimensional crystals, I will address Peierls' transitions in polyynes and polyacetylenes. (With Dr. Xiao He.)

(6) **Predictive calculations for molecular crystals.** I will present the applications of embedded-fragment, linear-scaling, electron-correlation methods to the electronic and (anharmonic) vibrational structures of solid hydrogen fluoride under pressure, solid carbon dioxide under pressure, and proton-disordered, hexagonal phase of ice (phase Ih). I will address the crystal structures of these crystals, their pressure dependence and solid-to-solid phase transition, the assignments of infrared and Raman bands and their crystal-field splitting, phonon dispersion and density of states, the interpretation of inelastic neutron scattering, and the pressure dependence of Fermi doublets in carbon dioxide as a spectroscopic geo-barometer. (With Olofsson Sode, Dr. Xiao He, and Dr. Sotiris Xantheas.)

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