Quantum chemistry for crystals

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

(1) Thermodynamic limit. Why is energy extensive and is an 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: the kinetic, Coulomb, exchange, and correlation energies.

(2) Size-consistency theorems. I will discuss how this analysis guides the design of size-consistent electronic and vibrational many-body methods. Our findings 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 criteria for determining size consistency of a method for extensive and intensive quantities; The extensive-intensive operator consistency theorem, which stipulates the balance between the determinant spaces reached by extensive and intensive operators. A charge-consistent redefinition of Fock integrals is also proposed on this basis, which is inevitable from a formal size-consistency viewpoint and also has certain practical advantages. (With Dr. Yu-ya Ohnishi.)

(3) Predictive calculations for molecular crystals. I will present the applications of fragment-based, linear-scaling, many-body perturbation theory (MBPT) to the electronic and (anharmonic) vibrational structures of three-dimensional solid hydrogen fluoride and carbon dioxide under pressure. On the basis of these predictive calculations, I will address the crystal structures of these solids, 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 as well as the interpretation of inelastic neutron scattering, and the pressure dependence of Fermi doublets in carbon dioxide as a spectroscopic geo-barometer. (With Olaseni Sode.)

(4) Size-extensive vibrational self-consistent field method. I will introduce the diagrammatically size-extensive vibrational self-consistent field (XVSCF) method. 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 Murat Keçeli and Matthew Hermes.)

(5) New algorithms for crystal orbital theory. A distance-based truncation of lattice sums of interactions in a local basis corresponds, via a Fourier transform, to down-sampling of wave vectors in reciprocal space integrations. I will introduce two down-sampling schemes, the mod-*n* (uniform down-sampling) and log-*n* (exponential down-sampling) methods, which have made second-order MBPT and even third-order MBPT and coupled-cluster singles and doubles (CCSD) routine for at least one-dimensional solids for the first time. I will also discuss a reciprocal space hybrid of second-order MBPT and CCSD, which applies the latter only for bands near the Fermi surface, potentially resolving both the cost issue of CCSD and the divergence problem of MBPT in metals. (With Dr. Yu-ya Ohnishi.)

This work has been supported by the NSF, DOE, Camille & Henry Dreyfus Foundation, and Research Corporation for Science Advancement.