Local correlation-energy increments for solids – ground and excited states

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Possibilities to determine solid-state properties by means of many-body expansions in terms of finite subsystems are critically reviewed. Different variants are shown to be needed for molecular crystals, ionic solids, and semiconductors.

At the example of LiH, it is demonstrated that milli-Hartree accuracy for the cohesive energy, E_{coh}, can be obtained both for the Hartree-Fock and the correlation piece of E_{coh}, by expansions based on suitably prepared zeroth-order model systems [1].

Difficulties due to delocalization and transferability problems for incremental expansions in metals are discussed, and several suggestions to overcome these problems for group 1, 2 (11, 12) metals are compared [2].

Finally, calculation of electron correlation effects for excited states and band structures within incremental approaches is considered. While for localized excitations a direct determination of energy increments with extension of an initial orbital space is possible [3], increments for both diagonal and off-diagonal matrix elements between intermediate quasi-particle states are needed in the delocalized case. Two possible routes for the latter purpose ('correlate then localize' and 'localize then correlate') are critically compared, in the light of new results [4].

[1] Stoll, H., Doll, K. *J. Chem. Phys.*, 136:074106, 2012.

[2] Paulus, B., Stoll, H. in *Accurate Condensed-Phase Quantum Chemistry*, Manby, F.R. (ed.), CRC Press, p. 57, 2010; Stoll, H., Doll, K. *Chem. Phys. Lett.*, 501:283, 2011.

[3] Mata, R.A., Stoll, H. *J. Chem. Phys.*, 134:034122, 2011.

[4] Stoyanova, A., Hozoi, L., Fulde, P., Stoll, H. *Phys. Rev. B*, 83:205119, 2011; Stoll, H., Mitrushchenkov, A.O., Werner, H.-J., Stoyanova, A., Hozoi, L., Fulde, P. *J. Chem. Theory Comput.*, submitted.