Breaking covalent bonds in the context of the many-body expansion

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The Many-Body Expansion (MBE) is a concept based on combinatorial mathematics and is usually employed to count the number of elements in the union of finite sets. In 1970 was applied for the first time to chemical physics problems considered individual water molecules as “bodies” connected via hydrogen bonds as it was used to estimate the non-additive three-body term by partitioning the energy of a water trimer.[1]

The purpose of the MBE in quantum chemistry is twofold: in analysis, to understand the composition of interatomic and intermolecular interactions, and in practice, to facilitate calculations of large systems.[2-3] The application of MBE in covalent structures, especially metallic ones, is full of challenges due to the complex electronic structure and short-range interactions exhibited by such systems. Both dynamic and non-dynamic correlation may be necessary to capture the multi-coordinated bonding of metals, in addition to considerations of different spins among the intermediate structures of open shell metals.[4]

In this presentation, a novel implementation of the MBE to account for the breaking of covalent bonds is analyzed. The central concept of the new implementation is the *in situ* atomic electronic state of an atom in a molecule that casts the one-body term as the energy required to promote it to that state from its ground state.[5] The rest of the terms correspond to the individual diatomic, triatomic, etc., fragments. Here, the MBE for the 1st and 2nd group metals and for the XH_n series, X = C, Si, Ge, Sn and n = 1–4) is examined and analyzed via coupled cluster, perturbation theory, and multireference configuration interaction methodologies.[5-7]

References:
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