Translationally transformed coupled-cluster theory in a local basis for periodic systems

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There are a lot of interesting problems in surface chemistry where quantum chemistry could give great insight, like reaction mechanisms in heterogeneous catalysis, the effect of surface functionalization on semiconductors, or the influence of defects on the reactivity of crystal surfaces.

Plane wave based methods applied to crystals cannot handle problems that are localized in nature like surface defects and adsorbates. On the other hand, molecular electronic structure techniques, which describe these effects and the locality of the electronic correlation well, are too computationally expensive to use on these systems.

A new approach based on coupled-cluster (CC) theory is proposed. This scheme reformulates the electronic amplitudes to incorporate the periodicity of crystals *and* the locality of electronic interaction. This avoids the calculation of redundant amplitudes. Perfectly periodic surfaces are envisioned as reference wavefunctions for localized defects and chemical reactions.

The working equations are derived starting from the amplitude equations of conventional CC on an infinite system and rearranging them such that the distance to an anonymous cell is an explicit degree of freedom. The formally infinite summations can be truncated by systematically neglecting numerically insignificant amplitudes.

The theory and the details of the computer implementation will be presented, as well as first tests of the equations on 1-dimensional electronic systems.