Cluster embedding method with non-orthogonal wave functions

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When we theoretically study processes in large or infinite electron systems we have to treat the whole quantum system as two subsystems: small fragment of the system (cluster) and the remaining part of it. Problem "cluster in the field of the rest of system" is successfully solved in the framework of embedded molecular cluster (EMC) model[1] with *orthogonal* wave functions. Unfortunately, standard realization of EMC model leads to well-pronounced boundary effects[2]. To overcome limitations of standard EMC model, we have developed modified EMC model[2] treating cluster embedding problem in the frameworks of one-electron approximation with *non-orthogonal* wave functions. We have demonstrated[2] that our embedding method radically reduces boundary effects.

Further applications require generalization of our embedding approach on the case of DFT Kohn-Sham one-electron equations. We demonstrate[3] that our variation procedure is compatible with Kohn-Sham method and may be combined with time-dependent DFT and quantum transport theory.

We have compared, too, our embedding equations with the equations theory of pseudopotentials gives[4]. Among other results we have established that generalized Phillips-Kleinman equations may be transformed to eigenvalue equations[4].

To use our cluster embedding method for theoretical treatment of processes in quantum systems, we should overcome limitations of one-electron approximation. It may be done by configurations interaction (CI) and perturbation theory (PT) methods if electron transitions are described correctly. For this purpose we need occupied and vacant cluster states of the same localization. Our initial embedding equations[2] are established to give delocalized vacant states[5]. To get the same localization degree for the both occupied and vacant states, modified equations are proposed[5]. As the result, initially developed for Hartree-Fock calculation scheme, our embedding method became compatible with DFT, CI, and PT for the both ground and excited states.

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