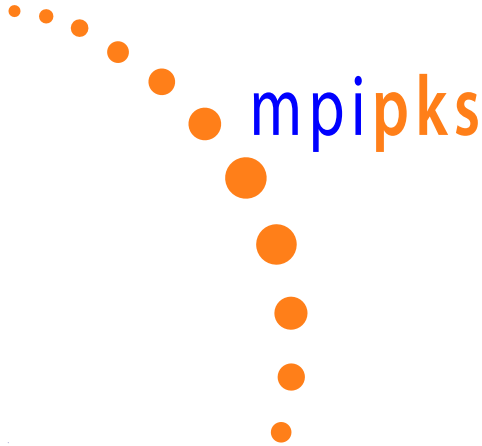

Development of a wavefunction-based ab-initio method for group II metals applying the method of increments

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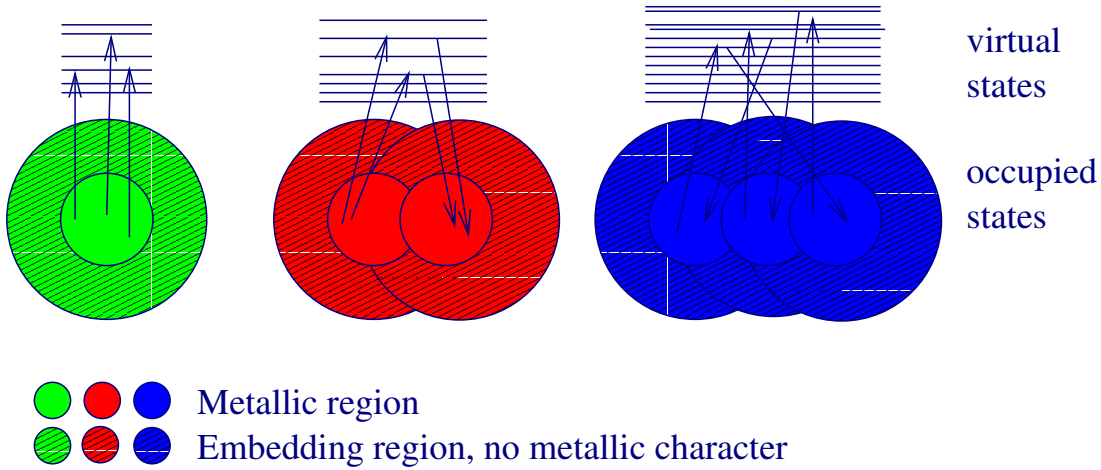
1 Method of increments for metals

Idea: Electronic correlations are of short range

Many-body expansions of the correlation energy of the infinite system in terms of localized entities i, j, k,



Correlation energy for the infinite system per unit cell:

$$E_{\text{corr}} = \sum_{i \in \text{u.c.}} \epsilon_i + \frac{1}{2!} \sum_{\substack{i \neq j \\ i \in \text{u.c.} \\ j \in \text{solid}}} \Delta\epsilon_{ij} + \frac{1}{3!} \sum_{\substack{i \neq j \neq k \\ i \in \text{u.c.} \\ j \in \text{solid}}} \Delta\epsilon_{ijk} + \ldots$$

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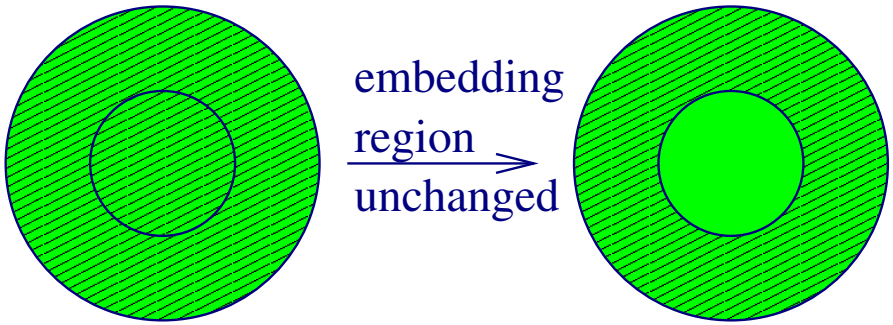
1.1 Embedding scheme for metals

1. Calculation with only s functions on all atoms;
   Localization of the orbitals

   $\Rightarrow$ Localized orbitals mimic the electrostatic and van der Waals interaction,
   no metalicity described



Metallic region
Embedding region, no metallic character

2. Reoptimizing the orbitals on the central part with better basis functions, where the surrounding kept unchanged.
   Metallic character can be developed in the central part.
   - No charge flow to the surface of the cluster
   - Localized orbitals on atoms to be correlated
   - Metalicity described with incremental scheme

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2 First application to mercury

- Mercury is not bound at the HF level, metallic binding due to correlation
- Very good agreement of the cohesive energy with the experimental value

- Experimental rhombohedral structure is the ground-state structure:

  Deviations for the lattice parameters below 1.5%

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3 Content of the Project

- Application of the methods to other metals: Magnesium and Beryllium
- Comparison of different embedding schemes for metals
- Test of localized non-orthogonal orbitals
- Incremental expansions relying on Kohn-Sham orbitals
- Multi-reference incremental scheme for quasi-degenerate metallic bands