Mosaico: A technique for linear-scaling energy optimization in semiempirical, HF, and DFT calculations

L. Seijo

Departamento de Química, Universidad Autónoma de Madrid, 28049 Madrid, Spain.

A method is presented for the energy minimization step of semiempirical and first-principles Hartree-Fock and DFT calculations on very large molecules or solids, whose computational demands grow linearly with the size of the system. A few monitoring calculations are presented that show some potentiallities and limits of the method: Extended Hückel calculations and DFT calculations performed with the Siesta code (periodic boundary conditions, LCAO using atom centered numerical basis sets, linear-scaling computation of the one electron effective Hamiltonian matrix).

The Mosaico method [1] is based on the on-the-fly variational calculation of the localized orbitals (LMOs) of any localization method of choice; the LMOs are represented with orbital-specific basis sets. This basic strategy makes the method useful only to systems with not a very small gap. The full set of LMOs of a large molecule is seen as an orbital mosaic where each tile or *tessera* is made of only a few LMOs. The *tesserae* are computed out of a set of embedded cluster pseudoeigenvalue coupled equations which are solved in a building-block self-consistent fashion. In each iteration, the embedded cluster or embedded *tessera* equations are solved independently of each other and, as a result, the method is parallel at a high level of the calculation.

In addition to full system calculations, the method enables to perform simpler, much less demanding embedded cluster calculations. In these, one profits from the transferability of the LMOs of a given localization method between similar molecules and variationally computes only a fraction of the LMOs, while the rest are taken from a similar system and frozen.

[1] L. Seijo and Z. Barandiarán, J. Chem. Phys. **121**, 6698 (2004).