

## **BOSS: A bond order dissection approach for efficient electronic structure calculations**

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### **Summary**

The coupling of the micro- and the mesoscale of chemical reactions is currently a field of intensive research. Where the microscale is the realm of quantum mechanical effects, the mesoscale is described by statistical mechanics and macroscopic thermodynamics. Numerically, the microscale is usually treated with Hartree-Fock (HF), Coupled Cluster (CC), Configuration Interaction (CI) or Density Functional Theory (DFT) methods that yield approximate solutions to the underlying quantum-mechanical (QM) Schrödinger equation (SE). The mesoscale on the other hand is examined by classical molecular mechanics (MM) methods that use Newton mechanics with empirically fitted potentials.

In this field the ultimate goal would be a seamless coupling of quantum mechanical computations where needed and classical molecular mechanics simulations where sufficient. Any starting point of such an approach must be the general Schrödinger equation for the electrons and for the nuclei of the system under consideration. It however has a dimensional complexity of  $3(N + M)$ , where  $N$  denotes the number of electrons and  $M$  the number of nuclei. This renders any direct numerical treatment impossible due to the curse of dimension and we have to resort to model approximations. As a first step, in the Ehrenfest and Born-Oppenheimer molecular dynamics (MD) approaches, the wave functions of the nuclei and electrons are separated, the subsystem of the nuclei is treated classically with Newton mechanics and the remaining  $3N$ -dimensional electronic Schrödinger equation is further approximated by some of the aforementioned methods. The potential needed for Newton mechanics is obtained from the electronic solution by the Hellmann-Feynman theorem. Then, there are numerous approaches that concentrate on the locality of electronic wave functions or the interface problem between reaction site (QM) and environment (MM).

We propose a new more general coupling method, enabling both linear scaling and reaction site-environment schemes. Generally, the ansatz is sparked off the idea that also made empirical many-body potential such as Tersoff's successful, where the energy and the forces of an atom are assumed to depend on its local coordination. We use this chemical knowledge between nuclei to sensibly neglect terms in an ANOVA-like decomposition of the  $R^{3(M+N)}$  space of the Schrödinger equation. We exploit locality, however not by a cutoff radius, but instead implicitly when dissecting the inherent bond structure of a molecular system. To this end, we employ molecular graph theory and modern graph algorithms to create the local subproblems as overlapping fragments of the molecular system. Hydrogeni-

sation is used to close shells and saturate cut bonds. The local subproblems may be evaluated with any of the aforementioned approximative QM techniques. Thus, the  $3(M + N)$  complexity is broken down linearly to those of  $i$  components with an upper bound  $\max_i \{M_i^{(k)}\}$  controlled by a single parameter  $k$  that we coin the *bond order* of the approximation. Specifically, this combines the smaller prefactor of the cubic scaling methods with a general linear scaling behaviour in electronic structure calculations. We tested the implementation on a small set of molecules and carbon and boron-nitride nanotubes and come to promising results.

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