Multiscale Computation in Chemistry

The quantum-mechanical equations that govern molecular chemistry are fully known. If efficient solvers were available, all chemistry could in principle be computerized, yielding detailed understanding of molecular and macromolecular structures and interactions.

The basic reasons for the immense complexity of molecular computations are the very *high dimensionality* of the fundamental equations, and the huge *scale gap*, that exists between the microscopic scale at which the physical laws (or even their low-dimensional approximations) are given and the macroscopic scale of the phenomena we wish to understand. This gap implies, first of all, a huge number of *variables* (e.g., many gridpoints in electronic-structure calculations, or many atoms in molecular dynamics simulations) and even much larger number of *interactions* (e.g., each atom interacting electrostatically with each other).

Furthermore, this gap involves other *scale difficulties*. First, the simulations are limited to steps at the scale of the fast atomic vibrations, roughly 10^{-15} of a second. Moreover, the molecular energy landscape includes many basins with large *energy barriers* between them. Huge number of simulation steps are needed per each switch to a new basin. This difficulty is compounded many times over since small-scale energy basins are nested within larger-scale basins, and so on at all scales.

In various areas of physics and engineering, our past work has shown that all such scaling difficulties can be overcome by *multiscale* computational methods.

Our research consists of isolating these complexity factors and constructing the mujltiscale methods designed to overcome each of them, in the following areas:

1. Multiscale path integrals. A general approach to solve the $3N$-dimensional Schrödinger equation for an N-particle system is by Monte-Carlo methods, using Feynmann path integral representation of the time evolution operator. The main problem with this approach is the extreme oscillatory nature of the path contributions. A multiscale packing of paths, organized in a multigrid structure, can eliminate the problem, using also a multigrid method for instantly updating large-matrix determinants.

2. Multigrid quantum chemistry. A very good low-dimensional approximation used in ab-initio quantum chemistry is the nonlinear Kohn-Sham system, in which a large number N of eigenfunctions (representing N electrons) need be calculated for the 3D differential operator $-\Delta + V$, whose potential V at each point depends on the positions of nuclei and on global integrals involving the eigenfunctions. A multiscale collective representation of the eigenbasis has been developed, eliminating the need for a separate representation of each eigenfunction and for orthogonalizing it with respect to all others. Together with multigrid solvers for the equations associated with the global integrals, the entire problem can be solved in $O(N \log N)$ operations, even when the external calculation of positioning the nuclei to achieve minimal total energy is included.

3. Multiscale molecular dynamics. Even with the vastly simplified models of molecular dynamics, computing costs rise very steeply with problem size, restricting the simulations to relatively small systems and to Monte-Carlo steps many orders of magnitude smaller than needed. This steep rise can be radically reduced by *multiscale Monte-Carlo*, which involves renormalization-type derivation of increasingly coarser molecular Hamiltonians. Each coarsening step involves:
(A) Decomposing long-range interactions into the sum of smooth interactions and local ones. The smooth interactions can be transferred directly to the coarse level.
(B) All the local coarse-level interactions are then constructed by iteratively comparing local simulations at the coarse level with such simulations at the fine level.

As a result of the multiscale algorithm it is expected to achieve the following:

- *There is no need for a huge number of variables*, since the coarse-level *equations* (unlike the large-scale *solutions*) can be derived just by local simulations at *representative* small volumes.

- *No need for summation of long-range interactions*.

- *No slowness*: Large equilibrium-simulation steps can be done at the coarse levels, effectively averaging over smaller-scale vibrations and attraction basins.

- Proceeding this way to sufficiently coarse levels, the *macroscopic equations* of the material should emerge, which is often the very objective of the entire calculations.