Description of the Path Integral MD and Path Integral Ab Initio MD

Basic overview: Path Integral MD or Path Integral Ab Initio MD includes nuclear quantum effects on a single ground state electronic surface. Thus, phenomena like tunneling and zero point energy can be investigated. However, motion on multiple electronic surfaces and phenomena like intersystem crossing cannot be treated at present. Path Integral QM/MM can be performed but will not be discussed here.

Path Integrals are a mathematically exact formalism that maps quantum mechanics onto the classical mechanics of ring polymers. Assuming Boltzman statistics, each particle in the system expanded from a single point to a P-bead ring polymer with harmonic nearest neighbor internal interactions. The particles interact amonst themselves via the usual potential reduced in strength by P (dividing the potential by the scalar double, P). These interactions are "bead-order" in that bead "k" of particle 'i' interacts with bead "k" of particle "j", only! Thus, the system is replicated, creating P copies with almost perfect parallelization (except for the internal interactions).

In *ab-initio* path integral molecular dynamics, P-independent *ab-initio* calculations are spawned. They do not interact with one another. They each interact only with their "bead". That is, the "k" *ab initio* calculation has an external potential formed by considering the "kth" bead of all the particles. The coupling is induced indirectly through the harmonic interactions of the polymer chains!!

The basic components of a Path Integral or *ab initio* Path Integral calculation are:

1. An external interaction potential for the atoms/ions (Coulombs Law, Lennard-Jones interactions, empirical interactions from a force field). Each atom "i" of bead "k" interacts with atom "j" of bead "k" as they normally would in standard classical calculation.

2. Boundary conditions of the problem used to treat the long range forces. Long range force routines such as PME or Ewald are performed P-times, once for each set of particles with the same bead number.

3. If an Path Integral *ab initio* calculation is required, P ab initio calculations are created, 1 for each set of particles with the same bead number "k".

In order to perform a Path Integral calculation, the following data is needed:

1. P sets of electronic orbitals which, ultimately, are described in terms of a set of coefficients for expansion in a basis set (plane waves). For Car-Parrinello calculations, we also need P sets of fictitious velocities and forces for the coefficients.

2. P sets of positions, velocities, and forces for atoms.

The basic steps for Path Integral MD are as follows:

1. Perform P-independent ab-initio calculations and get forces on coefs and particles.

2. Perform P-independent classical force evaluations and get particle forces.

3. Get the intrapolymer forces N independent calculations of $P-1$ nearest-neighbor beads where N is the total number of atoms in a single classical system.

4. Numerical Integration of the particles occurs in a coordinate system formed by N independent transformations of size P. Both the particle positions and the particle forces must be transformed. The computational cost of the transformation is of order "P" in scalar.