Q&A Lecture 9

In computer simulations of Car-Parrinello, is the electronic mass treated as a hyperparameter, that is increased as much as possible, to get the largest timestep, or is the physical mass used?

It's a hyperparameter that is chosen small enough to ensure that Born-Oppenheimer is mimicked and large enough not to reduce the time step too much.

Also, isn't Born-Oppenheimer much less expensive computationally than CP, since the minimization should take less steps than calculating the evolution of the densities?

It really depends on how many iterations are needed in the non-linear conjugate gradient minimization in BO. This, in turn, depends crucially on the initial guess in the iterative algorithm used for the minimization and on the tolerance imposed on the result. CP is less expensive (and faster, can be up a factor of 10 for fixed total time) but BO is more accurate if the tolerance is small enough

Generally, is Car-Parrinello method better than Born-Oppenheimer approximation in terms of the accuracy?

No. If the Born-Oppenheimer minimization is accurately converged, then the resulting dynamics is more accurate. The finite mass of the electronic degrees of freedom in Car-Parrinello implies that - in particular for long runs needed to get good statistical averages - there is a violation of the adiabatic condition and "tricks". In practice, however, the observed differences are not very large and Car-Parrinello continues to be a very popular algorithm.

Are there any criteria to adopt each method?

Mostly cost: Car-Parrinello is cheaper so, if the size of the system and the runtime need to be large, it is preferred. In all other cases, Born-Oppenheimer is selected.

What kind of expressions the inertia parameter are?

Not sure what you mean with expression. The meaning of the inertia parameter is that they are quantities that play the role of a mass for variables that are not positions. This means that, when we construct evolution equations for, say an angle or (as in our case) variables that represent coefficients in a basis expansion, we consider their acceleration (i.e. second time derivative, that will have units of [unit of the angle/coefficient]/time^2) and to obtain a force we have to multiply by a quantity that will lead us to the units of a force for the product (these will not, in general, be kg). The physical meaning is that they represent the "resistance" (inertia) of the variables to changes in the velocities.

About MaZe, I am not sure if I understand well what this constraint force means, or where it comes from. If it is a force that is « invented » (non-existent in an actual real-life system), wouldn't it mess up the calculations, giving wrong results?

I have had a few questions along the same lines, so we'll discuss it more in detail in the next class. The "magic" of the algorithm is exactly that this force does not bias the ionic dynamics — good question, though.

I don't understand the constraint in the MaZe dynamics, how is it different from the minimization of the energy with respect to the density in Born-Oppenheimer dynamics?

The condition is the same. The key difference is that the electronic coefficients are treated as dynamical variables in MaZe and this has a number of advantages. There have been a few questions along these lines, so we'll discuss it more in detail in the next class.

Why do we choose to discretize the density function specifically into a plane wave representation?

I used the plane waves because they are part of the most used representation, in particular, for extended (solid) systems where electrons are delocalized. In actual calculations, one takes into account that different terms in the energy functional are represented more efficiently in different basis - coordinates and plane waves - so one changes basis in the code (like we saw in SOFT). For molecular systems, Gaussian localised basis are also used.

Why is MeZe method more advantageous over Car-Parrinello?

We'll discuss this more in detail in the next class. In short: the mass of the electronic degrees of freedom is set to zero, leading to complete adiabatic separation of the ionic and electronic degrees of freedom; the time-step does not need to be reduced compared to the ionic one; it can be proven that the correct ionic statistical ensemble is sampled.

How do you properly choose \mu, and how does the considered system influence this choice?

\mu needs to be sufficiently small to enforce (approximately) adiabatic separation. The latter implies that typical timescales of the motion of the ions are (a) smaller and (b) sufficiently different from those of the electronic degrees of freedom. One observable that provides access to these timescales (via frequencies) is the Fourier transform of the velocity time-correlation functions (we'll see more about this type of quantities in future lectures), known as the power spectrum. So, one can compute the power spectrum and look at the positions of peaks corresponding to ionic motions and electronic ones and assess (a) and (b).

How does the inability of the Car-Parrinello method to capture the correct physics affect the types of systems that can be studied using Car-Parrinello Molecular Dynamics compared to Born-Oppenheimer Molecular Dynamics?

Born-Oppenheimer is preferred whenever the size and time scales that need to be addressed is "small" (up to a hundred ions, nanoseconds). Car-Parrinello is cheaper and therefore used when larger systems are studied. The main pathology of CP is a shift in the infrared spectra of the ions that depends on the mass.

How do we incorporate the total electron number constraint in all three methods? In the BOMD approach, we can incorporate it using Lagrange multipliers, as discussed previously.

But how would we do so in the Car-Perrinello and Mass Zero Constraint Dynamics approaches?

Lagrange multipliers can (and are) used also in Car-Parrinello and MaZe.

How would we find a good basis for rho in Born-Oppenheimer approach?

There are two aspects to keep in mind. The first one is that we have to compute the various terms in the energy functional that depend on the density. The basis is then chosen depending on what is the most convenient to compute the different terms. Typically, this implies using the (discretized) coordinate representation for some terms and the basis of plane waves for others. One moves back and forth between the two via Fast Fourier Transforms (like we saw in the SOFT algorithm). The second aspect depends on the system: coordinates are “always” good, but plane waves may not be the most convenient choice. For example, they work well for solids - in which the electronic charge density is delocalised across the system - but not so well for molecular systems. For the latter, the electronic charge density has different localisation sites, typically close to ionic positions. In this case, a more convenient basis is that of Gaussians centered on the ionic positions.

According to the variational principle, we have $\mu = \delta E[\rho] / \delta \rho(r)$. According to the notes you put on moodle, $\mu = V_ext + delta F_TK[\rho] / delta \rho$. I didn’t fully understand the physical significance of the Lagrange multiplier μ. It seems that it’s the combination of the external potential and a potential related to F_HK. Since F_HK is a universal potential (i.e., system independent), if I understand correctly, μ is not related to the correlation between electrons? Is there a more intuitive explanation for the physical significance of \mu?

\mu is the Lagrange multiplier that intervenes (as a contribution to the intensity) in the force (and the related work) needed to keep the number of electrons in the system constant. You can read it in the other sense and say that to change the number of electrons you have to provide a work equal to “minus” the Lagrange multiplier. This estabishes a connection between \mu and the chemical potential for the system.

Why do we invent a second order differentiable equation for evolution of rho_G? Our goal is to find the solution for \partial E[\rho]/ \partial \rho_G = 0, i.e., to minimize E[\rho] with respect to rho_G. Why don’t we just use the first order differetiable equation, i.e., \partial E[\rho]/\partial \rho = \mu \dot{\rho_G}, which is just the formula of gradient descent algorithm. And 1/\mu is the learning rate.

A second order dynamics provides more flexibility in the path to solution. E.g. can you get our of “small” energy minima on the way to a global minimum using a first order dynamics? Note that the expensive part of the algorithm is in both cases the calculation of the force so a first order does not give an advantage in this respect.

How can we know that applying some fictional mechanics actually works in calculations?

Theory! One can study the formal properties of the fictional mechanics and understand, for example, what is the statistical ensemble that it samples.

Couldn't this method be applied in many problems?

Indeed, there is a family of algorithms know as extended Lagrangian methods that use (variations on) the idea. We'll see another example in class.

I don't understand how adding an extra term (the constraint) allows us to force the system to be in the electronic ground state. Why do we need to use a mass that takes a value of zero and how does that constrain the system?

The constraint imposes that the electronic variables minimize the energy functional. The mass must be taken to zero to ensure that this constraint does not bias the ionic motion. Since there have been several questions along these lines, I'll discuss MaZe (that goes beyond CPMD) in the next class.