

Q&A Lecture 6

What are the 'usual' error margins on the check of the energy? I can imagine that some systems have to be monitored much more closely than others as a result of stiffness. Can you provide some order of magnitude on what precision we would deal with? (In a general sense, not even very exotic systems)

Acceptable relative errors (as the one defined in class) on the energy are of the order of 10^{-4} - 10^{-5} . This is a very general rule applied to systems varying from simple gas to proteins. The stiffness of the potential, i.e. the maximum frequency of the motion, is a relevant parameter in determining a reasonable size of the time step. Typically, Δt is chosen 10 times smaller than the fastest time scale in the system. This provides a good "initial guess" for the time step that then is verified via the energy conservation criterion that we discussed.

The systems we are now looking at are all nicely behaving diatomic systems. However, let's say we look at more exotic examples, e.g. nuclear fission, Born-Oppenheimer would start to fall apart since nuclei are now suddenly no longer part of the same system. Can we recover anything from the algorithmic approach or is this so far out that we have to devise whole new ways of finding solutions?

Although the example considered in class was a diatomic, our methods are valid for more complicated systems and also allow for dissociation as illustrated via the example (so I am not sure what you mean when you say nuclei are no longer part of the same system). Fission would be a very different experiment because you are actually breaking the nucleus, and in that case, you need more than the type of quantum mechanics we discussed - not just an algorithmic problem.

What other methods could we have used to estimate the electronic potential energy acting on the nuclei? What are the main advantages and disadvantages of these alternative approaches, and why did we ultimately choose the variational method?

Alternatives include - for example - direct diagonalization of the electronic Hamiltonian in a convenient basis set, diffusion (quantum) Monte Carlo. The variational method, in its various incarnations that will be discussed also in future lectures, is the best compromise between accuracy and efficiency in the context of dynamical simulations.

Also, when we take the derivative of E with respect to C and equate it 0, we get an equation with 2 unknowns C_m and C_n . How do we find them with one equation? Did using a delta function to solve $\langle n | \phi | m \rangle$ mean that the constants are equal?

After the derivative is taken, there is only one set of unknowns. This can be immediately seen by recalling the summation index in one of the two sums like the other. Also, we don't get one equation but a system of equations in a number equal to the number of coefficients to be determined. This can be seen because we must take the derivative (independently, one derivative one equation) with respect to all coefficients.

You mentioned $E_0(R)$ is the electronic potential, does it mean it includes both electronic kinetic energy, electron-electron repulsion, and electron-nuclei attraction? Because from the name electronic potential, it seems to mean that this energy is just potential, but does not include kinetic energy.

Indeed, the name might be misleading but E_0 includes also the electronic kinetic energy. All terms are in there.

We also discussed the variational principle using a continuous “trial basis”. Is this really a good idea given that the bound eigenstates of the electronic Hamiltonian are supposed to be discrete?

It is possible to represent the eigenstates of discrete eigenvalues in a continuous representation. Think about the eigenfunctions of the harmonic oscillator or the particle in a box in the coordinate basis representation.

Can we use alternative higher order schemes for the ODE approximation, such as Runge–Kutta methods, or is it in practice never necessary?

The velocity Verlet algorithm is in fact the most commonly used. This is because it represents a very good combination of accuracy and numerical cost. Furthermore, it preserves by construction important properties of classical mechanics such as time-reversibility and conservation of the volume of phase space. This is not the case for alternatives such as Runge-Kutta.

Can you possibly give me two examples where the variational principle is used in the continuous representation and the discrete one, as this remains very abstract to me?

Hartree-Fock is an example of using a continuous representation, but since I am not sure I understand the question in relation to what has been done in class by Edrick I think that he may give a better answer. If not, I'll try again.

By using the Born-Oppenheimer approximation, we consider the nucleus as a classical particle. So, why can we use continuous trial functions in the variational principle? Doesn't it make the electrons also act as classical particles?

The electrons remain quantum, and we need to solve the time-independent Schrodinger equation to determine their ground state for each nuclear configuration. The different treatments (classical and quantum) are justified based on the different relevant masses and time-scales. The Born-Oppenheimer approximation - also known as classical adiabatic approximation - implies that there is no significant energy exchange between the electronic and nuclear system on the time-scales considered and therefore that the classical nature of the nuclei does not “disrupt” the quantum one of the electrons.

Is there any connection or requirement between the Born-Oppenheimer approximation and the trial functions that we use?

No

What is the ratio between coulomb and exchange energy, usually or how much can the exchange term stabilize the system?

The Coulomb term is typically bigger than the exchange - say between 10^{-2} and 10^4 . However, this is strongly system dependent and incorrect account of the exchange can substantially affect stability of the system in particular for strongly correlated systems and affect physical properties such as phase diagrams and/or band gaps.

In addition to the energy conservation criterion, what are other possible indicators for a stable trajectory? I guess probably the RMSD fluctuations, but do some others exist?

In practical calculations, in the NVE ensemble, not much else is routinely checked. Other indicators are more expensive (e.g. check conservation of the phase space volume by computing the Jacobian of the transformation between the time propagated and zero time

phase space variables) or require reinitialization of the run (e.g. time-reversibility: propagate, stop the propagation, invert sign of all momenta and check how well the trajectory retraces itself). As you say, checking stability of the averages of observables provides at least a sanity check.

What was the motivation to consider the determinant product of states in the Hartree-Fock model?

The determinant is antisymmetric under exchanges of two rows or columns (i.e. it changes sign). This is consistent with the Pauli principle that must be respected by electronic wave functions.

We discussed energy conservation as one of the criteria for the stability of our simulation. I've heard of two other: symplecticity and monodromy matrices. How are they related to one another? Are they completely different or do they have some similarities in the approach? I want to explicitly understand what we are stabilizing and how in a more general way, rather than just saying energy.

Energy is indeed only one of the respected conservation laws with respect to classical evolution. Momentum and phase space volume (so the Jacobian of the transformation constructed via the monodromy matrices) are additional conserved quantities. Volume conservation is related to energy conservation: it would not hold, e.g., for a dissipative system. Time-reversibility is also respected by velocity Verlet. The monodromy matrices are not individually conserved but this is correct (i.e. they are not conserved analytically).

Are other conservation laws e.g., momentum, angular momentum, (approximately) respected by the velocity Verlet algorithm?

Momentum is conserved, the conservation of angular momentum is usually broken not so much as a consequence of the Verlet but because of other conditions adopted in simulation setups, in particular the use of orthorhombic cells and periodic boundary conditions. We'll say a bit more about this in future lectures.

Can a functional derivative be thought of as a gradient with respect to a basis in the function space?

Not sure I understand. You can take a gradient with respect to variables, not basis...also, if you want to stretch a bit the definition in what we discussed, the functional derivative is taken with respect to the coefficient (i.e. $\phi(y)$) of the expansion in the coordinate basis.

Is there a theoretical bound of the compound error for the time stepping algorithm, even if only for some special cases?

By compound, you mean after N time-steps with N large? If so, it is of the order dt^2 both for velocities and positions. Note that the local (i.e. per time-step) error - as determined via the Liouvillian derivation of the algorithm, is of order dt^3 .