

# Computational Quantum Mechanics

## One-body problem

For time-independent 1D SE, we use **the Numerov algorithm**. It uses the central difference approximation of the second derivative to get the next point from the previous two.

## MPS

No thank you!

## Monte-Carlo methods

**MC integration:**  $\int f(x)dx = \sum_{x_i} f(x_i)/N$ .

**Importance sampling:**  $\int f(x)dx = \int f(x)/p(x) \cdot p(x)dx = \sum_{x_i} f(x_i)/p(x_i)$ ,  $x_i$  sampled from pdf  $p(x)$ .

**MCMC:**  $x_i$  generated from Markov Chain For  $x_i$  to be distributed as  $p(x)$ , it is sufficient that **detailed balance** is fulfilled:

$$T(x \rightarrow x')p(x) = T(x' \rightarrow x)p(x')$$

For the **metropolis method**,  $T(x \rightarrow x') = \omega_{xx'} A_{xx'}$ , where  $\omega$  is a symmetric, stochastic matrix which should be interpreted as a proposal distribution and  $A_{xx'}$  is to be treated as acceptance probabilities.

The **Wolff algorithm** can be useful when simulating the Ising model using MCMC. It proposes new states where entire clusters of spins are flipped, instead of just one.

We can also use MCMC for **quantum spin systems**. To do so, we must use a quantum to classical mapping:

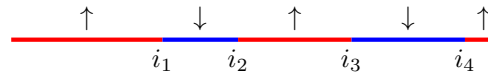
$$Z = \text{tr} \left[ e^{-\beta \hat{H}} \right] = \sum_C W(C)$$

$$\langle \hat{m} \rangle = \text{tr} \left[ \hat{m} e^{-\beta \hat{H}} \right] = \sum_C m(C) W(C)$$

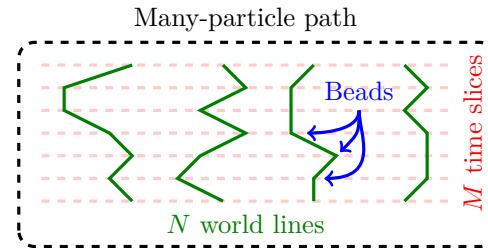
It turns out that we can always make a mapping from a d-dimensional quantum system to a (d+1)-dimensional classical system. For a single spin-1/2 you can accomplish it by splitting the exponential into a product of  $M$  factors and inserting a resolution of identity between all of them:

$$Z = \sum_i \langle i | U^M | i \rangle = \sum_{\{i_1, \dots, i_M\}} \langle i_1 | U | i_2 \rangle \langle i_2 | \dots | i_M \rangle \langle i_M | U | i_1 \rangle$$

Increasing  $M$  to infinity, the probability of having two neighbouring sites with opposite spin goes to 0 at a rate such that the total number of domain walls remains finite. Therefore, we can change our description to only keep track of where the domain walls are.



**Quantum Monte Carlo for particles** is yet another application of MC methods this time to  $N$  quantum particles in  $d$  dimensions in a thermal state. Do again subdivision into  $M$  factors and resolution of identity, though this time with  $\int |R\rangle \langle R| dR$ . This gives a high dimensional integral which we calculate with MCMC methods. The configuration being sampled is the many-particle paths. Updates are proposed by choosing a single time slice of a single world line (a **bead**) and moving it a bit (gaussian proposal).



The goal of **Diffusion Monte Carlo** is to find the ground state of a bosonic system. Instead of fixing  $\beta$  and splitting it into  $\Delta\tau M$  and wiggling the world lines, we fix  $\tau$  and apply  $e^{-\Delta\tau \hat{H}}$  a bunch of times. The state is  $M$  walkers with positions and weights (initially random/1). Applying the operator consists of drawing displacements from a gaussian, which incorporates the kinetic energy part of  $\hat{H}$ , and updating the weights using the potential. We then remove walkers with low weights and add copies of ones with high weights. This is an alternative method to the acceptance probability previously discussed.

## Electronic structure

How do we find the energy eigenstates of a molecule? The relevant Hamiltonian is

$$\begin{aligned} H &= - \sum_j^{N_e} \frac{\hbar^2}{2m_e} \nabla_{r_j}^2 - \sum_\ell^{N_n} \frac{\hbar^2}{2m_\ell} \nabla_{R_\ell}^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} \\ &\quad + \frac{1}{2} \sum_{\ell \neq m} \frac{Z_\ell Z_m e^2}{|R_\ell - R_m|} - \sum_{j, \ell}^{N_e, N_n} \frac{Z_\ell e^2}{|r_j - R_\ell|} \\ &= T_e + T_n + V_{ee} + V_{nn} + V_{ne} \end{aligned}$$

The first step is to use the **Born-Oppenheimer Approximation**: nuclei are heavy compared to electrons, so they're effectively frozen when solving for the electron wave functions.

The **Hartree** method is assuming non-interacting electrons in a mean field. You first guess some wavefunctions for the individual electrons and then, using these as the wavefunction the electrons interact with, calculate new wavefunctions and iterate until it seems to converge. Once converged, take a Slater determinant to find the ground state.

The **Hartree-Fock** method also assumes independent (but not non-interacting) electrons in a mean field, but the asymmetry is considered from the beginning. First take some orthonormal set of single-electron wave functions  $\phi_i$ . Then take some new single-electron wave functions that are linear combinations of these:  $\varphi_k = \sum_i \alpha_{ik} \phi_i$ . Letting  $\Psi$  be the many body wave function gotten from a Slater determinant of the  $\varphi_k$ , minimize  $\langle \Psi | H_{BO} | \Psi \rangle$ . Writing it out gives rise to an *exchange term* owing to the Pauli principle.

## Density Functional Theory