## Computational Quantum Mechanics
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One-body problem

For time-independent 1D SE, we use **the Numerov algorithm**. It solves $f''(x) = k(x)f(x)$. To do this, Taylor expand f and add $f(x+\Delta x) + f(x-\Delta x)$. In that expression, replace the fourth derivative by the finite difference approximation to the second derivative of f'', and f'' by $k(x)f(x)$. To get started, you thus need two points, Δx apart. Bound states can be found using the **Bidirectional-Shooting method**. Perform Numerov from right and left and scale them so they match. Vary b until the derivatives match too.
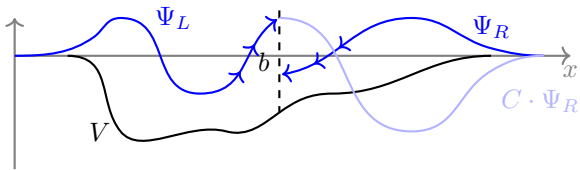
For higher dimensions, try using symmetries first because partial differential equation solvers are a lot more difficult to handle. Try factorizing $\psi(\mathbf{r}) = \psi_x(x)\psi_y(y)\psi_z(z)$. Or if the potential has a spherical symmetry, try an ansatz with the spherical harmonics.

For solving the time-*dependent* Schrödinger equation, we either use **spectral methods** – expressing the initial wave function as a linear combination of energy eigenfunctions and evolving those – but this is only tractable for small systems since we need an eigenbasis. The other method is direct numerical integration for which we use the **split operator method**.

$$e^{-i\Delta t(\hat{T}+\hat{V})} \approx e^{-i\ \Delta t\hat{V}/2}e^{-i\Delta t\hat{T}}e^{-i\Delta t\hat{V}/2}$$

for small Δt.

Many-body problems

In quantum mechanics, particles like the electron are *indistinguishable* and exchanging two of them cannot affect any observable. Thus, the wavefunction can only differ with a phase ± 1. Therefore, not every function in $\mathcal{H}^{\otimes N}$ is a valid wave function. A product state $\psi(r_1, r_2, \ldots, r_N) = \psi_1(r_1)\psi_2(r_2)\ldots\psi_N(r_N)$ has to be replaced by a sum of all of the possible permutations, with the appropriate phase. For bosonic systems, it's just the sum of all permutations, while

for fermionic systems the odd permutations are added with a phase of -1. This can be written as a **Slater determinant**. Note that the general (fermionic) state is a *sum* of Slater determinants, and only special states can be written as a single Slater determinant, analogously to product states.

In second quantization, and given a set of single particle wave functions $\{\phi_i\}_i$ we write a state as

$$|n_1 n_2 n_3 \ldots\rangle = \prod_i (a_i^\dagger)^{n_i} |0\rangle$$

Note that while bosonic creation and annihilation operators commute, fermionic anticommute, so the order matters. For example, $a_2^\dagger |1000\rangle = -|1100\rangle$.

Quantum Spin Models

We've talked about three spin models, the **Transverse Field Ising Model**, with the Hamiltonian

$$H = J\sum_{\langle i,j\rangle} \hat{S}_i^z \hat{S}_j^z + \sum_i hS_i^x,$$

the **Heisenberg Model**, with the Hamiltonian

$$H = J\sum_{\langle i,j\rangle} \hat{\vec{S}}_i \hat{\vec{S}}_j,$$

and the more general **XXZ** model, which is like an anisotropic version of the Heisenberg model,

$$H = J\sum_{\langle i,j\rangle} \hat{S}_i^x \hat{S}_j^x + \hat{S}_i^y \hat{S}_j^y + \Delta \hat{S}_i^z \hat{S}_j^z$$

Matrix Product States / Operators

No thank you!

Monte-Carlo methods

MC integration: $\int f(x)\mathrm{d}x = \sum_{x_i} f(x_i)/N$.
Importance sampling: $\int f(x)\mathrm{d}x = \int f(x)/p(x) \cdot p(x)\mathrm{d}x = \sum_{x_i} f(x_i)/p(x_i)$, 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:

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

For the **metropolis method**, $T(x \to x') = \omega_{xx'}A_{xx'}$, where ω 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:

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

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

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:

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

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.
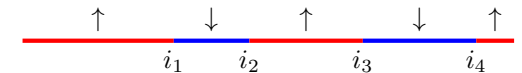
Quantum Monte Carlo for particles is yet another application of MC methods this time to N quantum particles in d dimensions in a thermal state. Do again subdivision into M factors and resolution of identity, though this time with $\int |R\rangle \langle R|\,\mathrm{d}R$. This gives a high dimensional 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).

Many-particle path
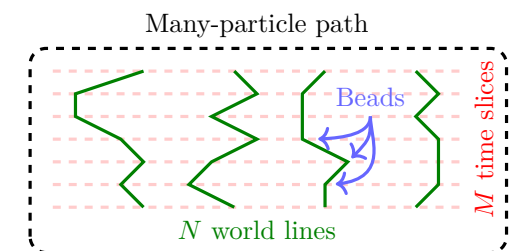
The goal of **Diffusion Monte Carlo** is to find the ground state of a bosonic system. Instead of fixing β and splitting it into $\Delta\tau M$ and wiggling the world lines, we fix τ and apply $e^{-\Delta\tau\hat{H}}$ a bunch of times. The state is M walkers with positions and weights (initially random/1). 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.

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Electronic structure

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

$$H = -\sum_j^{N_e} \frac{\hbar^2}{2m_e}\nabla_{r_j}^2 - \sum_\ell^{N_n} \frac{\hbar^2}{2m_\ell}\nabla_{R_\ell}^2 + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|r_i - r_j|}$$

$$+ \frac{1}{2}\sum_{\ell\neq m}\frac{Z_\ell Z_m e^2}{|R_\ell - R_m|} - \sum_{j,\ell}^{N_e,N_n}\frac{Z_\ell e^2}{|r_j - R_\ell|}$$

$$= T_e + T_n + V_{ee} + V_{nn} + V_{ne}$$

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 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 ϕ_i. Then take some new single-electron wave functions that are linear combinations of these: $\varphi_k = \sum_i \alpha_{ik}\phi_i$. Letting Ψ be the many body wave function gotten from a Slater determinant of the φ_k, minimize $\langle\Psi|\,H_{\mathrm{BO}}\,|\Psi\rangle$. Writing it out gives rise to an *exchange term* owing to the Pauli principle.

Density Functional Theory is concerned with the electron ground state density n_0, rather than the actual wavefunction. There is a one-to-one correspondence between n_0 and V_{ext}. In the case of molecules, $V_{\mathrm{ext}} = V_{ne}$, but we could have a more general external potential. The clever point is that everything that is not V_{ext} is the same no matter which system we are

trying to solve. The energy functional that we minimize is

$$E_{[v_{\mathrm{ext}}]}[n] = \min_{\Psi\to n}\langle\Psi|T_e + V_{ee} + V_{\mathrm{ext}}\,|\Psi\rangle$$

$$= \min_{\Psi\to n}\langle\Psi|T_e + V_{ee}|\Psi\rangle + \int \mathrm{d}r v_{\mathrm{ext}}(r)n(r)$$

The first term we call $F[n]$ and that is universal – it does not depend on the specific problem. The $\Psi\to n$ notation means Ψ such that the density is n.

Unfortunately, since the correlations in Ψ can be complicated (i.e. it is not a single Slater determinant state), this is still not an easy problem. The **Kohn-Sham solution scheme** tries to remedy this by trying to find a non-interacting (i.e. it *is* a single Slater determinant state) system with the same density as the exact one. To compensate for the errors coming from this ignoring of the correlation, we add an additional term including the unknown correction called the exchange-correlation functional E_{XC}:

$$E[n] = E_k[n] + E_c[n] + E_{XC}[n] + V_{\mathrm{ext}}[n]$$

Minimizing this under the condition $\int n\mathrm{d}n = N_e$ using lagrange multipliers gives single-particle equations called the Kohn-Sham equations.

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + V_{\mathrm{eff}}(r)\right]\varphi_j = \varepsilon_j\varphi_j$$

$$V_{\mathrm{eff}}(r) = \int \mathrm{d}r'\frac{n}{|r - r'|} + V_{XC}(r) + V_{\mathrm{ext}}(r)$$

Note that this is in principle just a trick to find the density, you should not expect the single particle energies ε_j to actually correspond to the single particle energies of the system.