Computational Quantum Physics

Lecture Summary
(Spring Semester 2015)

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Disclaimer

This is a summary of the *Computational Quantum Physics* lecture [2] taught by Prof. Troyer during the spring semester 2015 at the ETH Zürich and was written by me as a preparation for the oral exam. All of the equations shown in this summary have been presented during the lecture, which is based on [3]; equations taken from other sources are appropriately referenced in the text.

Quantum Mechanics in One Hour

Basis of Quantum Mechanics

Wave Functions and Hilbert Spaces

- Pure state of quantum system is described by a wave function

$$|\Psi\rangle \in \mathcal{H} \quad , \tag{1}$$

  where $\mathcal{H}$ is a Hilbert space.

- Wave functions are usually normalized

$$\| \, |\Psi\rangle \, \| = \sqrt{\langle \Psi \rangle} = 1 \quad . \tag{2}$$

- Spin-$1/2$ system describes the two spin states of an electron

  - $\mathcal{H} = \mathbb{C}^2$ with basis vectors

$$|\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad , \tag{3}$$

$$|\downarrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad . \tag{4}$$

- Quantum spin can exist in any complex superposition

$$|\Psi\rangle = \alpha\,|\uparrow\rangle + \beta\,|\downarrow\rangle \quad , \tag{5}$$

  where Eq. (2) requires that

$$|\alpha|^2 + |\beta|^2 = 1 \quad . \tag{6}$$

  - The state

$$|\rightarrow\rangle = 1/\sqrt{2}\,(|\uparrow\rangle + |\downarrow\rangle) \tag{7}$$

    is a superposition that describes the spin pointing in the positive x-direction.

Mixed States and Density Matrices

- General state of a quantum system in nature is described by the density matrix ρ with unit trace

$$\mathrm{Tr}\,\rho = 1 \quad . \tag{8}$$

- Density matrix of a pure state:

$$\rho_{\text{pure}} = |\Psi\rangle\,\langle\Psi| \quad . \tag{9}$$

  - Density matrix of a spin pointing in the positive x-direction is

$$\rho_{\rightarrow} = |\rightarrow\rangle\,\langle\rightarrow| = \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix} \quad . \tag{10}$$

  - Density matrix of a spin pointing up with 50% probability and pointing down with a 50% probability is

$$\rho_{\text{mixed}} = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix} \quad . \tag{11}$$

Observables

- A physical observable is represented by a self-adjoint linear operator acting on the Hilbert space.
  - In a finite-dimensional Hilbert space, the operator can be represented by a Hermitian matrix.
- For the spin-$1/2$ system, the spin is given by

$$\underline{\mathbf{S}} = (\mathbf{S_x}, \mathbf{S_y}, \mathbf{S_z})^T = \frac{\hbar}{2}(\boldsymbol{\sigma_x}, \boldsymbol{\sigma_y}, \boldsymbol{\sigma_z})^T = \frac{\hbar}{2}\underline{\boldsymbol{\sigma}} \quad , \tag{12}$$

  where

$$\boldsymbol{\sigma_x} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} , \quad \boldsymbol{\sigma_y} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} , \quad \boldsymbol{\sigma_z} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} . \tag{13}$$

  are the Pauli matrices.
  - The observables $\mathbf{S_x}, \mathbf{S_y}, \mathbf{S_z}$ do not commute, i.e.,

$$[\mathbf{S_x}, \mathbf{S_y}] \neq 0 \quad , \tag{14}$$
$$[\mathbf{S_y}, \mathbf{S_z}] \neq 0 \quad , \tag{15}$$
$$[\mathbf{S_z}, \mathbf{S_x}] \neq 0 \quad , \tag{16}$$
$$\tag{17}$$

    which is the root difference between classical and quantum mechanics, since due to Eqs. (15), (16) and (17) the observables $\mathbf{S_x}, \mathbf{S_y}, \mathbf{S_z}$ cannot be measured simultaneously.

The Measurement Process

- Measurement of quantum system is intrusive and not deterministic, meaning that the measurement process will change the state of the quantum system.
  - After measuring an observable A, the new wave function of the quantum system will be an eigenvector of A and the outcome of the measurement the corresponding eigenvalue.
- Expectation value of a measurement
  1. from a wave function Ψ:

$$\langle A \rangle = \langle \Psi | \, A \, | \Psi \rangle \quad . \tag{18}$$

  2. from a density matrix ρ:

$$\langle A \rangle = \mathrm{Tr}(\rho A) \quad . \tag{19}$$

The Uncertainty Relation

- If two observables A and B do not commute, i.e.,

$$[A, B] \neq 0 \quad , \tag{20}$$

  then both observables cannot be measured simultaneously.
  - When measuring A, the wave function is changed to an eigenstate of A, which changes the result of a subsequent measurement of B.
  - Heisenberg uncertainty relation: if two observables A and B do not commute but satisfy $[A, B] = \mathrm{i}\hbar$, then

$$\Delta A \Delta B \geq \hbar/2 \tag{21}$$

    has to be satisfied, where ΔA is the root-mean-square deviation of A.

The Schrödinger Equation

The Time-Dependent Schrödinger Equation

- The wave function $|\Psi\rangle$ of a quantum system evolves according to

$$\mathrm{i}\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = H |\Psi(t)\rangle \quad , \tag{22}$$

  where H is the Hamilton operator.

The Time-Independent Schrödinger Equation

- Using the Ansatz

$$|\Psi(t)\rangle = \exp\{-\mathrm{i}Et/\hbar\} |\Psi(t)\rangle \quad , \tag{23}$$

  where E is the energy of the quantum system, the Schrödinger equation simplifies to a linear eigenvalue problem

$$H |\Psi(t)\rangle = E |\Psi(t)\rangle \quad . \tag{24}$$

A Quantum Particle in Free Space

- Hilbert space: complex functions $\in C^2(\mathbb{R}^n)$
  - The wave functions $\langle\Psi|$ are complex valued functions $\Psi(\mathbf{x})$ in n-dimensional space
- Position operator:

$$\hat{x} = \mathbf{x} \quad . \tag{25}$$

- Momentum operator:

$$\hat{p} = -\mathrm{i}\hbar\nabla \quad . \tag{26}$$

- Schrödinger equation of a quantum particle in an external potential $V(\mathbf{x})$

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi = -\frac{\hbar^2}{2m}\nabla^2\Psi + V(\mathbf{x})\Psi \tag{27}$$

  can be obtained from the classical Hamilton function by replacing $\mathbf{x}$ and $\mathbf{p}$ by the operators in Eqs. (25) and (26).

  – Classical Hamilton function:

$$H(\mathbf{x},\mathbf{p}) = \frac{\mathbf{p}^2}{2m} + V(\mathbf{x}) \quad . \tag{28}$$

  – Quantum mechanical Hamiltonian operator:

$$H(\mathbf{x},\mathbf{p}) = \frac{\hat{p}^2}{2m} + V(\hat{x}) \quad = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{x}) \quad . \tag{29}$$

The Quantum One-Body Problem

The Time-Independent 1D Schrödinger Equation

- Time-Independent one-dimensional Schrödinger Equation for a particle with mass m in a potential $V(x)$:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x)}{\partial x^2} + V(x)\Psi(x) = E\Psi(x) \quad . \tag{30}$$

The Numerov Algorithm

- After rewriting second order differential equations to a coupled system of two first order differential equations, any ODE solver (e.g. Runge-Kutta method) could be applied, but there exist better methods.

- For the special form

$$\Psi''(x) + k(x)\,\Psi(x) = 0 \quad , \tag{31}$$

  with

$$k(x) = 2m[E - V(x)]/\hbar^2 \tag{32}$$

  for the Schrödinger equation the Numerov algorithm can be used.

- Numerov algorithm (locally of 5th order, globally of 4th order):

$$\left(1+\frac{\Delta x^2}{12}k_{n+1}\right)\Psi_{n+1} = 2\left(1-\frac{5\Delta x^2}{12}k_n\right)\Psi_n - \left(1+\frac{\Delta x^2}{12}k_{n-1}\right)\Psi_{n-1} + O(\Delta x^6) \quad , \tag{33}$$

  where $\Psi_n = \Psi(x_n)$ and $k_n = k(x_n)$.

  - Derivation of the Numerov algorithm

    1. Start from the Taylor expansion of Ψ_n:

$$\Psi_{n\pm1} = \Psi_n \pm \Delta x\Psi' + \frac{\Delta x^2}{2}\Psi''_n \pm \frac{\Delta x^3}{6}\Psi^{(3)}_n \pm \frac{\Delta x^4}{24}\Psi^{(4)}_n + O(\Delta x^6) \quad . \tag{34}$$

    2. Add Ψ_{n+1} and Ψ_{n-1}:

$$\Psi_{n+1} + \Psi_{n-1} = 2\Psi_n + \Delta x^2\Psi''_n + \frac{\Delta x^4}{12}\Psi^{(4)}_n \quad . \tag{35}$$

    3. Replace in Eq. (35) the fourth derivatives by a finite difference second derivative of the second derivatives:

$$\Psi^{(4)}_n = \frac{\Psi''_{n+1} + \Psi''_{n-1} - 2\Psi''_n}{\Delta x^2} \quad . \tag{36}$$

    4. Use Eq. (31) to substitute $\Psi''(x)$ with $-k(x)\Psi(x)$ in Eq. (35).

Numerov Algorithm: Initial Values

- For potentials $V(x)$ with reflective symmetry, i.e., $V(x) = V(-x)$ the wave functions need to be either even ($\Psi(x) = \Psi(-x)$) or odd ($\Psi(x) = -\Psi(x)$) under reflection

- Since a step of the Numerov algorithm (Eq. (33)) depends on both Ψ_n and Ψ_{n-1}, to start the algorithm we need the wave function at two initial values.

  - For the even solution using a half-integer mesh with mesh points

$$x_{n+1/2} = (n+1/2)\Delta x \tag{37}$$

    and therefore pick initial values

$$\Psi(x_{-1/2}) = \Psi(x_{1/2}) = 1 \quad . \tag{38}$$

  - For the odd solution:

1. Due to $\Psi(0) = -\Psi(0)$ it follows that for the first starting value one gets $\Psi(0) = 0$
2. Using an integer mesh with mesh points $x_n = n\Delta x$ one picks $\Psi(x_1) = 1$ as the second starting value

- For potentials $V(x)$ vanishing at large distances, i.e., $V(x) = 0$ for $|x| \geq a$ the exact solution of the Schrödinger equation at large can be used to define the starting points, e.g.

$$\Psi(-a) = 1 \quad , \tag{39}$$

$$\Psi(-a - \Delta x) = \exp\{-\Delta x\sqrt{2mE}/\hbar\} \quad . \tag{40}$$

- For potentials $V(x)$ that do not vanish, we need to begin with a single starting value $\Psi(x_0)$ and obtain the second starting value $\Psi(x_1)$ by performing an integration over the first space step Δx with an Euler or Runge-Kutta algorithm.

The One-Dimensional Scattering Problem

- Scattering problem is the numerically easiest quantum problem, since solutions exist for all energies $E > 0$ if the potential vanishes at large distances, i.e., $V(x) \to 0$ for $x \to \infty$
- Potential barrier: $V(x) > 0 \ \forall x \in [0, a]$ and $V(x) = 0 \ \forall x \neq [0, a]$
  - For a particle approaching the barrier from the left, i.e., $x < 0$, the following ansatz can be made:

$$\Psi_L(x) = A\exp\{\mathrm{i}qx\} + B\exp\{-\mathrm{i}qx\} \quad , \tag{41}$$

    where A is the amplitude of the incoming wave and B the amplitude of the reflected wave
  - For a particle approaching from the right, i.e., $x > a$, we can make the following ansatz:

$$\Psi_R(x) = C\exp\{\mathrm{i}qx\} \quad . \tag{42}$$

  - A, B, C have to be determined by matching to a numerical solution of the Schrödinger equation in the interval $[0, a]$ and is done the following way:
    * Set $C = 1$ and use two points a and $a + \Delta x$ as starting points for a Numerov integration.
    * Integrate the Schrödinger equation numerically - backwards in space, from a to 0 - using the Numerov algorithm.
    * Match numerical solution of the Schrödinger equation for $x < 0$ to Eq. (41) to determine A, B.

- Reflection probability:

$$R = \frac{|B|^2}{|A|^2} \tag{43}$$

- Transmission probability:

$$T = \frac{1}{|A|^2} \tag{44}$$

Bound States and Solution of the Eigenvalue Problem

- Bound state describes a system where a particle is subject to a potential such that the particle has a tendency to remain localised in one or more regions of space.
- Scattering states exist for all energies $E > 0$.
- Bound states solutions of the Schrödinger equation with $E < 0$ exist only for discrete energy eigenvalues.
  - Integrating the Schrödinger equation from $-\infty$ to ∞ generates solutions that diverge to $\pm\infty$ as $x \to \infty$ for almost all values.
    - These solutions cannot be normalized and thus are not valid solutions for the Schrödinger equation.
    - Only for some special eigenvalues E will the solution converge to 0 as $x \to \infty$.
  - Find suitable solutions of the Schrödinger equation

$$\Psi''(x) + \frac{2m}{\hbar^2}[E - V(x)]\,\Psi(x) = 0 \tag{45}$$

  for $E < 0$ using the following methods:

  1. Method 1: Shooting method
     a) $V(x) = 0 \quad \forall x \notin [0, a]$
     b) Start with an initial guess for E
     c) Integrate from $x = 0$ to $x_f \gg a$ and obtain $\Psi_E(x_f)$
     d) Use a root solver (e.g. bisection method) to look for an energy E with $\Psi_E(x_f) \approx 0$
  2. Method 2: Matching method, that is, integrate the Schrödinger equation from both sides towards the center
     a) Pick starting point b and choose $E = V(b)$
     b) Integrate $\Psi_L(x)$ from $x = 0$ to a chosen point b and obtain $\Psi_L(b)$; then, numerically estimate

$$\Psi'_L(b) = \frac{\Psi_L(b) - \Psi_L(b - \Delta x)}{\Delta x} \quad . \tag{46}$$

c) Integrate $\Psi_R(x)$ from $x = a$ to the chosen point b and obtain $\Psi_R(b)$; then, numerically estimate

$$\Psi'_R(b) = \frac{\Psi_R(b) - \Psi_R(b - \Delta x)}{\Delta x} \quad . \tag{47}$$

d) At point b the wave functions and their first two derivatives have to match, since the solution $\Psi(x)$ of the Schrödinger equation has to be in $C^2(\mathbb{R})$; the following conditions are obtained from these facts:

$$\Psi_L(b) = \alpha\Psi_R(b) \tag{48}$$
$$\Psi'_L(b) = \alpha\Psi'_R(b) \tag{49}$$
$$\Psi'_L(b) = \alpha\Psi''_R(b) \tag{50}$$

* The conditions in Eqs. (48) and (49) can be combined to the condition that the logarithmic derivatives should vanish:

$$\left.\frac{\mathrm{d}\log\Psi_L}{\mathrm{d}x}\right|_{x=b} = \frac{\Psi'_L(b)}{\Psi_L(b)} = \frac{\Psi'_R(b)}{\Psi_R(b)} = \left.\frac{\mathrm{d}\log\Psi_R}{\mathrm{d}x}\right|_{x=b} \quad . \tag{51}$$

* The condition shown in Eq. (50) is automatically fulfilled for $V(b) = E$, since $\Psi''(b)$ evaluates to 0 (see Eq. (45))

e) Find the root using a shooting method, e.g. bisection algorithm.

The Time-Independent Schrödinger Equation in Higher Dimensions

Factorization Along the Coordinate Axis

- For the three-dimensional Schrödinger equation in a cubic box with potential $V(\mathbf{r}) = V(x, y, z) = V(x)V(y)V(z)$, using the product ansatz

$$\Psi(\mathbf{r}) = \Psi_x(x)\Psi_y(y)\Psi_z(z) \tag{52}$$

the PDE factorizes into three ODEs which can be solved with the previous methods.

Potential With Spherical Symmetry

- For spherically symmetric potentials with $V(\mathbf{r}) = V(\|\mathbf{r}\|)$ an ansatz using spherical harmonics is used:

$$\Psi_{l,m}(\mathbf{r}) = \Psi_{l,m}(r, \theta, \phi) = \frac{u(r)}{r} Y_{l,m}(\theta, \phi) \quad . \tag{53}$$

- Using Eq. (53) the three-dimensional Schrödinger equation can be reduced to a one-dimensional one for the radial wave function $u(r)$ in $[0, \infty)$:

$$\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{\hbar^2\, l\,(l+1)}{2mr^2} + V(r)\right) u(r) = Eu(r) \quad . \tag{54}$$

  - Given the singularity at $r \to 0$, a numerical integration should start at large distances r and integrate towards $r = 0$.
    * Largest errors are only accumulated at the last steps of the integration.

Finite Difference Methods

- Discretize the three-dimensional Schrödinger equation ($\hbar = 1$)

$$\nabla^2 \Psi(\mathbf{r}) + 2m(E - V(\mathbf{r}))\Psi(\mathbf{r}) = 0 \quad , \tag{55}$$

  the space is discretized and the system of linear equations

$$\begin{aligned} 1/\Delta x^2 \; & [\Psi(x_{n+1}, y_n, z_n) + \Psi(x_{n-1}, y_n, z_n) + \Psi(x_n, y_{n+1}, z_n)] \\ & \Psi(x_n, y_{n-1}, z_n) + \Psi(x_n, y_n, z_{n+1}) + \Psi(x_n, y_n, z_{n-1})] \\ & + [2m(E - V(\mathbf{r})) - 6/\Delta x^2]\Psi(x_n, y_n, z_n) = 0 \quad . \end{aligned} \tag{56}$$

  - For small matrices, use a direct solver.
  - For large matrices the discretization results in a sparse matrix; use optimized iterative numerical algorithms.
  - To calculate bound states, an eigenvalue problem has to be solved.
    * For small systems (full matrix can be stored in memory) use direct solvers.
    * For bigger systems, use sparse solvers (e.g. Lanczos algorithm).

Variational Solutions Using a Finite Basis Set

- For general potentials or for systems consisting of more than two particles we need to employ a PDE solver, since it is not possible to reduce the Schrödinger equation to a one-dimensional problem.

- Expand the wave functions in terms of a finite set of basis functions

$$|\Phi\rangle = \sum_{i=1}^{N} a_i \, |u_i\rangle \quad . \tag{57}$$

- The ground state energy is estimated by minimizing the energy of the variational wave function

$$E^* = \frac{\langle \Phi | \, H \, | \Phi \rangle}{\langle \Phi | \, \Phi \rangle} \quad . \tag{58}$$

  - E^* will converge towards the true ground state energy E_0 by increasing the siz eof the basis set.

- The matrix elements of the Hamilton operator H are defined as

$$H_{ij} = \langle u_i | \, H \, | u_j \rangle = \int \mathrm{d}\mathbf{r} \; u_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 + V \right) u_j(\mathbf{r}) \quad . \tag{59}$$

- The matrix elements of the overlap matrix are given by

$$S_{ij} = \langle u_i | \, u_j \rangle = \int \mathrm{d}\mathbf{r} \; u_i^*(\mathbf{r}) u_j(\mathbf{r}) \quad . \tag{60}$$

  - For an orthogonal basis set, $\underline{\mathbf{S}}$ is the identity matrix.

- By minimizing Eq. (58) we obtain the generalized eigenvalue problem

$$\sum_j H_{ij} a_j = E \sum_k S_{ik} a_k \;\text{ for }\; i = 1, \ldots, N \quad \Leftrightarrow \quad \underline{\mathbf{H}}\,\mathbf{a} = E\,\underline{\mathbf{S}}\,\mathbf{a} \quad . \tag{61}$$

  - For an orthogonal basis set, Eq. (61) reduces to an ordinary eigenvalue problem and can be solved using a sparse solver, e.g. Lanczos algorithm.

- In general, to solve Eq. (61) orthogonal matrices $\underline{\mathbf{U}}$ have to be found such that $\underline{\mathbf{U}}^T \underline{\mathbf{S}} \underline{\mathbf{U}}$ is the identity matrix.
  - By introducing $\mathbf{b} = \underline{\mathbf{U}}^{-1}\mathbf{a}$ the problem given by Eq. (61) can be rearranged into

$$\begin{aligned} &\underline{\mathbf{H}}\,\mathbf{a} = E\,\underline{\mathbf{S}}\,\mathbf{a} \\ \Leftrightarrow\; &\underline{\mathbf{H}}\,\underline{\mathbf{U}}\,\mathbf{b} = E\,\underline{\mathbf{S}}\,\underline{\mathbf{U}}\,\mathbf{b} \\ \Leftrightarrow\; &\underline{\mathbf{U}}^T\,\underline{\mathbf{H}}\,\underline{\mathbf{U}}\,\mathbf{a} = E\,\underline{\mathbf{U}}^T\,\underline{\mathbf{S}}\,\underline{\mathbf{U}}\,\mathbf{b} = E\mathbf{b} \end{aligned} \tag{62}$$

    and we end up with a standard eigenvalue problem for $\underline{\mathbf{U}}^T\,\underline{\mathbf{H}}\,\underline{\mathbf{U}}$, which can be solved by eigensolvers for generalized eigenvalue problems.

The Time-Dependent Schrödinger Equation

Spectral Methods

1. To calculate the time evolution of a state $|\Psi(t_0)\rangle$ from time t_0 to t first solve the stationary eigenvalue problem

$$H \, |\Phi\rangle = E \, |\Phi\rangle \quad , \tag{63}$$

   and calculate the eigenvectors $|\Phi_n\rangle$ with eigenvalues ϵ_n.

2. Represent the initial wave function $|\Psi\rangle$ by a spectral decomposition

$$|\Psi(t_0)\rangle = \sum_n c_n \, |\Phi_n\rangle \quad . \tag{64}$$

3. At time t we then obtain (each $|\Phi_n\rangle$ is an eigenvector of H)

$$|\Psi(t)\rangle = \sum_n c_n \exp\{-\mathrm{i}\epsilon_n(t-t_0)/\hbar\}\ |\Phi_n\rangle \quad . \tag{65}$$

- Drawback: this approach is only useful for very small problems since diagonalizing the matrix takes huge computational effort.

Direct Numerical Integration

- Choose direct numerical integration if the Hamiltonian changes over time, i.e., $H(t)$ or if the number of basis states is too large too perform a complete diagonalization of the Hamiltonian
- After choosing a set of basis functions, a set of coupled ODEs which can be evolved for each point along the time line by standard ODE solvers.
- The exact quantum evolution

$$\Psi(x, t+\Delta t) = \exp\{-\mathrm{i}H\Delta t/\hbar\}\Psi(x,t) \tag{66}$$

  is unitary, i.e., $\underline{\mathbf{U}}^*\underline{\mathbf{U}} = \underline{\mathbf{U}}\underline{\mathbf{U}}^* = \underline{\mathbf{I}}$ and thus conserves the norm.
  - The Forward Euler method does not conserve the norm and is thus not suitable for this task.
- The following unitary approximant is used as integrator, since it conserves the norm:

$$\begin{aligned}\Psi(x,t+\Delta t) &= \left(1+\frac{\mathrm{i}\Delta t}{2\hbar}H\right)^{-1}\left(1-\frac{\mathrm{i}\Delta t}{2\hbar}H\right)\Psi(x,t)\\ \Leftrightarrow \left(1+\frac{\mathrm{i}\Delta t}{2\hbar}H\right)\Psi(x,t+\Delta t) &= \left(1-\frac{\mathrm{i}\Delta t}{2\hbar}H\right)\Psi(x,t) \quad .\end{aligned} \tag{67}$$

  1. Taylor expansion of the exact time evolution operator presented in Eq. (66) is given by

$$\exp\{-\mathrm{i}H\Delta t/\hbar\} = \left(1-\frac{\mathrm{i}\Delta t}{2\hbar}H\right) + O(\Delta t^2) \quad . \tag{68}$$

  2. Reformulate time evolution operator using Eq. (68):

$$\begin{aligned}\exp\{\mathrm{i}H\Delta t/2\hbar\} &= (\exp\{-\mathrm{i}H\Delta t/2\hbar\})^{-1}\ \exp\{-\mathrm{i}H\Delta t/2\hbar\}\\ &= \left(1+\frac{\mathrm{i}\Delta t}{2\hbar}H\right)^{-1}\left(1-\frac{\mathrm{i}\Delta t}{2\hbar}H\right) + O(\Delta t^3) \quad .\end{aligned} \tag{69}$$

     The resulting operator is unitary and is used in the unitary integrator algorithm shown in Eq. (67).

- The integrator presented in Eq. (67) is an implicit integrator, meaning that at each timestep a linear system of equations needs to be solved.
  - For one-dimensional problems H is often tridiagonal and a tridiagonal solver can be used.
  - In higher dimensions H will not be tridiagonal, but still sparse, meaning we can use iterative algorithms.

The Split Operator Method

- Split the Hamilton operator as follows:

$$H = \hat{T} + \hat{V} \quad , \tag{70}$$

  with

$$\hat{T} = \frac{1}{2m}\hat{p}^2 \tag{71}$$

$$\hat{V} = V(\mathbf{x}) \tag{72}$$

  - $\hat{T}$ is diagonal in momentum space
  - $\hat{V}$ is diagonal in position space

- Split the time evolution:

$$\begin{aligned} \exp\{-\mathrm{i}\Delta t H/\hbar\} = &\exp\{-\mathrm{i}\Delta t\hat{V}/(2\hbar)\} \\ &\cdot \exp\{-\mathrm{i}\Delta t\hat{T}/\hbar\} \\ &\cdot \exp\{-\mathrm{i}\Delta t\hat{V}/(2\hbar)\} + O(\Delta t^3) \quad . \end{aligned} \tag{73}$$

- Perform individual time evolutions in real space (Eq. (74)) and momentum space (Eq. (75)):

$$[\exp\{-\mathrm{i}\Delta t\hat{V}/(2\hbar)\}\ |\Psi\rangle](\mathbf{x}) = \exp\{-\mathrm{i}\Delta t\hat{V}/(2\hbar)\}\,\Psi(\mathbf{x}) \quad , \tag{74}$$

$$[\exp\{-\mathrm{i}\Delta t\hat{T}/\hbar\}\ |\Psi\rangle](\mathbf{k}) = \exp\{-\mathrm{i}\Delta t\,\hbar\,\|k\|^2/(2m)\}\,\Psi(\mathbf{k}) \quad . \tag{75}$$

  - Quantum state can be represented by a superposition of basis states.
    - $\Psi(\mathbf{x})$ is said to be the *wave function in position space* if the eigenfunctions of the position operator are chosen as a set of basis functions:

      .

$$\Psi(\mathbf{x}) = \sum_j \Phi_j \Psi_j(\mathbf{x}) \tag{76}$$

    - $\Phi(\mathbf{k})$ is said to be the *wave function in momentum space* if the eigenfunctions of the momentum operator are chosen as a set of basis functions:

.

$$\Phi(\mathbf{k}) = \sum_j \Psi_j \Phi_j(\mathbf{k}) \tag{77}$$

  - Basis change from real to momentum space is performed using a Fast Fourier Transform (FFT).

- The split operator method results in a fast and unitary integrator

Exact Diagonalization of Quantum Spin Models

Quantum Spin Models

- Single quantum particle is described by a Hilbert space $\mathcal{H}$ of dimension $\dim \mathcal{H} = d$.
- N distinguishable quantum particles are described by the tensor product of N Hilbert spaces

$$\mathcal{H}^{(N)} \equiv \mathcal{H}^{\otimes N} = \otimes_{i=1}^{N} \mathcal{H} \quad , \tag{78}$$

  with dimension d^N.

- A single spin-$1/2$ particle has Hilbert space $\mathcal{H} = \mathbb{C}^2$ with $\dim \mathcal{H} = 2$
  - N spin-$1/2$ particles have a Hilbert space $\mathcal{H}^{(N)} = \mathbb{C}^{2N}$ with $\dim \mathcal{H} = 2^N$.
    - The basis for $N = 30$ spin-$1/2$ particles is already of size $2^{30} \approx 10^9$
      - Small and moderately sized systems of up to 30 spin-$1/2$ can be evaluated by direct calculations. To go to larger systems, quantum Monte Carlo methods can be used (for bosonic systems, and approximate methods for fermions that reduce the many-particle problem to a single-particle problem)

The Transverse Field Ising Model

- The transverse field Ising model (TFIM) adds a magnetic field in the x direction to a lattice of spin-$1/2$ particles coupled by an Ising interaction:

$$H = \sum_{\langle i,j \rangle} J_{ij} \sigma_i^z \sigma_j^z - \Gamma \sum_i \sigma_i^x \quad . \tag{79}$$

  - $\langle i, j \rangle$ denotes the sum over all bonds in the lattice.
  - The Pauli matrix σ_x flips an $\uparrow$-spin to a $\downarrow$-spin, thus introducing quantum dynamics to the Ising model.

The Quantum Heisenberg Model

- Hamiltonian of the quantum Heisenberg model:

$$H = \sum_{\langle i,j \rangle} J_{ij} \mathbf{S_i S_j} = \sum_{\langle i,j \rangle} J_{ij} [1/2 \, (S_i^+ S_j^- + S_i^- S_j^+) + S_i^z S_j^z] \quad . \quad . \tag{80}$$

  - $S^+ = S_x + iS_y$, is a raising (creation) operator.
  - $S^- = S_x - iS_y$ is a lowering (annihilation) operator.
  - Both ladder operators in Eq. (80) are used to keep the total magnetization unchanged.

The Quantum XXZ Model

- Magnetic materials might not have the same coupling strength in all spin direction (often weaker or stronger coupling along one direction).
- Hamiltonian of the quantum XXZ model:

$$H = \sum_{\langle i,j \rangle} J_{ij}^x / 2 (S_i^+ S_j^- + S_i^- S_j^+) + J_{ij}^z S_i^z S_j^z \quad . \tag{81}$$

Exact Diagonalization

- Exact diagonalization: solving a quantum model by using an iterative eigensolver to calculate the ground state and low-lying excited states.
- Matrix representation of the model Hamiltonian is typically sparse, but still huge regarding memory requirement.
  - We have $O(N^2)$ terms in the Hamiltonian, resulting in $O(N^2)$ non-zero elements per row and column of the matrix $\implies$ $O(N^2 \, 2^N)$ non-zero elements in the resulting matrix.
- Memory usage is minimized by only storing the three vectors required for the Lanczos recurrence relations.
  - The Lanczos algorithm requires the computation of matrix-vector products but does not store the full matrix.

Lanczos Algorithm

- The goal of the Lanczos algorithm is to find the k largest/smallest eigenvalues and eigenvectors
  - Run-time is $\mathcal{O}(N^2)$ for a dense and $\mathcal{O}(N)$ for a sparse matrix

The algorithm:

1. Build a Krylov basis $\{\mathbf{v}_1, \mathbf{v}_2, \ldots, \mathbf{v}_M\}$ spanning the Krylov subspace $\mathcal{K}_M = \text{span}\{\mathbf{u}_1, \mathbf{u}_2, \ldots, \mathbf{u}_M\}$ by doing M iterations of the power method

$$\mathbf{u}_{n+1} = \frac{\underline{\mathbf{A}}\,\mathbf{u}_n}{\|\underline{\mathbf{A}}\,\mathbf{u}_n\|} \tag{82}$$

2. The iteration equation is given by

$$\beta_{n+1}\mathbf{v}_{n+1} = \underline{\mathbf{A}}\mathbf{v}_n - \alpha_n\mathbf{v}_n - \beta_n\mathbf{v}_{n-1} \tag{83}$$

   - Advantage: we only need to store 3 vectors of length N, namely $\mathbf{v}_{n+1}, \mathbf{v}_n$, and $\mathbf{v}_{n-1}$; dense matrix eigensolvers require storage of order N^2

3. In the Krylov basis the matrix $\underline{\mathbf{A}}$ is tridiagonal; the eigenvalues of $\underline{\mathbf{A}}$ in the Krylov basis are good approximations of the eigenvalues of $\underline{\mathbf{A}}$
   - The extreme eigenvalues converge very fast, i.e., $M \ll N$ iterations are sufficient to obtain those eigenvalues

Table A.1: Time and memory complexity for operations on sparse and dense $N \times N$ matrices

operation	time	memory
storage		
dense matrix	—	N^2
sparse matrix	—	$\mathrm{O}(N)$
matrix-vector multiplication		
dense matrix	$\mathrm{O}(N^2)$	$\mathrm{O}(N^2)$
sparse matrix	$\mathrm{O}(N)$	$\mathrm{O}(N)$
matrix-matrix multiplication		
dense matrix	$\mathrm{O}(N^{\ln 7/\ln 2})$	$\mathrm{O}(N^2)$
sparse matrix	$\mathrm{O}(N) \ldots \mathrm{O}(N^2)$	$\mathrm{O}(N) \ldots \mathrm{O}(N^2)$
all eigen values and vectors		
dense matrix	$\mathrm{O}(N^3)$	$\mathrm{O}(N^2)$
sparse matrix (iterative)	$\mathrm{O}(N^2)$	$\mathrm{O}(N^2)$
some eigen values and vectors		
dense matrix (iterative)	$\mathrm{O}(N^2)$	$\mathrm{O}(N^2)$
sparse matrix (iterative)	$\mathrm{O}(N)$	$\mathrm{O}(N)$

Exact Diagonalization for the Transverse Field Ising Model

- Core of the code is a matrix-vector multiplication function that computes

$$|\Phi\rangle = H\,|\Psi\rangle \quad . \tag{84}$$

- 2^N basis states of a quantum spin-$1/2$ TFIM can be represented by N-bit strings.
  - 2^N configurations are enumerated by the integers $0, \ldots, 2^N - 1$.
  - i-th bit of an integer corresponds to the orientation of the i-th spin in that configuration.
    - 0 denotes an $\uparrow$-spin.
    - 1 denotes an $\downarrow$-spin.

Bit-Operators in C++

- `bit_arg << shift_arg`
  - Shift bits of `bit_arg` `shift_arg` places to the left.
  - Or: multiplication by $2^{\texttt{shift\_arg}}$.
- `bit_arg >> shift_arg`
  - Shift bits of `bit_arg` `shift_arg` places to the right.
  - Or: integer division by $2^{\texttt{shift\_arg}}$.
- Bitwise AND: `left_arg & right_arg`
- Bitwise OR: `left_arg | right_arg`
- Bitwise XOR: `left_arg ^ right_arg`
  - `A XOR B` sets the i-th bit of the result to 1 if the i-th bit of A, B is not equal; else it sets it to 0.

Implementation of the Transverse Field Ising Model

- Hamiltonian of the transverse field Ising model:

$$H = \underbrace{\sum_{\langle i,j \rangle} J_{ij} \sigma_i^z \sigma_j^z}_{\text{Ising term}} - \underbrace{\Gamma \sum_i \sigma_i^x}_{\text{Transverse field term}} \quad . \tag{85}$$

- `state_dimension = 1 << N` $= 2^N$
  - Dimension of the tensor product of N Hilbert spaces $H^{(N)}$
- Calculation of the Ising term:

```
for( state_t s = 0; s < dimension; ++s ) {
  double jtotal = 0.;
  for( int r = 0; r < N - 1; ++r )
    jtotal += ((s >> r)^(s >> (r+1))) & 1 ? -J: +J;
  phi[s] = jtotal * psi[s];
}
```

  - $s \in [0, 2^N - 1]$ is used to represent all the available 2^N states.
  - $r \in [0, N - 1]$ is used to address the i-th bit of the state s, which represents the orientation of the i-th spin.
  - `jtotal += ((s >> r)^(s >> (r+1)))& 1 ? -J: +J;`
    1. With `s >> r`, the r-th bit of the state s is moved to the right-most position of the state (same for the $(r+1)$-th bit with $s >> (r+1)$), i.e., the information about the spin direction of the r-th and $(r+1)$-th spin is moved to the right-most position of the bit-string.
    2. Both bit-strings are then compared using the XOR-operator; the resulting bit-string is called k.
       * We are using the XOR-operator, since if both spins are equal (either both are up or both are down) it will evaluate to the same value, i.e., 0.
    3. Since we are only interested in the right-most bit of k, we *select* that bit using the bitwise AND-operator with $1 = 000\ldots0001$.
       * If the result of `(((s >> r)^(s >> (r+1)))& 1)` is 1, then both spins have different orientation and we get $-J$, since `c = a ^ b` sets the i-th bit of `c` to 1 if the i-th bit of `a` and the i-th bit of `b` are different.
       * Else, if the result is 0, then both spins have the same orientation and we get $+J$.

- Calculation of the transverse field term:

```
for( state_t s = 0; s < dimension; ++s ) {
  double jtotal = 0.;
  for( int r = 0; r < N - 1; ++r ){
    state_t sflip = s ^ (1<<r);
    phi[sflip] -= Gamma*psi[s];
  }
  phi[s] = jtotal * psi[s];
}
```

Exact Diagonalization for the Quantum XXZ and Heisenberg Models

- Heisenberg model does conserve the total magnetization. This allows to restrict the diagonalization to a subspace of fixed magnetization.

- These states have a fixed number of $N/2+M^z$ up-spins and $N/2-M^z$ down-spins.
  - States can be characterized by all N-bit strings that have $N/2 - M^z$ bits set to 0.
- Handling of the fixed magnetization basis states:

```
for (state_type s=0;s<index_.size();++s)
  if(alps::popcnt(s)==Ndown) {
    states_.push_back(s);
    index_[s]=states_.size()-1;
  }
  else
    // invalid state
    index_[s]=std::numeric_limits<index_type>::max();
```

  - `states_` is an array of size $N/2 - M^z$ that contains all states s with the required number of down-spins
  - `item_` is an array of length 2^N that contains the index of state s within the `states_` array, i.e., `s = states_[index_[s]]`.

Time Evolution of Quantum Spin Systems

The Trotter-Suzuku Decomposition

- Goal: calculate the matrix potential $\exp\{-\mathrm{i}Ht)\}$.
- Split Hamiltonian into a sum of K terms:

$$H = \sum_{k=1}^{K} h_k \quad , \tag{86}$$

  which can be easily exponentiated.
- First order version of the Trotter-Suzuku decomposition for a small time step Δt is

$$\exp\{-\mathrm{i}H\Delta t)\} = \prod_{k=1}^{K} \exp\{-\mathrm{i}h_k t)\} + O(\Delta t^2) \tag{87}$$

- Second order version of the Trotter-Suzuku decomposition for a small time step Δt is

$$\exp\{-\mathrm{i}H\Delta t)\} = S(\Delta t/2) + O(\Delta t^3) \quad , \tag{88}$$

  where S is defined as

$$S(\Delta t) = \left(\prod_{k=1}^{K} \exp\{-\mathrm{i}h_k t)\}\right)\left(\prod_{k=K}^{1} \exp\{-\mathrm{i}h_k t)\}\right) \quad . \tag{89}$$

Time Evolution for the Transverse Field Ising Model

- Hamiltonian of the transverse field Ising model:

$$H = \overbrace{\sum_{\langle i,j \rangle} J_{ij} \sigma_i^z \sigma_j^z}^{\text{Ising term } H^z :=} + \overbrace{\left(-\Gamma \sum_i \sigma_i^x \right)}^{\text{Transverse field term } H^x :=} \quad . \tag{90}$$

- Ising term H^z can be easily exponentiated since it is diagonal, and results in diagonal matrix:

$$\exp\{\mathrm{i} H^z \Delta t\} = \prod_{\langle i,j \rangle} \exp\{-\mathrm{i} \Delta t J_{ij} \sigma_i^z \sigma_j^z\} \quad . \tag{91}$$

- Transverse field term H^x splits into N commuting terms for each spins:

$$\exp\{\mathrm{i} H^x \Delta t\} = \prod_i \exp\{-\mathrm{i} \Delta t \Gamma \sigma_i^x\} \quad . \tag{92}$$

Higher Spin

- A quantum spin-S has $2S+1$ states.
- S^z components are $-S, -S+1, \ldots, S-1, S$.
- For a spin-S we will need $\lceil \log(2S+1) \rceil$ bits.
- The spin operators S^x, S^y, S^z are represented by $(2S+1) \times (2S+1)$ matrices (higher-dimensional generalizations of the Pauli matrices).

Quantum Computing

Quantum Bits and Quantum Gates

Quantum Bits

- Basic memory element is the quantum bit, or qubit for short.
- Up-spin state is associated with the 0 bit, down-spin state with the 1 bit:

$$|0\rangle = |\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad , \tag{93}$$

$$|1\rangle = |\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad . \tag{94}$$

- Quantum bit can exist in an arbitrary superposition of these two states:

$$|\Psi\rangle = \alpha\,|0\rangle + \beta\,|1\rangle \quad . \tag{95}$$

  where the normalization condition from Eq. (2) requires that $|\alpha|^2 + |\beta|^2 = 1$.
  - $|0\rangle, |1\rangle$ are the basis vectors and α, β the corresponding amplitudes.
  - In the $|0\rangle$-$|1\rangle$-basis, $|\Psi\rangle$ can also be written as

$$|\Psi\rangle = \alpha\,|0\rangle + \beta\,|1\rangle \quad = \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad . \tag{96}$$

  - Such a state requires infinite number of classical bits to describe α, β in a binary representation.

- Two quantum bits can be represented as

$$\alpha\,|00\rangle + \beta\,|01\rangle + \gamma\,|10\rangle + \delta\,|11\rangle \quad , \tag{97}$$

  where $|ab\rangle$ is the state where the first qubit has value a and the second qubit value b.

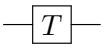
- Register of N qubits can store the wave function of N spin-$1/2$s, or N spin-orbitals for fermions.
  - This would require exponential memory on classical computers.

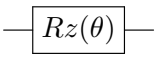
Quantum Gates

- The quantum mechanical time evolution is unitary, thus awe can only perform unitary operations on quantum bits and measurements.
- Gate which acts on k qubits is represented by a $2^k \times 2^k$ unitary matrix.

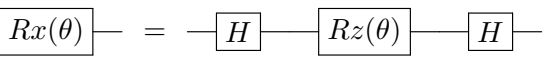
Single Qubit Gates

1. Pauli-X —$\boxed{X}$—
   - Quantum analog of a classical NOT gate.
2. Pauly-Y —$\boxed{Y}$—
3. Pauli-Z —$\boxed{Z}$—
4. Hadamard gate —$\boxed{H}$—
   - 90 degree rotation around the y axis, rotating a state aligned with z to x.
5. Phase gate —$\boxed{S}$—

6. T gate or $\pi/8$ gate 

7. $Rz(\theta)$ gate 

   - Rotation around the z axis in spin space

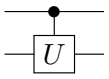
8. 

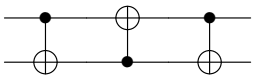
   - Swap z and x with a Hadamard gate, perform a rotation around the z axis and then rotate it back.

Two-qubit gates

- Common two-qubit gates are controlled gates, consistinng of a control bit and a target bit.
- Controlled version CU of a single qubit gate U performs the single qubit operation U on the target qubit only if the control qubit is set to 1.
  - Since quantum computers use reversible logic, to generate a two-qubit output we need a two-qubit input, which is provided by a controlled version of a single qubit gate.
- Let $\underline{\mathbf{U}} = \begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix}$ be the matrix representation of the gate U; then the matrix representation of CU in a basis $\{|00\rangle, |01\rangle, |10\rangle, |11\rangle\}$ is

$$\left(\begin{array}{cc|cc} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ \hline 0 & 0 & U_{11} & U_{12} \\ 0 & 0 & U_{21} & U_{22} \end{array}\right) \tag{98}$$

  - Quantum circuit for the controlled gate is: 

- Most important two-qubit gate is the controlled-NOT-gate (CNOT), and is typically drawn as 
- The swap gate, which swaps the states of two qubits can be built from three CNOT gates as 
- The Hadamard, $\pi/8$ and CNOT gates are universal gates, meaning they are sufficient to implement any quantum circuit; all the other gates can be built from these gates.

Quantum Algorithms

Quantum Teleportation

- Quantum teleportation lets us transmit a quantum state by sending just two classical bits.
- A Bell state is defined as a maximally entangled quantum state of two qubits.
  - Quantum entanglement: quantum states of two or more objects have to be described with reference to each other, even though the individual objects may be spatially separated; this leads to correlations between observable physical properties of the systems.
  - It is possible to prepare two particles in a single quantum state such that when one is observed to be spin-up, the other one will always be observed to be spin-down and vice versa, this despite the fact that it is impossible to predict, according to quantum mechanics, which set of measurements will be observed.

Deutsch Algorithm

- Deutsch problem: Analysis of the single bit binary functions

$$f(x) : \{0, 1\} \to \{0, 1\} \quad . \tag{99}$$

  - There are four such functions, which can be divided into two groups:
    1. *constant* functions, for which $f(x)$ is independent of x.
    2. *balanced* functions, for which $f(x)$ is zero for one value of x and unity for the other.
- It might be possible to determine the value $f(0) \oplus f(1)$ ($a \oplus b$ equals 0 if a and b are the same, and 1 if the are different) using only one evaluation of f as long as the calculation is performed using a quantum computer.
- Since quantum computers use reversible logic, the binary function f cannot be implemented directly.
  - Define propagator U_f which captures f in within a reversible transformation by using a system with two input qubits and two output qubits as follows

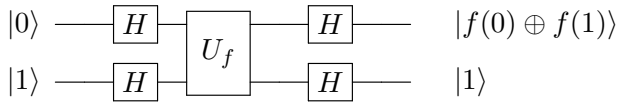
$$|x\rangle\,|y\rangle \xrightarrow{U_f} |x\rangle\,|y \oplus f(x)\rangle \quad . \tag{100}$$

- It is not necessary to start with the system in some eigenstate; instead it is possible to begin with a superposition of states:

$$\left(\frac{|0\rangle + |1\rangle}{\sqrt{2}}\right)\left(\frac{|0\rangle - |1\rangle}{\sqrt{2}}\right)$$
$$\xrightarrow{U_f} (-1)^{f(0)}\left(\frac{|0\rangle + (-1)^{f(0)\oplus f(1)}|1\rangle}{\sqrt{2}}\right)\left(\frac{|0\rangle - |1\rangle}{\sqrt{2}}\right) \quad . \tag{101}$$

  - $f(0) \oplus f(1)$ is encoded in the relative phase of the two states contributing to the superposition.
  - The relative phase can be measured, and so the value of $f(0) \oplus f(1)$ has been determined using only one application of the propagator U_f, that is only one evaluation of the function f.
  - The input eigenstates used in Equation (101) can be generated using Hadamard gates on the eigenstates $|0\rangle, |1\rangle$.
  - After having applied the propagator U_f another pair of Hadamard gates can be used to convert the superpositions back into eigenstates which encode the desired result.

- Quantum circuit for solving Deutsch's problem:



Simulating Quantum Systems

Time Evolution of a Quantum Spin Model

- The TFIM Hamiltonian is presented in Eq. (90).
- For the time evolution on a quantum compjuter we still have to use a Trotter decomposition just like in the classical case.
- We only need N qubits instead of 2^N complex numbers in a classical code and only $O(N)$ instead of $O(2^N)$ operatiions are required.

Adiabatic state preparation

- Adiabatic theorem: A physical system remains in its instantaneous eigenstate if a given perturbation is acting on it slowly enough and if there is a gap between the eigenvalue and the rest of the Hamiltonian's spectrum
- Implement time evolution under the unitary operation $\exp\{-\mathrm{i}Ht\}$ to prepare ground state of quantum system
  - Quantum computer can only do unitary operations, so using the power method or Lanczos algorithm for this task is not feasible

- Start with Hamiltonian H_0, of which the ground state is known; the ground state of an unknown Hamiltonian H_f is found by and adiabatically interpolating between H_0 and H_f with

$$H(t) = (1 - \frac{t}{t_f})H_0 + \frac{t}{t_f}H_f \quad , \tag{102}$$

and by choosing t_f long enough (exponentially small errors)

–

$$t_f \ll \mathcal{O}(\min_t \Delta(t)^{-2}), \tag{103}$$

$$\Delta(t) = E_1(t) - E_0(t) \tag{104}$$

- Landau-Zener Problem: the probability for a diabatic transition, i.e., probability for not ending in the ground state is given by

$$P = \exp\{-2\pi\Gamma\} \quad , \tag{105}$$

with $\Gamma = \epsilon^2/(2\hbar v)$. Choose $v \ll \epsilon^2/2 = \Delta^2/8$ to have an exponentially small error probability P

Indistinguishable Particles: Fermions and Bosons

Bosons

- General many-body wave function has to be symmetric:

$$\Psi^{(S)} = \mathcal{S}_+\psi(\mathbf{q}_1, \ldots, \mathbf{q}_N) \equiv \mathcal{N}_S \sum_p \psi(\mathbf{q}_{p(1)}, \ldots, \mathbf{q}_{p(N)}) \quad , \tag{106}$$

where the sum goes over all permutations p of N and $\mathcal{N}_S$ is a normalization factor.

Fermions

- General many-body wave function has to be asymmetric:

$$\Psi^{(S)} = \mathcal{S}_+\psi(\mathbf{q}_1, \ldots, \mathbf{q}_N) \equiv \mathcal{N}_A \sum_p \text{sign}(p)\psi(\mathbf{q}_{p(1)}, \ldots, \mathbf{q}_{p(N)}) \quad , \tag{107}$$

where the sum goes over all permutations p of N and $\mathcal{N}_A$ is a normalization factor.

– Consequence of the antisymmetrization:

$$\psi(\mathbf{q}_1, \mathbf{q}_2) = \Phi(\mathbf{q}_1)\Phi(\mathbf{q}_2) \implies$$
$$\Psi(\mathbf{q}_1, \mathbf{q}_2) = \psi(\mathbf{q}_1, \mathbf{q}_2) - \psi(\mathbf{q}_2, \mathbf{q}_1) = \Phi(\mathbf{q}_1)\Phi(\mathbf{q}_2) - \Phi(\mathbf{q}_2)\Phi(\mathbf{q}_1) = 0 \quad ,$$

i.e., no two fermions can be in the same state as a wavefunction

Fock Space

- Hilbert space describing the many-body system with $N = 0, 1, \ldots, \infty$ particles is called the Fock space:

$$H = \bigoplus_{n=0}^{\infty} S_{\pm} \mathcal{H}^{\otimes N} \quad , \tag{108}$$

  where H is the Fock space, $\mathcal{H}$ is a single-particle Hilbert space and $\mathcal{H}^{\otimes N}$ N-particle Hilbert spaces; S_+ is the symmetrization operator used for bosons and S_- the antisymmetrization operator used for fermions

- Single-particle Hilbert space $\mathcal{H}$ is spanned by the basis $\{|\Phi_1\rangle, \ldots, |\Phi_L\rangle\}$ consisting of L single-particle wave functions $|\Phi\rangle_i$
- Wave function of state $|n_1, \ldots, n_L\rangle$ is given as symmetrized and normlaized product of single-particle wave functions
  - n_i is the number of particles occupying the ith state
    - For bosons: $n_i \in \mathbb{N}_{\geq 0}$
    - For fermions: $n_i \in \{0, 1\}$
  - $|1, 1\rangle$ means that a single particle occupies state 1 and another single particle occupies state 2

Slater Determinant

- Describes the wave function of a multi-fermionic system
- Antisymmetrized and normalized product of N single-particle wave functions Φ_i is given by the Slater determinant

$$\mathcal{S}_- \prod_{i=1}^{N} \Phi(\mathbf{q}_i) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Phi_1(\mathbf{q}_1) & \ldots & \Phi_N(\mathbf{q}_1) \\ \vdots & & \vdots \\ \Phi_1(\mathbf{q}_N) & \ldots & \Phi_N(\mathbf{q}_N) \end{vmatrix} \quad . \tag{109}$$

  - Note: fermionic many-body wave function is a linear superposition of many Slater determinants

Creation and Annihiliation Operators

- The L basis functions $|\Phi\rangle_i$ factor into:
  - $L/(2S+1)$ orbital wave functions $f(\mathbf{q}_i)$
  - $2S+1$ spin wave functions $|\sigma\rangle$, where $\sigma = -S, -S+1, \ldots, S$
- Annhilation operator: $a_{i,\sigma} |\Phi\rangle_j = \delta_{ij} |0\rangle$

  - σ is the spin index; i is the orbital index

- Creation operator: $|\Phi\rangle_i = a^\dagger_{i,\sigma} |0\rangle$
- Basis state $|n_1, \ldots, n_L\rangle$ for bosons in the occupation number basis can be expressed using creation operators:

$$|n_1, \ldots, n_L\rangle = \prod_{i=1}^{L} (a_i^\dagger)^{n_i} |0\rangle = (a_1^\dagger)^{n_1} \cdot \cdots \cdot (a_L^\dagger)^{n_L} \tag{110}$$

Quantum Monte Carlo

Path Integral Monte Carlo

- **Goal:** Permit to calculate static properties of systems of Bosons at thermal equilibrium by means of Monte Carlo methods using path integrals
- Non-relativistic Hamiltonian:

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \Delta_i + V(\mathbf{R}) \quad . \tag{111}$$

- The static properties of a quantum many-body system in thermal equilibrium are obtainable from the thermal density matrix $\exp\{-\beta \hat{H}\}$
  - Expectation value:

$$\langle \hat{O} \rangle = \mathrm{tr} \left(\hat{O} \exp\{-\beta \hat{H}\} \right) / Z \tag{112}$$

  - Partition function Z:

$$Z = \mathrm{tr} \left(\exp\{-\beta \hat{H}\} \right) \tag{113}$$

- Thermal density matrix in coordinate representation:

$$\rho(\mathbf{R}, \mathbf{R}', \beta) = \langle \mathbf{R} | \exp\{-\beta \hat{H}\} | \mathbf{R}' \rangle \tag{114}$$

  - Partition function Z in coordinate representation:

$$Z(N, T, V) = \int \rho(\mathbf{R}, \mathbf{R}, \beta) \, \mathrm{d}\mathbf{R} \tag{115}$$

  - Product property of the density matrix:

$$\exp\{-(\beta_1 + \beta_2)\hat{H}\} = \exp\{-\beta_1 \hat{H}\} \exp\{-\beta_2 \hat{H}\} \tag{116}$$

$$\Leftrightarrow \rho(\mathbf{R}_1, \mathbf{R}_3, \beta_1 + \beta_2) = \int \rho(\mathbf{R}_1, \mathbf{R}_2, \beta_1) \, \rho(\mathbf{R}_2, \mathbf{R}_3, \beta_2) \, \mathrm{d}\mathbf{R}_2 \tag{117}$$

- Problem: $\rho(\mathbf{R}_j, \mathbf{R}_{j+1})$ are generally unknown
  - Solution: Short time / high temperature approximation using

$$\tau = \frac{\beta}{M} = \frac{1}{k_B T M} \tag{118}$$

    with a large M
  - With this approximation $\rho(\mathbf{R}_j, \mathbf{R}_{j+1})$ we get a multi-dimensional integral of known functions

- Density matrix at β is the same as the product of M density matrices at the inverse temperature $\tau = \beta/M$:

$$\exp\{-\beta\hat{H}\} = \left(\exp\{-\tau\hat{H}\}\right)^M \quad , \tag{119}$$

  with τ being the time step
  - In coordinate representation:

$$\rho(\mathbf{R}_1, \mathbf{R}_{M+1}, \beta) = \int \dots \int \mathrm{d}\mathbf{R}_2 \dots \mathrm{d}\mathbf{R}_M \tag{120}$$

$$\rho(\mathbf{R}_1, \mathbf{R}_2, \tau) \dots \rho(\mathbf{R}_M, \mathbf{R}_{M+1}, \tau) \tag{121}$$

- The coordinate representation of the density matrix is psoitive definite; it is known that many-variable integrals of positive functions can be calculated efficiently by means of Monte Carlo methods

- Primitive approximation: neglect all terms beyond the one which is linear in τ

$$\exp\{-\tau(\hat{T} + \hat{V}) + \tau^2/2\,[\hat{T}, \hat{V}] + \dots\} = \exp\{-\tau\hat{T}\}\exp\{-\tau\hat{V}\} \tag{122}$$

  - In the limit of a large Trotter number M Eq. (119) remains exact if we use the primitive approximation, which is guaranteed by the Trotter formula:

$$\exp\{-\tau(\hat{T} + \hat{V})\} = \lim_{M\to\infty} [\exp\{-\tau\hat{T}\}\exp\{-\tau\hat{V}\}]^M \tag{123}$$

- Using the primitive approximation, we arrive at the following $dN(M-1)$-dimensional integral:

$$\rho(\mathbf{R}_1, \mathbf{R}_{M+1}, \beta) \cong \int \dots \int \prod_{j=2}^{M} \mathrm{d}\mathbf{R}_j \prod_{j=1}^{M} \left(\rho^{\text{free}}(\mathbf{R}_j, \mathbf{R}_{j+1}, \tau)\exp\{-\tau V(\mathbf{R}_j)\}\right) \quad , \tag{124}$$

  where

$$\rho^{\text{free}}(\mathbf{R}, \mathbf{R}', \tau) \equiv \langle\mathbf{R}|\exp\{-\tau\hat{T}\}|\mathbf{R}'\rangle \tag{125}$$

- The Trotter formula guarantees that in the limit $M \to \infty$ this is an exact equation
- If M is large but finite, Monte Carlo can be used to evaluate the integral
- The partition function is given by

$$Z(N,V,T)\rho(\mathbf{R}_1,\mathbf{R}_1,\beta) = \cong \int \dots \int \prod_{j=1}^{M} \mathrm{d}\mathbf{R}_j \prod_{j=1}^{M} \left(\rho^{\text{free}}(\mathbf{R}_j,\mathbf{R}_{j+1},\tau)\exp\{-\tau V(\mathbf{R}_j)\}\right) \tag{126}$$

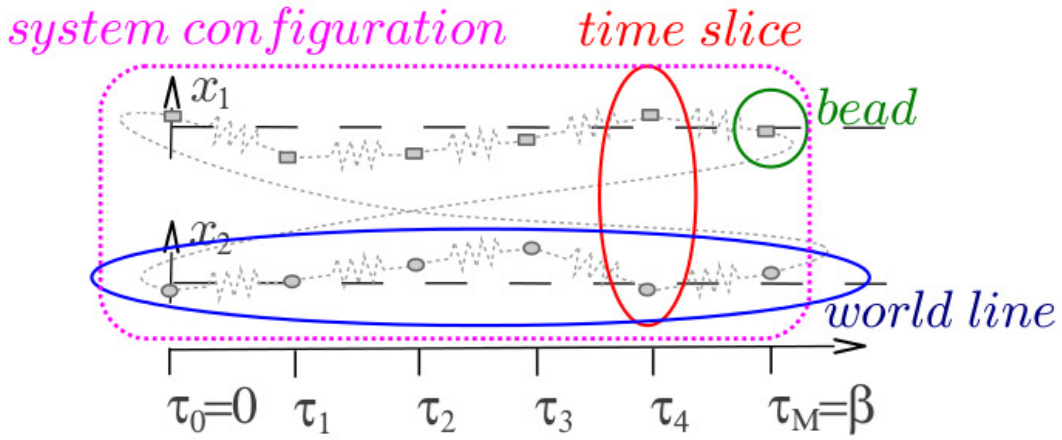


Figure 1: Definitions regarding PIMC. *System configuration:* set of the dNM coordinates $\mathbf{R}_1,\dots,\mathbf{R}_M$. *Time-slice:* j-th term of a system configuration; contains the dN coordinates of the N particles at imaginary time $(j-1)\,\tau$. *World line:* the world line i is the set of coordinates describing the path of the particle i in imaginary time, i.e., $\{\mathbf{r}_1^i,\dots,\mathbf{r}_j^i,\dots,\mathbf{r}_M^i\}$. *Beads:* the M components of a world line [1]

- Feynman's mapping of a quantum system to a classical system consisting of polymers
  - Partition function of a classical system of polymers
  - Polymer is a necklace of beads interacting as if connected by ideal springs
  - Primitive approximation: beads within the same time slice j interact via interparticle potential $v(\mathbf{r})$
    - Higher order approximations possible
- The partition function shown in Eq. (126) is not symmetrical under particle exchange, so it holds only for distinguishable particles. *Problem:* Bosons and fermions are indistinguishable

  - Symmetrize the density matrix by summing over all possible permutations
  - Sign problem: In the case of fermions, the Fermi partition function would lead to an exponentially small signal to noise ratio going to large N and small T due to alternating $+$ (for even permutations) and $-$ (for odd permutations) signs in front of each term

Path Sampling Methods

- Detailed balance condition: Let $P(X, X')$ be the probability to transition from configuration X to X'; then, if the transition matrix $P(X, X')$ satisifies

$$\pi(X)P(X, X') = \pi(X')P(X', X) \quad , \tag{127}$$

  the random walk samples points with probability $\pi(X) = w(X)/Z$, where $w(X)$ is the weight of the state X and Z the partition function

- Metropolis algorithm:
  1. Propose transition from X to X' with an arbitrary probability $T(X, X')$
  2. Acceptance / rejection stage: accept transition proposal with probability

$$A(X, X') = \min(1, \chi(X, X')) \quad , \tag{128}$$

     where

$$\chi(X, X') = \frac{\pi(X')T(X', X)}{\pi(X)T(X, X')} \tag{129}$$

Diffusion Monte Carlo

- **Goal:** study the ground-state properties of quantum systems, i.e., simulate many-body systems at zero temperature. When applied to bosons, diffusion Monte Carlo (DMC) provides the exact result for the ground-state energy
- DMC is based on the solution of the time-dependent Schrödinger equation written in imaginary time:

$$\frac{\partial}{\partial\beta}\Phi(\mathbf{R}, \beta) = \hat{H}\Phi(\mathbf{R}, \beta) \quad , \tag{130}$$

  where $\beta = \mathrm{i}t/\hbar$
- The solution of Eq. (130) is

$$\Phi(\mathbf{R}, \beta) = \exp\{-\beta\hat{H}\}\Phi(\mathbf{R}, 0) \tag{131}$$

- If we expand $\Phi(\mathbf{R}, \beta)$ on the basis of the eigenstates $\Phi_n(\mathbf{R}, \beta)$

$$\Phi(\mathbf{R}, \beta) = \sum_{n=0}^{\infty} c_n \Phi_n(\mathbf{R}, \beta) = \sum_{n=0}^{\infty} c_n \exp\{-E_n \beta\} \quad , \tag{132}$$

  we get that in the long time limit $\beta \to \infty$ Eq. (132) reduces to

$$\Phi(\mathbf{R}, \beta) = c_0 \Phi_0(\mathbf{R}) \exp\{-E_0 \beta\} \quad , \tag{133}$$

  meaning that the contribution of the ground state dominates the sum in Eq. (132)

Electronic Structure of Molecules and Atoms

Electronic Structure Problem

- Electronic structure problems arise from the Born-Oppenheimer approximation: the nuclei of atoms are so much heavier than the electrons that we can view them as classical particles and can consider them as stationary for the purpose of calculating the properties of electrons; the Hamiltonian operator for the electrons thus becomes

$$H = \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}_i) \right) + \sum_{i<j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad , \tag{134}$$

  where the potential of the M atomic nucleai with charges $Z_i\, e$ at the locations $\mathbf{R}_i$ is given by

$$V(\mathbf{r}) = -e^2 \sum_{i=1}^{M} \frac{Z_i}{|\mathbf{R}_i - \mathbf{r}|} \tag{135}$$

Basis Functions

Electron Gas

- The electron-electron interactions are completely neglected, i.e., $V(\mathbf{r}_i) = \mathbf{0} \, \forall i$ in Eq. (135)
- Ideal choice for basis functions are plane waves

$$\psi_k(\mathbf{r}) = \exp\{-\mathrm{i}\mathbf{k}\mathbf{r}\} \tag{136}$$

Atoms and Molecules

- Slater-Type-Orbitals (STO): consist of a product between a radial ($R(r)$) and angular wave function ($Y_{l,m}(\theta, \phi)$)

  - Advantage: these wave functions have the correct asymptotic radial dependence and the correct angular dependence
  - Disadvantage: the matrix elements of the Hamiltonian do not have closed form solutions

- Gauss-Type-Orbitals (GTO): use Gaussian functions
  - Advantage: the matrix elements of the Hamiltonian have closed form solutions, since Gaussians can be easily integrated
  - Disadvantage: Non-orthogonal

Electrons in Solids

- Use linear augmented plane waves (LAPW): smoothly cross over from localized wave function behaviour near the nuclei to plane waves in the region between the atoms

The Hartree-Fock Method

- The Hartree-Fock approximation is based on the assumption of independent electrons
- Ansatz: N-particle wave function is a Slater determinant of N single-particle wave functions:

$$\Phi(\mathbf{r}_1,\sigma_1;\ldots;\mathbf{r}_N,\sigma_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \Phi_1(\mathbf{r}_1;\sigma_1) & \ldots & \Phi_N(\mathbf{r}_1;\sigma_1) \\ \vdots & & \vdots \\ \Phi_1(\mathbf{r}_N;\sigma_N) & \ldots & \Phi_N(\mathbf{r}_N;\sigma_N) \end{vmatrix} . \tag{137}$$

  - The orthogonal single-particle wave functions Φ_n are chosen such that the energy is minimal

- Hartree-Fock method :
  1. Hartree-Fock wave function (Slater determinant) can be written in second quantized form

$$|\Phi\rangle = \prod_{\mu,\sigma} c^\dagger_{\mu\sigma}\,|0\rangle \quad , \tag{138}$$

     where $c^\dagger_{\mu\sigma}$ is orthogonal and creates an electron in the orbital $\phi_\mu(\mathbf{r},\sigma)$
  2. Expand $c^\dagger_{\mu\sigma}$ in terms of creation operators $\hat{a}^\dagger_{n\sigma}$, which are not necessarily orthonormal:

$$c^\dagger_{\mu\sigma} = \sum_{n=1}^{L} d_{\mu n}\hat{a}^\dagger_{n\sigma} \tag{139}$$

     where $\hat{a}^\dagger$ can be a STO or GTO, with σ being the spin and n being the orbital

3. Minimize the energy E_0 by changing the $d_{\mu\sigma}$ under the condition that the $|\Phi\rangle_\mu$ are normalized; use Lagrange multipliers to enforce the normalization constraint
4. The result is a generalized eigenvalue problem of the form

$$\underline{\mathbf{A}}[\mathbf{x}]\mathbf{x} = \lambda \underline{\mathbf{B}}\mathbf{x} \quad , \tag{140}$$

where $\underline{\mathbf{A}}$ is the Fock matrix, $\underline{\mathbf{B}}$ the overlap matrix and λ the eigenvalue; $\underline{\mathbf{A}}$ depends on the solution $\mathbf{x}$ (self-consistent field theory)

- Eq. (140) is solved iteratively until convergence to a fixed point is achieved

Density Functional Theory

- Many-body wave function living in $\mathbb{R}^{3N}$ is replaced by the electron density, which lives in $\mathbb{R}^3$
- Compared to the Hartree-Fock method, DFT could be an exact theory, if the exchange-correlation functional would be known
- Hohenberg-Kohn theorems:
  1. The ground state energy E_0 of an electronic system in an external potential V is a functional of the electron density $\rho(\mathbf{r})$:

$$E_0 = E[\rho] = \int \mathrm{d}^3\mathbf{r}\, V(\mathbf{r})\rho(\mathbf{r}) + F[\rho] \quad , \tag{141}$$

  with a universal functional F
  2. The density of the ground state wave function minimizes the functional E_0 shown in Eq. (141)
- DFT:
  1. Start with Ansatz

$$F[\rho] = \underbrace{E_h[\rho]}_{\text{Hartree term}} + \overbrace{E_k[\rho]}^{\text{Kinetic term}} + \underbrace{E_{xc}[\rho]}_{\text{Exchange-correltation term (unknown)}} \tag{142}$$

  - E_h is given by the Coulomb repulsion between two electrons
  - E_k is the kinetic energy of a non-interacting electron gas with the same density
  - E_{xc} is the unknown contribution
  2. To calculate the ground state density we have to minimize the energy given in Eq. (141):

$$\partial E[\rho] = 0 \tag{143}$$

Local Density Approximation

- Approximate the potential v_{xc} arising from the functional $E_{xc}[\rho]$ by replacing v_{xc} with the potential of a uniform gas with the same density. In this case, we ignore the fact that the functional E_{xc} may depend on $\rho, \nabla\rho, \nabla^2\rho, dots$ and assume that it takes the local density:

$$E_{xc}[\rho](\mathbf{r}) = E_{\text{LDA}}(\rho(\mathbf{r})) \tag{144}$$

Car-Parinello Molecular Dynamics

- Atomic nuclei are propagated using classical molecular dynamics, but the electronic forces which move the nuclei are estimated using DFT

Quantum Monte Carlo Algorithms for Lattice Models

World Line Representations for Quantum Lattice Models

- Problem: Monte Carlo method cannot be directly applied except in the classical case where the Hamiltonian $\mathcal{H}$ is diagonal
  - The partition function is an operator expression (and not a simple sum over classical configurations):

$$Z = \text{tr}\left(\exp\{-\beta\mathcal{H}\}\right) \tag{145}$$

- Solution: map the quantum system to an equivalent *classical* system:

$$Z = \text{tr}\left(\exp\{-\beta\mathcal{H}\}\right) = \sum_c w(c) \tag{146}$$

  - The magnetization for example is given by

$$\langle m\rangle = \sum_c m(c)P(c) \quad , \tag{147}$$

    where $P(c) = w(c)/Z$

A Spin-$1/2$ in a Magnetic Field

- Hamilton operator for a single quantum mechanical spin-$1/2$ in a longitudinal magnetic field h and transverse magnetic field Γ:

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_x = -hS^z - \Gamma S^x \quad , \tag{148}$$

  where S^i are the Pauli matrices with a given basis set $\{|1/2\rangle, |-1/2\rangle\}$ in which the z-component of the spin operator is diagonal, however H is not diagonal

Discrete Time Path Integrals

- Use discrete imaginary time steps $\delta\tau = \beta/M$
- Approximate the quantum transfer matrix using the lowest-order Taylor expansion for the exponential function:

$$\exp\{-\Delta_\tau \mathcal{H}\} = 1 - \Delta_\tau \mathcal{H} + \mathcal{O}(\Delta_\tau^2) \tag{149}$$

- In the discrete time path integral formulation, the partition function Z in Eq. (145) is evaluated by rewriting the trace as a sum over all basis states $|i\rangle$:

$$Z = \mathrm{tr}\left(\exp\{-\beta\mathcal{H}\}\right) = \mathrm{tr}\left(\exp\{-\Delta_\tau\mathcal{H}\}^M\right) = \mathrm{tr}\left([1 - \Delta_\tau\mathcal{H} + \mathcal{O}(\Delta_\tau^2)]^M\right) \tag{150}$$

$$= \sum_{(i_1,\ldots,i_M)} \langle i|_1 U |i_2\rangle \langle i|_2 U |i_3\rangle \cdot \cdots \cdot \langle i|_M U |i_1\rangle + \mathcal{O}(\Delta_\tau) \tag{151}$$

  - The expression in Eq. (151) is identical to the partition function of a one-dimensional chain of classical Ising spins $\sigma_i = \pm 1$ of length M with periodic boundary conditions $\sigma_M = \sigma_1$
  - Any d-dimensional Ising model can be mapped to a $(d+1)$-dimensional classical Ising model

Continuous Time Path Integrals

- Modern world line QMC algorithm are based on a continuous time representation, i.e., they work in the limit $\Delta_\tau \to 0 (M \to \infty)$
  - Number of spins M diverges as $\Delta_\tau \to 0$, however the average number of domain walls between parallel spins remains finite $\implies$ store the values of the spins in the j-th domain ($j = 1, \ldots, n$) and the location of the last spin of the j-th domain
- The continuous time interpretation is obtained by integrating the continuous time expression over all possible domain walls and summing over all possible number of domain walls n

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