Problem Set 3: Path integrals and density matrices
Graduate Quantum I
Physics 6572

James Sethna
Due Monday September 24
Last correction at October 1, 2012, 8:02 pm

Reading

Sakurai and Napolitano, sections 2.6, 3.4

3.1 **Momentum-space propagator**, Sakurai exercise (2.33).

3.2 **Exponentials of matrices.** (Math) ③

In quantum mechanics, one often takes exponentials of operators. The exponential of a matrix $\exp(M)$ can be computed using several different equivalent relations.

First, one can compute it as a power series:

$$\exp(M) = \sum_{n=0}^{\infty} M^n/n! \tag{1}$$

Let's take the exponential $\exp(-i\phi\sigma_2/2)$, where $\sigma_2 = \left(\begin{smallmatrix} 0 & -i \\ i & 0 \end{smallmatrix}\right)$ is the second Pauli matrix (also known as σ_y). This is the definition of how spin $\frac{1}{2}$ particles transform under rotations.

(a) Note that $\sigma_2^2 = 1$*. Separate the infinite series into even and odd terms, and express* $\exp(-\mathrm{i}\phi\sigma_2/2)$ *as a linear combination of the identity matrix* $\mathbb{1}$ *and the matrix* σ_2*. In your answer, note that a* $360°$ *rotation is not equal to the identity, but to minus the identity!*

Secondly, one can compute it as an infinite product of infinitesimal transformations:

$$\exp(M) = \lim_{n\to\infty} \exp(M/n)^n = \lim_{n\to\infty} (\mathbb{1} + M/n)^n. \tag{2}$$

This will be the basic trick we use to generate the path-integral formulation of quantum mechanics. It is also the way we generate symmetry operations (like rotations) from infinitesimal generators (like angular momentum).[1] For example, in two dimensions the angular momentum operator is $J = \mathrm{i}\hbar \left(\begin{smallmatrix} 0 & 1 \\ -1 & 0 \end{smallmatrix}\right)$.

(b) Show that a 2x2 rotation matrix by an angle θ/n*, in the limit* $n \to \infty$*, can be written as* $\mathbb{1} + (C\theta/n)J$*. What is the constant* C*? Argue, without calculation, that the product in eqn 2 must generate the finite-angle rotations.*

---

[1] Continuous groups like the rotations are called *Lie groups*. The corresponding infinitesimal generators, and their commutation relations, are called the *Lie algebra* for the group.

Finally, most matrices which arise in quantum mechanics (symmetric matrices, Hermitian matrices, and the more general category of *normal matrices*) can be diagonalized by a unitary change of basis: $D = \left(\begin{smallmatrix} \lambda_1 & 0 & \cdots \\ 0 & \lambda_2 & \cdots \\ 0 & 0 & \cdots \end{smallmatrix}\right) = U^\dagger M U$, with $U^\dagger = (U^T)^* = U^{-1}$. Thus $M^n = (UDU^\dagger)^M = UD(U^\dagger U)D \cdots DU^\dagger = UD^nU^\dagger$. For these matrices, we can compute the exponential of a matrix by doing a coordinate change to the basis that diagonalizes it:

$$\exp(M) = \sum_{n=0}^{\infty} M^n/n! = \sum_{n=0}^{\infty} UD^nU^\dagger/n! = U\left(\sum_{n=0}^{\infty} D^n/n!\right)U^\dagger = U\left(\begin{smallmatrix} e^{\lambda_1} & 0 & \cdots \\ 0 & e^{\lambda_2} & \cdots \\ 0 & 0 & \cdots \end{smallmatrix}\right)U^\dagger \quad (3)$$

Let's apply this to the time evolution operator $\exp(-iHt/\hbar)$ for the Hamiltonian we studied in the Eigen exercise (3.1): $H = \left(\begin{smallmatrix} 0 & -4 \\ -4 & 6 \end{smallmatrix}\right)$.

(c) Apply the relation eqn 3 to calculate the 2x2 time evolution operator $\exp(-iHt/\hbar)$ *for our Hamiltonian. Apply the resulting time evolution operator to the state* $\psi(0) = \left(\begin{smallmatrix} 1 \\ 0 \end{smallmatrix}\right)$ *to calculate* $\psi(t)$*. Also write the time evolved state as* $\sum_n \exp(-iE_nt/\hbar)|n\rangle\langle n|\psi\rangle$*, where* $|n\rangle$ *are the eigenstates of* H*. Do the two methods agree?*

3.3 **Propagators to Path Integrals.** (PathIntegrals) ③

In class, we calculated the propagator for free particles, which Sakurai also calculates (eqn 2.6.16):

$$K(x', t; x_0, t_0) = \sqrt{\frac{m}{2\pi i\hbar(t-t_0)}} \exp\left[\frac{im(x'-x_0)^2}{2\hbar(t-t_0)}\right]. \quad (4)$$

Sakurai also gives the propagator for the simple harmonic oscillator (eqn 2.6.18):

$$\begin{aligned} K(x', t; x_0, t_0) =& \sqrt{\frac{m\omega}{2\pi i\hbar \sin[\omega(t-t_0)]}} \quad (5) \\ & \times \exp\left[\left\{\frac{im\omega}{2\hbar\sin[\omega(t-t_0)]}\right\}\left[(x'^2+x_0^2)\cos[\omega(t-t_0)] - 2x'x_0\right]\right]. \end{aligned}$$

In deriving the path integral, Feynman approximates the short-time propagator in a potential $V(x)$ using the 'trapezoidal' rule:

$$K(x_0+\Delta x, t_0+\Delta t; x_0, t_0) = N_{\Delta t}\exp\left[\frac{i\Delta t}{\hbar}\left\{\tfrac{1}{2}m(\Delta x/\Delta t)^2 - V(x_0)\right\}\right], \quad (6)$$

where the expression in the curly brackets is the straight-line approximation to the Lagrangian $\frac{1}{2}m\dot{x}^2 - V(x)$. Check Feynman's approximation: is it correct to first order in Δt for the free particle and the simple harmonic osillator? For simplicity, let's ignore the prefactors (coming from the normalizations), and focus on the terms inside the exponentials.

Taking $t = t_0 + \Delta t$ *and* $x' = x_0 + \dot{x}\Delta t$*, expand to first order in* Δt *the terms in the exponential for the free particle propagator (eqn 4) and the simple harmonic oscillator* *(eqn 5). Do they agree with Feynman's formula?* (Hint: For the simple harmonic oscillator, the first term is proportional to $1/\Delta t$, so you'll need to keep the second term to second order in Δt.)

3.4 **Spin density matrix.**[2] (Quantum) ③

Let the Hamiltonian for a spin be

$$\mathcal{H} = -\frac{\hbar}{2}\mathbf{B}\cdot\vec{\sigma}, \tag{7}$$

where $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ *are the three Pauli spin matrices, and* $\mathbf{B}$ *may be interpreted as a magnetic field, in units where the gyromagnetic ratio is unity. Remember that* $\sigma_i\sigma_j - \sigma_j\sigma_i = 2\mathrm{i}\epsilon_{ijk}\sigma_k$*. Show that any* 2×2 *density matrix may be written in the form*

$$\boldsymbol{\rho} = \frac{1}{2}(\mathbf{1} + \mathbf{n}\cdot\vec{\sigma}). \tag{8}$$

Show that the equations of motion for the density matrix $\mathrm{i}\hbar\partial\boldsymbol{\rho}/\partial t = [\mathcal{H}, \boldsymbol{\rho}]$ *can be written as* $\mathrm{d}\mathbf{p}/\mathrm{d}\mathbf{t} = -\mathbf{B}\times\mathbf{p}$.

3.5 **Density Matrices and Statistical Mechanics.** (Quantum Stat Mech) ③

Quantum tunneling of atoms dominates the low temperature properties of glasses (as discovered at Cornell by Robert Pohl and his Master's student Zeller). Defects in crystals also have important quantum tunneling properties; indeed, tunneling defects in alkali halides were a major field of study here in the 60's and 70's (Pohl, Sievers, Silsbee, Krumhansl, …). For example, if you substitute a (small) lithium atom for a (larger) potassium in KCl, it lowers its energy by sitting off-center, nestled into a corner of the cube formed by its six Cl neighbors. But quantum mechanically, it has six such off-center positions, and can tunnel between them.

Here we'll study the simpler case of an atom with two equilibrium positions. Let the Hamiltonian for an atom in a symmetric double well be approximated by

$$\mathcal{H}_0 = \begin{pmatrix} 0 & -\Delta \\ -\Delta & 0 \end{pmatrix} \tag{9}$$

where the basis states $|L\rangle = \left(\begin{smallmatrix}1\\0\end{smallmatrix}\right)$ and $|R\rangle = \left(\begin{smallmatrix}0\\1\end{smallmatrix}\right)$ are localized in the left and right wells, and where $\Delta > 0$ is the tunneling matrix element (calculated, for example, by WKB or instantons). This two-level system approximation is the starting point for many theories of defect tunneling and glasses.

(a) Find the eigenvalues and eigenvectors of $\mathcal{H}_0$*.*

At a temperature T, quantum statistical mechanics tells us that the density matrix is

$$\rho = \exp(-\mathcal{H}/k_BT)/\mathrm{Tr}(\exp(-\mathcal{H}/k_BT)) \tag{10}$$

---

[2] Adapted from exam question by Bert Halperin, Harvard University, 1976.

(b) Find the density matrix $\rho(T)$ for $\mathcal{H}_0$. (Hint: There are lots of different ways to exponentiate the matrix. Your final answer should be written without any infinite sums, and the diagonal elements should make sense.)

(c) Find the expectation value for the energy $U(T) = \langle H \rangle$ by taking an appropriate trace involving ρ. Find the specific heat $c(T) = \mathrm{d}U/\mathrm{d}T$.

Your formula should give a peak in the specific heat near $k_B T = \Delta$. This is called a Schottky peak, and is often a clear signal of a tunneling defect.

Statistical mechanics is often formulated in the energy basis. Every energy eigenstate $|E_\alpha\rangle$ is weighted by a Boltzmann factor $\exp(-E_\alpha/k_B T)$, so the probability of being in that state is $p_\alpha = \exp(-E_\alpha/k_B T)/Z$.

$$\rho = \sum_\alpha p_\alpha |E_\alpha\rangle\langle E_\alpha|. \tag{11}$$

Here the partition function $Z = \sum_\alpha \exp(-E_\alpha/k_B T)$ is seen as the normalization factor for the Boltzmann sum.

(d) Calculate the expectation value for the energy by summing over the eigenstates. Check your answer from part (c).

Why bother with density matrices, when eigenstates will do? In many cases, the eigenstate basis isn't natural. For example, when our double-well atom is put in an electric field or under strain, the couplings are simple in the position basis, and quite ugly and unnatural in the energy eigenstates. For example, if the left and right wells are separated by a distance Q and the ion has charge e, the total Hamiltonian might be $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_I$, with an interaction Hamiltonian

$$\mathcal{H}_I = eEX = eE \begin{pmatrix} -Q/2 & 0 \\ 0 & Q/2 \end{pmatrix}. \tag{12}$$

(d) Write $\mathcal{H}_I$ in the energy basis. (Hint: The answer isn't so messy, but only because it's a symmetric double well.)

3.6 **Does entropy increase in quantum systems?.** (Mathematics, Quantum) ③

One can show (Exercise (5.7) in my text, 'Entropy, Order Parameters, and Complexity') that in classical Hamiltonian systems the non-equilibrium entropy $S_{\text{nonequil}} = -k_B \int \rho \log \rho$ is constant in a classical mechanical Hamiltonian system. Here you will show that in the microscopic evolution of an isolated quantum system, the entropy is also time independent, even for general, time-dependent density matrices $\rho(t)$.

Using the evolution law $\partial\rho/\partial t = [\mathcal{H}, \rho]/(\mathrm{i}\hbar)$, prove that $S = -\mathrm{Tr}\,(\boldsymbol{\rho} \log \boldsymbol{\rho})$ is time independent, where $\boldsymbol{\rho}$ is any density matrix. (Hint: Go to an orthonormal basis ψ_i which diagonalizes ρ. Show that $\psi_i(t)$ is also orthonormal, and take the trace in that basis. Use the cyclic invariance of the trace.)