**1.** Calculate the partition function of the hydrogen atom at room temperature. What is the probability for the atom to be in the ground state at room temperature? Is this consistent with what we know about hydrogen? If not, what's wrong?

2. Consider the scattering of a quantum particle by a potential step of height V_0. Let E be the energy of the particle and assume that it satisfies the inequality $E > V_0$.
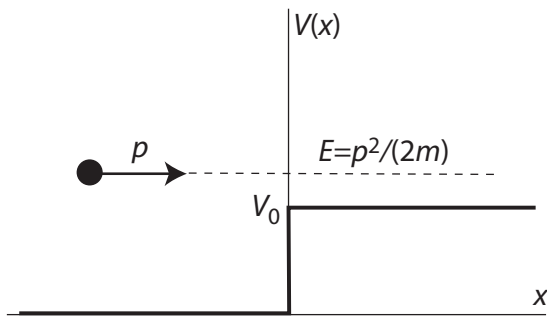
This problem is solved in just about every quantum mechanics textbook, where it is shown that the probability for the particle to be reflected back is given by

$$R = \left(\frac{k-k'}{k+k'}\right)^2 = \left(\frac{p-p'}{p+p'}\right)^2$$

where $p = \sqrt{2mE} \equiv \hbar k$ and $p' = \sqrt{2m(E-V_0)} \equiv \hbar k'$ are the momenta of the particle to the left and to the right of the barrier (and k and k' are the corresponding wavevectors). Notice that Planck's constant does not enter the above expression at all. Since quantum mechanics is a better theory than classical mechanics, we thus expect nonzero reflection probability for any particle (quantum or classical), which is in contradiction with our knowledge that classical particle would behave deterministically and continue moving in the same direction, as long as its energy is higher than the barrier V_0. Explain this paradox.

3. To describe the behavior of Brownian particles (or molecules) in liquids, one often uses the Langevin equation of the form:

$$m\ddot{x} = -\gamma \dot{x} - V'(x) + f(t)$$

Here we assume that the particle of mass m is subjected to a potential $V(x)$, to a viscous drag force proportional to its velocity, and to a random force $f(t)$ that describes the particle's collisions with the surrounding solvent molecules.

A. Let $x(t)$ be a particle's trajectory obtained by solving the above equation. Now consider a time reversed trajectory, $x(-t)$. If someone gave you both $x(-t)$ and $x(t)$ but did not tell you which one is which, would you be able to find out by yourself?

B. In computer simulations, it is often beneficial to run trajectories backward in time to discover the system's past based on its current state. In the case of Newtonian dynamics, where the equation of motion is $m\ddot{x} = -V'(x)$, this simply amounts to reversing the initial velocity $v = dx/dt$, $v(0) \rightarrow -v(0)$. Then the substitution $t \rightarrow -t$ results in exactly the same equation as before (as expected since Newtonian dynamics is time-reversible). In the case of Langevin dynamics, what is the appropriate equation to describe the past of the particle?

4. Time evolution of many molecular systems can be described by the master equation of the form:

$$dp_i / dt = \sum_{j \neq i} k_{j \rightarrow i} p_j - \sum_{j \neq i} k_{i \rightarrow j} p_i$$

where p_i is the probability of finding a system in state i and $k_{i \rightarrow j}$ is a rate coefficient describing the probability of making transition from i to j per unit time. This equation, for instance, can be used to describe vibrational relaxation of a molecule, where the states i represent different vibrational energy levels. Or it can be used to describe the diffusion of an atom on a metal surface, where i would enumerate different lattice sites. To be specific, consider vibrational relaxation in a molecule, which is in contact with a large reservoir at temperature T. Show that the above equation cannot have oscillatory solutions. More precisely, if the above master equation is rewritten in the form,

$$\frac{d\mathbf{p}}{dt} = \mathbf{Kp}$$

where $\mathbf{p}$ is the vector whose components are the probabilities p_1, p_2, ..., prove that the eigenvalues of the matrix $\mathbf{K}$ are real numbers.

5.

A. In the 1s state of hydrogen atom, the z and x components of the electron's angular momentum have definite values equal to zero. Given that the operators L_x and L_z do not commute, what about the uncertainty principle?

B. The energy of the ground state of a one-dimensional rigid rotor is zero, in apparent contradiction to the uncertainty principle. Is there really a contradiction?