Assignment 13: Advanced Exercises in Monte Carlo and Minimization Techniques

1. Study the function:

$$E(x,y) = ax^2 + by^2 + c\,(1-\cos\gamma x) + d\,(1-\cos\delta y)\,. \qquad \text{(D.11)}$$

   Note that is has many local minima and a global minimum at $(x,y) = (0,0)$. Minimize $E(x,y)$ with $a = 1, b = 2, c = 0.3$, $\gamma = 3\pi$, $d = 0.4$, and $\delta = 4\pi$ by the standard simulated annealing method. Use the starting point $(1,1)$ and step perturbations $\Delta x = 0.15$, and set β in the range of 3.5 to 4.5. Limit the number of steps to ~ 150. Now implement the *variant* of the simulated annealing method where acceptance probabilities for steps with $\Delta E < 0$ are proportional to $\exp(-\beta E^g \Delta E)$, with the exponent $g = -1$. Analyze and compare the efficiency of the searches in both cases. It will be useful to plot all pairs of points (x,y) that are generated by the method and distinguish 'accepted' from 'rejected' points.

2. Devise a different variant of the basic simulated annealing minimization method that would incorporate *gradient* information to make the searches more efficient.

3. Consider the following global optimization deterministic approach based on the *diffusion equation* as first suggested by Scheraga and colleagues (L. Piela, J. Kostrowicki, and H. A. Scheraga, "The Multiple-Minima Problem in Conformational Analysis of Molecules. Deformation of the Potential Energy Hypersurface by the Diffusion Equation Method", *J. Chem. Phys.* **93**, 3339–3346 (1989)).
   The basic idea is to deform the energy surface smoothly. That is, we seek to make "shallow" wells in the potential energy landscape disappear iteratively until we reach a global minimum of the deformed function. Then we "backtrack" by successive minimization from the global minimum of the transformed surface in the hope of reaching the global minimum of the real potential energy surface. This idea can be implemented by using the heat equation where T represents the temperature distribution in space x, and t represents time:

$$\frac{\partial^2 T}{\partial x^2} = \frac{\partial T}{\partial t} \qquad \text{(D.12)}$$

$$T(x,0) = E(x)\,. \qquad \text{(D.13)}$$

   Here, the boundary condition at time $t = 0$ equates the initial temperature distribution with the potential energy function $E(x)$. Under certain conditions (e.g., E is bounded), a solution exists. Physically, the application of this equation exploits the fact that the heat flow (temperature distribution) should eventually settle down.

To formulate this idea, let us for simplicity consider first a one-dimensional problem where the energy function E depends on a scalar x. Let $E^{(n)}(x)$ represent the nth derivative of E with respect to x and define the transformation operator $\mathcal{S}$ on the energy function E for $\beta > 0$ as follows:

$$\mathcal{S}[E(x)] = E(x) + \beta E^{(2)}(x)\,. \tag{D.14}$$

That is, we have:

$$\begin{aligned}
\mathcal{S}^0 E &= E \\
\mathcal{S}^1 E &= E + \beta E^{(2)} \\
\mathcal{S}^2 E &= E + 2\beta E^{(2)} + \beta^2 E^{(4)} \\
\mathcal{S}^3 E &= E + 3\beta E^{(2)} + 3\beta^2 E^{(4)} + \beta^3 E^{(8)} \\
\vdots &\qquad\qquad \vdots \\
\mathcal{S}^N E &= (1 + \beta d^2/dx^2)^N E\,.
\end{aligned}$$

Now writing $\beta = t/N$ where t is the time variable, and letting $N \to \infty$, we write:

$$\exp\left(t d^2/dx^2\right) E \equiv \exp(A(t))\, E = \left[1 + A + \frac{A^2}{2!} + \frac{A^3}{3!} + \cdots\right]. \tag{D.15}$$

Thus we can define $T(t)$ as

$$T(t) = \exp((A(t)) = \exp(t d^2/dx^2)\,. \tag{D.16}$$

In higher dimensions, let x represent the collective vector of n independent variables; we replace the differential operator above d^2/dx^2 by the *Laplacian operator*, that is

$$\Delta = \sum_{i=1}^{n} \partial^2/\partial x_i\,.$$

Using this definition, we can also write

$$T(t) = T_1(t)\, T_2(t)\, \cdots T_n(t)$$

where

$$T_i = \exp(t\partial^2/\partial x_i)\,.$$

This definition produces the heat equation (D.12, D.13) since

$$\begin{aligned}
\frac{\partial T(t)[E(x)]}{\partial t} &= \left[\frac{dA}{dt} + \frac{2A}{2}\frac{dA}{dt} + \frac{3A^2}{3!}\frac{dA}{dt} + \cdots\right][E] \\
&= \left[1 + A + \frac{A^2}{2} + \cdots\right]\frac{d^2}{dx^2}[E]
\end{aligned}$$

$$= \frac{\partial^2 T(t)}{\partial x^2}[E(x)]\,.$$

In practice, the diffusion equation method for global optimization is implemented by solving the heat equation by Fourier techniques (easy, for example, if we have dihedral potentials only) or by solving for T up to a sufficiently large time t. This solution, or approximate solution (representing $E(x,t)$ for some large t), is expected to yield a deformed surface with one (global) minimum. With a local minimization algorithm, we compute the global minimum x^* of the deformed surface, and then begin an iterative deformation/minimization procedure from x^* and $E(x,t)$ so that at each step we deform backwards the potential energy surface and obtain its associated global minimum ($E(x,t) \longrightarrow E(x,t-\Delta t)$ and x^* to x^1, $E(x,t-\Delta t) \longrightarrow E(x,t-2\Delta t)$ and x^1 to x^2, $\cdots$ $E(x,0) \longrightarrow x^k$). Of course, depending on how the backtracking is performed, different final solutions can be obtained.

(a) To experiment with this interesting diffusion-equation approach for global minimization, derive a general form for the deformation operator $T(t) = \exp(td^2/dx^2)$ on the following special functions $E(x)$: (*i*) polynomial functions of degree n, and (*ii*) trigonometric functions $sin\omega x$ and $cos\omega x$, where ω is a real-valued number (frequency). What is the significance of your result for (*ii*)?

(b) Apply the deformation operator $T(t) = \exp(td^2/dx^2)$ to the quadratic function

$$E(x) = x^4 + ax^3 + bx^2\,, \tag{D.17}$$

with $a = 3$ and $b = 1$. Evaluate and plot your resulting $T(t)E(x)$ function at $t = 0, \Delta t, 2\Delta t, ...$, for small time increments Δt until the global minimum is obtained.

(c) Apply the deformation operator $T(t)$ for the two-variable function in eq. (D.11). Examine behavior of the deformation as $t \to \infty$ as a function of the constants a and b. Under what conditions will a unique minimum be obtained as $t \to \infty$?

4. Use Newton minimization to find the minimum of the two-variable function in equation (D.11) and the one-variable function in equation (D.17). It is sufficient for the line search to use simple bisection: $\lambda = 1, 0.5$, etc., or some other simple backtracking strategy. For the quartic function, experiment with various starting points.