

which is discussed in many texts (see Griffiths for example). It is also possible to compute  $T$  from averages over  $(x_j - x_{j-1})^2$ , but the virial theorem yields a smaller variance. The ground state wave function  $\phi(x)$  is obtained from the normalized probability  $P(x)\Delta x$  by dividing by  $\Delta x$  and taking the square root.

We can also find the thermodynamic properties of a particle that is connected to a heat bath at temperature  $T = 1/\beta$  by not taking the  $\beta = N\Delta\tau \rightarrow \infty$  limit. To obtain the ground state, which corresponds to the zero temperature limit ( $\beta \gg 1$ ), we have to make  $N\Delta\tau$  as large as possible. However, we need  $\Delta\tau$  to be as small as possible to approximate the continuum time limit. Hence, to obtain the ground state we need a large number of time intervals  $N$ . For the finite temperature simulation, we can use smaller values of  $N$  for the same level of accuracy as the zero temperature simulation.

The path integral method is very flexible and can be generalized to higher dimensions and many mutually interacting particles. For three dimensions,  $x_j$  is replaced by the three-dimensional displacement  $\mathbf{r}_j$ . Each real particle is represented by a ring of  $N$  "atoms" with a spring-like potential connecting each atom within a ring. Each atom in each ring also interacts with the atoms in the other rings through an interparticle potential. If the quantum system is a fluid where indistinguishability is important, then we must consider the effect of exchange by treating the quantum system as a classical polymer system where the "atoms" represent the monomers of a polymer, and where polymers can split up and reform. Chandler and Wolynes discuss how the quantum mechanical effects due to exchanging identical particles can be associated with the chemical equilibrium of the polymers. They also discuss Bose condensation using path integral techniques.

### Problem 16.31 Path integral calculation

- Write a program to implement the path integral algorithm for the one-dimensional harmonic oscillator potential with  $V(x) = x^2/2$ . Use the structure of your Monte Carlo Lennard-Jones program from Chapter 15 as a guide.
- Let  $N\Delta\tau = 15$  and consider  $N = 10, 20, 40$ , and  $80$ . Equilibrate for at least 2000 Monte Carlo steps per atom and average over at least 5000 mcs. Compare your results with the exact result for the ground state energy given by  $E_0 = 0.5$ . Estimate the equilibration time for your calculation. What is a good initial configuration? Improve your results by using larger values of  $N\Delta\tau$ .
- Find the mean energy  $\langle E \rangle$  of the harmonic oscillator at the temperature  $T$  determined by  $\beta = N\Delta\tau$ . Find  $\langle E \rangle$  for  $\beta = 1, 2$ , and  $3$  and compare it with the exact result  $\langle E \rangle = \frac{1}{2} \coth(\beta/2)$ .
- Repeat the above calculations for the Morse potential  $V(x) = 2(1 - e^{-x})^2$ . ■

## 16.11 ■ PROJECTS

Many of the techniques described in this chapter can be extended to two-dimensional quantum systems. The `Complex2DFrame` tool in the `frames` package is designed to show two-dimensional complex scalar fields such as quantum wave functions. Listing 16.13 in Appendix 16A shows how this class is used to show a two-dimensional Gaussian wave packet with a momentum boost.

### Project 16.32 Separable systems in two dimensions

The shooting method is inappropriate for the calculation of eigenstates and eigenvalues in two or more dimensions with arbitrary potential energy functions  $V(\mathbf{r})$ . However, the special case of separable potentials can be reduced to several one-dimensional problems that can be solved using the numerical methods described in this chapter. Many molecular modeling programs use the Hartree-Fock self-consistent field approximation to model nonseparable systems as a set of one-dimensional problems. Recently, there has been significant progress motivated by a molecular dynamics algorithm developed by Car and Parrinello.

Write a two-dimensional eigenstate class `Eigenstate2d` that calculates eigenstates and eigenvalues for a separable potential of the form

$$V(x, y) = V_1(x) + V_2(y). \quad (16.106)$$

Test this class using the known analytic solutions for the two-dimensional rectangular box and two-dimensional harmonic oscillator. Use this class to model the evolution of superposition states. Under what conditions are there wave function revivals? ■

### Project 16.33 Excited state wave functions using quantum Monte Carlo

Quantum Monte Carlo methods can be extended to compute the excited state wave functions using a Gram-Schmidt procedure to insure that each excited state is orthogonal to all lower lying states (see Roy et al.). A quantum Monte Carlo method is used to compute the ground state wave function. A trial wave function for the first excited state is then selected and the ground state component is subtracted from the trial wave function. This subtraction is repeated after every iteration of the Monte Carlo algorithm. Because excited states decay with a time constant  $e^{-(E_j - E_0)}$ , the lowest remaining excited state dominates the remaining wave function. After the first excited state is obtained, the second excited state is computed by subtracting both known states from the trial wave function. This process is repeated to obtain additional wave functions.

Implement this procedure to find the first few excited state wave functions for the one-dimensional harmonic oscillator. Then consider the one-dimensional double-well oscillator

$$V(x) = -\frac{1}{2}kx^2 + a_3x^3 + a_4x^4, \quad (16.107)$$

with  $k = 40$ ,  $a_3 = 1$ , and  $a_4 = 1$ . ■

### Project 16.34 Quantum Monte Carlo in two dimensions

The procedure described in Project 16.33 can be used to compute two-dimensional wave functions (see Roy et al.).

- Test your program using a separable two-dimensional double-well potential.
- Find the first few excited states for the two-dimensional double-well potential

$$V(x, y) = -\frac{1}{2}k_x x^2 - \frac{1}{2}k_y y^2 + \frac{1}{2}(a_{xx}x^4 + 2a_{xy}x^2y^2 + a_{yy}y^4), \quad (16.108)$$

with  $k_x = k_y = 20$  and  $a_{xx} = a_{yy} = a_{xy} = 5$ . Repeat with  $k_x = k_y = 20$  and  $a_{xx} = a_{yy} = a_{xy} = 1$ . ■