5.1 [10] The Lennard-Jones 6-12 potential is commonly used as a model to describe the potential of an atom in the neighborhood of another atom. Classically, the energy is given by

\[ E = \frac{1}{2} m x^2 + 4\varepsilon \left[ \left( \frac{\sigma}{x} \right)^{12} - \left( \frac{\sigma}{x} \right)^6 \right]. \]

(a) [6] Find the minimum \( x_{\text{min}} \) of this potential, and expand the potential to quadratic order in \( (x - x_{\text{min}}) \).

The potential is minimized when the derivative vanishes, so we have

\[ 0 = \frac{dV}{dx} = 4\varepsilon \frac{d}{dx} \left[ \left( \frac{\sigma}{x} \right)^{12} - \left( \frac{\sigma}{x} \right)^6 \right] = 4\varepsilon \left[ -\frac{12\sigma^{12}}{x^{13}} + \frac{6\sigma^6}{x^7} \right] = \frac{24\varepsilon \sigma^6}{x^7} \left( 1 - \frac{2\sigma^6}{x^6} \right) \]

The minimum of this potential is therefore \( x_{\text{min}} = 2^{1/6} \sigma \). If we expand this potential out to order \( (x - x_{\text{min}})^2 \), we have

\[ V(x) \approx V(x_{\text{min}}) + V'(x_{\text{min}})(x - x_{\text{min}}) + \frac{1}{2} V''(x_{\text{min}})(x - x_{\text{min}})^2 \]

\[ = 4\varepsilon \left[ \left( \frac{\sigma}{\sigma^2} \right)^{12} - \left( \frac{\sigma}{\sigma^2} \right)^6 \right] + 0 + \frac{1}{2} \cdot 4\varepsilon \left[ \frac{156\sigma^{12}}{(\sigma^2)^{14}} - \frac{42\sigma^6}{(\sigma^2)^{15}} \right] (x - x_{\text{min}})^2 \]

\[ = 4\varepsilon \left( \frac{1}{4} - \frac{1}{2} \right) + \frac{4\varepsilon}{2\sigma^2} \left[ 156 \cdot 2^{12} - 42 \cdot 2^4 \right] (x - x_{\text{min}})^2 = -\varepsilon + \frac{4\varepsilon [39 - 21]}{2\sigma^2 2^{13}} (x - x_{\text{min}})^2 \]

\[ = -\varepsilon + 9 \cdot 2^{5/3} \frac{\varepsilon}{\sigma^2} (x - x_{\text{min}})^2. \]

(b) [4] Determine the classical frequency \( \omega \), and calculate the quantum mechanical minimum energy, as a function of the various parameters.

The Harmonic oscillator is normally written as \( E = \frac{1}{2} m \dot{x}^2 + \frac{1}{2} k x^2 \). Comparing this with our energy expression, we see that the role of the spring constant is played by the combination

\[ k = 9 \cdot 2^{8/3} \frac{\varepsilon}{\sigma^2}. \]

The angular frequency is given by \( \omega = \sqrt{k/m} \), so we have

\[ \omega = \sqrt{\frac{9 \cdot 2^{8/3} \varepsilon}{m \sigma^2}} = \frac{3 \cdot 2^{4/3}}{\sigma} \sqrt{\frac{\varepsilon}{m}}. \]
The ground state energy is normally \( E_0 = \frac{1}{2} \hbar \omega \), but the energy has been shifted downwards by an amount \(-\varepsilon\), so we have

\[
E_0 = -\varepsilon + \frac{1}{2} \hbar \omega = -\varepsilon + 3 \cdot 2^{1/3} \frac{\hbar}{\sigma} \sqrt{\frac{\varepsilon}{m}}.
\]

5.2 [10] At \( t = 0 \), a single particle is placed in a harmonic oscillator \( H = \frac{P^2}{2m} + \frac{1}{2} m \omega^2 X^2 \) in the superposition state \( |\Psi(t=0)\rangle = \frac{1}{\sqrt{5}} |1\rangle + \frac{2}{\sqrt{5}} |2\rangle \), that is, in a superposition of the first and second excited states.

(a) [3] What is the wave function \( |\Psi(t)\rangle \) at subsequent times?

The wave function has been written in terms of eigenstates of the Hamiltonian, so this makes it relatively easy. The energy of the state \( |n\rangle \) is \( \hbar \omega (n + \frac{1}{2}) \), and therefore the state will evolve as

\[
|\Psi(t)\rangle = \frac{1}{\sqrt{5}} |1\rangle e^{-i3\omega t/2} + \frac{2}{\sqrt{5}} |2\rangle e^{-i5\omega t/2} = \frac{3}{5} |1\rangle e^{-i3\omega t/2} + \frac{4}{5} |2\rangle e^{-i5\omega t/2}.
\]

(b) [7] What are the expectation values \( \langle X \rangle \) and \( \langle P \rangle \) at all times?

These are most easily calculated using the raising and lowering operators

\[
\langle X \rangle = \sqrt{\frac{\hbar}{2m\omega}} \langle \Psi | (a + a^\dagger) | \Psi \rangle = \sqrt{\frac{\hbar}{2m\omega}} \left( \frac{1}{5} \langle 1 | e^{i3\omega t/2} + \frac{4}{5} \langle 2 | e^{i5\omega t/2} \right) (a + a^\dagger) \left( \frac{1}{5} | 1 \rangle e^{-i3\omega t/2} + \frac{4}{5} | 2 \rangle e^{-i5\omega t/2} \right)
\]

\[
= \sqrt{\frac{\hbar}{2m\omega}} \left( \frac{1}{5} \langle 1 | e^{i3\omega t/2} + \frac{4}{5} \langle 2 | e^{i5\omega t/2} \right) \left[ \frac{1}{5} \langle 0 | + \frac{4}{5} \langle 2 | \right] + \frac{4}{5} \left( \sqrt{2} | 1 \rangle + \sqrt{3} | 3 \rangle \right) e^{-i5\omega t/2} \right]
\]

\[
= \sqrt{\frac{\hbar}{2m\omega}} \frac{1}{2} \frac{\sqrt{2}}{2} \left( e^{-i\omega t} + e^{i\omega t} \right) = \frac{24}{25} \sqrt{\frac{\hbar}{m\omega}} \cos(\omega t),
\]

and

\[
\langle P \rangle = i \frac{\sqrt{\hbar m\omega}}{2} \langle \Psi | (a^\dagger - a) | \Psi \rangle = i \frac{\sqrt{\hbar m\omega}}{2} \left( \frac{1}{5} \langle 1 | e^{i3\omega t/2} + \frac{4}{5} \langle 2 | e^{i5\omega t/2} \right) (a^\dagger - a) \left( \frac{1}{5} | 1 \rangle e^{-i3\omega t/2} + \frac{4}{5} | 2 \rangle e^{-i5\omega t/2} \right)
\]

\[
= i \frac{\sqrt{\hbar m\omega}}{2} \left( \frac{1}{5} \langle 1 | e^{i3\omega t/2} + \frac{4}{5} \langle 2 | e^{i5\omega t/2} \right) \left[ \frac{1}{5} \langle 2 | - | 0 \rangle \right] e^{-i3\omega t/2} + \frac{4}{5} \left( \langle 3 | - | 2 \rangle \right) e^{-i5\omega t/2} \right]
\]

\[
= i \frac{\sqrt{\hbar m\omega}}{2} \frac{3}{2} \frac{\sqrt{2}}{2} \left( e^{i\omega t} - e^{-i\omega t} \right) = -\frac{24}{25} \sqrt{\hbar m\omega} \sin(\omega t).
\]