Physics 741 – Graduate Quantum Mechanics 1

Solutions to Chapter 5

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

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

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 $x_{\min} = 2^{1/6}\sigma$. If we expand this potential out to order $(x - x_{\min})^2$, we have

$$\begin{aligned}
V(x) &\approx V(x_{\min}) + V'(x_{\min})(x - x_{\min}) + \tfrac{1}{2}V''(x_{\min})(x - x_{\min})^2 \\
&= 4\varepsilon\left[\left(\frac{\sigma}{\sigma 2^{1/6}}\right)^{12} - \left(\frac{\sigma}{\sigma 2^{1/6}}\right)^6\right] + 0 + \frac{1}{2}\cdot 4\varepsilon\left[\frac{156\sigma^{12}}{\left(\sigma 2^{1/6}\right)^{14}} - \frac{42\sigma^6}{\left(\sigma 2^{1/6}\right)^8}\right](x - x_{\min})^2 \\
&= 4\varepsilon\left(\frac{1}{4} - \frac{1}{2}\right) + \frac{4\varepsilon}{2\sigma^2}\left(156\cdot 2^{-7/3} - 42\cdot 2^{-4/3}\right)(x - x_{\min})^2 = -\varepsilon + \frac{2\varepsilon}{\sigma^2 2^{1/3}}(39 - 21)(x - x_{\min})^2 \\
&= -\varepsilon + 9\cdot 2^{5/3}\frac{\varepsilon}{\sigma^2}(x - x_{\min})^2 .
\end{aligned}$$

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

The Harmonic oscillator is normally written as $E = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2$. 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

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

5.2 [10] At $t = 0$, a single particle is placed in a harmonic oscillator $H = P^2/2m + \frac{1}{2}m\omega^2 X^2$ in the superposition state $\left|\Psi(t=0)\right\rangle = \frac{3}{5}\left|1\right\rangle + \frac{4}{5}\left|2\right\rangle$, that is, in a superposition of the first and second excited states.

(a) [3] What is the wave function $\left|\Psi(t)\right\rangle$ 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 $\left|n\right\rangle$ is $\hbar\omega\left(n+\frac{1}{2}\right)$, and therefore the state will evolve as

$$\left|\Psi(t)\right\rangle = \tfrac{3}{5}\left|1\right\rangle e^{-i3\hbar\omega t/2\hbar} + \tfrac{4}{5}\left|2\right\rangle e^{-i5\hbar\omega t/2\hbar} = \tfrac{3}{5}\left|1\right\rangle e^{-i3\omega t/2} + \tfrac{4}{5}\left|2\right\rangle e^{-i5\omega t/2}.$$

(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

$$\begin{aligned}
\langle X\rangle &= \sqrt{\frac{\hbar}{2m\omega}}\left\langle\Psi\right|\left(a+a^\dagger\right)\left|\Psi\right\rangle = \sqrt{\frac{\hbar}{2m\omega}}\left(\tfrac{3}{5}\left\langle 1\right| e^{i3\omega t/2} + \tfrac{4}{5}\left\langle 2\right| e^{i5\omega t/2}\right)\left(a+a^\dagger\right)\left(\tfrac{3}{5}\left|1\right\rangle e^{-i3\omega t/2} + \tfrac{4}{5}\left|2\right\rangle e^{-i5\omega t/2}\right)\\
&= \sqrt{\hbar/(2m\omega)}\left(\tfrac{3}{5}\left\langle 1\right| e^{i3\omega t/2} + \tfrac{4}{5}\left\langle 2\right| e^{i5\omega t/2}\right)\left[\tfrac{3}{5}\left(\left|0\right\rangle + \sqrt{2}\left|2\right\rangle\right) + \tfrac{4}{5}\left(\sqrt{2}\left|1\right\rangle + \sqrt{3}\left|3\right\rangle\right)e^{-i5\omega t/2}\right]\\
&= \sqrt{\hbar/(2m\omega)}\,\tfrac{3}{5}\cdot\tfrac{4}{5}\sqrt{2}\left(e^{-i\omega t} + e^{i\omega t}\right) = \tfrac{24}{25}\sqrt{\hbar/(m\omega)}\cos(\omega t),
\end{aligned}$$

and

$$\begin{aligned}
\langle P\rangle &= i\sqrt{\tfrac{1}{2}\hbar m\omega}\left\langle\Psi\right|\left(a^\dagger - a\right)\left|\Psi\right\rangle\\
&= i\sqrt{\tfrac{1}{2}\hbar m\omega}\left(\tfrac{3}{5}\left\langle 1\right| e^{i3\omega t/2} + \tfrac{4}{5}\left\langle 2\right| e^{i5\omega t/2}\right)\left(a^\dagger - a\right)\left(\tfrac{3}{5}\left|1\right\rangle e^{-i3\omega t/2} + \tfrac{4}{5}\left|2\right\rangle e^{-i5\omega t/2}\right)\\
&= i\sqrt{\tfrac{1}{2}\hbar m\omega}\left(\tfrac{3}{5}\left\langle 1\right| e^{i3\omega t/2} + \tfrac{4}{5}\left\langle 2\right| e^{i5\omega t/2}\right)\left[\tfrac{3}{5}\left(\sqrt{2}\left|2\right\rangle - \left|0\right\rangle\right)e^{-i3\omega t/2} + \tfrac{4}{5}\left(\sqrt{3}\left|3\right\rangle - \sqrt{2}\left|1\right\rangle\right)e^{-i5\omega t/2}\right]\\
&= i\sqrt{\tfrac{1}{2}\hbar m\omega}\,\tfrac{3}{5}\cdot\tfrac{4}{5}\sqrt{2}\left(e^{i\omega t} - e^{-i\omega t}\right) = -\tfrac{24}{25}\sqrt{\hbar m\omega}\sin(\omega t).
\end{aligned}$$