PHYS 661 - Quantum Mechanics II

Modern Quantum Mechanics by *J. J. Sakurai*

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Homework 4

Problem 1 - Harmonic Oscillator Wave Functions in the WKB Approximation
In the lecture we calculated the energy of the 1D harmonic oscillator [potential $V(x) = \frac{1}{2}m\omega_0^2 x^2$] in the WKB approximation. Compare numerically the WKB wave function $\psi_n^{(\mathrm{WKB})}(0)$ at the origin to the exact harmonic oscillator wave function for $n = 0, 1, 2, \ldots, 8$. Interpret your results. The WKB wave function is normalized as follows (no need to prove that this is the correct normalization): in the classically allowed region $\psi^{(\mathrm{WKB})}(x) = \frac{A}{\sqrt{p(x)}} \cos\left(\frac{1}{\hbar}\int_b^x \mathrm{d}x' p\left(x'\right) - \frac{\pi}{4}\right)$ has $A^2 = \left[\int_b^a \frac{1}{2p(x)}\,\mathrm{d}x\right]^{-1}$ where a and b are the turning points.

Solution. The WKB wave function in the classically allowed region is given by

$$\psi^{(\mathrm{WKB})}(x) = \frac{A}{\sqrt{p(x)}} \cos\left(\frac{1}{\hbar}\int_b^x p\left(x'\right)\mathrm{d}x' - \frac{\pi}{4}\right),$$

where

$$A = \left[\int_b^a \frac{1}{2p(x)}\,\mathrm{d}x\right]^{-\frac{1}{2}}$$

is the normalization constant.

For the harmonic oscillator, we have

$$p(x) = \sqrt{2m\left(E - \frac{1}{2}m\omega_0^2 x^2\right)}.$$

We need to find the turning points for the harmonic oscillator. We know that, at the turning points, the potential is equal to the energy. Then

$$V(x_0) = \frac{1}{2}m\omega_0^2 x_0^2 = E \implies x_0 = \pm\sqrt{\frac{2E}{m\omega_0^2}},$$

$$\implies a = \sqrt{\frac{2E}{m\omega_0^2}} = x_0 \qquad \text{and} \qquad b = -\sqrt{\frac{2E}{m\omega_0^2}} = -x_0.$$

Notice that $b = -a$. By replacing in the normalization constant A, we get

$$
\begin{aligned}
A &= \left[\int_b^a \frac{1}{2p(x)}\,\mathrm{d}x\right]^{-\frac{1}{2}} \\
&= \left[\int_{-x_0}^{x_0} \frac{1}{2\sqrt{2m\left(E-\frac{1}{2}m\omega_0^2x^2\right)}}\,\mathrm{d}x\right]^{-\frac{1}{2}} \\
&= \left[\frac{1}{2}\int_{-x_0}^{x_0} \frac{1}{\sqrt{2mE-m^2\omega_0^2x^2}}\,\mathrm{d}x\right]^{-\frac{1}{2}} \\
&= \left[\frac{1}{2\sqrt{2mE}}\int_{-x_0}^{x_0} \frac{1}{\sqrt{1-\frac{m\omega_0^2}{2E}x^2}}\,\mathrm{d}x\right]^{-\frac{1}{2}} \\
&= \left[\frac{1}{2\sqrt{2mE}}\int_{-x_0}^{x_0} \frac{1}{\sqrt{1-\frac{x^2}{x_0^2}}}\,\mathrm{d}x\right]^{-\frac{1}{2}} \\
&= \left[\frac{1}{2\sqrt{2mE}}\left(x_0\arcsin\left(\frac{x}{x_0}\right)\right)_{-x_0}^{x_0}\right]^{-\frac{1}{2}} \\
&= \left[\frac{\pi x_0}{2\sqrt{2mE}}\right]^{-\frac{1}{2}} \\
&= \left[\frac{\pi}{2\sqrt{2mE}}\sqrt{\frac{2E}{m\omega_0^2}}\right]^{-\frac{1}{2}} \\
&= \left[\frac{\pi}{2m\omega_0}\right]^{-\frac{1}{2}} \\
&= \sqrt{\frac{2m\omega_0}{\pi}}.
\end{aligned}
$$

By replacing in the wave function, we get

$$\begin{aligned}
\psi^{(\mathrm{WKB})}(x) &= \frac{A}{\sqrt{p(x)}}\cos\left(\frac{1}{\hbar}\int_b^x p\left(x'\right)\mathrm{d}x' - \frac{\pi}{4}\right) \\
&= \sqrt{\frac{2m\omega_0}{\pi p(x)}}\cos\left[\frac{1}{\hbar}\int_{-x_0}^x \sqrt{2m\left(E-\frac{1}{2}m\omega_0^2 x'^2\right)}\,\mathrm{d}x' - \frac{\pi}{4}\right] \\
&= \sqrt{\frac{2m\omega_0}{\pi}}\left(2m\left(E-\frac{1}{2}m\omega_0^2x^2\right)\right)\cos\left[\frac{\sqrt{2mE}}{\hbar}\int_{-x_0}^x \sqrt{1-\frac{m\omega_0^2}{2E}x'^2}\,\mathrm{d}x' - \frac{\pi}{4}\right] \\
&= \sqrt{\frac{\omega_0}{\pi}}\left(\frac{4m}{2E-m\omega_0^2x^2}\right)^{\frac{1}{4}}\cos\left[\frac{\sqrt{2mE}}{\hbar}\,\frac{x_0\arcsin\left(\frac{x'}{x_0}\right)+x'\sqrt{1-\frac{x'^2}{x_0^2}}}{2}\Bigg|_{-x_0}^{x} - \frac{\pi}{4}\right] \\
&= \sqrt{\frac{\omega_0}{\pi}}\left(\frac{4m}{2E-m\omega_0^2x^2}\right)^{\frac{1}{4}}\cos\left[\frac{\sqrt{2mE}}{\hbar}\left(\frac{x_0\arcsin\left(\frac{x}{x_0}\right)+x\sqrt{1-\frac{x^2}{x_0^2}}}{2}+\frac{\pi}{4}x_0\right) - \frac{\pi}{4}\right] \\
&= \sqrt{\frac{\omega_0}{\pi}}\left(\frac{4m}{2E-m\omega_0^2x^2}\right)^{\frac{1}{4}}\cos\left[\frac{\sqrt{2mE}}{\hbar}x_0\left(\frac{\arcsin\left(\frac{x}{x_0}\right)+\frac{x}{x_0}\sqrt{1-\frac{x^2}{x_0^2}}}{2}+\frac{\pi}{4}\right) - \frac{\pi}{4}\right] \\
&= \sqrt{\frac{\omega_0}{\pi}}\left(\frac{4m}{2E-m\omega_0^2x^2}\right)^{\frac{1}{4}}\cos\left[\frac{E}{\omega_0\hbar}\left(\arcsin\left(\frac{x}{x_0}\right)+\frac{x}{x_0}\sqrt{1-\frac{x^2}{x_0^2}}+\frac{\pi}{2}\right) - \frac{\pi}{4}\right] \\
&= \sqrt{\frac{\omega_0}{\pi}}\left(\frac{4m}{2E-m\omega_0^2x^2}\right)^{\frac{1}{4}}\cos\left[\left(n+\frac{1}{2}\right)\left(\arcsin\left(\frac{x}{x_0}\right)+\frac{x}{x_0}\sqrt{1-\frac{x^2}{x_0^2}}+\frac{\pi}{2}\right) - \frac{\pi}{4}\right] \\
&= \sqrt{\frac{\omega_0}{\pi}}\left(\frac{4m}{2E-m\omega_0^2x^2}\right)^{\frac{1}{4}}\cos\left[\left(n+\frac{1}{2}\right)\left(\arcsin\left(\frac{x}{x_0}\right)+\frac{x}{x_0}\sqrt{1-\frac{x^2}{x_0^2}}+\frac{\pi}{2}\right) - \frac{\pi}{4}\right].
\end{aligned}$$

Recall that the exact harmonic oscillator wave function is given by

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}}H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right)\mathrm{e}^{-\frac{m\omega}{2\hbar}x^2},$$

where H_n are the n-th order Hermite polynomials.
To find the error, we take the absolute difference of the functions. In particular, we do so for the origin at $x = 0$ and only consider values up to $n = 8$.
The exact wave function at $x = 0$ is

$$\psi_n(0) = \frac{1}{\sqrt{2^n n!}}H_n(0)\mathrm{e}^0 = \frac{H_n(0)}{\sqrt{2^n n!}}.$$

The WKB approximation of the wave function at $x = 0$ is

$$\psi^{(\mathrm{WKB})}(0) = \sqrt{\frac{\omega_0}{\pi}}\left(\frac{2}{E}\right)^{\frac{1}{4}}\cos\left[\frac{\pi}{2}\left(n+\frac{1}{2}\right)-\frac{\pi}{4}\right].$$

The error at $x = 0$ for each n is given by

$$\text{Error} = \left|\psi_n(0) - \psi^{(\mathrm{WKB})}(0)\right|.$$

- **For n = 0:** Error $= 1 - \sqrt{\frac{2}{\pi}}$.
- **For n = 1:** Error $= 0$.

- **For n = 2:** Error $= \frac{1}{\sqrt{2}} - \frac{1}{5^{\frac{1}{4}}}\sqrt{\frac{2}{\pi}}$.
- **For n = 3:** Error $= 0$.
- **For n = 4:** Error $= \frac{1}{2}\sqrt{\frac{3}{2}} - \frac{1}{9^{\frac{1}{4}}}\sqrt{\frac{2}{\pi}}$.
- **For n = 5:** Error $= 0$.
- **For n = 6:** Error $= \frac{\sqrt{5}}{4} - \frac{1}{13^{\frac{1}{4}}}\sqrt{\frac{2}{\pi}}$.
- **For n = 7:** Error $= 0$.
- **For n = 8:** Error $= \frac{1}{8}\sqrt{\frac{35}{2}} - \frac{1}{17^{\frac{1}{4}}}\sqrt{\frac{2}{\pi}}$.

For large n, we can see that the error decreases, which means that the WKB approximation better matches the exact wave function. ■

Problem 2 - Number of Bound States of a Potential
Consider the 1D potential $V(x) = V_0 \operatorname{sech}^2(x/a)$ with $V_0 < 0$.

(a) Find the bound state energies in the WKB approximation. What is the number of bound states as a function of V_0?

(b) For a generic 1 D potential $U(x)$, by using the WKB approximation, estimate the number of bound states. Does your result agree with the estimate you get from part 1 above? How about in the case of the harmonic potential?

Solution. (a) In the WKB approximation, the quantization condition for bound states is given by

$$\frac{1}{2\pi\hbar}\oint p(x)\,\mathrm{d}x = \left(n + \frac{1}{2}\right),$$

where a and b are the turning points such that

$$\oint p(x)\,\mathrm{d}x = 2\int_b^a p(x)\,\mathrm{d}x \qquad \text{and} \qquad p(x) = \sqrt{2m(E - V(x))}.$$

Finding the classical turning points, we have

$$V(x_\pm) = V_0 \operatorname{sech}^2\left(\frac{x_\pm}{a}\right) = E \implies x_\pm = \pm a \operatorname{sech}^{-1}\left(\sqrt{\frac{E}{V_0}}\right).$$

By replacing in the integrand of the above condition, we have

$$\begin{aligned}
\int_b^a p(x)\,\mathrm{d}x &= \int_{x_-}^{x_+} \sqrt{2m(E - V(x))}\,\mathrm{d}x \\
&= \int_{x_-}^{x_+} \sqrt{2m\left(E - V_0 \operatorname{sech}^2\left(\frac{x}{a}\right)\right)}\,\mathrm{d}x \\
&= 2\sqrt{2mE}\int_0^{x_+} \sqrt{1 - \frac{V_0}{E}\operatorname{sech}^2\left(\frac{x}{a}\right)}\,\mathrm{d}x.
\end{aligned}$$

Let $u = \operatorname{sech}^2\left(\frac{x}{a}\right) \implies \mathrm{d}u = -\frac{2}{a}\operatorname{sech}^2\left(\frac{x}{a}\right)\tanh\left(\frac{x}{a}\right)\mathrm{d}x = -\frac{2}{a}u\sqrt{1-u}$. The limits of integration become from 1 to $\frac{E}{V_0}$. Replacing, we have

$$\begin{aligned}
\int_b^a p(x)\,\mathrm{d}x &= 2\sqrt{2mE}\int_0^{x_+}\sqrt{1-\frac{V_0}{E}\operatorname{sech}^2\left(\frac{x}{a}\right)}\,\mathrm{d}x \\
&= -2\sqrt{2mE}\int_1^{\frac{E}{V_0}}\sqrt{1-\frac{V_0}{E}u}\frac{a}{2u\sqrt{1-u}}\,\mathrm{d}u \\
&= -a\sqrt{2mE}\int_1^{\frac{E}{V_0}}\frac{\sqrt{1-\frac{V_0}{E}u}}{u\sqrt{1-u}}\,\mathrm{d}u \\
&= -a\sqrt{2mE}\left(-\frac{\ln(-1)\left(\sqrt{EV_0}-E\right)}{E}\right) \\
&= \mathrm{i}\pi a\sqrt{2mE}\left(\frac{\sqrt{EV_0}-E}{E}\right) \\
&= \mathrm{i}\pi a\sqrt{2m}\left(\sqrt{V_0}-\sqrt{E}\right).
\end{aligned}$$

We have that $V_0 < 0$, then we can write $V_0 = -|V_0|$. Applying the WKB quantization condition for a potential with two sloping walls, we get

$$\begin{aligned}
\frac{1}{2\pi\hbar}\oint p(x)\,\mathrm{d}x &= n-\frac{1}{2} \\
&= \frac{1}{\pi\hbar}\int_b^a p(x)\,\mathrm{d}x \\
&= \frac{\mathrm{i}a\sqrt{2m}}{\hbar}\left(\sqrt{V_0}-\sqrt{E}\right) \\
\implies n-\frac{1}{2} &= \frac{\mathrm{i}a\sqrt{2m}}{\hbar}\left(\sqrt{V_0}-\sqrt{E}\right) \\
\sqrt{V_0}-\sqrt{E} &= \frac{\hbar}{\mathrm{i}a\sqrt{2m}}\left(n-\frac{1}{2}\right) \\
\sqrt{V_0}\left(1-\sqrt{\frac{E}{V_0}}\right) &= \frac{\hbar}{\mathrm{i}a\sqrt{2m}}\left(n-\frac{1}{2}\right) \\
\sqrt{\frac{E}{V_0}} &= 1-\frac{\hbar}{\mathrm{i}a\sqrt{2mV_0}}\left(n-\frac{1}{2}\right) \\
\sqrt{\frac{E}{V_0}} &= 1+\frac{\mathrm{i}\hbar}{a\sqrt{2mV_0}}\left(n-\frac{1}{2}\right) \\
\sqrt{\frac{E}{V_0}} &= 1+\frac{\hbar}{a\sqrt{2m|V_0|}}\left(n-\frac{1}{2}\right) > 0.
\end{aligned}$$

We can thus find the upper bound for n, *i.e.* the maximum number of bound states. Then

$$n_{\max} = \frac{a}{\hbar}\sqrt{2mV_0}+\frac{1}{2}.$$

(b) The bound state energy is

$$E = V_0\left[\frac{\hbar}{a\sqrt{2mV_0}}\left(n_{\max}-\frac{1}{2}\right)-1\right]^2.$$

For some number of induced modes, we have that $m = n+1$ and then

$$\theta = \frac{1}{2\pi}\oint p(x)\,\mathrm{d}x = \left(n+\frac{1}{2}+\frac{m}{4}\right)\hbar, \qquad n = 0,1,2,\ldots,$$

where m is the number of hard walls.

Solving for n, we get

$$n = \frac{1}{2\pi\hbar} \oint \sqrt{2m(E - V_0)}\, \mathrm{d}x \pm \frac{1}{2} - \frac{m}{4},$$

where the $\pm$ depends on the potential of the problem. Thus,

$$n = \frac{\sqrt{2mE}}{2\pi\hbar} \oint \sqrt{1 - \frac{U(x)}{E}}\, \mathrm{d}x \pm \frac{1}{2} - \frac{m}{4},$$

where $U(x)$ is some arbitrary potential. For $U(x) = V(x)$ (our problem), we do not have any hard walls ($m = 0$), and thus

$$n = \frac{\sqrt{2mE}}{2\pi\hbar} \oint \sqrt{1 - \frac{U(x)}{E}}\, \mathrm{d}x \pm \frac{1}{2}.$$

■

Problem 3 - Vibration of NH_3
The ammonia molecule NH_3 forms a shallow pyramid structure with a triangular base of hydrogen and nitrogen on the top. The nitrogen on top vibrates like a harmonic oscillator with frequency 950 cm^{-1} [in wavenumber units] separating the two lowest modes. In practice, the lowest two modes are seen to have small splittings of 0.8 cm^{-1} and 36 cm^{-1}, respectively. Interpret the splitting to be arising from N tunneling from the top of the pyramid to the bottom (inverting the pyramid upside-down), estimate the value for $\phi = \frac{1}{\hbar}\int_{-x_i}^{x_i} \mathrm{d}x' \left|p\left(x'\right)\right|$ for the two modes. Comment on the result.

Solution. The energy level splitting of the double well potential in the WKB approximation is given by

$$E_{n,\pm} \approx \hbar\omega_0 \left(n + \frac{1}{2} \pm \frac{1}{2\pi}\mathrm{e}^{-\phi_n}\right).$$

Due to the nitrogen atom tunnelling across the barrier of the hydrogen atoms, we have the following energy level splittings

- **For n = 0:**

$$\begin{aligned} E_{0,+} - E_{0,-} &= 0.8\,\mathrm{cm}^{-1} \\ &= \hbar\omega_0 \left(\frac{1}{2} + \frac{1}{2\pi}\mathrm{e}^{-\phi_0}\right) - \hbar\omega_0 \left(\frac{1}{2} - \frac{1}{2\pi}\mathrm{e}^{-\phi_0}\right) \\ &= \frac{\hbar\omega_0}{2\pi}\mathrm{e}^{-\phi_0} \\ \implies \frac{\hbar\omega_0}{2\pi}\mathrm{e}^{-\phi_0} &= 0.8 \\ \mathrm{e}^{-\phi_0} &= \frac{2\pi(0.8)}{\hbar\omega} \\ \phi_0 &= -\ln\left(\frac{1.6\pi}{\hbar\omega}\right). \end{aligned}$$

- **For n = 1:**

$$\begin{aligned} E_{1,+} - E_{1,-} &= 36\,\mathrm{cm}^{-1} \\ &= \hbar\omega_0 \left(\frac{1}{2} + \frac{1}{2\pi}\mathrm{e}^{-\phi_1}\right) - \hbar\omega_0 \left(\frac{1}{2} - \frac{1}{2\pi}\mathrm{e}^{-\phi_1}\right) \\ &= \frac{\hbar\omega_0}{2\pi}\mathrm{e}^{-\phi_1} \\ \implies \frac{\hbar\omega_1}{2\pi}\mathrm{e}^{-\phi_1} &= 36 \\ \mathrm{e}^{-\phi_1} &= \frac{2\pi(36)}{\hbar\omega} \\ \phi_1 &= -\ln\left(\frac{72\pi}{\hbar\omega}\right). \end{aligned}$$

Additionally, we know that the Nitrogen vibrates like a harmonic oscillator with frequency 950 cm^{-1}. Then

$$\Delta = E_1 - E_0 = \hbar\omega_0 = 950\,\mathrm{cm}^{-1}.$$

By replacing in the equations for ϕ, we get

$$\phi_0 \approx 5.9344 \qquad \text{and} \qquad \phi_1 \approx 2.1282.$$

We can conclude that the phase is larger for the ground state because the approximation is better in that case. This shows that, as energy increases, the WKB approximation performs worse since the energy might eventually be greater than the central barrier. ■