

The harmonic potential $V_h(x) = \frac{1}{2}kx^2$ in Quantum Mechanics ...

Why is the harmonic potential important in Quantum Mechanics?

- The general solution to the time-independent SE, namely:

$$\left(\frac{-\hbar^2}{2m}\right) \frac{d^2u(x)}{dx^2} + V(x)u(x) = Eu(x) , \quad (5.154)$$

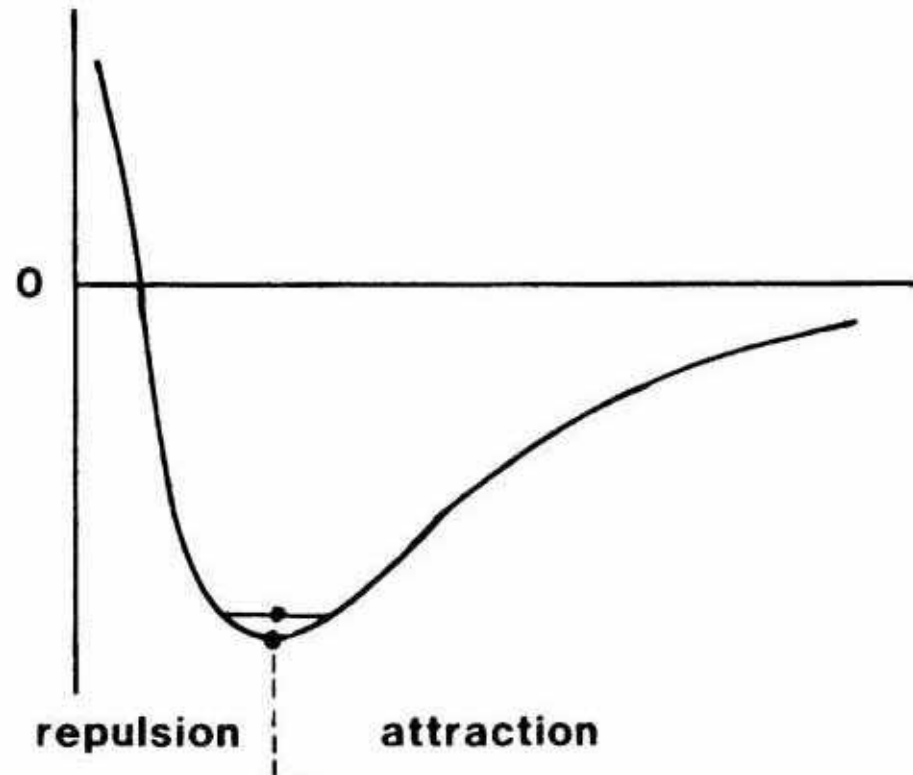
is known analytically, for only a few special cases.

- In general, the solutions must be worked out numerically.
- Sometimes, you are only interested in the first few states of a binding potential, E_0 , the ground state, E_1 , the first excited state, and so on.
- It can be shown that the first few low-lying states can be estimated by doing a fit of the harmonic potential, to an arbitrary, binding potential.

Here is the demonstration:

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Consider a binding potential, such as in this schematic representation¹² of the potential energy, $V(x)$, for two adjacent atoms as a function of internuclear separation, r .



In the vicinity of the minimum, x_0 , do a Taylor expansion of the form:

$$V(x) = V(x_0) + V'(x_0)(x - x_0) + \frac{1}{2}V''(x_0)(x - x_0)^2 + \mathcal{O}[(x - x_0)^3] . \quad (5.155)$$

¹²Unashamedly pilfered from the internet after a google images search for "binding potential".

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The $V'(x_0)$ denotes the derivative of $V(x)$ with respect to x , evaluated at x_0 and $V''(x_0)$ the double derivative of $V(x)$ with respect to x , evaluated at x_0 .

$$V_h = V(x_0) + V'(x_0)(x - x_0) + \frac{1}{2}V''(x_0)(x - x_0)^2 . \quad (5.156)$$

The first derivative, $V'(x_0) = 0$ at the minimum, and with the identification of $V''(x_0)$ as the spring constant, k , and $V(x_0) = V_0$ as the minimum we have identified the harmonic potential approximation to $V(x)$.

$$V_h = V_0 + \frac{1}{2}k(x - x_0)^2 . \quad (5.157)$$

The quantum mechanical solution of this is well known, and we shall describe it soon.

The major result of the quantum-mechanical analysis is a full description of the wavefunctions as well as the energy quantization:

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right) \quad (5.158)$$

$$n = 0, 1, 2 \dots \quad (5.159)$$

$$\omega = \sqrt{\frac{k}{m}} . \quad (5.160)$$

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Only a few potentials in the Schrödinger equation have been completely characterized in terms of wavefunctions and energy levels.

Most $V(x)$'s have not. However, before resorting to some numerical work to characterize the solutions, performing the harmonic approximation gives one the chance of at least approximating the first few lowest bound states, as well as their wavefunctions.

An illustration is in order ... the Morse interatomic force.

The Morse potential is given by:

$$V(x) = V_0(1 - e^{-a(x-x_0)})^2 - V_0, \quad (5.161)$$

where the parameter a controls the width of the potential.

It is easily determined that:

$$V(x_0) = -V_0 \quad (5.162)$$

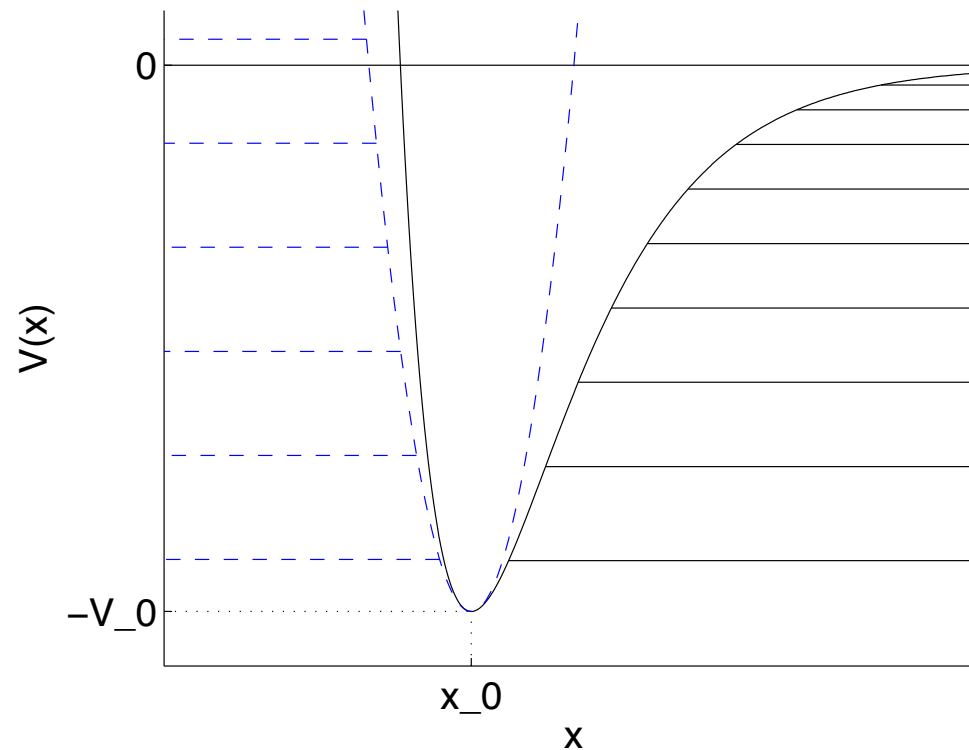
$$V'(x_0) = 0 \quad (5.163)$$

$$k = 2V_0a^2. \quad (5.164)$$

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The Morse potential is shown in the solid black curve, similar in shape to the schematic on the near (5.155).

The horizontal solid lines are the ground state and the first 8 excited states of the Morse potential.

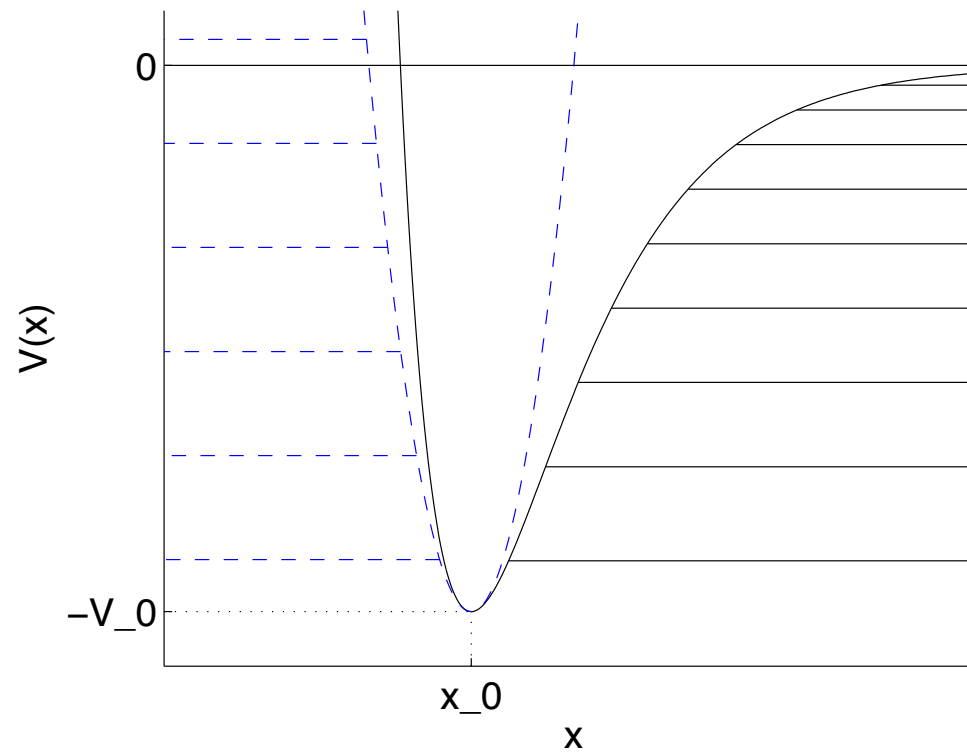


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The Morse potential has the following energy levels:

$$E_n = \hbar\omega (n + 1/2) - \frac{[\hbar\omega (n + 1/2)]^2}{4V_0} . \quad (5.165)$$

The dashed lines represent the harmonic approximation. The first few energy levels of the harmonic approximation are quite good, but then it deteriorates for higher excitation levels.

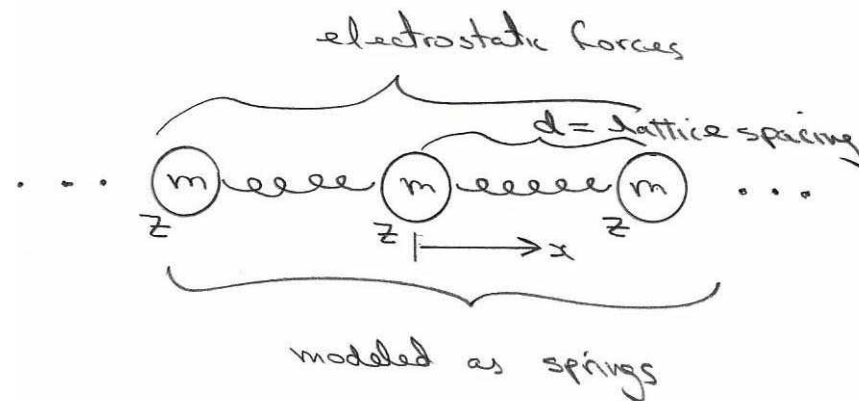


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Another example: Vibrations in a metal crystal

The atoms in crystals are held together by attractive electrostatic forces.

Consider the following model for a 1D crystal, where d is the lattice spacing. We are considering the atom near its equilibrium position, $x_0 = 0$.



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This potential, and its harmonic approximation are given by;

$$V(x) = \frac{Z^2}{4\pi\epsilon_0} \left[\frac{1}{d+x} + \frac{1}{d-x} \right] \quad (5.166)$$

$$V_0 = \frac{Z^2}{2\pi\epsilon_0 d} \quad (5.167)$$

$$V'(x) = \frac{Z^2}{4\pi\epsilon_0} \left[\frac{1}{(d+x)^2} - \frac{1}{(d-x)^2} \right] \quad (5.168)$$

$$V'(0) = 0 \quad (5.169)$$

$$V''(x) = \frac{Z^2}{4\pi\epsilon_0} \left[\frac{2}{(d+x)^3} + \frac{2}{(d-x)^3} \right] \quad (5.170)$$

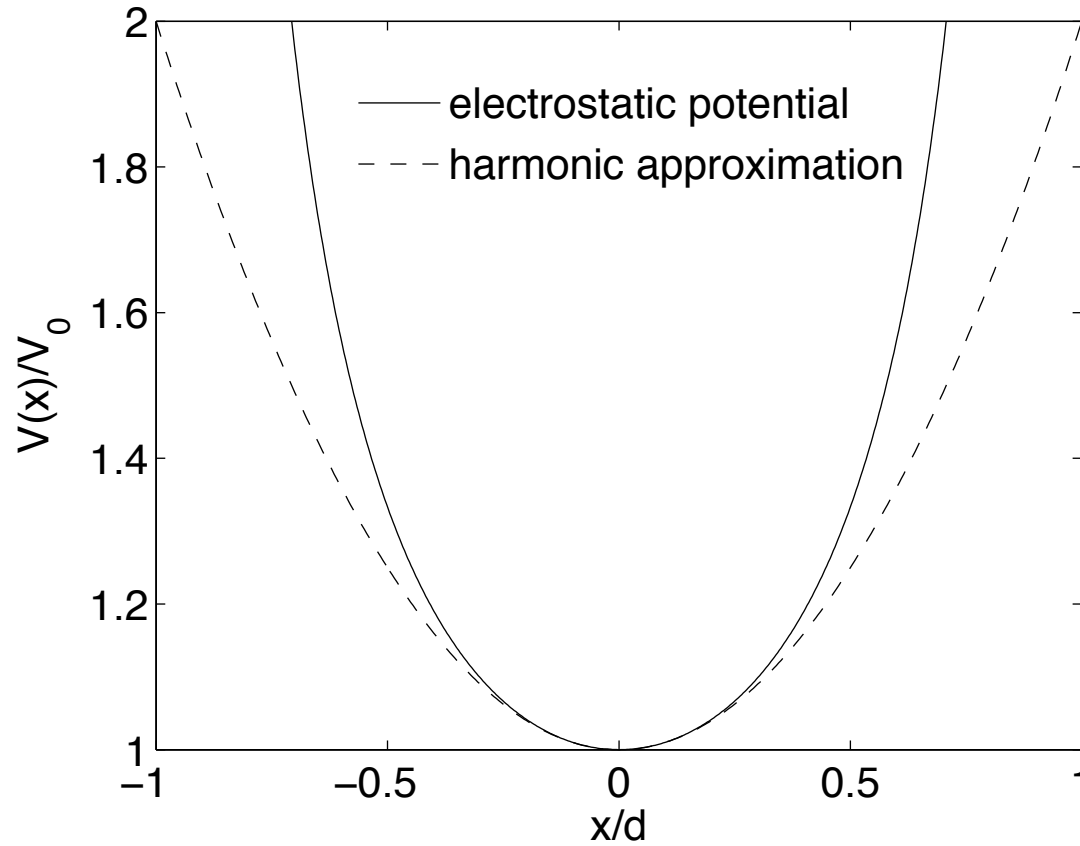
$$k = \frac{Z^2}{\pi\epsilon_0 d^3} \quad [\text{Since } k = V''(0)] \quad (5.171)$$

Therefore, the harmonic approximation is given by

$$V_h(x) = \frac{Z^2}{2\pi\epsilon_0 d} + \frac{1}{2} \frac{Z^2}{\pi\epsilon_0 d^3} x^2. \quad (5.172)$$

A graphical comparison is given on the next page.

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The QM solution of the harmonic oscillator ...

It starts with the time-independent SE with the harmonic potential, namely:

$$\frac{-\hbar^2}{2m}u''(x) + \frac{1}{2}kx^2u(x) = Eu(x) , \quad (5.173)$$

Which can be found by the Frobenius method.¹³ After considerable work ...

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right) \quad (5.174)$$

$$n = 0[\text{the ground state}], 1, 2 \dots \quad (5.175)$$

$$\omega^2 = \frac{k}{m} \quad (5.176)$$

$$u_n(x) = \left(\frac{\alpha}{2^n n! \sqrt{\pi}} \right)^{1/2} e^{(-[\alpha x]^2/2)} H_n(\alpha x) \quad (5.177)$$

[The H_n are the “Hermite polynomials”]

$$\alpha = \left(\frac{mk}{\hbar^2} \right)^{1/4} = \left(\frac{m\omega}{\hbar} \right)^{1/2} \quad (5.178)$$

$$\langle n|m \rangle = \delta_{mn} \quad (5.179)$$

¹³More information can be found at:

Wikipedia: http://en.wikipedia.org/wiki/Frobenius_method (general discussion)

Online supplemental notes: <http://www.umich.edu/~ners311/CourseLibrary/Harmonic%20Potential.pdf> (Frobenius applied to (5.173) — 27 pages!)

You can also google: “Hermite polynomials”, “Charles Hermite” (1822-1901), “Ferdinand Georg Frobenius” (1849-1917)

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Note that:

$$\begin{aligned}\langle n|m\rangle &= \int_{-\infty}^{\infty} dx \left(\frac{\alpha}{2^n n! \sqrt{\pi}} \right)^{1/2} e^{(-[\alpha x]^2/2)} H_n(\alpha x) \left(\frac{\alpha}{2^m m! \sqrt{\pi}} \right)^{1/2} e^{(-[\alpha x]^2/2)} H_m(\alpha x) \\ &= \frac{1}{\sqrt{\pi}} \left(\frac{1}{2^{(n+m)} n! m!} \right)^{1/2} \int_{-\infty}^{\infty} dz e^{-z^2} H_n(z) H_m(z) \\ &\quad [z = \alpha x, \text{ and some reorganization}] \\ &= \frac{1}{\sqrt{\pi}} \left(\frac{1}{2^n n!} \right) \int_{-\infty}^{\infty} dz e^{-z^2} H_n^2(z) = 1 \quad [\text{for } n = m] \\ &= 0 \quad [\text{for } n \neq m]\end{aligned}\tag{5.180}$$

These integrals are easily checked using Mathematica with the code:

n = any integer >= 0

m = any integer >= 0

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Sqrt[(1/2^n)*(1/n!)]*Sqrt[(1/2^m)*(1/m!)]*(1/Sqrt[Pi])*
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Integrate[HermiteH[n,z]HermiteH[m,z] Exp[-z^2],{z,-Infinity,Infinity}]}}
```

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One can also calculate (see the supplemental notes) that for any n ,

$$\langle n|V|n\rangle = \langle n|K|n\rangle = E_n/2 = \frac{\hbar\omega}{2} \left(n + \frac{1}{2} \right), \quad (5.181)$$

where $\mathcal{V} \equiv kx^2/2$ is the potential energy “operator” and \mathcal{K} is the kinetic energy operator. This result agrees with the classical result we found at the start of this chapter.

Properties of the H_n 's

The explicit forms of the of the Hermite polynomials are:

$$\begin{aligned} H_0(z) &= 1 \\ H_1(z) &= 2z \\ H_2(z) &= 4z^2 - 2 \\ H_3(z) &= 8z^3 - 12z \\ H_4(z) &= 16z^4 - 48z^2 + 12 \\ &\vdots \end{aligned} \quad (5.182)$$

Note that $H_n(z)$ always starts with a $(2z)^n$.

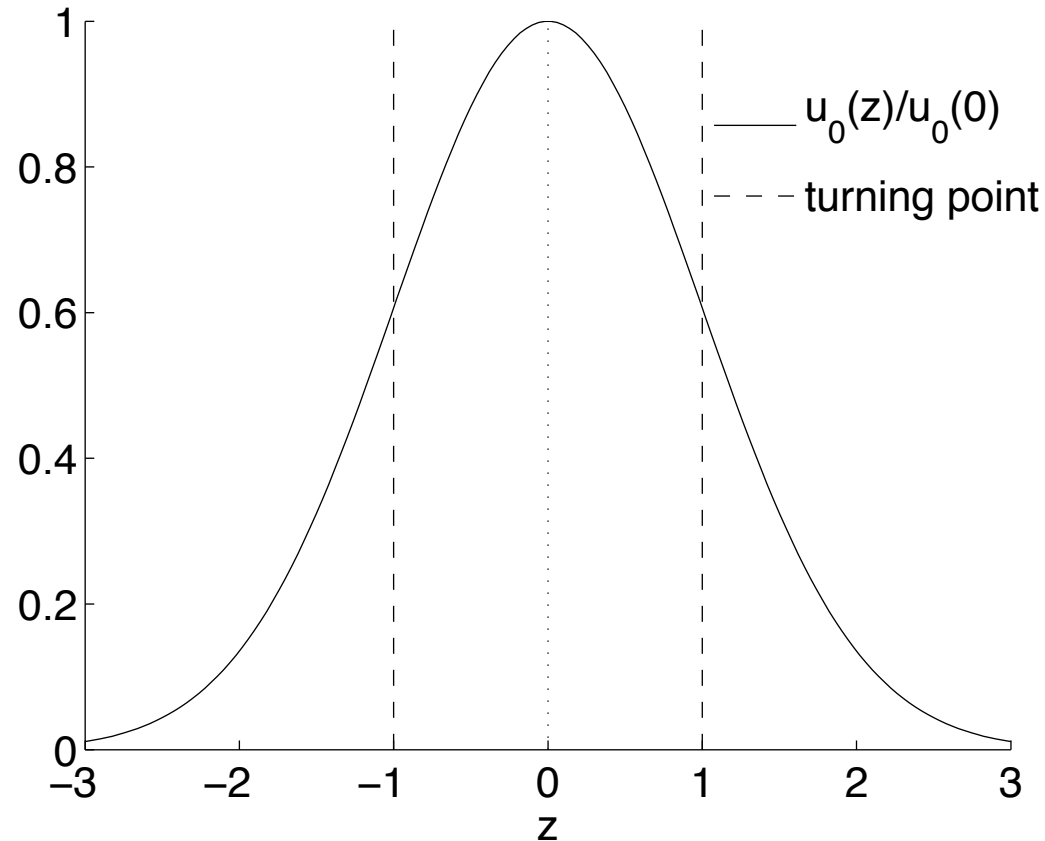
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Recursion relationship to obtain the H_n 's

$$H_{n+1}(z) = 2zH_n(z) - 2nH_{n-1}(z) \quad \text{for } n \geq 1 \quad (5.183)$$

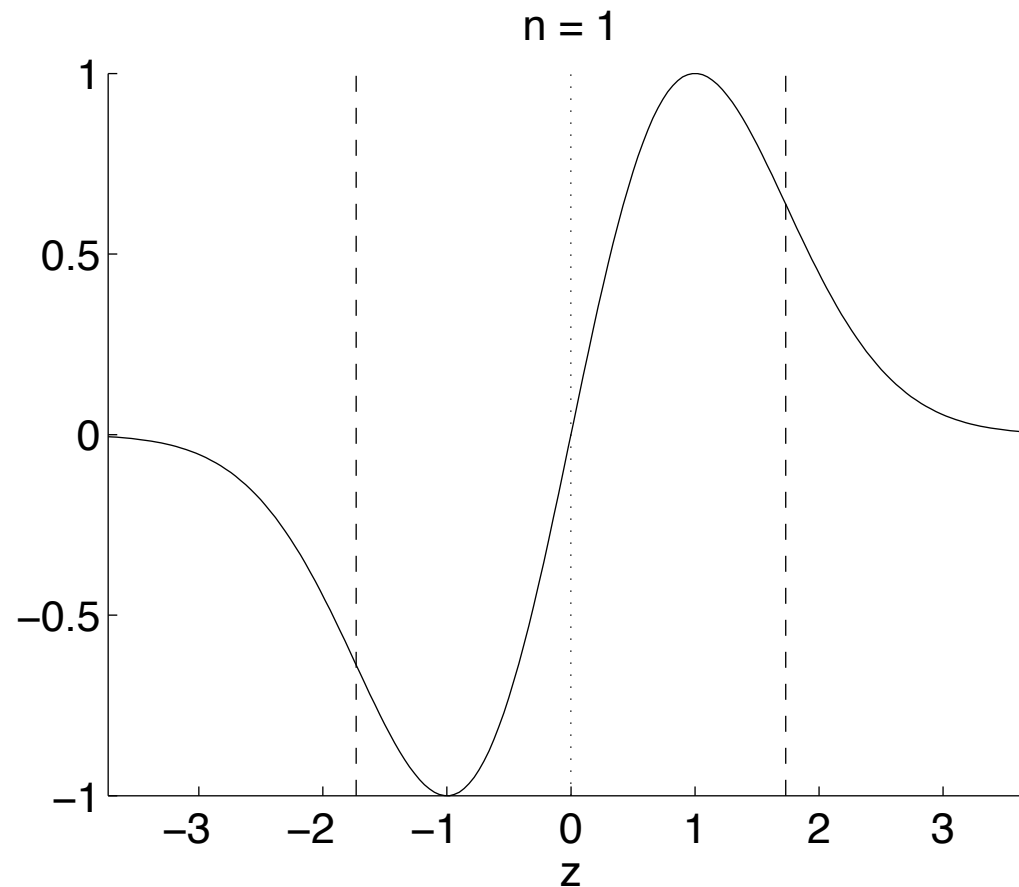
The wavefunctions are plotted on the next few pages.

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One can show that the “classical turning point”, the maximum extent of the classical trajectory of a particle in harmonic potential, at the energy of the quantum state, E_n , is given by $z_{\max} = \sqrt{2n + 1}$.

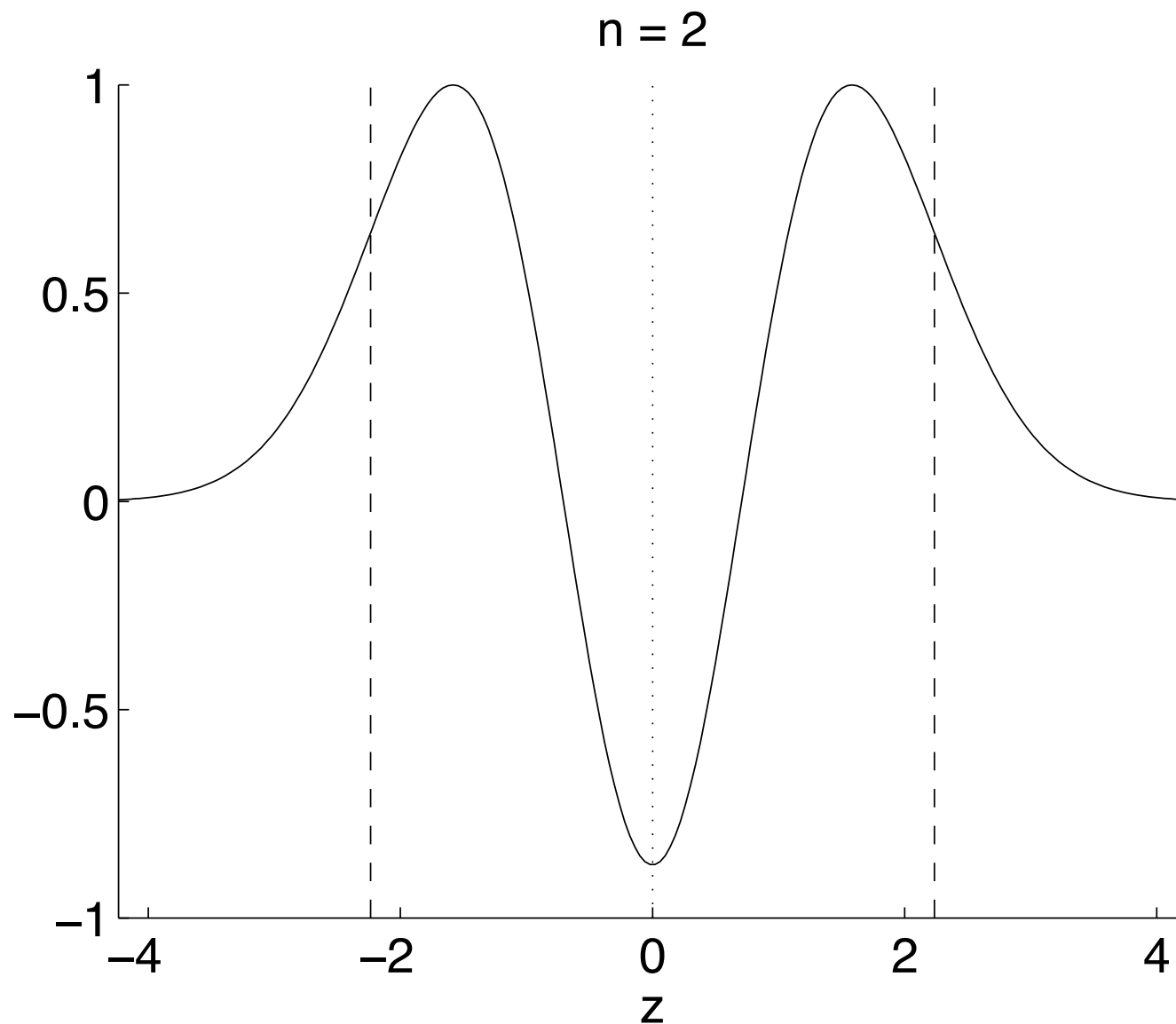
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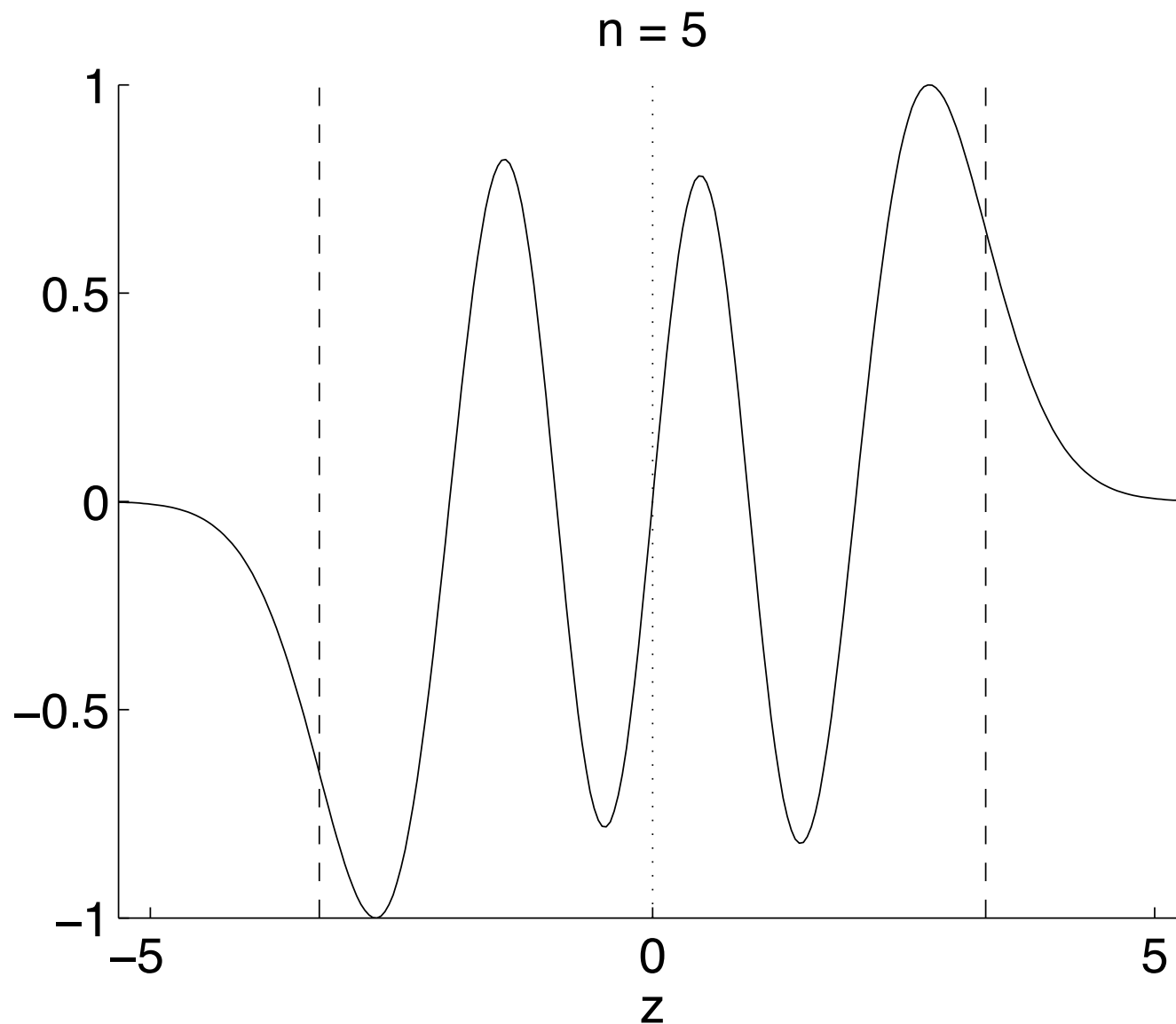
For presentation purposes, these wavefunctions are not normalized, and are scaled to between ± 1 on the vertical axis.

Note that the odd-numbered wavefunctions have odd parity.

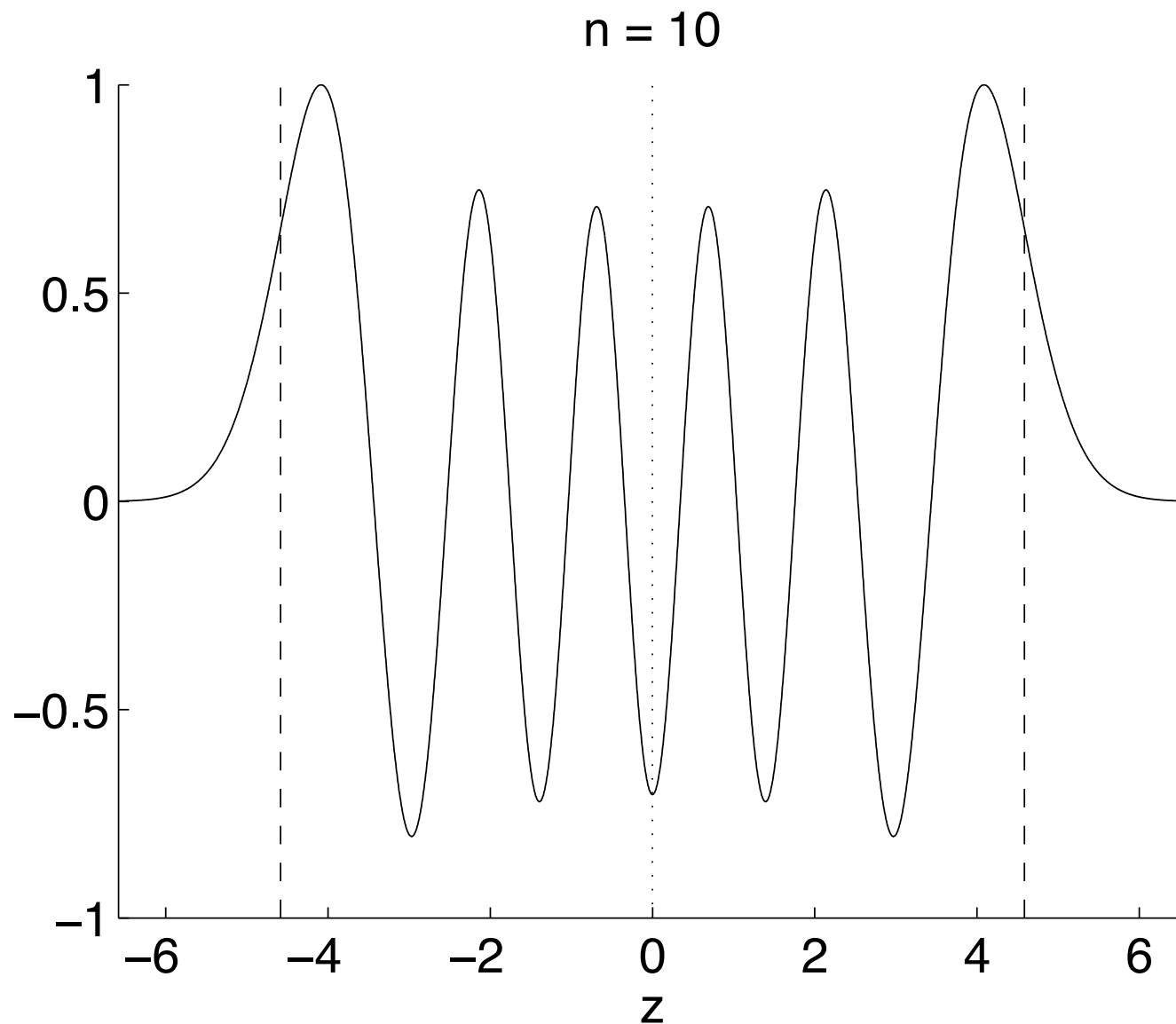
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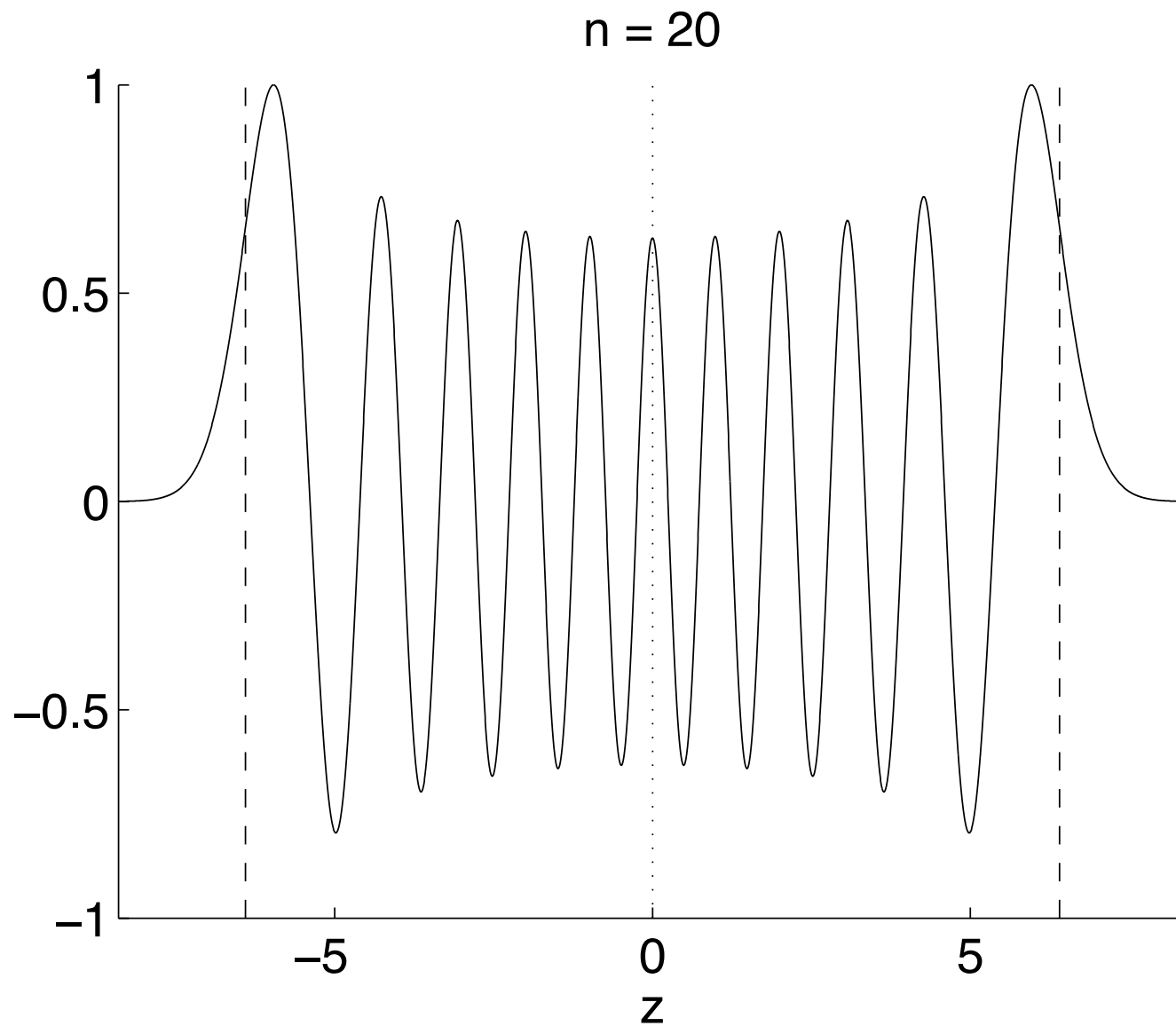
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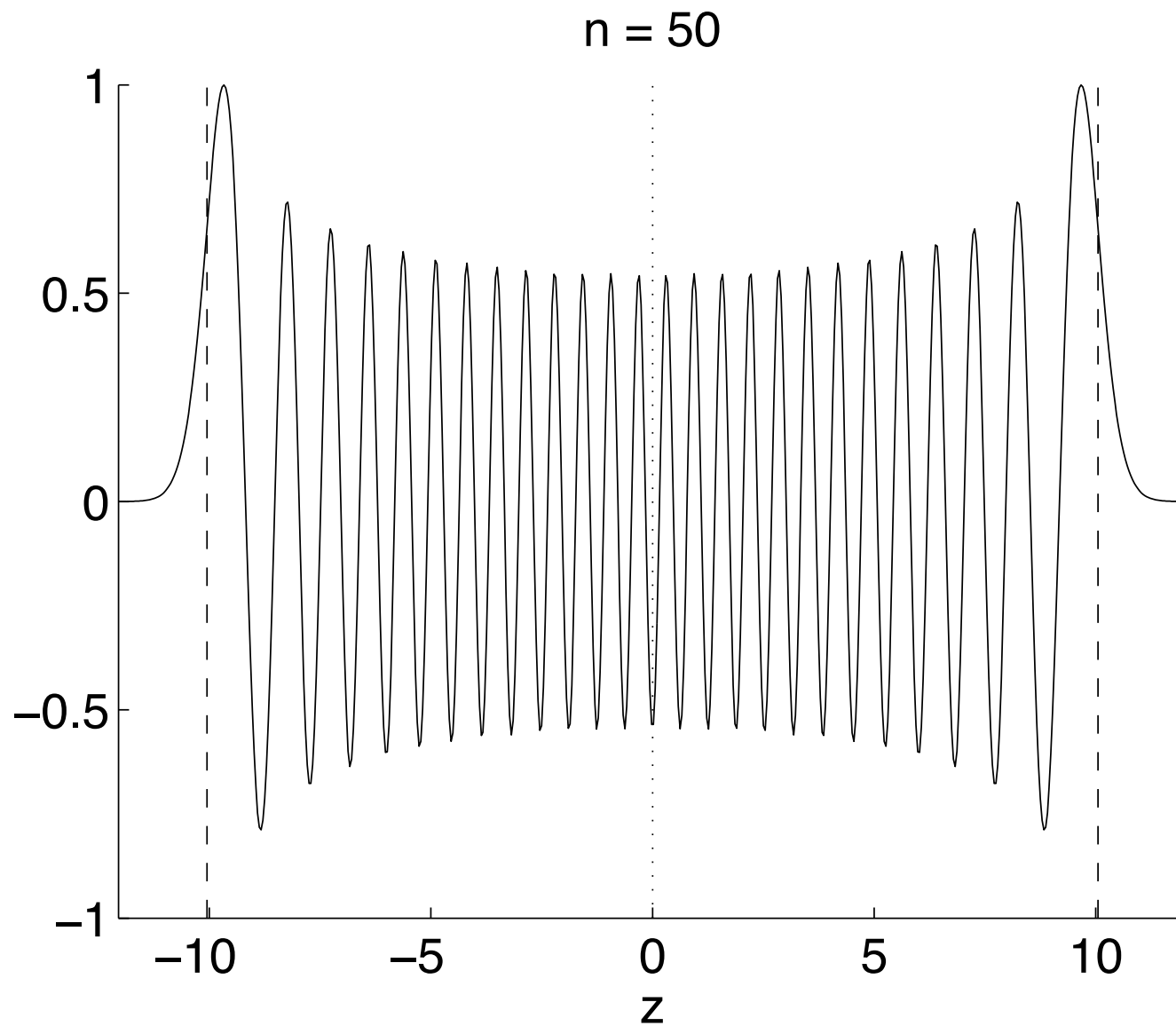
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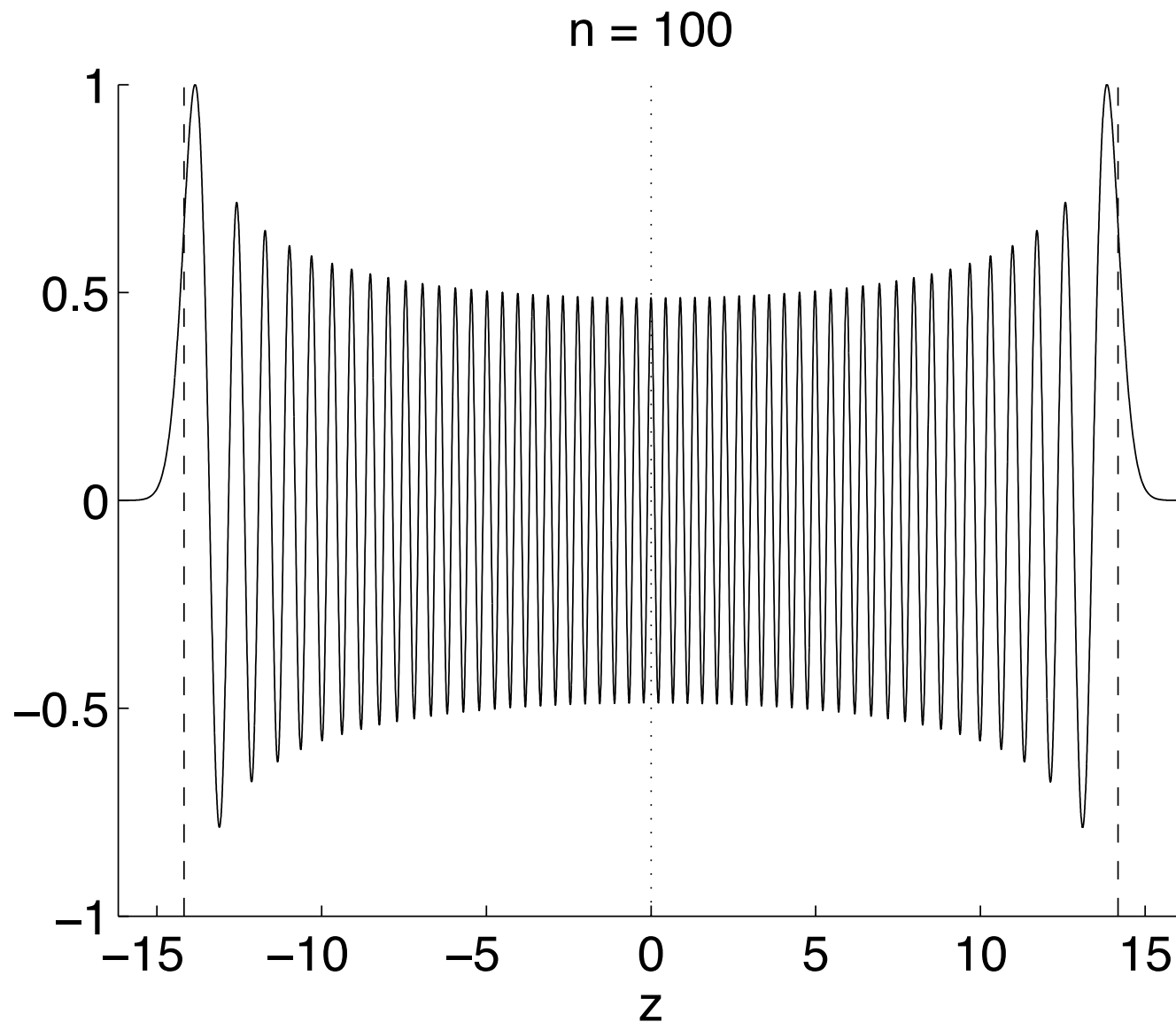
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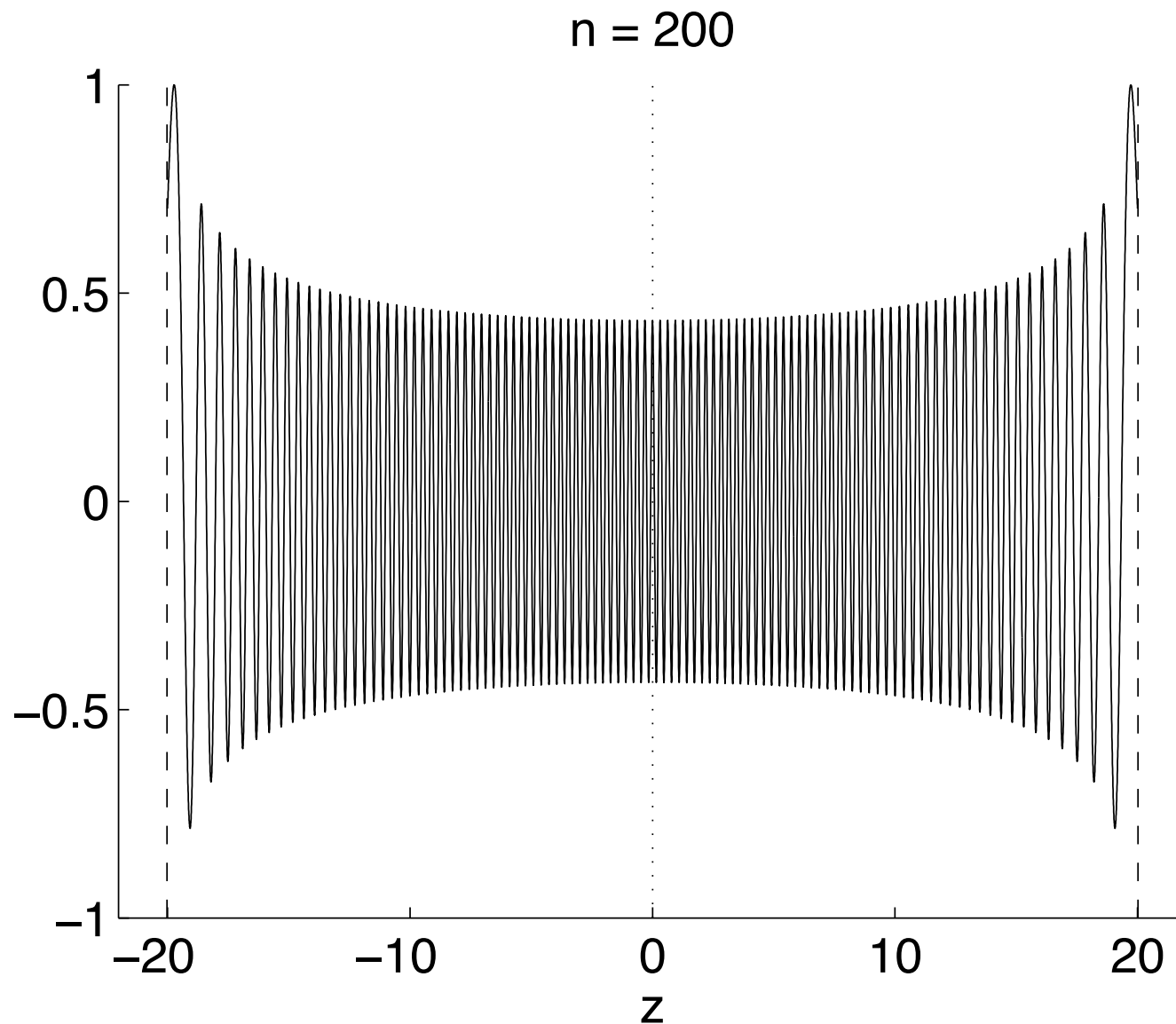
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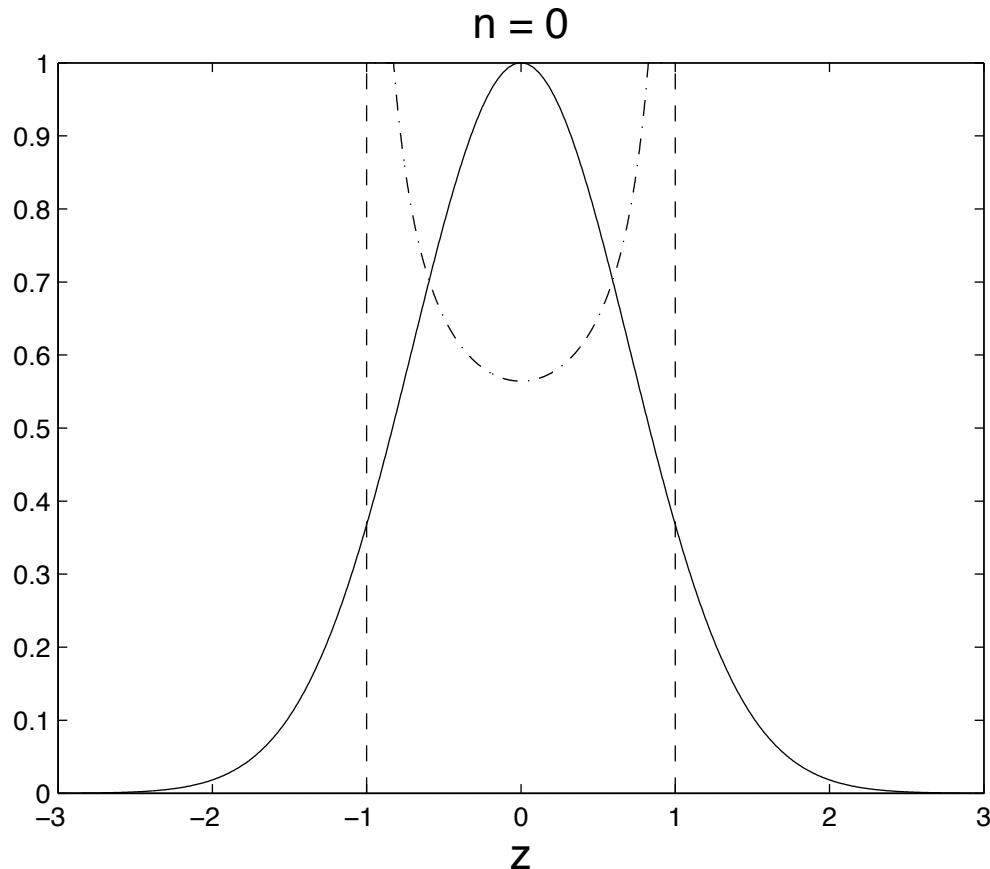


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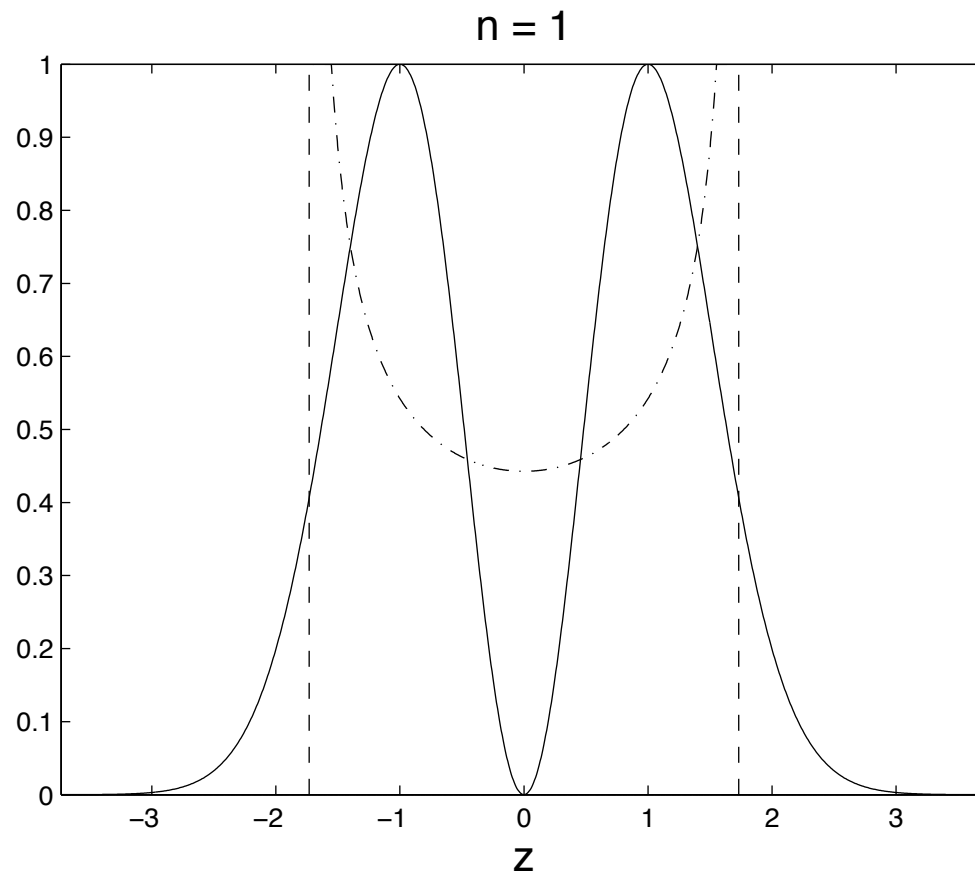
The probability densities:



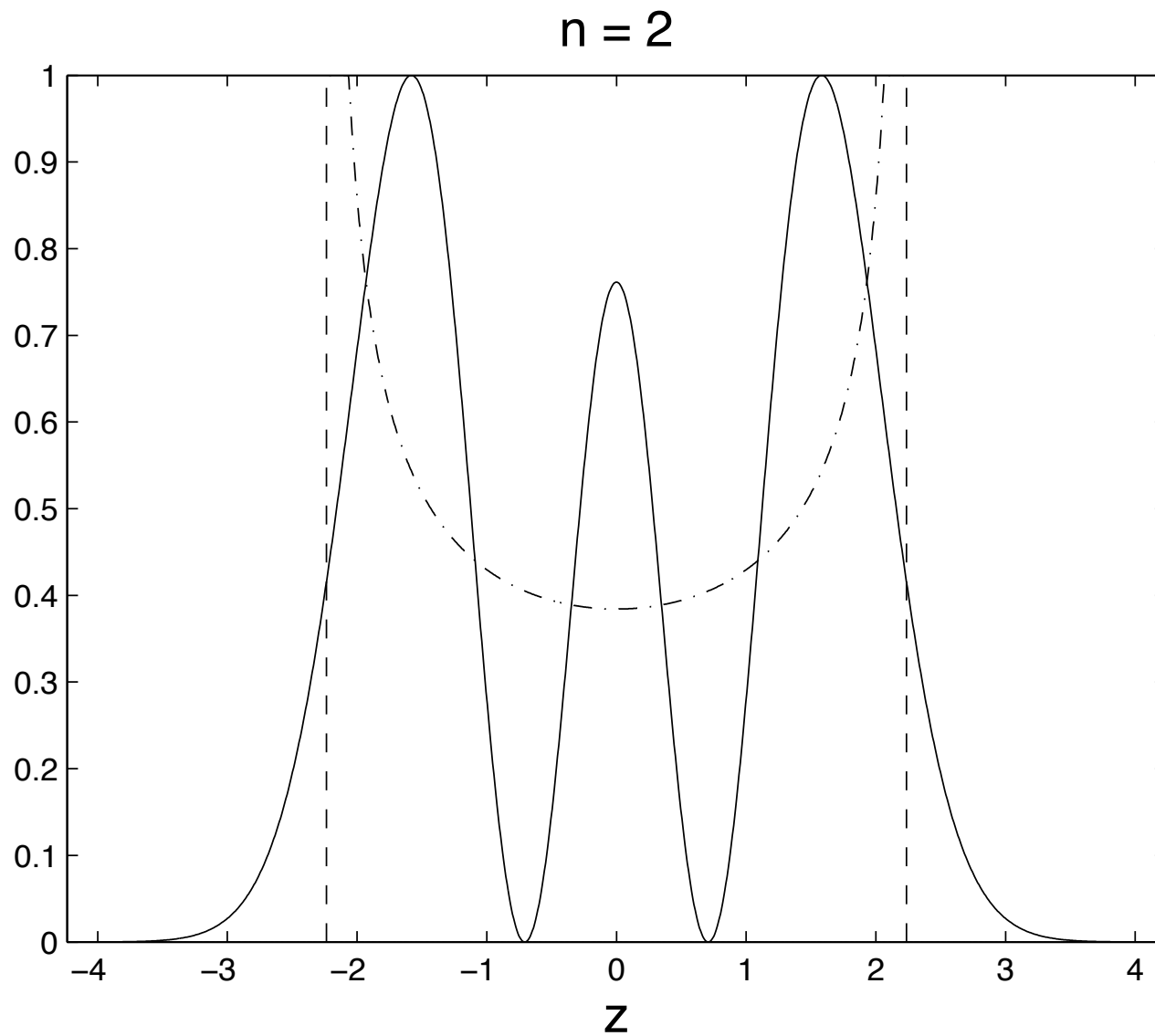
For presentation purposes, these probability densities are not normalized, and are scaled to have a maximum value of 1.

The dash-dot line represents the classical trajectory.

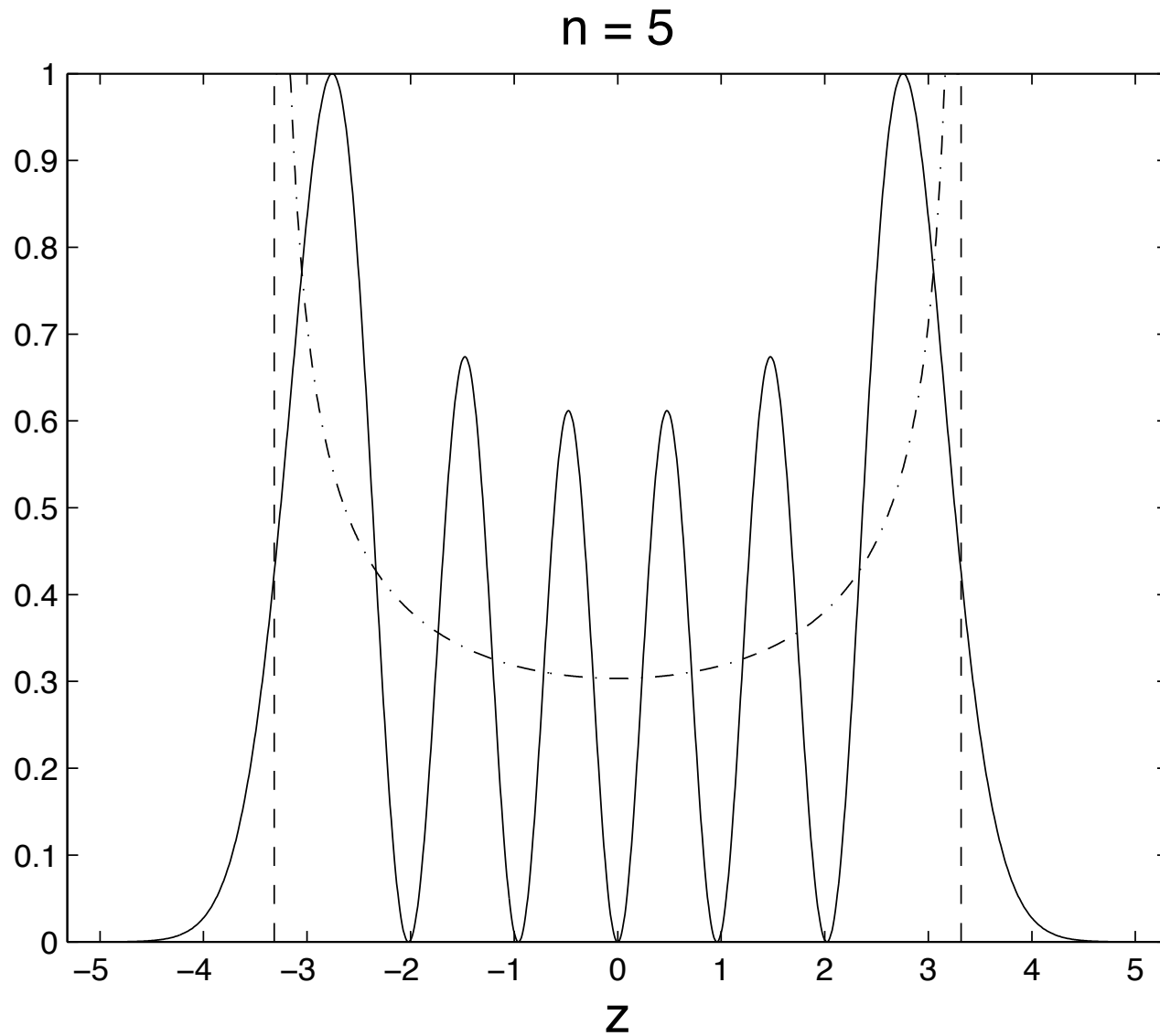
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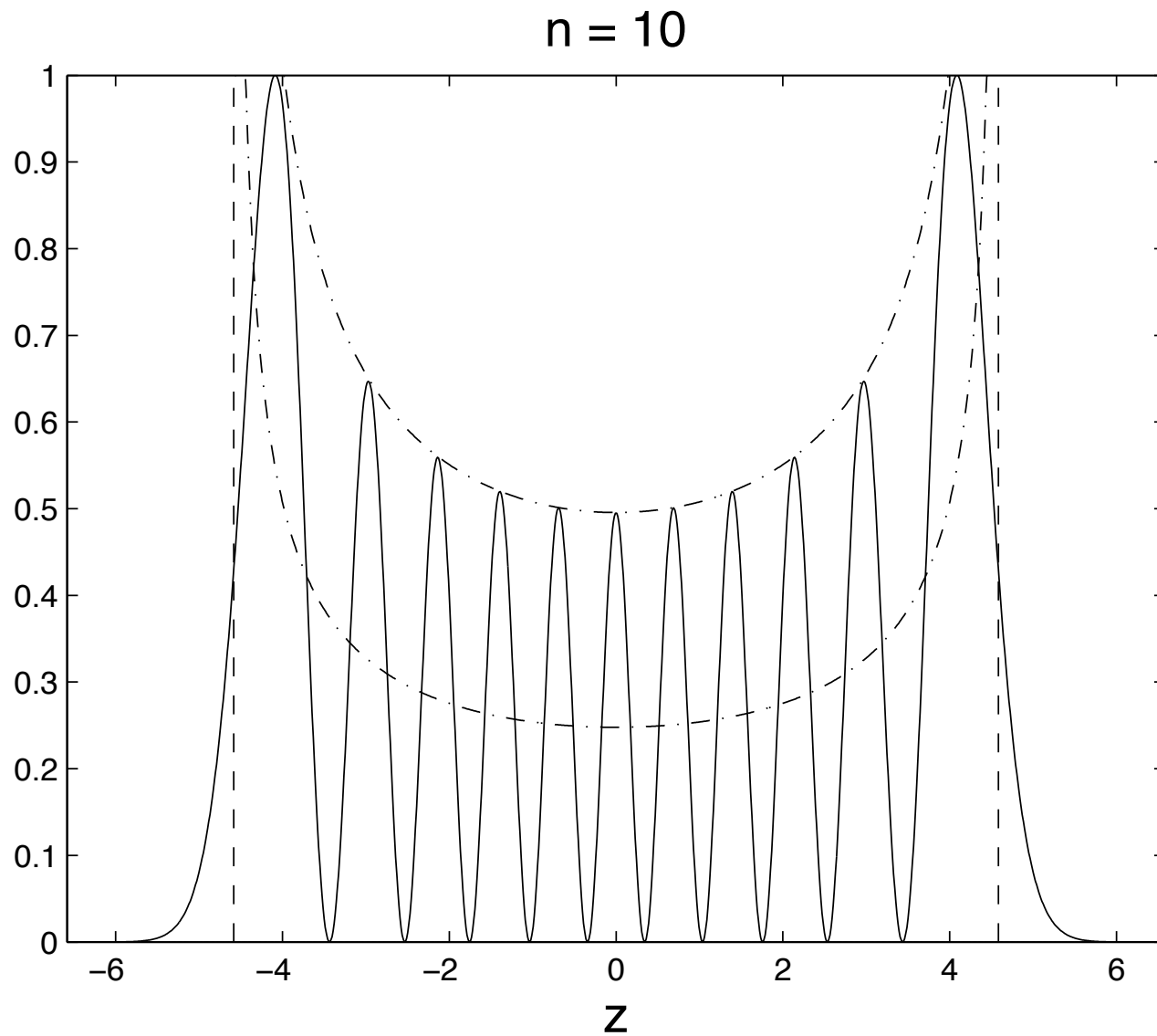
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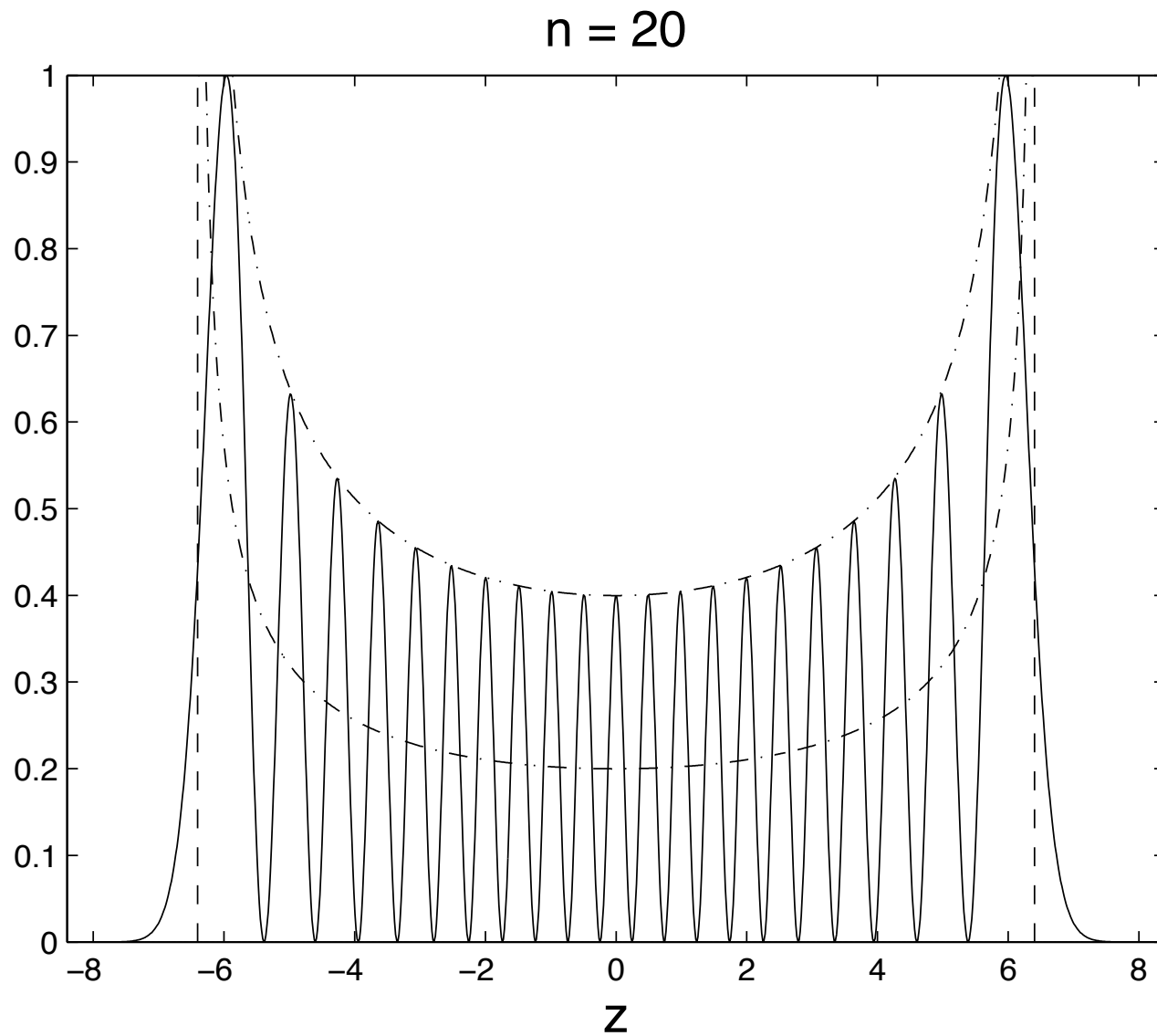
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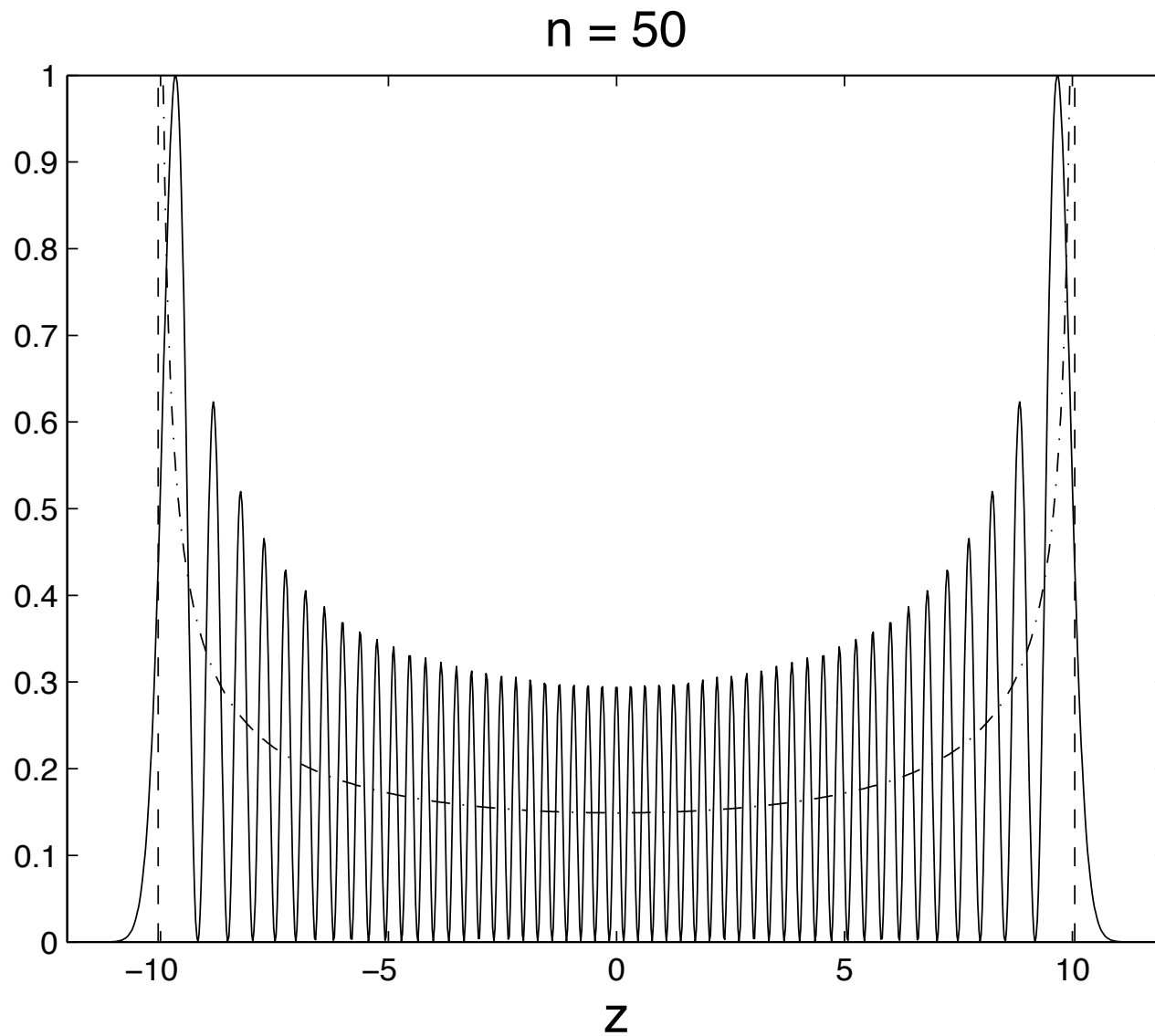
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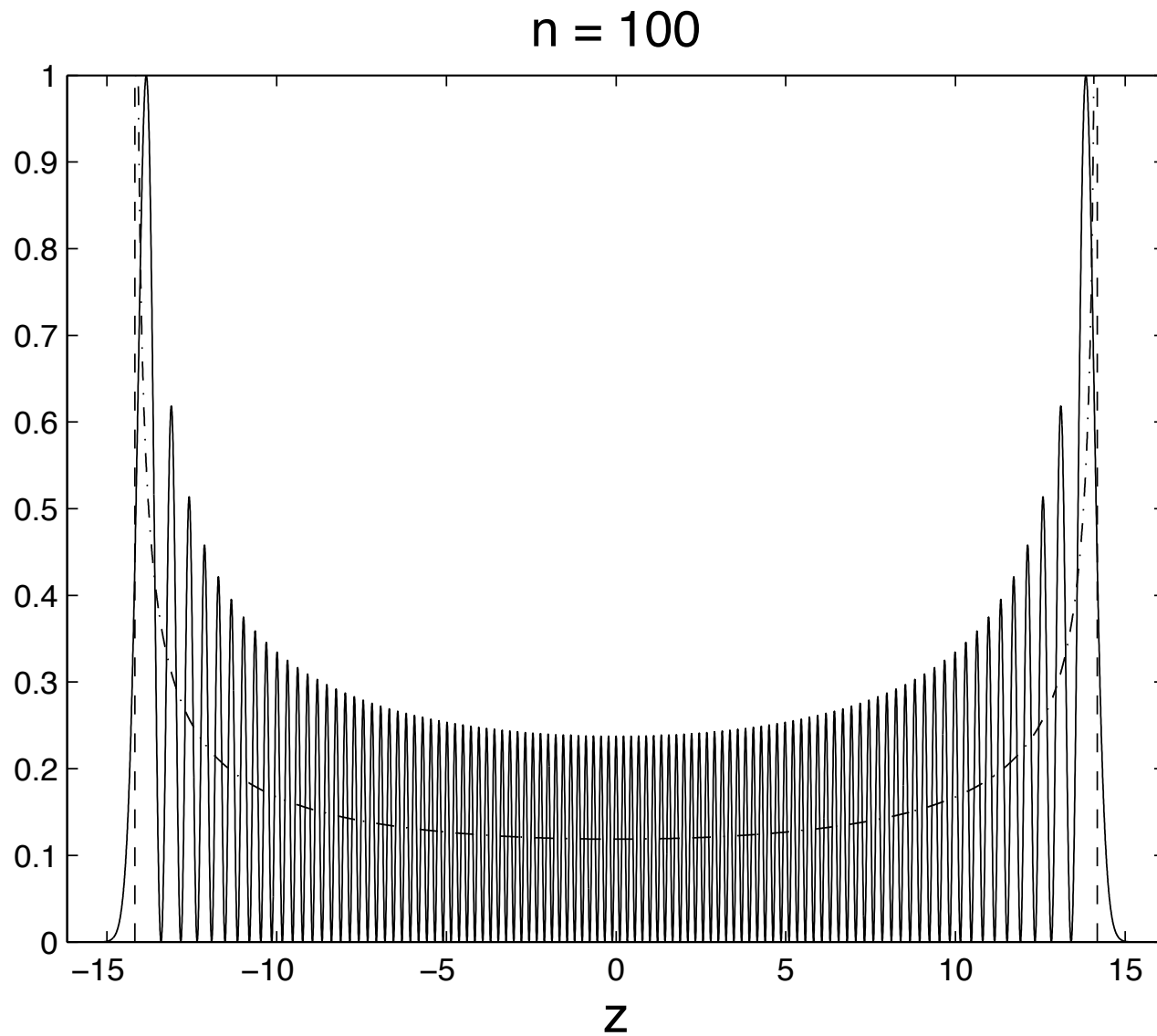
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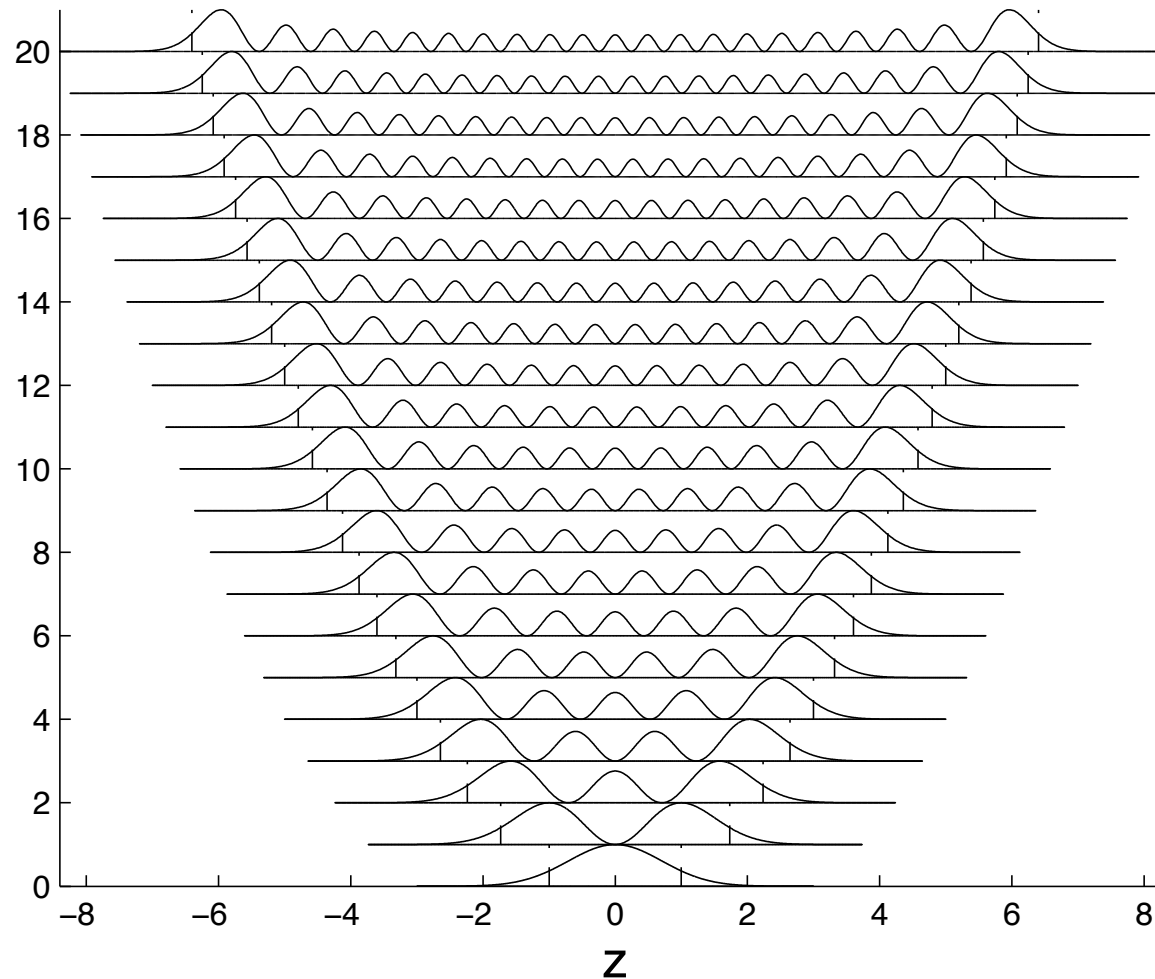


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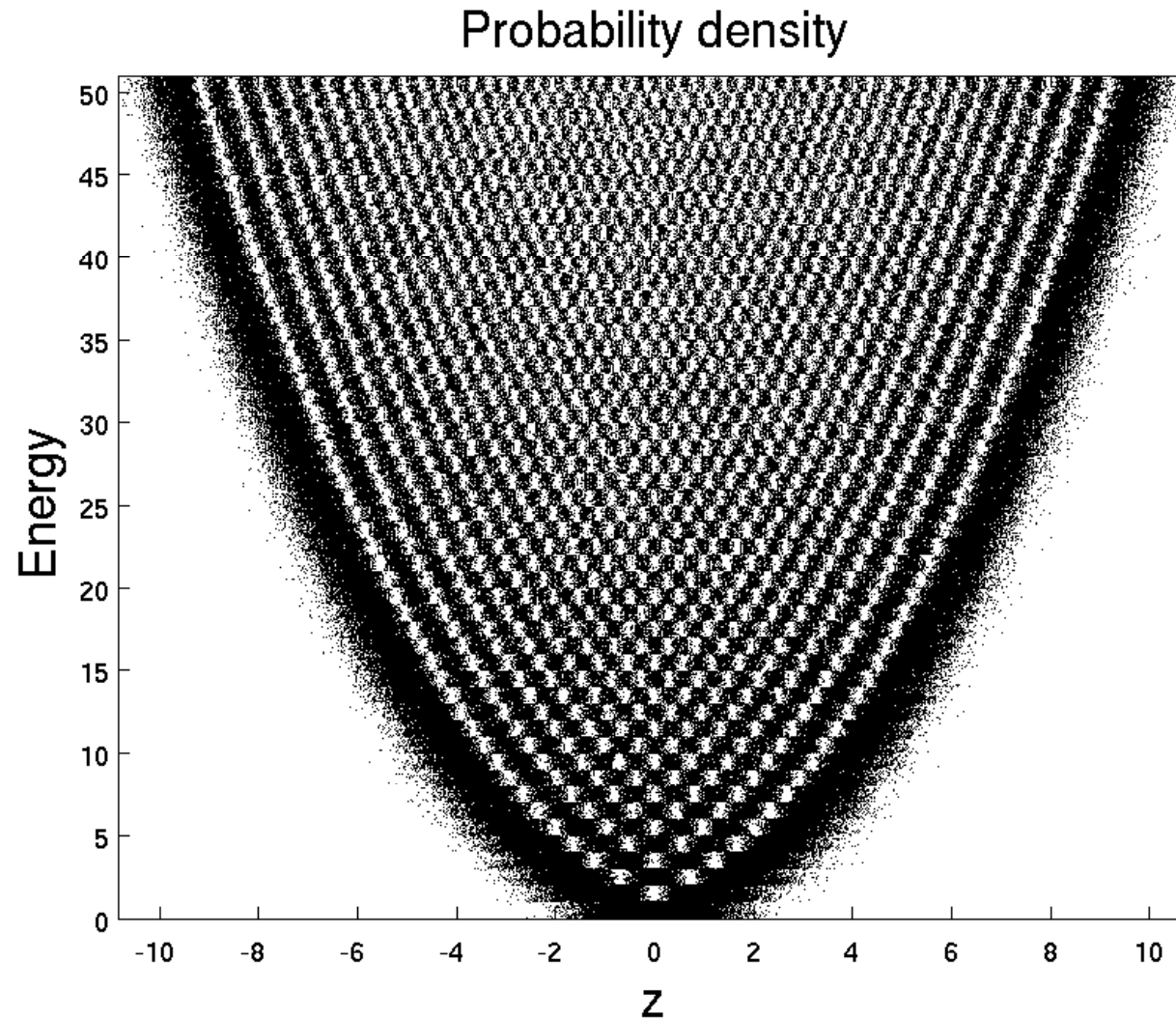
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An offset-overlay of $P(x)$ for $n = 0, 1, 2, \dots, 20$.



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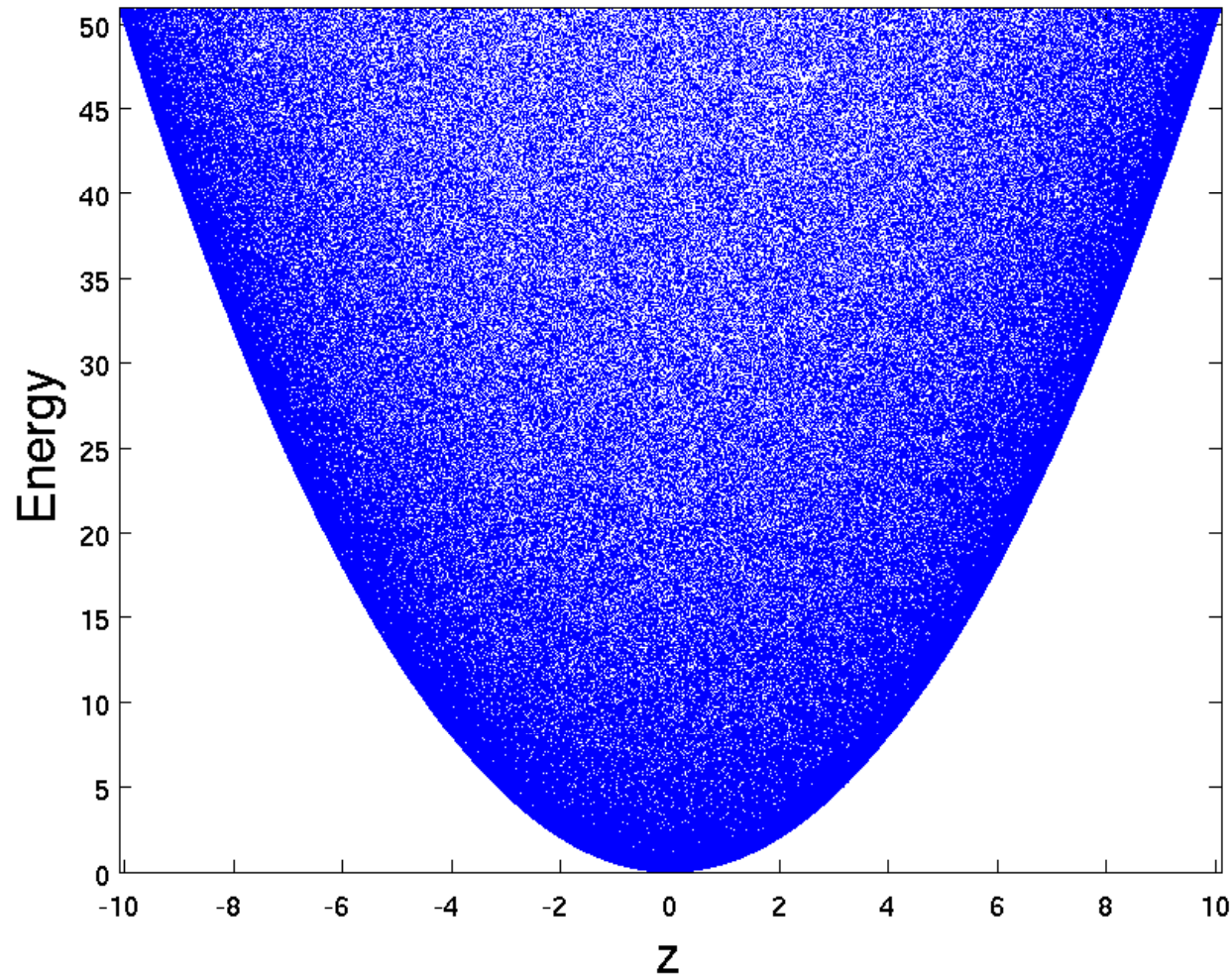
Random samples of $P(x)$ for $n = 0, 1, 2, \dots, 50$.



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Random samples of $P(x)$ for $n = 0, 1, 2, \dots, 50$ for a classical trajectory.

Classical particle snapshots



... The QM solution of the harmonic oscillator

Random samples of $P(x)$ for $n = 0, 1, 2, \dots, 50$ for both.

Classical and Quantum together

