Anharmonicity

In real molecules, highly sensitive vibrational spectroscopy can detect overtones, which are transitions originating from the n = 0 state for which Δn = +2, +3, …

Overtones are due to anharmonicity. A good approximation of realistic anharmonicity is given by the Morse potential.

$$V(r) = D_e[1 - e^{-\alpha(r-r_0)}]^2$$

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Put x = r – r_0 and Taylor expand:

$$V(x) = D_e(1 - 2e^{-\alpha x} + e^{-2\alpha x})$$

$$\approx D_e(1 - 2[1 - \alpha x + \tfrac{1}{2}\alpha^2 x^2] + [1 - 2\alpha x + \tfrac{1}{2}4\alpha^2 x^2]) = D_e\alpha^2 x^2$$

Comparing to the harmonic oscillator $V(x) = \tfrac{1}{2}kx^2$

we see that $k = 2D_e\alpha^2$

$$\alpha = \left(\frac{k}{2D_e}\right)^{1/2} = \left(\frac{\mu\omega^2}{2D_e}\right)^{1/2}$$

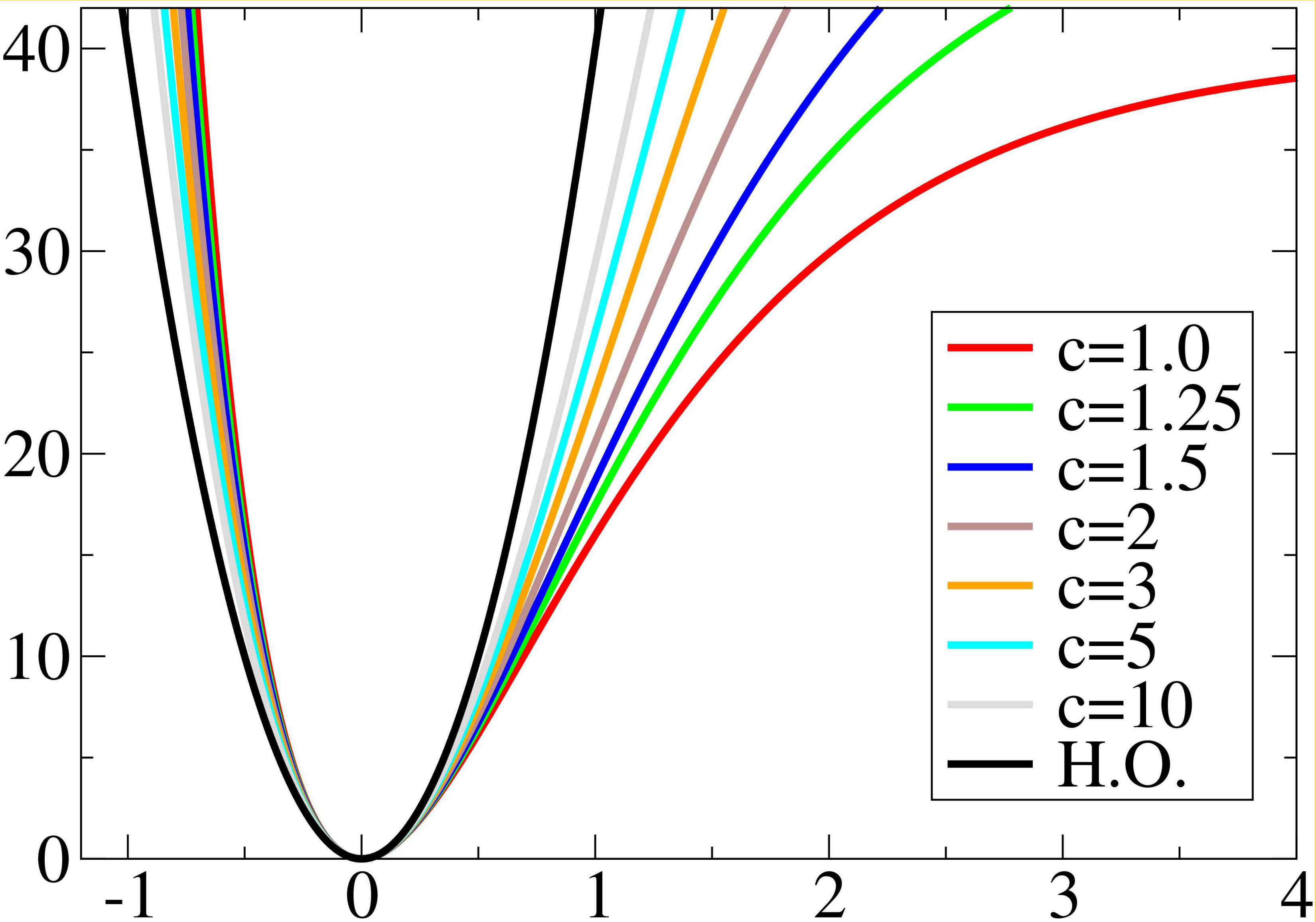
So we do $D_e \rightarrow cD_e$

$$\alpha \rightarrow \frac{\alpha}{\sqrt{c}}$$

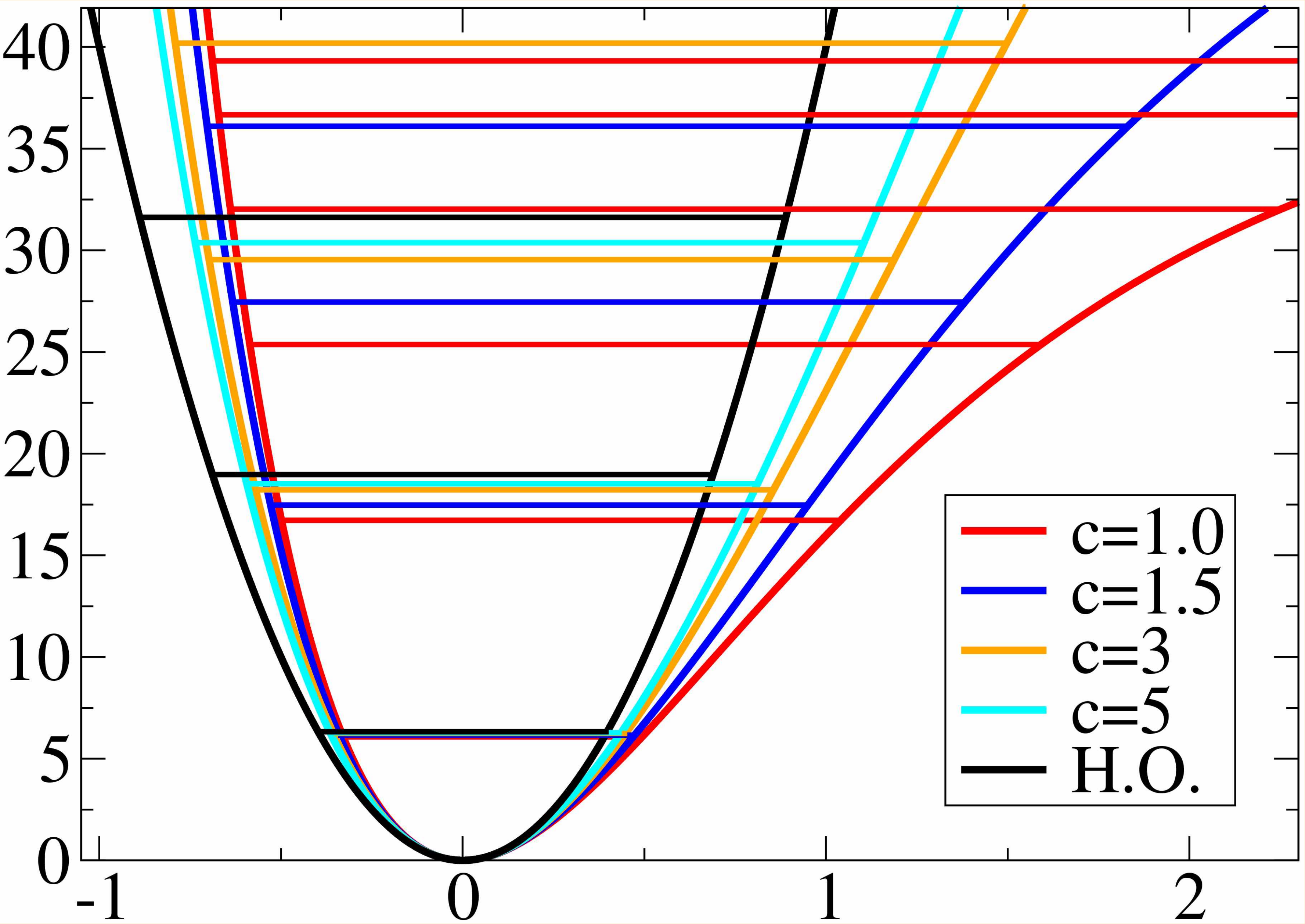
to keep the force constant the same but change the anharmonicity

$$V(x) = D_e[1 - e^{-\alpha x}]^2$$

use D_e = 40, α = 1;
then scale by *c*



Energy levels



Morse model

$$E_n = 2\alpha D_e^{1/2}\left[(n+1/2) - (n+1/2)^2 \frac{\alpha}{2D_e^{1/2}}\right]$$

$$\psi_n(x) = N_n y^{\beta - n - 1/2} e^{-y/2} L_n^{2\beta - 2n - 1}(y)$$

$$0 \le n < \frac{D_e^{1/2}}{\alpha} - \frac{1}{2}$$ **dissociated above this**

$$N_n = \left[\frac{\alpha(2\beta - 2n - 1)n!}{\Gamma(2\beta - n)}\right]^{1/2}$$

$$y = 2\beta e^{-\alpha x}$$

$$\beta = \frac{D_e^{1/2}}{\alpha}$$

$L_n^a(x)$ **are the generalized Laguerre polynomials**

Harmonic oscillator model

$$E_n^{MORSE} = 2\alpha D_e^{1/2}\left[(n+1/2) - (n+1/2)^2 \frac{\alpha}{2D_e^{1/2}}\right]$$

$$E_n^{HO} = 2\alpha D_e^{1/2}(n+1/2)$$

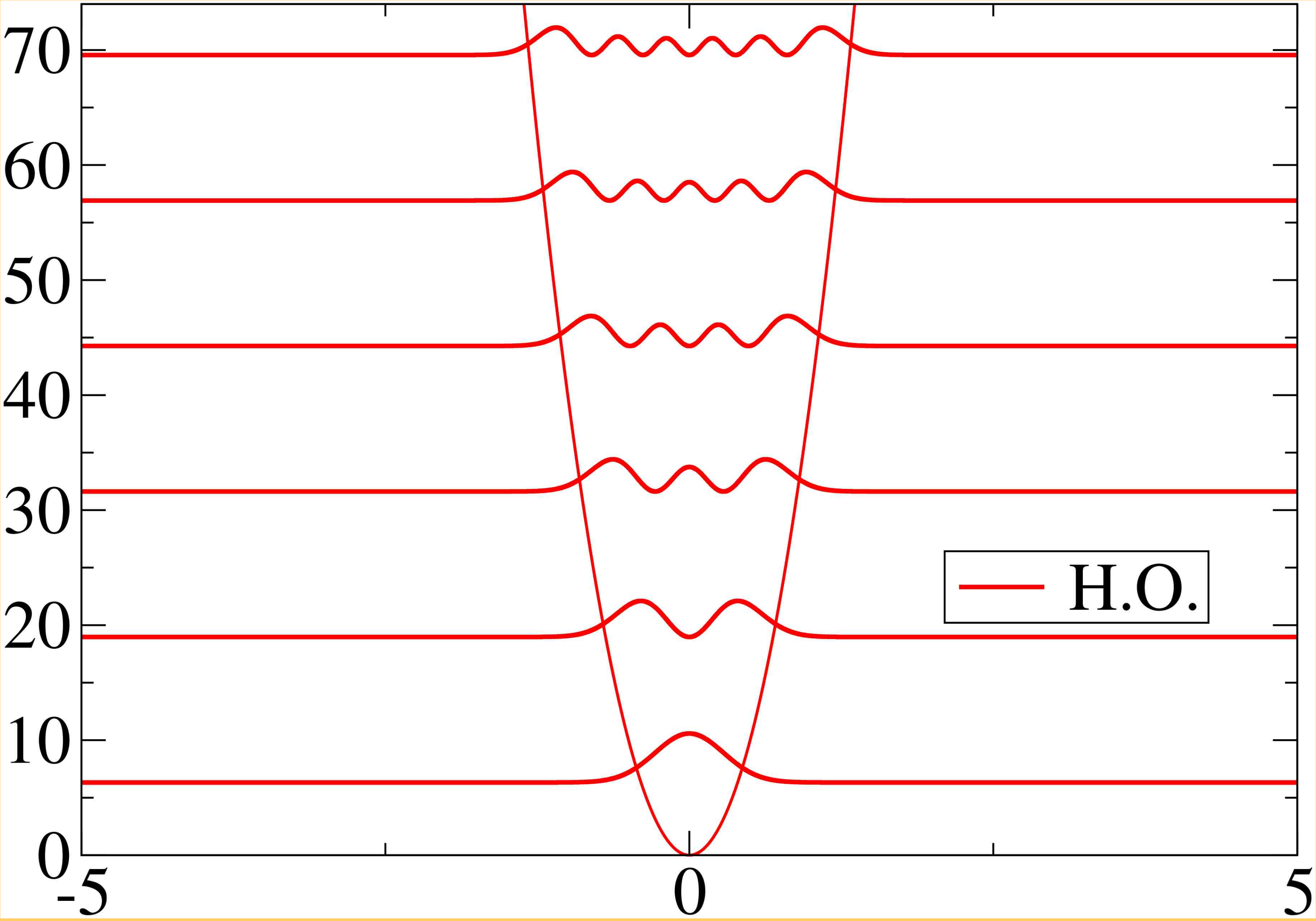
$$\psi_n(x) = N_n H_n(\alpha^{1/2} x) e^{-\alpha x^2/2}$$

$$\alpha = \left(\frac{k\mu}{\hbar^2}\right)^{1/2}$$

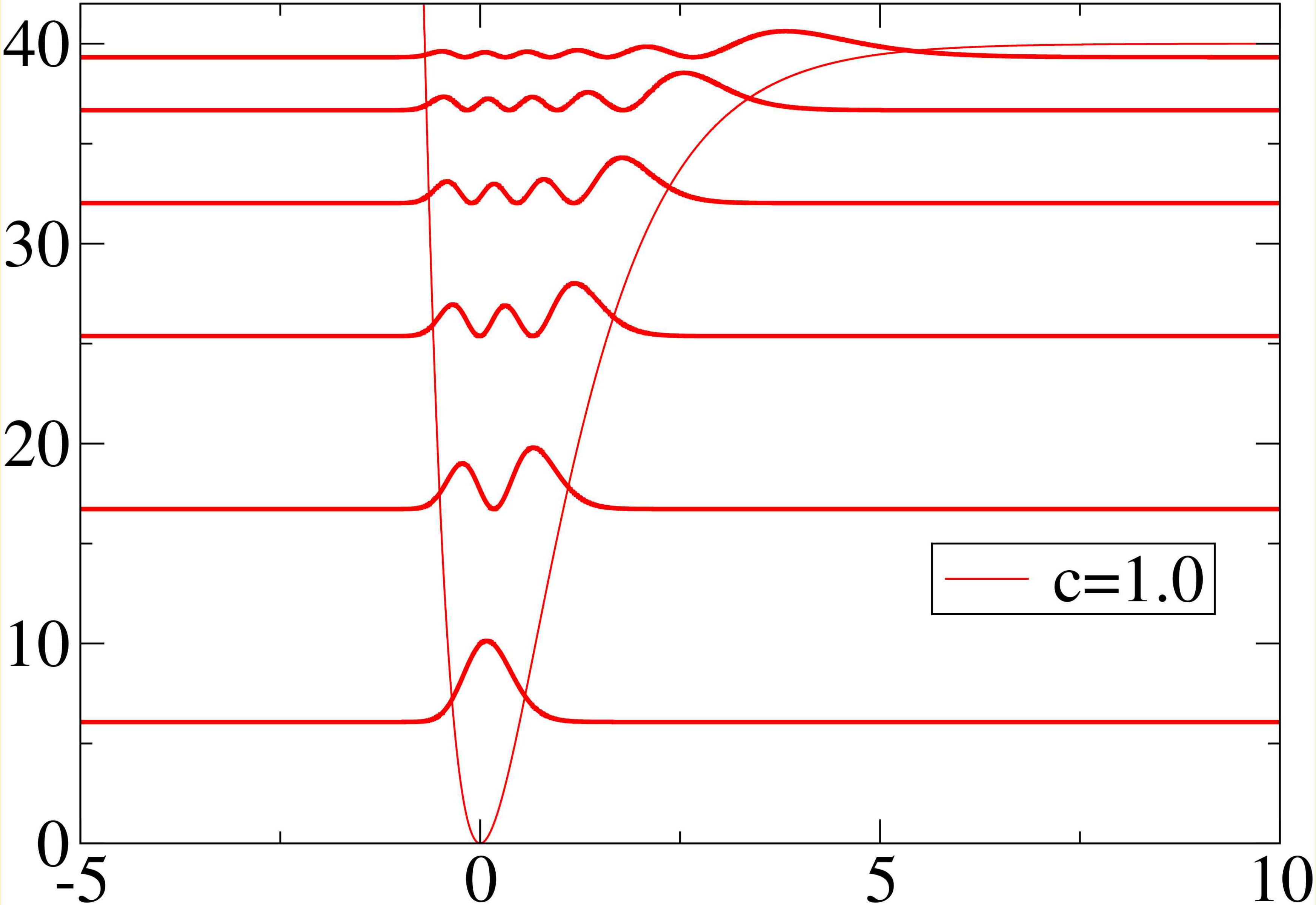
$$N_n = \frac{1}{(2^n n!)^{1/2}}\left(\frac{\alpha}{\pi}\right)^{1/4}$$

$H_n(x)$ **are the Hermite polynomials**

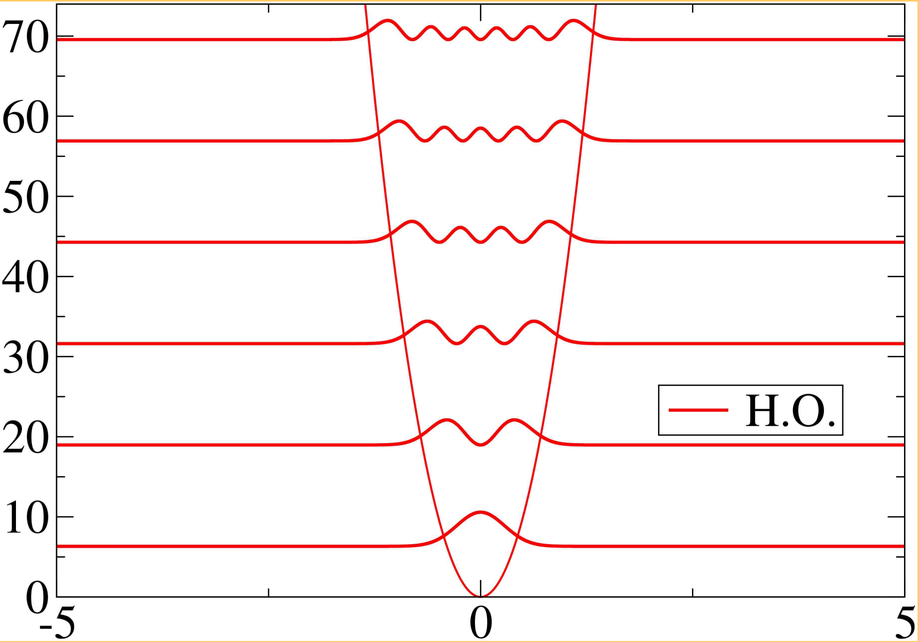
Wavefunctions: harmonic oscillator

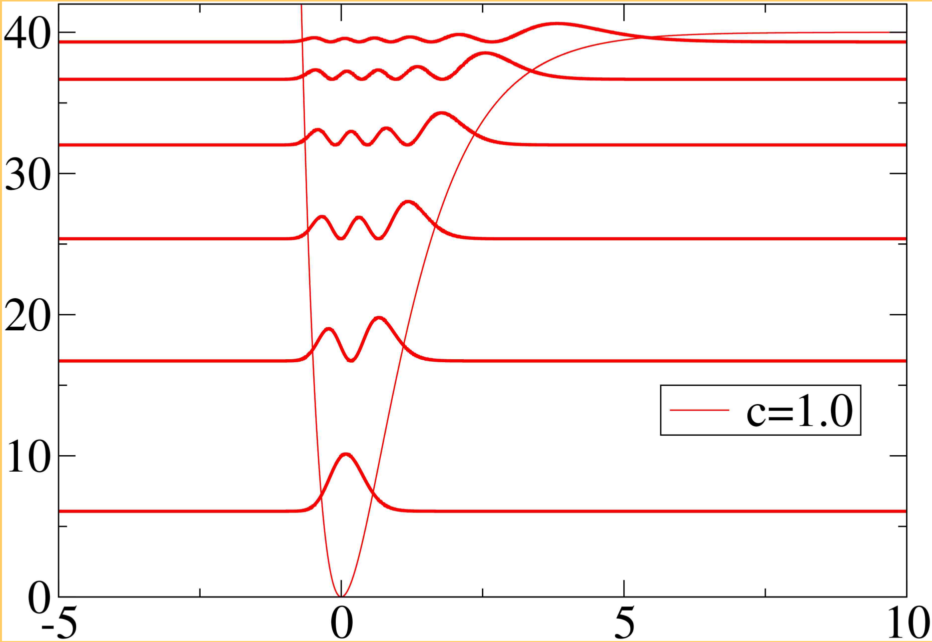


Wavefunctions: Morse oscillator

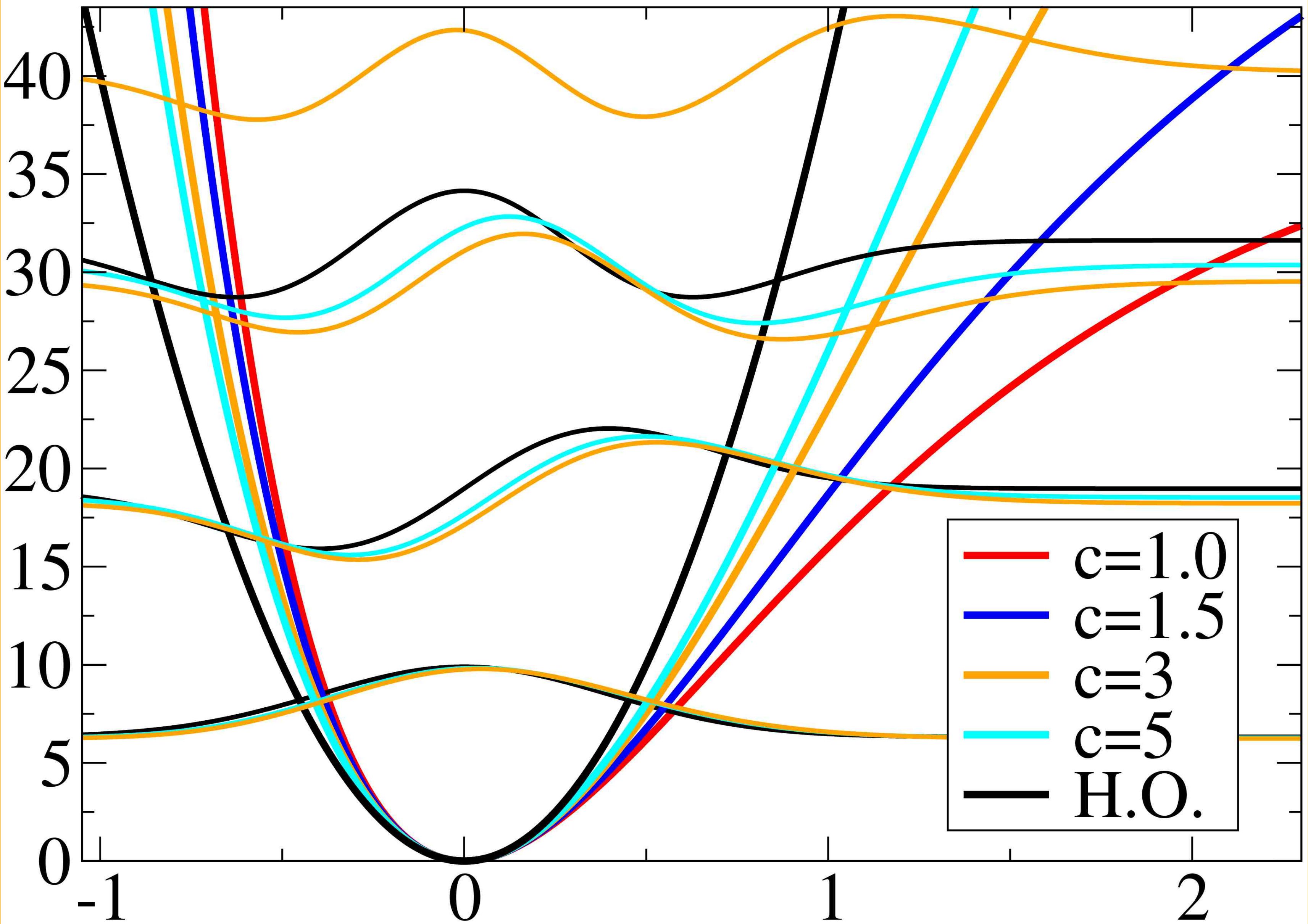


Wavefunctions: harmonic vs. Morse

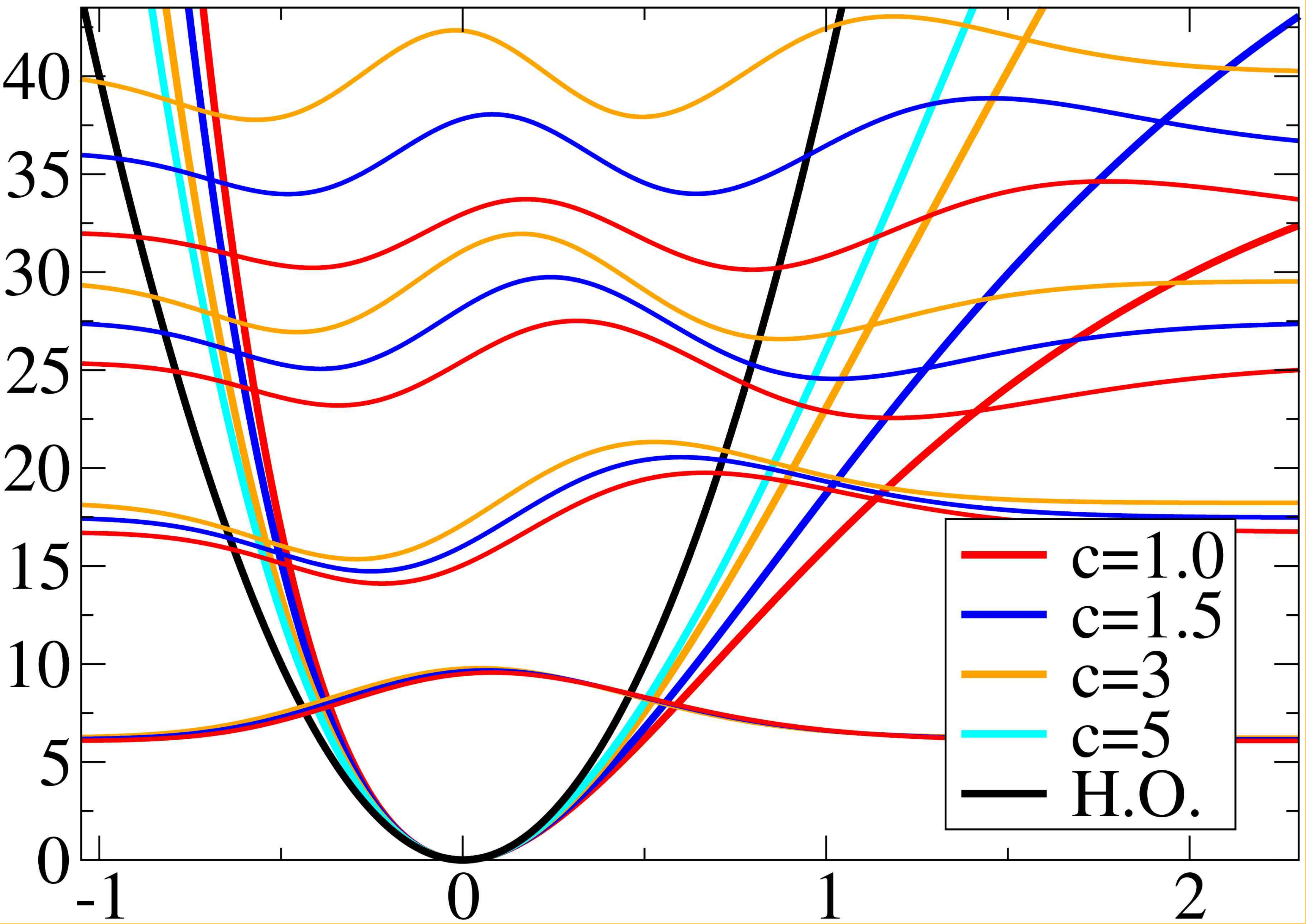




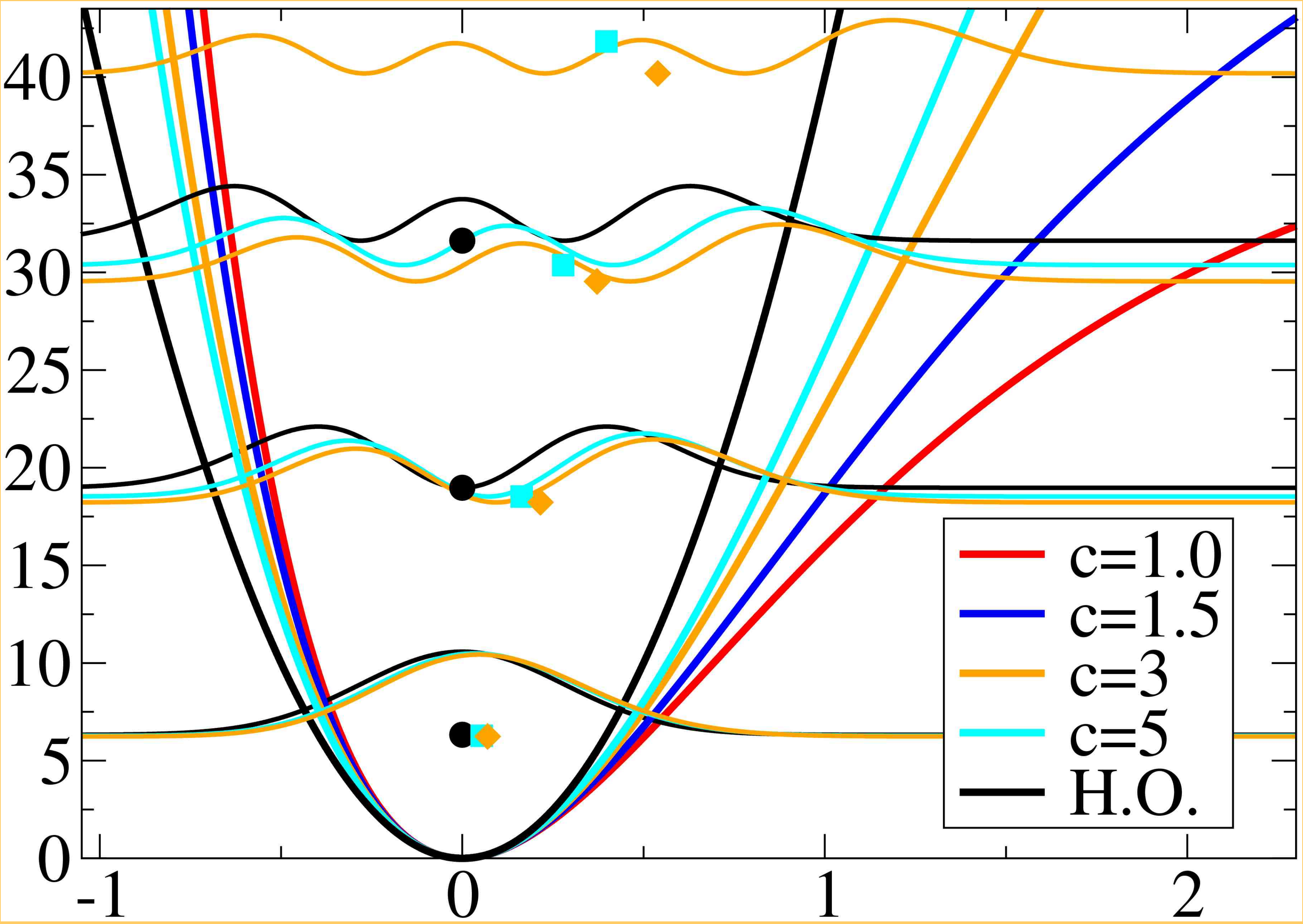
Wavefunctions



Wavefunctions



Expectation value of position



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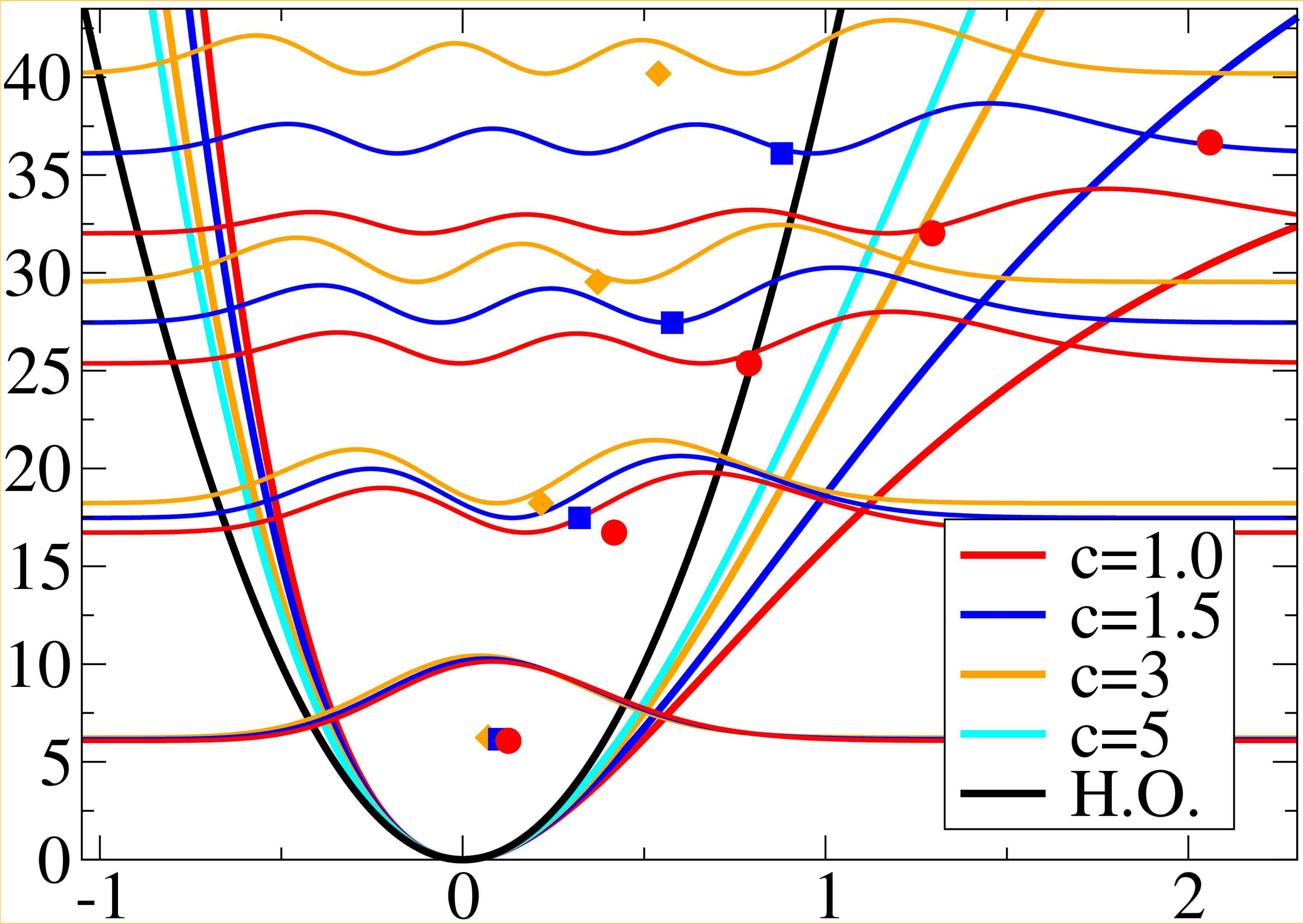
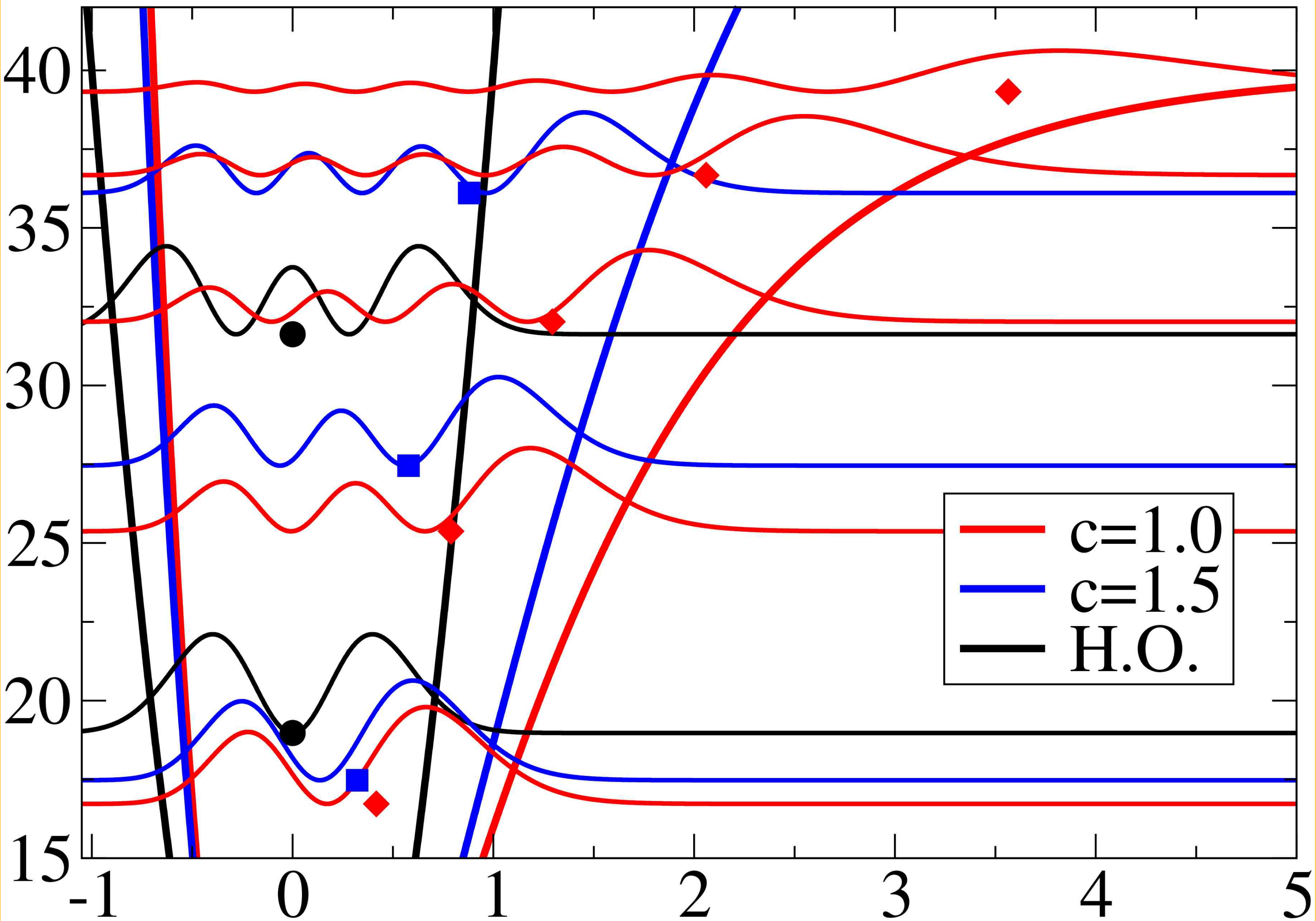
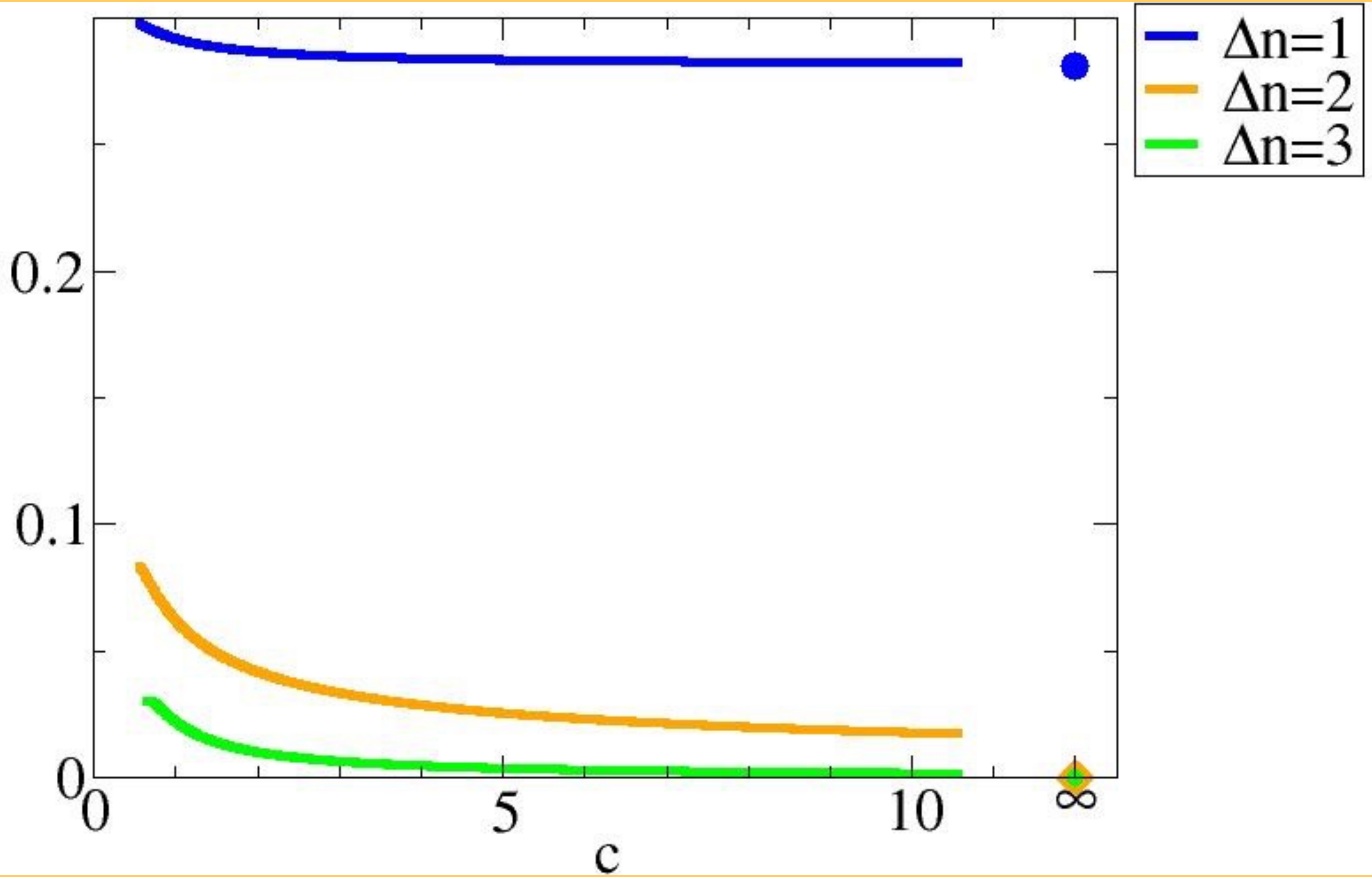


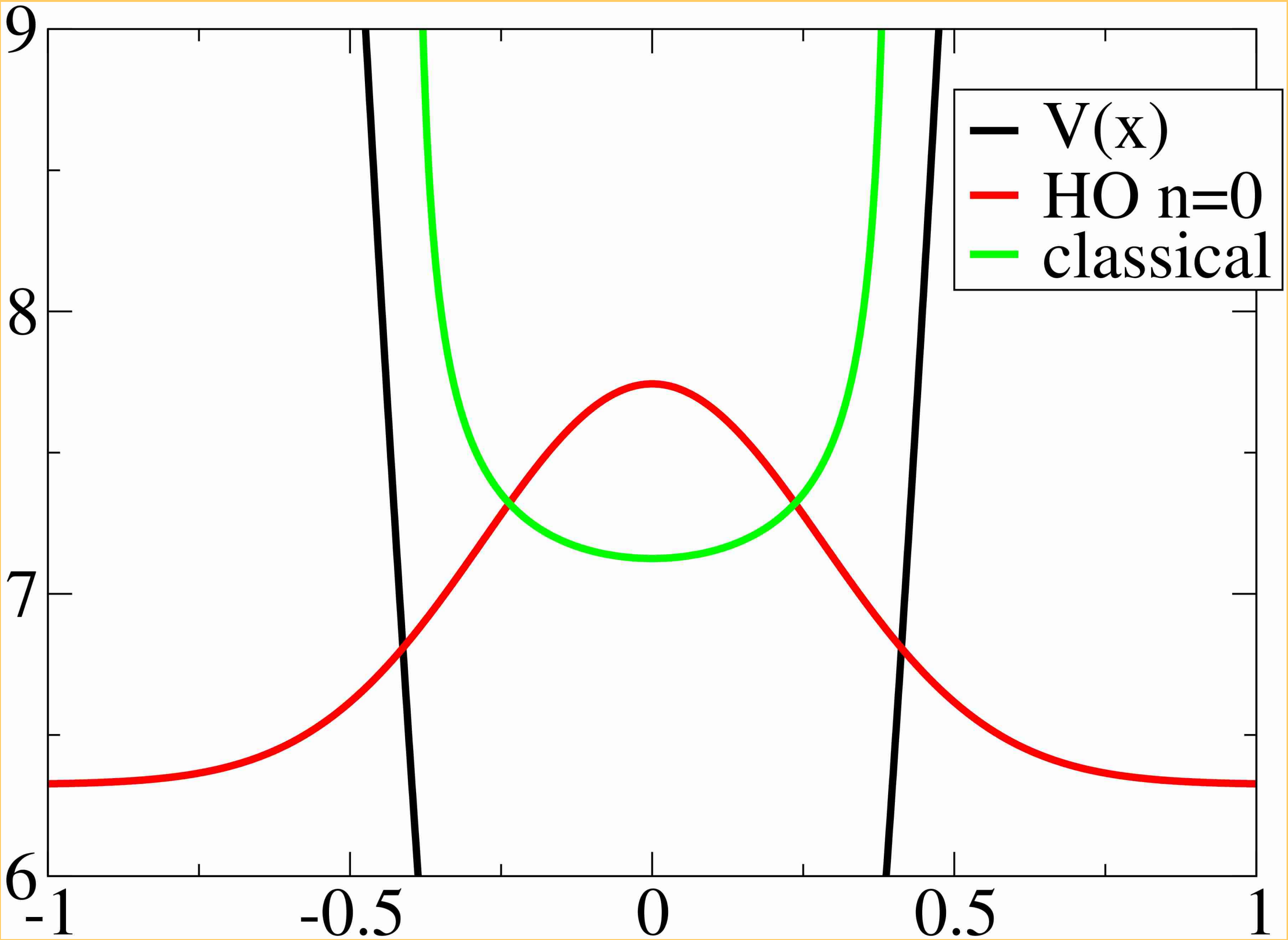
Expectation value of position



Selection rules



Correspondence principle

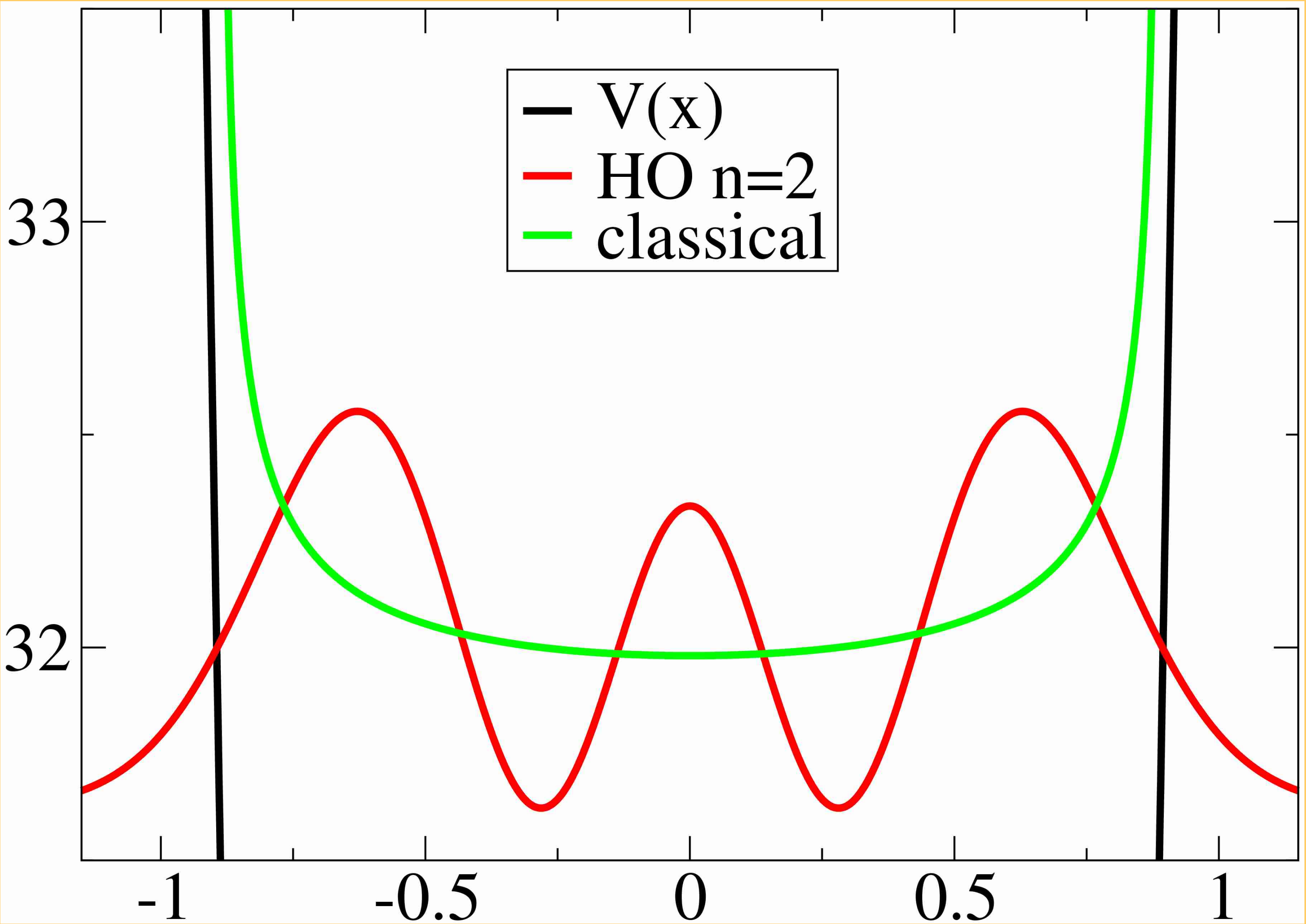


$$P_{classical}(x) = \left(\pi\sqrt{2E/k - x^2}\right)^{-1}$$

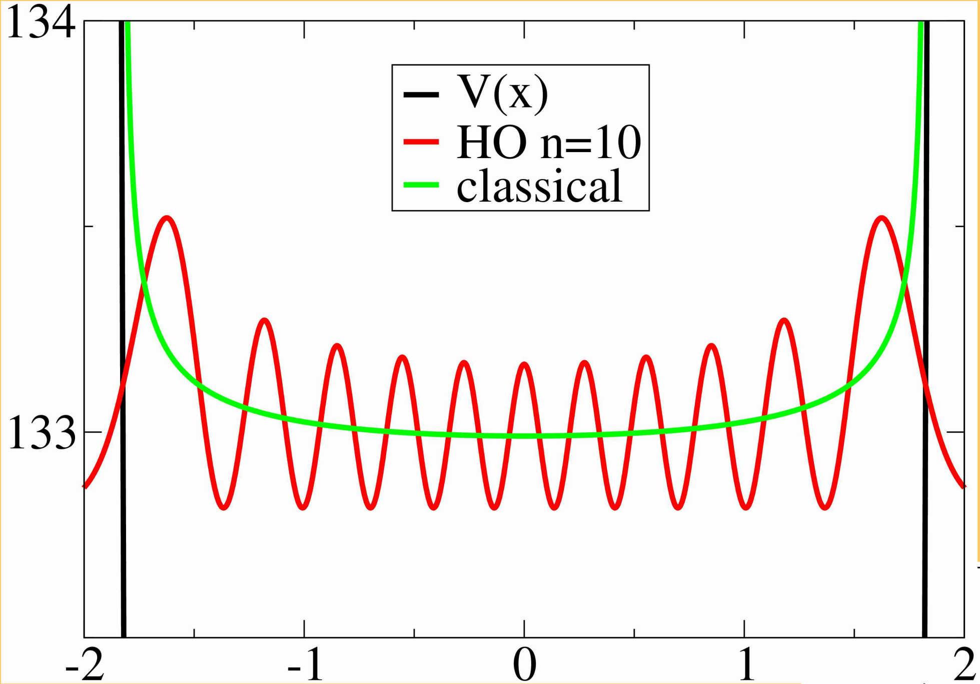
$$2E/k = x^2_{turn}$$

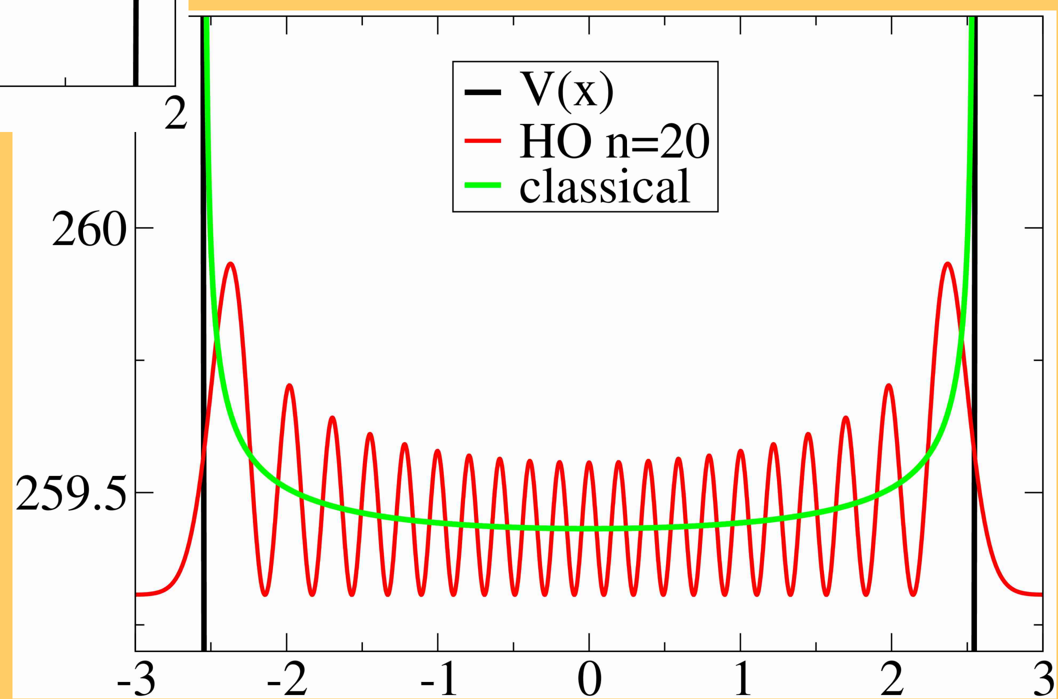
Where x_{turn} is the maximum value of x

Correspondence principle



Correspondence principle





Correspondence principle