Chemical Physics Letters 633 (2015) 208–213

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Quantum revivals of Morse oscillators and Farey-Ford geometry

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ARTICLE INFO

Article history:
Received 18 March 2015
In final form 20 May 2015
Available online 4 June 2015

ABSTRACT

Analytical eigensolutions for Morse oscillators are used to investigate quantum resonance and revivals and show how Morse anharmonicity affects revival times. A minimum semi-classical Morse revival time $T_{min-rev}$ found by Heller is related to a complete quantum revival time T_{rev} using a quantum deviation δ_N parameter that in turn relates T_{rev} to the maximum quantum beat period $T_{max-beat}$. Also, number theory of Farey and Thales-circle geometry of Ford is shown to elegantly analyze and display fractional revivals. Such quantum dynamical analysis may have applications for spectroscopy or quantum information processing and computing.

1. Introduction

Wavepacket dynamics has a long history that has more recently been accelerated by graphics that exhibit space–time behavior. Such studies began with revivals in cavity QED simulations by Eberly [1] and later simulations of molecular rovibronic dynamics [2,3]. Ultrafast laser spectroscopy made it possible to observe wavepacket resonance and localized periodic motion in experimental situations [4–6] involving AMOP dynamics [6,7]. This helped reveal new physics and chemistry of ultrafast spectroscopy [7,8].

Some of this involves symmetry and number theoretic properties of wavepacket space–time structure, a still largely unexplored field. The following development is based upon earlier *Cn*-group and Farey-sum-tree [9] analysis of quantum rotors [10,11] as cited by Schleich et al. [12,13] for possible numeric factorizing applications. That work treated only R(2) rings or 1D infinite-wells but nevertheless revealed general symmetry properties.

Here Morse oscillators are shown to share Farey-sum revival structure of R(2) rings or 1D infinite-wells. Moreover, Morse revivals reveal concise ways to find complete revival times T_{rev} along with new ways to quantify quantum wavepacket dynamics using Ford circles [14,15].

The Morse oscillator potential Eq. (1a) is an anharmonic potential [16] used to describe covalent molecular bonding. Some dynamics of Morse states have been studied [17–21] as a model of vibrational anharmonicity.

$$V_M(x) = D(1 - e^{-\alpha x})^2 \tag{1a}$$

Coordinate x is variation of bond from equilibrium where the potential has its minimum and zero value at $x = 0$. Coefficient D is bond dissociation energy and its maximum inflection value at infinite x. D relates harmonic frequency ω_e in Eq. (1b) and anharmonic frequency ω_χ in Eq. (1c) that gives width parameter α. The latter is related to reduced mass μ and anharmonic frequency ω_χ.

$$D = \frac{{\omega_e}^2}{4\omega_\chi}\hbar \tag{1b}$$

$$\alpha = \sqrt{\frac{2\omega_\chi \mu}{\hbar}} = \sqrt{\frac{\omega_e^2 \mu}{2D}} \tag{1c}$$

McCoy [22] revived interest in exact eigenfunctions and eigenvalues [23] of Morse oscillator used in Eqs. (2) and (3a) below and allows analysis of its quantum dynamics that may be relevant to anharmonic dynamics in general.

The Morse oscillator, being anharmonic, has varying spacing of its energy levels in contrast to uniform (harmonic) spacing. At high quanta n, energy levels $E_n = \hbar\omega_n$ have low-n spacing $\Delta E = \hbar\omega_e$ compressed for positive anharmonic frequency ω_χ in Eq. (2).

$$E_n = \hbar\omega_n = \hbar\omega_e\left(n + \frac{1}{2}\right) - \hbar\omega_\chi\left(n + \frac{1}{2}\right)^2 \tag{2}$$

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http://dx.doi.org/10.1016/j.cplett.2015.05.035
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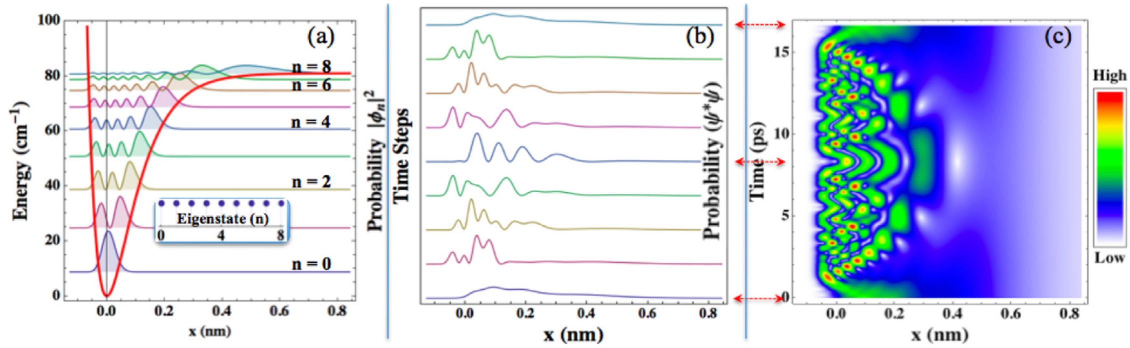

Figure 1. The Morse oscillator with a harmonic frequency $\omega_e/2\pi c = 18\,\mathrm{cm}^{-1}$ and an anharmonic frequency $\omega_\chi/2\pi c = 1\,\mathrm{cm}^{-1}$. (a) Each of its stationary eigenstate $|\phi_n|^2$ was list-plotted on a energy level of eigenvalue E_n in the potential well (red-color-line), these wave functions are normalized (indicated by the same-height dotted-line). (b) The wave packet $\psi^*\psi$ is propagated along the time steps. (c) The probability density map of the wave packet $|\psi|$ as a function of space and time. The double arrows connecting (b) and (c) indicate the corresponding time events. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

The corresponding Morse eigenfunctions of the eigenvalues are given by Eq. (3a) where L_n^{2s} represents a generalized associated Laguerre polynomial [22].

$$\phi_n(x) = e^{\frac{-y(x)}{2}} y(x)^{s(n)} \sqrt{\frac{\alpha(\nu - 2n - 1)n!}{\Gamma(\nu - n)}} L_n^{2s(n)}(y(x)) \tag{3a}$$

Exponentially scaled $y(x)$ has exponent $s(n)$ as given.

$$y(x) = \nu e^{-\alpha x} \tag{3b}$$

$$s(n) = \frac{1}{2}(\nu - 2n - 1) \tag{3c}$$

The scaling parameter ν is as follows:

$$\nu = \frac{4D}{\hbar\omega_e} \tag{3d}$$

Dynamic waves are combinations of eigenfunctions.

$$\psi(x, t) = \sum_{n=0}^{n_{\max}} c_n \phi_n(x) e^{-i\frac{E_n t}{\hbar}} \tag{4}$$

Here n_{max} is the highest bound state. Its eigenvalue is nearest to dissociative limit D. To get maximum beating we assume equal Fourier coefficients $c_n = 1$ (we do not consider shorter revivals had by zeroing select c_n). For instance, amplitude of beat $\omega_A - \omega_B$ between two states $|A\rangle$ and $|B\rangle$ is related to the standing-wave-ratio $SWR = (A - B)/(A + B)$ of amplitude A and B given to each state. Clearly, this is maximum at 100% modulation when $A = B$. However, having all amplitudes equal is not always desirable particularly if the result is chaotic. A gradual turn-on and turn-off of a select range of frequencies may lead to a more revealing waveform. This involves the art of band-pass windowing and the Lorentzian or Gaussian windows are among the best known [11].

A sample Morse oscillator potential shown in Figure 1(a) has a total of nine stationary bound states (from $n = 0$ to $n_{max} = 8$). The initial wave packet (Eq. (4) at $t = 0$) is a sum of these stationary bound states and evolves as shown in Figure 1(b) ending in its lowest $\psi(x, T)^* \psi(x, T)$ trace as the initial shape fully revived.

Space–time plots of the norm $|\psi(x, t)|$ in Figure 1(c) show resonant beat nodes and anti-nodes that outline semi-classical trajectories $x(t)$ corresponding to energy values E_n ranging from the lowest ground state E_0 up to the highest bound state $E_{n_{\max}}$.

2. Analysis

An essential part of wave packet dynamics analysis of anharmonic systems is to predict if and when exact wave packet revival might occur. If T_{rev} is a time for a Morse oscillator revival, then Wang and Heller [21] have shown

$$T_{rev} = \frac{\pi}{\omega_\chi}\mathbb{M} \tag{5a}$$

where $\mathbb{M}$ is an integer. This revealed two facts about Morse oscillator dynamics. First, there may be minimum or fundamental revival period at

$$T_{\min-rev} = \frac{\pi}{\omega_\chi} \tag{5b}$$

This is the shortest revival time for Morse oscillator found by Wang and Heller [21]. Second, any complete revival period is made of integer numbers of the fundamental period. That is, any complete quantum revival must contain integer numbers of semiclassical-trajectory-profile periods (minimum revival period) which is approximately outlined by a classical particle oscillating with a frequency of $2\omega_\chi$ in the Morse potential.

For a simple illustration of the relationship between quantum periods and semiclassical-trajectory-profile periods, consider three cases of classical particles with corresponding quantum eigenvalue energies orbiting in a Morse potential as shown in Figure 2(a). Here the rainbow-shape trajectory of a classical particle with energy E_2 has a classical oscillating period T close to the fundamental period of π/ω_χ, while a classical trajectory with energy $E_3 = D$ is of a particle barely escaping from its Morse potential well.

The preceding case has a simple revival period formula. More analysis is required to determine a specific integer $\mathbb{M}$ of Eq. (5a) for Morse revivals for a given (ω_e, ω_χ).

Beating of waves with nearby frequency plays a key role in quantum dynamics. The maximum beat period $T_{max-beat}$ due to the closest bound energy level pair in the Morse well is one key to finding its revival period. A complete revival of $|\Psi(x, t)|^2$ at time T_{rev} must contain integer numbers of all beat periods including at least one fundamental time period $T_{max-beat}$ for the slowest beat frequency. This relates it to revival period.

$$T_{rev} = T_{\max-beat}\mathbb{N} \tag{6}$$

Here $\mathbb{N}$ is an integer. The Morse energy level Eq. 2 gives a beat-gap between neighboring energy.

$$\Delta E = E_n - E_{n-1} = \hbar(\omega_e - 2\omega_\chi n) \tag{7}$$

The ΔE is the minimum for maximum n occurring between the highest bound quantum numbers n_{max} and n_{max-1}. Planck's relation $E = \hbar\omega$ gives maximum beat period.

$$T_{\max-beat} = \frac{2\pi}{(\Delta\omega)_{\min}} = \frac{2\pi}{E_{n_{\max}} - E_{n_{\max-1}}}\hbar = \frac{2\pi}{\omega_e - 2\omega_\chi n_{\max}} \tag{8}$$