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Morse Oscillator Propagator Using its Coherent States: Exact and Approximate

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Abstract
Morse oscillator coherent states are employed to derive an analytical expression of its off-diagonal propagator. An exact expression for the Morse oscillator propagator is provided. Additionally, an approximately good expression is also derived. A closed-form expression of the Morse oscillator diagonal propagator is given as well. This expression seems to be relatively *easier* and numerically much more stable than those in the literature. The stability issue is critical when dealing with Morse oscillator arising dynamics and integrals as divergence becomes a lingering problem. For this reason, the presented closed-form expression of the Morse oscillator diagonal propagator herein should be useful, especially numerically.

Keywords Approximate form of Morse oscillator propagator · Morse oscillator coherent states · Numerical stability of the anharmonic system propagator

1 Introduction

Many important time-dependent phenomena in physics, chemistry, and biology are modeled by employing harmonic oscillators. However, some of those phenomena tend to exhibit anharmonic behavior and treating them harmonically would yield erroneous results and hence wrong conclusions. Therefore, having the right tool to probe quantum dynamics of anharmonic oscillators is of paramount importance. The most commonly utilized anharmonic oscillator is that of Morse, for which the reason it will be the central component of this paper. [1, 2] One way to handle time dependent quantities is to apply the relevant propagator, which is typically derived, or calculated, using path integral techniques. [2–6]. The remarkable work of Duru [4] was the first to derive an expression

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for the Feynman propagator of Morse oscillator using path integral techniques. His work, however, leads to a double-integral expression of which the integrand is a product of Bessel functional and exponential functional. The complexity of the integrand poses a challenge for the traditional integration routines, causing numerical difficulties and uncertainties. [7, 8]

In light of the above, this paper is to find an expression of the off-diagonal propagator of Morse oscillator using its coherent states relying on previous work. [9–14] These anharmonic coherent states are less straightforward and more difficult to deal with than their harmonic counterparts and as a result they pose some challenges: Morse oscillator bound states (comprising a subspace of bound states) are incomplete due to the presence of continuum states; Morse oscillator coherent states have a harder integration measure [12]; the arising commutators are hard to handle; and, finally, they have harder inner product to deal with mathematically as opposed to that of harmonic oscillator. For this reason, utmost care must be practiced when employing Morse oscillator coherent states to solving problems. However, one may circumvent the incompleteness issue physically by assuming that the vibrating system of interest does not undergo dissociation and therefore the continuum subspace (spanned by unbound states of Morse potential) would be of no significance to completeness and thus the error is negligible, if any at all. For example, consider a molecule whose anharmonic vibration may be described by a Morse oscillator; if this molecule escapes dissociation upon vibration, the unbound states would not be of essence or material. [15–17]

In this paper, the Morse oscillator propagator is recast in terms of its coherent states, assuming the system of interest escapes dissociation (continuum states are of no significance). The motivation for this work is to find a relatively easier form of the propagator of Morse oscillator, whereby it may more readily be utilized analytically and numerically than what has already been reported in the literature. [16–19] Numerical stability is of paramount importance when dealing with Morse oscillator dynamics that involve integrals. Several studies [18–21] have discussed the divergent dynamics, as a consequence of the divergent integrals, that arise in the wake of probing Morse oscillator spectral and dynamical properties. As such, seeking simpler and more manageable numerical uncertainty results should be valuable in that respect.

2 Theoretical Background and Morse Oscillator Coherent States

Consider a system experiencing anharmonic vibrations that may be modeled by Morse oscillator of which Hamiltonian is

$$H = \frac{P^2}{2\mu} + D_e[1-\exp(-ax)]^2, \tag{1}$$

defined over $-\infty < x < \infty$. While P and x are the momentum and position, D_e and a (often called Morse parameter) are the depth and width of Morse potential well, respectively, and μ is the oscillator mass. The eigenfunctions of $\hat{H}$ are expressed in terms of the generalized Laguerre polynomials, $L_m^{2\varepsilon-2m-1}(y)$,

$$\Phi_m(y) = \sqrt{\frac{\Gamma(m+1)2s}{\Gamma(2\varepsilon-m)}} y^{\varepsilon-m-\frac{1}{2}} e^{\frac{-y}{2}} L_m^{2\varepsilon-2m-1}(y), \tag{2}$$

where $\Gamma(.)$ is Gamma function and $\varepsilon = \sqrt{2\mu D_e}/a\hbar$ is the number of Morse potential bound states. (It should be noted the constraint condition for this system is $2s = 2\mathcal{E}-2m-1$ as dictated by Landau and Lifshitz. [16] To simplify notation and the forthcoming mathematical operations, we set $y = 2\varepsilon e^{-ax}$ (often called *Morse coordinate*)

$$\Phi_m(y) = \sqrt{\frac{\Gamma(m+1)2s}{\Gamma(2\varepsilon - m)}} y^s\, e^{-\frac{y}{2}}\, L_m^{2s}(y), \tag{3}$$

of which the normalization condition with respect to Morse coordinate becomes [14].

$$\int_0^{+\infty} \frac{|\Phi_m(y)|^2}{ay}\, dy = 1. \tag{4}$$

Morse oscillator coherent states may be written as a linear combination of the Morse oscillator eigenstates $|m\rangle$ as [9–11].

$$|\alpha\rangle = \sum_{m=0}^{N/2} \frac{\alpha^m}{\sqrt{\rho(m)}} |m\rangle \tag{5}$$

where $\rho(m)$ will be obtained by using the other definition of Klauder-Perelomov coherent states, *un-normalized*, namely

$$|\alpha\rangle = exp\left(zA^\dagger\right)|0\rangle, \tag{6}$$

where $A^\dagger$ is the creation operator and $|0\rangle$ is the ground state of Morse oscillator. Expanding the above exponential in Taylor series and carrying out the $A^\dagger$ operation yields [11].

$$\rho(m) = \frac{\mathrm{N}^{\mathrm{m}}\Gamma(m+1)\Gamma(N-m+1)}{\Gamma(N+1)} \tag{7}$$

Assuming that Morse potential will have N/2 finite bound states, the inner product of two coherent states is [9].

$$\langle\alpha|\beta\rangle = \sum_{m=0}^{N/2} \frac{(\alpha^*\beta)^m}{\rho(m)}. \tag{8}$$

The closure relation of Morse coherent oscillator coherent states is

$$\int d\sigma|\alpha\rangle\langle\alpha| = I, \tag{9}$$

where the integration measure dσ has been evaluated by several groups, [9, 10, 20, 21] but the form I use herein is written quite differently since I have chosen my coherent states to be un-normalized, as Popov has established in [9].

$$d\sigma = \frac{(N+1)}{\pi N\left(1 + \frac{|\alpha|^2}{N}\right)^{N+2}} d^2\alpha. \tag{10}$$

3 Morse Oscillator Propagator in Terms of its Coherent States

The off-diagonal Propagator of Morse oscillator is given by

$$\mathcal{F}(x_1, x_2; t) = \left\langle x_1 | e^{-\frac{i\hat{H}t}{\hbar}} | x_2 \right\rangle \tag{11}$$

This propagator may also be defined as

$$\mathcal{F}(x_1, x_2; t) = \sum_{m=0}^{N} \ e^{-\frac{iE_m t}{\hbar}} \Phi_{\mathrm{m}}^*(x_1) \Phi_{\mathrm{m}}(x_2) + \int_0^\infty dE \, e^{-\frac{iEt}{\hbar}} \, \Phi_{\mathrm{E}}^*(x_1) \Phi_{\mathrm{E}}(x_2). \tag{12}$$

The first term in Eq. (12) represents the bound states of Morse oscillator, whereas the second term signifies its continuum (unbound) states. Physically, while the bound states of Morse oscillator represent the quantized vibrations of the molecule at hand, the unbound states represent its dissociation. Assuming that the molecule will escape dissociation (scattering state) and therefore will remain fully quantized, thereby the unbound states in the continuum will have no contribution to its vibrational motion. For this reason, the second expansion term will be dropped in the treatment hereafter.

Morse oscillator coherent states may be utilized to cast $\mathcal{F}(x_1, x_2; t)$ as

$$\mathcal{F}(x_1, x_2; t) = \iint d\sigma_\alpha d\sigma_\beta \, \langle x_1 | \alpha \rangle \langle \beta | x_2 \rangle \left\langle \alpha | e^{-\frac{i\hat{H}t}{\hbar}} | \beta \right\rangle \tag{13}$$

where the integral measures are given by

$$d\sigma_\alpha = \frac{1}{\pi} \frac{(N+1) d_\alpha^2}{N\left(1 + |\alpha|^2/N\right)^{N+2}} \tag{13a}$$

and

$$d\sigma_\beta = \frac{1}{\pi} \frac{(N+1) d_\beta^2}{N\left(1 + |\beta|^2/N\right)^{N+2}} \tag{13b}$$

with N being related to the number of Morse oscillator bound states m, where $\langle x_1 | \alpha \rangle$ and $\langle \beta | x_2 \rangle$ are projecting coherent states α and β along $x_1$and x_2. Using the definition of a coherent state in Eq. (5) and eigenfunctions of Morse oscillator in Eq. (3) leads to

$$\langle x_1 | \alpha \rangle = \Psi^\alpha(x_1) = \sum_{m=0}^{\left[\frac{N}{2}\right]} \frac{\alpha^m}{\sqrt{\rho(m)}} \sqrt{\frac{\Gamma(m+1)2s}{\Gamma(2\varepsilon - m)}} x_1^s \, e^{-\frac{x_1}{2}} \, L_m^{2s}(x_1), \tag{14}$$

and

$$\langle x_2 | \beta \rangle = \Psi^\beta(x_2) = \sum_{n=0}^{\left[\frac{N}{2}\right]} \frac{\beta^{*n}}{\sqrt{\rho(n)}} \sqrt{\frac{\Gamma(n+1)2s}{\Gamma(2\varepsilon - n)}} x_2^s \, e^{-\frac{x_2}{2}} \, L_n^{2s}(x_2) \tag{15}$$

Note that s will remain the same along both projections. Further simplification of Eqs. (14) and (15) yields

$$\Psi^{\alpha}(x_1)=\sqrt{\Gamma(N+1)}\sum_{m=0}^{\left[\frac{N}{2}\right]}\alpha^{m}\sqrt{\frac{N-2m-1}{\Gamma(N-m)N^{m}}}\ \frac{x_1^{\frac{N-2m-1}{2}}}{\sqrt{\Gamma(N-m+1)}}\ e^{-\frac{x_1}{2}}L_m^{(N-2m-1)}(x_1), \tag{16}$$

and

$$\Psi^{\beta}(x_2)=\sqrt{\Gamma(N+1)}\sum_{n=0}^{\left[\frac{N}{2}\right]}\beta^{*n}\sqrt{\frac{N-2m-1}{\Gamma(N-n)N^{m}}}\ \frac{x_2^{\frac{N-2n-1}{2}}}{\sqrt{\Gamma(N-n+1)}}\ e^{-\frac{x_2}{2}}L_n^{(N-2n-1)}(x_2). \tag{17}$$

Utilizing the results in [7], one may write

$$\left\langle\alpha|e^{-\frac{i\hat{\mathrm{H}}t}{\hbar}}|\beta\right\rangle=\frac{e^{-\mathscr{y}}}{\sqrt{\pi}}\int_{-\infty}^{\infty}db\ e^{-b^{2}}\left(1+\frac{\alpha^{*}\beta e^{-2b\sqrt{v}-u}}{N}\right)^{N}, \tag{18}$$

where

$$\mathscr{y}=i\omega_0 t(1-\chi/2)/2, \tag{18a}$$

$$u=-i\omega_0 t(1-\chi),\ v=i\omega_0\chi t \tag{18b}$$

where ω_0 is the oscillator fundamental frequency and χ is the anharmonicity constant. Evaluating the integral in Eq. (18) yields

$$\left\langle\alpha|e^{-\frac{i\hat{\mathrm{H}}t}{\hbar}}|\beta\right\rangle=e^{-\mathscr{y}}\sum_{k=0}^{N}\binom{N}{k}\left(\frac{\alpha^{*}\beta}{N}\right)^{k}e^{vk^{2}-ku}, \tag{19}$$

Inserting the quantities in Eqs. (17)—(19) in Eq. (13) yields

$$\mathcal{F}(x_1,x_2;t)=e^{-\mathscr{y}}\iint d\sigma_{\alpha}d\sigma_{\beta}\Psi^{\alpha}(x_1)\Psi^{\beta}(x_2)\left(\sum_{k=0}^{N}\binom{N}{k}\left(\frac{\alpha^{*}\beta}{N}\right)^{k}e^{vk^{2}-ku}\right). \tag{20}$$

The above integral in Eq. (20) is considerably *simpler* to evaluate than that reported in [4]. Additionally, and more importantly, it is a more stable integral to evaluate numerically. This is because the work of Duru [4] leads to a double-integral expression of which the *integrand* is a product of Bessel *functional* and exponential *functional*, of which complexity poses a challenge for traditional numerical integration routines, causing numerical difficulties and uncertainties. [7, 8]

4 Calculations and Discussion

The integral in Eq. (20) shows the exact Morse oscillator propagator expressed in its coherent states representation for all kinds of anharmonic molecules, in the sense that the more anharmonic character a molecule has the less vibrational bound states it supports in its Morse potential well, and the converse is true. The number of Morse oscillator vibrational bound states is given by $\varepsilon=\frac{\sqrt{2\mu D_e}}{a\hbar}=\left[\frac{N}{2}\right]$, guided by Popov's notation, [11, 12], which may also be recast as $\left[\frac{N}{2}\right]=\frac{1}{2\chi}-1$. This section will introduce some assumptions which will lead to further simplification of Eq. (20).

Assuming intermediate to weak anahamonicity, $\chi \ll 1$, exhibited by molecules, for they will yield a considerable number of vibrational bound states. It turns out that this assumption will simplify the above propagator tremendously as will be shown below. Our numerical calculations indicate that as the anahamonicity constant χ gets smaller (giving rise to many vibrational bound states as is normally the case in diatomic molecules), allowing us to drop the quantum number m (n) without affecting Morse oscillator eigenfunctions or coherent states, which is especially true in the low temperature limit. [9] Fig. 1 reaffirms this conclusion. In light of this claim, one may assume that within the range of weak to intermediate anharmonicity, whereby $N-2m \sim N$ and $N-2n \sim N$, noting that N gives twice the actual number of vibrational bound states. As a result, Eq. (3), after renormalization, may be approximated as

$$\Phi_m(y) \approx \sqrt{\frac{\mathrm{N}\,\Gamma(m+1)}{\Gamma(N+m)}}\, y^{\frac{N-1}{2}}\, e^{-\frac{y}{2}}\, L_m^{N-1}(y), \tag{21}$$

The panels in Fig. 1 compare the exact Morse oscillator eigenfunctions in Eq. (3) to the approximate ones in Eq. (21) as χ gets smaller. Fig. 1 shows as χ gets smaller, the approximate functions start to approach the exact Morse oscillator eigenfucntions. (Note all of the used values of χ are within the range of those of diatomic molecules.) This should ratify the legitimacy of the herein made approximation. Therefore, one may recast the above sums in Eqs. (16) and (17) as

$$\Psi^{\alpha}(x_1) \approx \sqrt{\Gamma(N+1)}\, \sum_{m=0}^{\left[\frac{N}{2}\right]} \sqrt{\frac{N^{-m}\alpha^{2m}}{\Gamma(N-m+1)\Gamma(N+m)}}\; x_1^{(N-1)/2}\, e^{-\frac{x_1}{2}}\, L_m^{N-1}(x_1) \tag{22}$$

and

$$\Psi^{\beta}(x_2) \approx \sqrt{\Gamma(N+1)} \sum_{n=0}^{\left[\frac{N}{2}\right]} \sqrt{\frac{N^{-n}\,\beta^{*2n}}{\Gamma(N-n+1)\Gamma(N+n)}}\; x_2^{\frac{N-1}{2}}\, e^{-\frac{x_2}{2}}\, L_n^{N-1}(x_2). \tag{23}$$

Additionally, another observation, as a result of the above approximation, was made when doing the above numerical calculations. As a result of the assumed weak anharmonicity (typical in most diatomic molecules), hence large N, upon expanding the finite series only a few terms survive and the rest of the terms vanish. Employment of Gamma function series expansion and its properties [24] in the denominator of Eqs. (22) and (23) leads to

$$\Psi^{\alpha}(x_1) \approx x_1^{(N-1)/2}\, e^{-\frac{x_1}{2}} \sum_{m=0}^{\left[\frac{N}{2}\right]} \sqrt{\frac{N^{-m}\alpha^{2m}}{\Gamma(N)}}\; L_m^{N-1}(x_1) \tag{24}$$

and

$$\Psi^{\beta}(x_2) \approx\; x_2^{(N-1)/2}\, e^{-\frac{x_2}{2}} \sum_{n=0}^{\left[\frac{N}{2}\right]} \sqrt{\frac{N^{-n}\,\beta^{*2n}}{\Gamma(N)}}\, L_n^{N-1}(x_2). \tag{25}$$

Using the definition of associated Laguerre's polynomials [24] in this exact finite series [25].

$$\sum_{k=0}^{N} \frac{s^k}{(N-k)!}\; L_k^{\sigma-k}(\mathrm{z}) = s^N\, L_N^{\sigma-N}\left(\mathrm{z}-\frac{1}{s}\right), \tag{26}$$

one can make the following approximation

$$\sum_{m=0}^{\left[\frac{N}{2}\right]} \sqrt{\frac{N^{-m}\alpha^{2m}}{\Gamma(N)}}\, L_m^{N-1}(x_1) \cong \sqrt{\frac{1}{\Gamma(N)}} \left(\frac{\alpha}{\sqrt{N}}\right)^{\frac{N}{2}} L_{\frac{N}{2}}^{N-1}\left(x_1 - \frac{\sqrt{N}}{\alpha}\right), \tag{27}$$

provided that $\left|\frac{\alpha}{\sqrt{N}}\right| \gg 1$. I have run several calculations using the approximation in Eq. (27), the results are very good; hence it is reliable provided that $\left|\frac{\alpha}{\sqrt{N}}\right| \gg 1$. The inequality condition is legitimate in case of coherent states (be it harmonic or anharmonic) classically or quasi-classically since $\alpha \sim x_1 + i\,p$, where $x_1$and p are the coordinate and momentum, respectively. Therefore, $|\alpha|$ is much larger than $\sqrt{N}$ by orders of magnitude, hence the above assumption is justified.

Inserting Eq. (27) in Eqs. (24) and (25) leads to these approximate coherent states of Morse oscillator

$$\Psi^{\alpha}(x_1) = \sqrt{\frac{x_1^{(N-1)}\, e^{-x_1}}{\Gamma(N)}} \left(\frac{\alpha}{\sqrt{N}}\right)^{N/2} L_{\frac{N}{2}}^{N-1}\left(x_1 - \frac{\sqrt{N}}{\alpha}\right) \tag{28}$$

and

$$\Psi^{\beta}(x_2) = \sqrt{\frac{x_2^{(N-1)}\, e^{-x_2}}{\Gamma(N)}} \left(\frac{\beta^{\star}}{\sqrt{N}}\right)^{N/2} L_{\frac{N}{2}}^{N-1}\left(x_2 - \frac{\sqrt{N}}{\beta^{\star}}\right). \tag{29}$$

Substituting Eqs. (28) and (29) in Eq. (20) yields a much simpler expression of the propagator of the Morse oscillator than both Eq.(20) and that reported in Ref [4].

To this end, attention will be focused on the diagonal propagator for compactness purpose and to explicitly underscore the main point of this work: simpler and more manageable expression of the propagator of the Morse oscillator. As such, the propagator of interest reads

$$\mathcal{F}(x_1;t) = \frac{e^{-\mathcal{V}}}{\Gamma(N)} \times \iint d\sigma_{\alpha} d\sigma_{\beta}\, x_1^{(N-1)}\, e^{-x_1}\, L_{\frac{N}{2}}^{N-1}\left(x_1 - \frac{\sqrt{N}}{\beta^{\star}}\right) L_{\frac{N}{2}}^{N-1}\left(x_1 - \frac{\sqrt{N}}{\alpha}\right) \left(\frac{\beta^{\star}\alpha}{N}\right)^{\frac{N}{2}} \left\langle \alpha \middle| e^{-\frac{i\hat{H}t}{\hbar}} \middle| \beta \right\rangle. \tag{30}$$

Additionally, further approximation may be made to the argument of Laguerre functions. By looking at both arguments of Laguerre functions, one can infer that $\frac{\sqrt{N}}{\alpha}$ and $\frac{\sqrt{N}}{\beta^{\star}}$ would be too small to affect the value of Morse coordinate x_1 since $|\alpha| \gg \sqrt{N}$ and $|\beta^{\star}| \gg \sqrt{N}$. For this reason, their values contribute negligibly to x_1, leading to

$$\mathcal{F}(x_1;t) = \frac{e^{-\mathcal{V}}}{\Gamma(N)} \sum_{k=0}^{N} \binom{N}{k} vk^2 - ku \iint d\sigma_{\alpha} d\sigma_{\beta}\, x_1^{(N-1)}\, e^{-x_1} \left(L_{\frac{N}{2}}^{N-1}(x_1)\right)^2 \left(\frac{\beta^{\star}\alpha}{N}\right)^{N/2} \left(\frac{\alpha^{*}\beta}{N}\right)^{k} \tag{31}$$

Mathematically, both Eqs. (30) and (31) are simple, functionally well-behaved, and void of numerical uncertainty. The numerical stability is intuitively clear by direct inspection of both Eqs. (30) and (31) as will be ratified below by deriving a well-behaved expression in that respect.

Now I will find an analytical expression of the diagonal propagator by evaluation the integral in Eq. (31). I start by expressing α and β in polar coordinates as $\alpha = re^{i\theta}$ and $\beta = \delta e^{i\varphi}$, and the integral measures in polar coordinates are given by

$$d\sigma_{\alpha} = \frac{1}{\pi} \frac{(N+1)\, r dr d\theta}{N(1 + r^2/N)^{N+2}} \tag{32a}$$

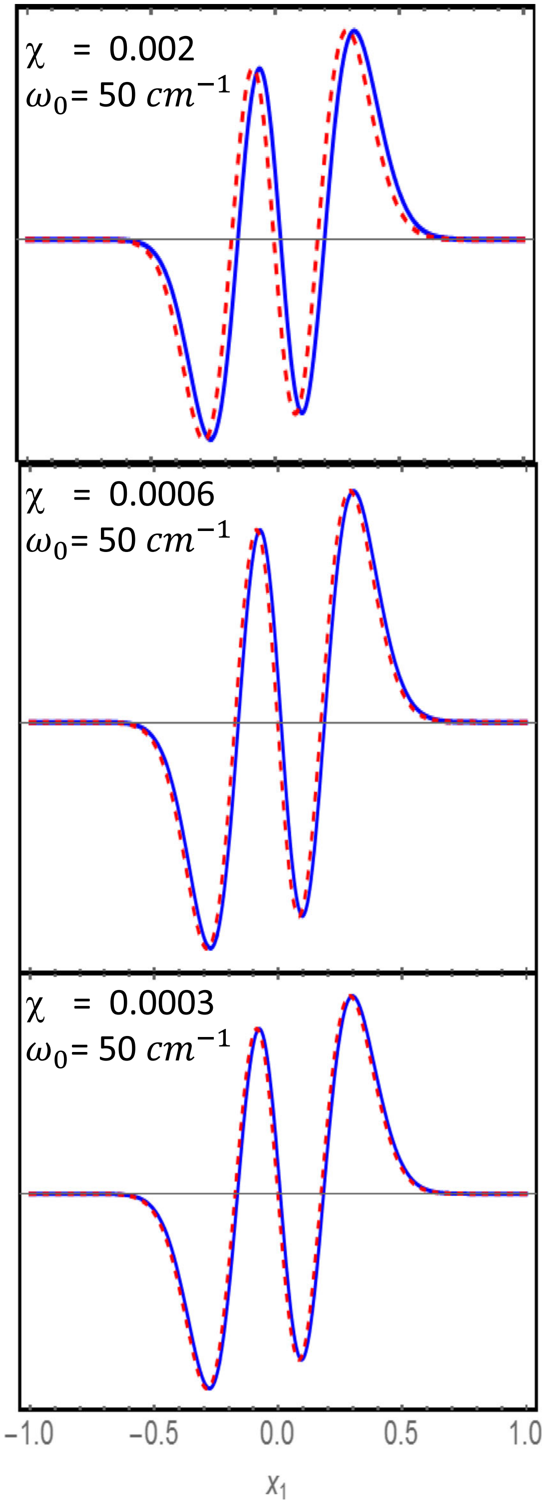
χ = 0.002
ω_0= 50 cm^{-1}
χ = 0.0006
ω_0= 50 cm^{-1}
χ = 0.0003
ω_0= 50 cm^{-1}
−1.0
−0.5
0.0
0.5
1.0
x_1

Fig. 1 Comparing the exact Morse oscillator third vibrational (m = 3) eigenfunctions (blue curve) to the approximate eigenfunctions (dashed red curve), which was calculated using Eq. (21) with different values of χ, as labelled in each panel of the Figure. Note the key premise of the validity of this approximation is weak anharmonicity as lucidly stated in the text. The bottom panel shows a wavefunction with $\chi = 0.0003$, for it this approximation shows that the red curve is getting much closer to the exact third eigenfunctions of Morse oscillator (blue curve)

and

$$d\sigma_{\beta} = \frac{1}{\pi} \frac{(N+1)\ \delta d\delta d\varphi}{N\left(1+\delta^{2}/N\right)^{N+2}} \tag{32b}$$

Utilizing this integral relationship [24].

$$\int_0^\infty \frac{x^{\mu-1}dx}{(p+qx^{\nu})^{n+1}} = \frac{1}{\nu p^{n+1}} \left(\frac{p}{q}\right)^{\mu/\nu} \frac{\Gamma(\mu/\nu)\Gamma(1+n-\mu/\nu)}{\Gamma(1+n)}, \qquad 0 < \frac{\mu}{\nu} < n+1 \tag{33}$$

to evaluate this integral

$$\int_0^\infty \frac{r^{\frac{N}{2}+k+1}\ dr}{\left(1+\frac{r^2}{N}\right)^{N+2}} = \frac{N^{\left(\frac{k}{2}+\frac{N}{4}+1\right)}}{2\Gamma(N+2)} \Gamma\left(\frac{2k+N+4}{4}\right) \Gamma\left(\frac{3N+4-2k}{4}\right), \tag{34}$$

which comes up while evaluating the integration in Eq. (31). Finally, inserting Eqs. (32 a, b–34) in Eq. (31) yields the final expression for the diagonal propagator

$$\mathcal{F}(x_1;t) = \left[N^{\left(\frac{N}{4}\right)} \frac{(N+1)}{\pi\Gamma(N+2)}\right]^2 \frac{e^{-y}}{\Gamma(N)} \frac{x_1^{(N-1)}}{e^{x_1}} \left(L_{\frac{N}{2}}^{N-1}(x_1)\right)^2 \sum_{k=0}^{N} \frac{\binom{N}{k}}{\left(k-\frac{N}{2}\right)^2} \frac{e^{\nu k^2-ku}}{N^{\left(\frac{N}{2}+k\right)}}$$
$$\times N^k \left[\Gamma\left(\frac{2k+N+4}{4}\right) \Gamma\left(\frac{3N+4-2k}{4}\right)\right]^2. \tag{35}$$

5 Concluding Remarks

The propagator tool is vitally important in time dependent systems, most of which are anharmonic. Having the propagator at our disposal allows us to probe the time evolution of the system of interest. In this article, a simple form of the propagator of Morse oscillator has been derived using Morse oscillator coherent states. As pointed out earlier, evaluating time dependent properties through employing Morse oscillator leads to divergent dynamics, hence strong numerical errors and uncertainties. [7, 8, 16–21] For this reason, numerical stability of Morse oscillator emerging integrals is of paramount importance in this case.

Thus far, an exact result of Morse oscillator propagator has been reported using Morse oscillator coherent states. Since the exact result of the propagator is complicated, and unappealing, an easier form has been derived through approximating the Morse oscillator eigenfunctions. The reliability and accuracy of the herein approximation has been tested, and seems to approach the exact eigenfunctions of Morse oscillator as the number of the Morse potential finite bound states increases, due to weak anharmonicity. Although this neat approximation has led to a more manageable expression of the propagator with better numerical stability, a simpler expression was also obtained using additional approximation to further simplify the argument of Laguerre's polynomials, leading to a closed-form expression of Morse oscillator propagator, which features both simplicity and high numerical stability.

In closing, a noteworthy issue is doing quantum dynamics in the low temperature limit where $kT \ll \hbar\omega_0$, calculations may be simplified considerably by taking the upper limit of the finite series to approach infinity, leading to a closed-form expression in the definition of the coherent states of Morse oscillator. This may be well justified as follows from statistical mechanics standpoint. The molecules composing the system are only very populated mostly in the lowest vibrational level and only very few molecules would occupy the next higher two vibrational levels, if any. This implies all the Morse potential bound states except the ground state are vacant and thereby diminishing all the subsequent finite series terms including those above and beyond $\frac{N}{2}$th vibrational level, justifying extending the upper series term to infinity. As such, this approximation is as good as exact. This should be part of future work.

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