Analytic dynamics of the Morse oscillator derived by semiclassical closures

Eric M. Heatwole and Oleg V. Prezhdo
Department of Chemistry, University of Washington, Seattle, Washington 98195-1700, USA

(Received 24 October 2008; accepted 25 May 2009; published online 29 June 2009)

The quantized Hamilton dynamics methodology [O. V. Prezhdo and Y. V. Pereverzev, J. Chem. Phys. 113, 6557 (2000)] is applied to the dynamics of the Morse potential using the SU(2) ladder operators. A number of closed analytic approximations are derived in the Heisenberg representation by performing semiclassical closures and using both exact and approximate correspondence between the ladder and position-momentum variables. In particular, analytic solutions are given for the exact classical dynamics of the Morse potential as well as a second-order semiclassical approximation to the quantum dynamics. The analytic approximations are illustrated with the O–H stretch of water and a Xe–Xe dimer. The results are extended further to coupled Morse oscillators representing a linear triatomic molecule. The reported analytic expressions can be used to accelerate classical molecular dynamics simulations of systems containing Morse interactions and to capture quantum-mechanical effects. © 2009 American Institute of Physics. [DOI: 10.1063/1.3154143]

I. INTRODUCTION

The Morse interaction potential carries great importance in chemical systems and has been studied exhaustively. It has been used to model water,1 alcohols,2 hydrocarbons,3,4 rare gases,5,6 metals,7,8 surfaces,9,10 semiconductor particles,11,12 carbon nanotubes,13,14 biomolecules,15 and many other types of systems. The Morse oscillator belongs to the class of supersymmetric potentials, which also include the harmonic oscillator and the Coulomb interaction.16,17 A variety of approaches18–22 including factorization methods,21 can be used to find the wave functions and energy spectrum of the Morse oscillator. It is known that the SU(2) group is the dynamical group for the bounded region of the Morse potential.23 Recently, the ladder operators associated with this SU(2) group have been explicitly constructed,18–22 see also Ref. 24. It is natural to consider the time evolution of these ladder operators, much like the time evolution of the raising and lowering operators of the harmonic oscillator25–27 or spin system.28,29 By considering equations of motion (EOM) for the ladder operators one can expect to extend stationary quantum mechanics to quantum dynamics and to obtain useful analytic expressions in time domain. Compared to the alternative representations of the Morse dynamics,24,30,31 the SU(2) operators provide a concise representation that limits the number of EOM.

The Heisenberg EOM for the Morse ladder operators21 form an infinite hierarchy of coupled linear differential equations. Valuable approximations to the exact hierarchy can be obtained using the recently developed quantized Hamilton dynamics (QHD) methodology.28,32–46 QHD truncates the hierarchy by closures47,48 and represents the higher-order expectations values of quantum-mechanical operators in terms of classical-like products of the lower-order expectation values. A number of semiclassical approximations can be obtained this way, depending on the decomposition level. Already at low orders, QHD can provide dramatic improvements over classical mechanics at very little cost. A closed analytic solution for the classical evolution of the Morse system can be helpful as well. It can replace the corresponding numerical solution used in molecular dynamics (MD) codes, substantially accelerate MD simulations in the great variety of systems1–15,49–52 and capture essential quantum-mechanical effects, such as zero-point energy and tunneling. For example, vibrational motions of chemical bonds involving hydrogen atoms are often described by Morse potentials. These motions are usually the fastest ones in molecular and solid state systems and, therefore, limit the length of the time step during numerical integration of MD EOM. Replacing the numerical solutions with analytic dynamics for the fast modes can speed up classical MD simulations. Further, dynamics of the hydrogen modes exhibit pronounced zero-point energy and tunneling features. These quantum-mechanical effects can be efficiently captured by the semiclassical QHD approximations,28,32–46 both numerically and especially if the solutions to the QHD EOM can also be given in an analytic form.

The current paper presents the first examples of QHD closures performed with the Morse raising and lowering operators, thereby extending the earlier studies carried out using the ordinary harmonic operators. It derives the second-order QHD EOM for the Morse oscillator and finds an analytic solution to these equations. The first-order QHD closure naturally leads to the classical dynamics of the Morse oscillator as well as to the exact and approximate analytic solutions to the classical dynamics. These formal results are illustrated with one and two-dimensional examples.

This paper is constructed as follows. First, we give a brief overview of the SU(2) ladder operators and examine some of their properties. In particular, we discuss how to

---

25–27
these ladder operators, much like the time evolution of the raising and lowering operators of the harmonic oscillator25–27 or spin system.28,29 By considering equations of motion (EOM) for the ladder operators one can expect to extend stationary quantum mechanics to quantum dynamics and to obtain useful analytic expressions in time domain. Compared to the alternative representations of the Morse dynamics,24,30,31 the SU(2) operators provide a concise representation that limits the number of EOM.

The Heisenberg EOM for the Morse ladder operators21 form an infinite hierarchy of coupled linear differential equations. Valuable approximations to the exact hierarchy can be obtained using the recently developed quantized Hamilton dynamics (QHD) methodology.28,32–46 QHD truncates the hierarchy by closures47,48 and represents the higher-order expectations values of quantum-mechanical operators in terms of classical-like products of the lower-order expectation values. A number of semiclassical approximations can be obtained this way, depending on the decomposition level. Already at low orders, QHD can provide dramatic improvements over classical mechanics at very little cost. A closed analytic solution for the classical evolution of the Morse system can be helpful as well. It can replace the corresponding numerical solution used in molecular dynamics (MD) codes, substantially accelerate MD simulations in the great variety of systems1–15,49–52 and capture essential quantum-mechanical effects, such as zero-point energy and tunneling. For example, vibrational motions of chemical bonds involving hydrogen atoms are often described by Morse potentials. These motions are usually the fastest ones in molecular and solid state systems and, therefore, limit the length of the time step during numerical integration of MD EOM. Replacing the numerical solutions with analytic dynamics for the fast modes can speed up classical MD simulations. Further, dynamics of the hydrogen modes exhibit pronounced zero-point energy and tunneling features. These quantum-mechanical effects can be efficiently captured by the semiclassical QHD approximations,28,32–46 both numerically and especially if the solutions to the QHD EOM can also be given in an analytic form.

The current paper presents the first examples of QHD closures performed with the Morse raising and lowering operators, thereby extending the earlier studies carried out using the ordinary harmonic operators. It derives the second-order QHD EOM for the Morse oscillator and finds an analytic solution to these equations. The first-order QHD closure naturally leads to the classical dynamics of the Morse oscillator as well as to the exact and approximate analytic solutions to the classical dynamics. These formal results are illustrated with one and two-dimensional examples.

This paper is constructed as follows. First, we give a brief overview of the SU(2) ladder operators and examine some of their properties. In particular, we discuss how to
express physical observables and the Morse Hamiltonian in terms of the ladder operators. Next, we derive approximate EOM for the ladder operators at the second-order in QHD and consider the first-order limit. The first-order of QHD allows us to derive a closed analytic form for the exact classical EOM of the Morse system. For some applications it may be desirable to have a simpler approximate form of the solution. The simpler solution is obtained in a closed analytic form by considering a harmonic-like correspondence between the ladder and position-momentum operators. The method is then expanded to a coupled linear chain of Morse oscillators. In this example the closed analytic EOM are not exact in the classical limit, however, they do provide an accurate representation of the classical dynamics. Once again, the harmonic-like operator correspondence is used to derive a simpler set of equations for the coupled Morse oscillators.

In both one and two-dimensional cases, the harmonic-like equations provide a great improvement over the true harmonic approximation of the Morse potential. Finally, the analytic results are exemplified with three chemical systems: the O–H stretch of water, the Xe–Xe dimer, and a linear triatomic. A number of initial conditions are considered for each example. Different amounts of kinetic energy are given to the one-dimensional systems. The initial conditions for the two-dimensional example are chosen to represent the symmetric stretch, the antisymmetric stretch and a mixed stretching motion. This paper concludes with a summary of our results and a discussion of possible extensions and applications.

II. THEORY

A. Ladder operators for the Morse potential

Setting the zero of energy at infinite separation, we define the following Morse potential:

$$V(x) = V_0(e^{-2\beta x} - 2e^{-\beta x}).$$

Here, $V_0$ is the depth of the potential well, $\beta$ is the width of the well, and $x$ is the distance from the equilibrium position, which is set at $x=0$. This Morse potential gives rise to the wave function of the following form:

$$\Psi_n^\nu(y) = N_n^\nu e^{-y^2/4}L_n^{2s}(y),$$

where variable $y$ is related to the coordinate $x$ by

$$y = \nu e^{-\beta x},$$

$L_n^{2s}(y)$ is the Laguerre function, and $N_n^\nu$ is the normalization constant

$$N_n^\nu = \sqrt{\frac{(\nu - 2n - 1)!\Gamma(n+1)}{\Gamma(\nu-n)}}.$$

The constants $\nu$ and $s$ depend on the well depth $V_0$ and width $\beta$, the total energy $E$, and the particle mass $\mu$. The Morse potential in the following way:

$$\hat{K}_-\Psi_n^\nu(y) = k_-\Psi_{n-1}^\nu(y),$$

$$\hat{K}_+\Psi_n^\nu(y) = k_+\Psi_{n+1}^\nu(y),$$

where the eigenvalues $k_-$ and $k_+$ are

$$k_- = \sqrt{n(\nu-n)},$$

$$k_+ = \sqrt{(n+1)(\nu-n-1)}.$$

The step-down operator, $\hat{K}_-$, destroys the ground state, while the step-up operator destroys the last bound state of the Morse potential, since $s=1$ for this state. It is now possible to define the algebra associated with the operators $\hat{K}_-$ and $\hat{K}_+$. By using Eq. (7) one can determine the commutator

$$[\hat{K}_+, \hat{K}_-]\Psi_n^\nu(y) = 2k_0\Psi_n^\nu(y),$$

where the eigenvalue $k_0$ is defined as

$$k_0 = n - \frac{\nu-1}{2}.$$

From this one can define the operator $\hat{K}_0$

$$\hat{K}_0 = \hat{n} - \frac{\nu-1}{2},$$

and establish the identity

$$\hat{K}_0 = \left(dy^2 + \frac{d}{dy} - \frac{s^2}{y} - \frac{y}{4} + n + \frac{1}{2}\right).$$

Now the following commutation relations can be found for the $\hat{K}_-$, $\hat{K}_+$, and $\hat{K}_0$ operators

$$[\hat{K}_+, \hat{K}_-] = 2\hat{K}_0,$$

$$[\hat{K}_0, \hat{K}_-] = -\hat{K}_-.$$

$$\nu = \sqrt{\frac{8\mu V_0}{\beta^2 h^2}},$$

$$s = \sqrt{-\frac{2\nu E}{\beta^2 h^2}}.$$
Utilizing the commutator relations for the Morse ladder operators as follows:32

\[ [\hat{K}_0, \hat{K}_s] = \hat{K}_s. \]  

(15)

This set of equations defines the SU(2) group for the Morse potential and allows the Hamiltonian to be written in the following simple form:

\[ \hat{H} = -\frac{\hbar \omega}{\nu} \hat{K}_0^2, \]  

(16)

where

\[ \omega = \frac{\hbar \beta^2 \nu}{2\mu}. \]  

(17)

B. Dynamics of the Morse oscillator

The set of operators defined in Sec. II A is useful for determining the static properties of the Morse oscillator.18–22 Can one apply these operators in order to obtain the evolution of a particle in the Morse potential? It turns out that the Heisenberg EOM for the ladder operators \( \hat{K}_-, \hat{K}_+, \) and \( \hat{K}_0 \) generate an infinite hierarchy of equations rather than a closed set as for the harmonic oscillator. Approximations are required in order to solve the hierarchy in a closed form. This can be done by utilizing the QHD approach.28,32–40,44–46

QHD is a simple approximation to quantum dynamics in the Heisenberg representation. Except for special cases, where the dynamic variables and the Hamiltonian form a closed Lie algebra, such as the harmonic oscillator or spin systems, the Heisenberg EOM result in an infinite hierarchy of linear differential equations. QHD approximates higher-order variables by products of lower-order variables, generating a closed set of nonlinear differential equations, much like in classical Hamilton dynamics. For example, a third-order variable can be decomposed in terms of the second and first-order variables as follows:32

\[ \langle ABC \rangle = \langle AB \rangle \langle C \rangle + \langle AC \rangle \langle B \rangle + \langle BC \rangle \langle A \rangle - 2 \langle A \rangle \langle B \rangle \langle C \rangle, \]  

(18)

preserving quantum effects to the second order. The higher is the order of the decomposition, the closer the approximation lies to the exact quantum result. Decomposition to the first-order gives classical mechanics.

Using Eq. (16) for the Hamiltonian allows us to write the general form of the Heisenberg EOM as

\[ \frac{d\hat{A}}{dt} = -\frac{i}{\hbar} [\hat{A}, \hat{H}] = \frac{i\omega}{\nu} [\hat{A}, \hat{K}_0^2]. \]  

(19)

Utilizing the commutator relations for the Morse ladder operators, Eq. (13), gives the following equations to the second order:

\[ \frac{d\langle \hat{K}_+(t) \rangle}{dt} = -\frac{2i\omega}{\nu} \langle \hat{K}_0 \hat{K}_0(t) \rangle_s, \]  

\[ \frac{d\langle \hat{K}_-(t) \rangle}{dt} = \frac{2i\omega}{\nu} \langle \hat{K}_0 \hat{K}_0(t) \rangle_s, \]  

where \( \langle \hat{K}_+ \hat{K}_0 \rangle_s \) terms refer to the symmetrized variables, \((\langle \hat{K}_- \hat{K}_0 \rangle + \langle \hat{K}_0 \hat{K}_- \rangle)/2\). The hierarchy continues indefinitely, since \( d\langle \hat{K}_+ \hat{K}_0 \rangle_s / dt \approx \langle \hat{K}_0 \hat{K}_1 \rangle_s \). Applying the QHD approach and using Eq. (18) to decompose the third-order variables to the second-order generates the following set of approximate equations:

\[ \frac{d\langle \hat{K}_+(t) \rangle}{dt} = -\frac{2i\omega}{\nu} \langle \hat{K}_+ \hat{K}_0(t) \rangle_s, \]  

\[ \frac{d\langle \hat{K}_-(t) \rangle}{dt} = \frac{2i\omega}{\nu} \langle \hat{K}_- \hat{K}_0(t) \rangle_s, \]  

\[ \frac{d\langle \hat{K}_0 \hat{K}_0(t) \rangle_s}{dt} = -\frac{2i\omega}{\nu} (2\langle \hat{K}_+ \hat{K}_0(t) \rangle \langle \hat{K}_0 \rangle) + (\langle \hat{K}_0^2(t) \rangle - 2\langle \hat{K}_0(t) \rangle^2) \langle \hat{K}_+(t) \rangle, \]  

\[ \frac{d\langle \hat{K}_- \hat{K}_0(t) \rangle_s}{dt} = \frac{2i\omega}{\nu} (2\langle \hat{K}_- \hat{K}_0(t) \rangle \langle \hat{K}_0 \rangle) + (\langle \hat{K}_0^2(t) \rangle - 2\langle \hat{K}_0(t) \rangle^2) \langle \hat{K}_-(t) \rangle. \]  

(21)

Because \( \hat{K}_0 \) is a constant of motion, the resultant set of differential equations is linear and can be solved analytically. Specifically, we obtain the following expressions for the time evolution of the expectation values of the raising and lowering operators:

\[ \langle \hat{K}_+(t) \rangle = \frac{e^{-2i\omega/t} \langle \hat{K}_0 \rangle (e^{-\eta} - e^{\eta}) (\langle \hat{K}_- \hat{K}_0(t) \rangle_s - \langle \hat{K}_0 \rangle \langle \hat{K}_+(0) \rangle)}{2 \sqrt{(\langle \hat{K}_0 \rangle^2 - \langle \hat{K}_0^2 \rangle)^2}}, \]  

\[ + \langle \hat{K}_+(0) \rangle e^{-2i\omega/t} \langle \hat{K}_0 \rangle (e^{-\eta} + e^{\eta})/2, \]  

\[ \langle \hat{K}_-(t) \rangle = \frac{e^{2i\omega/t} \langle \hat{K}_0 \rangle (e^{-\eta} - e^{\eta}) (\langle \hat{K}_- \hat{K}_0(t) \rangle_s - \langle \hat{K}_0 \rangle \langle \hat{K}_-(0) \rangle)}{2 \sqrt{(\langle \hat{K}_0 \rangle^2 - \langle \hat{K}_0^2 \rangle)^2}}, \]  

\[ + \langle \hat{K}_-(0) \rangle e^{2i\omega/t} \langle \hat{K}_0 \rangle (e^{-\eta} + e^{\eta})/2, \]  

(22)

where \( \eta = (2i\omega/\nu) \sqrt{(\langle \hat{K}_0^2 \rangle - \langle \hat{K}_0 \rangle^2)^2} \). This provides an analytic solution to the dynamics of the Morse oscillator that includes approximate quantum-mechanical effects. Further analysis of
Eq. (22) will continue in future work. In particular, determining the initial conditions for \( \langle \hat{K}, \hat{K}_0(0) \rangle \) and \( \langle \hat{K}_0^2 \rangle - \langle \hat{K}_0 \rangle^2 \) may be quite cumbersome in general. We will concentrate on the first-order limit for the remainder of this work.

C. The classical limit

The classical limit of Eq. (21) is obtained by decomposing all variables to the first-order,\(^{32}\)

\[
\frac{d\langle \hat{K}_\alpha(i) \rangle}{dt} = -\frac{i\omega}{\nu} \left( \langle \hat{K}_\alpha(\hat{K}_0(0)) \rangle + \langle \hat{K}_0(\hat{K}_\alpha(0)) \rangle \right),
\]

\[
\frac{d\langle \hat{K}_{\alpha}(i) \rangle}{dt} = \frac{i\omega}{\nu} \left( \langle \hat{K}_{\alpha}(\hat{K}_0(0)) \rangle + \langle \hat{K}_0(\hat{K}_{\alpha}(0)) \rangle \right).
\]

(23)

Since \( \langle \hat{K}_0 \rangle \) is a constant of motion, Eq. (23) are a set of linear differential equations and can be solved easily

\[
\langle \hat{K}_\alpha(t) \rangle = \langle \hat{K}_\alpha(0) \rangle \exp \left( -\frac{2i\omega}{\nu} \langle \hat{K}_0 \rangle t \right),
\]

\[
\langle \hat{K}_{\alpha}(t) \rangle = \langle \hat{K}_{\alpha}(0) \rangle \exp \left( \frac{2i\omega}{\nu} \langle \hat{K}_0 \rangle t \right).
\]

(24)

These first-order approximate solutions can also be obtained from the second-order solutions (22) by applying the commutator relations (13) to the \( \langle \hat{K}_\alpha, \hat{K}_0, \hat{K}_\beta \rangle \) terms and using the QHD decomposition, Eq. (18). The second-order solutions, Eq. (22), reduce to the classical solutions in the first order, as they should.

The expectation value of \( \hat{K}_0 \) can be identified with the value of \( s \) from Eq. (5) and related to the initial conditions using the form of the Hamiltonian from Eq. (16)

\[
\langle \hat{K}_0 \rangle = -s = -\sqrt{-\frac{2\mu E_0}{\beta^2 h^2}}.
\]

(25)

The initial total energy of the system \( E_0 \) is negative and should be handled with care, such that all contributions to the energy term are decomposed to the first order. It is now possible to rewrite the EOM (24) in the following way:

\[
\langle \hat{K}_{\alpha}(t) \rangle = \langle \hat{K}_{\alpha}(0) \rangle \exp(i\gamma t),
\]

\[
\langle \hat{K}_{\alpha}(t) \rangle = \langle \hat{K}_{\alpha}(0) \rangle \exp(-i\gamma t),
\]

(26)

where \( \gamma \) is given by

\[
\gamma = \frac{2s\omega}{\nu}
\]

and can be considered an effective frequency.

The effective frequency, Eq. (27), approaches the correct harmonic limit of \( \gamma = \omega \) as \( 2s \to \nu \) and goes to the correct classical frequency away from the harmonic limit. This can be seen by using the Bohr semiclassical condition and relating the classical action \( J = nh \) to the energy,\(^{53}\) allowing the use of the classical relationship

\[
\frac{dE_n}{dJ} = \nu t.
\]

(28)

The energy can be given in terms of the action as

\[
E = \beta \sqrt{\frac{2V_0}{\mu} - \frac{\beta^2}{2\mu} J^2}.
\]

(29)

and \( J = \nu t \). With these relationships, the classical frequency becomes

\[
\omega_{cl} = \omega - \hbar \beta^2 n,
\]

(30)

which is the same as Eq. (27) with \( 2s = 2n - \nu \).

At this point it is necessary to determine the initial conditions for \( \langle \hat{K}_\alpha \rangle \) and \( \langle \hat{K}_{\beta} \rangle \). For this purpose we represent \( d/dy \) as

\[
\frac{d}{dy} = -\frac{1}{\beta y} \frac{d}{dx} = -\frac{i}{\beta h} \frac{p_y}{y}
\]

(31)

and rewrite Eq. (6) in the following form:

\[
\hat{K}_\alpha = \left[ \frac{i}{\beta h} \hat{y} \hat{p}_x (2s + 1) + \frac{1}{y} s (2s + 1) - \frac{\nu}{2} \right] \sqrt{s + 1},
\]

\[
\hat{K}_{\beta} = \left[ \frac{i}{\beta h} \hat{x} \hat{p}_y (2s - 1) + \frac{1}{y} s (2s - 1) - \frac{\nu}{2} \right] \sqrt{s - 1}.
\]

(32)

Here, the \( \hat{y} \) operator precedes \( \hat{p}_x \), according to the convention originating from the chain rule used in Eq. (31). As a result, the initial conditions for the ladder operator are expressed in terms of the initial conditions for the classical momentum \( p_x \) and Morse coordinate \( y \), Eq. (3). Inversely, rearranging Eq. (32)

\[
\frac{p_x}{y} = i\hbar \left( \frac{K_+}{2(s - 1)} \sqrt{s \over s - 1} + \frac{K_-}{2(s + 1)} \sqrt{s \over s + 1} \right)
\]

\[
\frac{1}{y} = \frac{K_+}{2s(2s - 1)} \sqrt{s \over s - 1} + \frac{K_-}{2s(2s + 1)} \sqrt{s \over s + 1}
\]

\[
\frac{\nu}{(2s + 1)(2s - 1)}
\]

(33)

one can express the original \( x \) coordinate in terms of the Morse ladder operators

\[
x = \frac{1}{\beta} \ln \left( \frac{\nu K_+}{2s(2s - 1)} \sqrt{s \over s - 1} + \frac{\nu K_-}{2s(2s + 1)} \sqrt{s \over s + 1}
\]

\[
\frac{\nu^2}{(2s + 1)(2s - 1)} \right).
\]

(34)

It is now possible to write down a closed analytic expression for the dynamics of the Morse oscillator in the \( p_x \) and \( y \) coordinates.
\[
\frac{p_x(t)}{y(t)} = \frac{p_y(t)}{y(t)} \cos \gamma t - \frac{\beta h s}{y(t)} \sin \gamma t \\
+ \frac{\beta h vs}{(2s-1)(2s+1)} \sin \gamma t,
\]

\[
\frac{1}{y(t)} = \frac{p_y(t)}{y(t)} \sin \gamma t + \frac{\cos \gamma t}{y(t)} + \frac{\nu}{(2s-1)(2s+1)} (1 - \cos \gamma t).
\]

(35)

In going from Eqs. (33)–(35) we neglected two imaginary terms. These terms are inversely proportional to \(s\) and are small in the classical limit, in which the total energy far exceeds the zero-point energy, \(s \gg 1/2\), see Eq. (25). Equation (35) can be rearranged to give the following closed form for the usual \(x\) and \(p_x\) coordinates

\[
p_x(t) = \frac{p_x(0) \cos \gamma t - \frac{\beta h s}{y(0)} \sin \gamma t + \frac{y(0) \beta h vs}{(2s-1)(2s+1)} \sin \gamma t}{\frac{p_y(0)}{\beta h s} \sin \gamma t + \frac{\cos \gamma t}{y(0)} + \frac{\nu}{(2s-1)(2s+1)} (1 - \cos \gamma t)},
\]

\[
x(t) = \frac{1}{\beta} \ln \left( \frac{e^{\beta \nu_0 p_y(0)} \sin \gamma t + e^{\beta \nu_0 \cos \gamma t}}{2 \nu (2s-1)(2s+1) (1 - \cos \gamma t)} \right).
\]

(36)

It is easy to show using Eq. (35) that these are the exact solutions for the classical Morse oscillator with the constant value of \(s\), which depends on the initial conditions.

The steady-state solution of Eq. (35) is

\[
p_{x,eq} = 0,
\]

(37)

\[
y_{eq} = \frac{\nu}{2} + \frac{\nu^2 - 4}{2},
\]

which in the classical limit of \(\nu \gg 1\), Eq. (5), goes to

\[
p_{x,eq} = 0,
\]

(38)

\[
y_{eq} = \nu.
\]

This is the expected answer for the classical Morse oscillator.

D. The harmonic-like limit

It is useful to consider simpler forms for the above equations that will be valid near the harmonic limit. In the harmonic limit \(\nu \to \infty\), and the following approximations can be made

\[
2s = 2s + 1 = 2s - 1 \approx \nu,
\]

\[
\sqrt{\frac{s}{s + 1}} = \sqrt{\frac{s}{s - 1}} = 1.
\]

(39)

This allows us to approximate Eq. (33) as

\[
p_x = \frac{i}{2} \sqrt{2\mu \omega \hbar} \left( \frac{K_x}{\sqrt{\nu}} - \frac{K_y}{\sqrt{\nu}} \right),
\]

\[
1 - e^{-\beta \nu} = \sqrt{\frac{\hbar}{2m \omega \mu}} \left( \frac{K_x}{\sqrt{\nu}} + \frac{K_y}{\sqrt{\nu}} \right),
\]

(40)

where Eq. (17) was used. The above result was already obtained by Lemus.\(^{22}\) It converges to the correct harmonic limit, since \(K_x / \sqrt{\nu} \to a / a\).

The above approximations allow us to write the following simple analytic solution for the Morse oscillator

\[
p(t) = p_x(0) \cos \gamma t - \frac{z(0) \omega \mu}{\beta} \sin \gamma t,
\]

\[
z(t) = \frac{z(0)}{\beta} \cos \gamma t + \frac{p_x(0)}{\omega \mu} \sin \gamma t,
\]

(41)

where \(z = 1 - \exp(-\beta \nu)\). Rewriting the equations in terms of \(x\) and \(p\) we obtain

\[
p(t) = p(0) \cos \gamma t - \frac{\omega \mu}{\beta} z(0) \sin \gamma t,
\]

\[
x(t) = -\frac{1}{\beta} \ln \left( 1 - z(0) \cos \gamma t - \frac{\beta}{\omega \mu} p(0) \sin \gamma t \right).
\]

(42)

One can derive Eq. (42) starting from Eq. (35) and employing the same set of approximations. It should be emphasized that solution (42) is not equivalent to the harmonic approximation to the Morse potential. It provides a significantly better description of the dynamics of the Morse oscillator, as illustrated with examples below. Equation (42) does converge to the harmonic solution in the appropriate limit.

E. Linear triatomic

For a more complicated example than the simple one-dimensional Morse oscillator, consider a linear triatomic, in which the atoms are coupled via Morse potentials. Ignoring the translational and rotational components, the kinetic energy of the triatomic can be written as

\[
T = \frac{m}{2} (x_1^2 + x_2^2) + \frac{M}{2} x_3^2.
\]

(43)

Here, the end atoms \(x_1\) and \(x_3\) have mass \(m\), and the middle atom \(x_2\) has mass \(M\). The potential energy of the linear triatomic, in which the neighboring atoms interact by the Morse potential, is given by

\[
V(x) = V_0 e^{-2\beta (x_2^2 - x_1^2) - 2e^{-\beta (x_2 - x_1)} + V_0 e^{-2\beta (x_3^2 - x_1^2) - 2e^{-\beta (x_3 - x_1)}}.
\]

(44)

Following the standard procedure,\(^{54}\) the center of mass of the triatomic is set stationary, such that

\[
x_2 = -\frac{m}{M} (x_1 + x_3).
\]

(45)

Eliminating \(x_2\) in Eqs. (43) and (44) gives the following form for the kinetic:
Since the momentum can be defined as 

\[ p = \frac{\hbar}{i} \frac{\partial \hat{T}}{\partial \hat{x}} \]  

and potential 

\[ V(x) = V_0 \left( \exp \left( -2 \beta \left( \frac{1}{M} x_1 - \frac{m}{M} x_3 \right) \right) \right) \]

-2 \exp \left( -2 \beta \left( \frac{1}{M} x_1 - \frac{m}{M} x_3 \right) \right)

\[ + \exp \left( -2 \beta \left( \frac{1}{M} x_3 + \frac{m}{M} x_1 \right) \right) \]

\[ -2 \exp \left( - \beta \left( \frac{1}{M} x_3 + \frac{m}{M} x_1 \right) \right) \]

energies.

Defining the new variables \( u, v \)

\[ u = -\left( 1 + \frac{m}{M} \right) x_1 - \frac{m}{M} x_3, \]

\[ v = \frac{m}{M} x_1 + \left( 1 + \frac{m}{M} \right) x_3 \]

eliminates the cross terms in the potential energy and changes the kinetic energy to 

\[ T = \frac{m}{2(2m + M)} (u^2 + v^2) + 2muv. \]

Since the momentum can be defined as 

\[ p_i = \frac{\partial T}{\partial \dot{x}_i}, \]

the kinetic energy can be rewritten in terms of the momentum, and the total Hamiltonian for the triatomic system can be expressed as 

\[ H_{\text{tot}} = \frac{1}{2} p_u^2 + \frac{1}{2} p_v^2 + \frac{p_u p_v}{M} + V(u) + V(v), \]

where \( V(u) \) and \( V(v) \) are identical one-dimensional Morse potentials. The reduced mass \( \mu \) is defined as 

\[ \mu = \frac{m M}{m + M}. \]

Using Morse ladder operators, the Hamiltonians \( H_u \) and \( H_v \) for the noninteracting degrees of freedom \( u \) and \( v \), can be written as

\[ H_u = \frac{p_u^2}{2\mu} + \lambda^2 (1 - \exp(-\beta u))^2 = -\frac{\hbar^2}{\nu} (K_u^0)^2, \]

\[ H_v = \frac{p_v^2}{2\mu} + \lambda^2 (1 - \exp(-\beta v))^2 = -\frac{\hbar^2}{\nu} (K_v^0)^2. \]

The total Hamiltonian \( H_{\text{tot}} \) including the interaction term is

\[ H_{\text{tot}} = H_u + H_v - \frac{p_u p_v}{M}. \]

The \( u \) and \( v \) modes are coupled through the kinetic energy term. If the system is close to the harmonic limit, it is possible to use Eq. (40) and to rewrite the coupling term using the \( K_u, K_v \) operators. This produced the following form of the total Hamiltonian:

\[ H_{\text{tot}} = -\frac{\hbar \omega}{\nu} \left( (\hat{K}_u^0)^2 + (\hat{K}_v^0)^2 - \frac{\mu}{2M} (\hat{K}_u^0 \hat{K}_v^0 - \hat{K}_v^0 \hat{K}_u^0) \right. \]

\[ + \left. \hat{K}_u^0 \hat{K}_u^0 \right) . \]

The expression for the coupling term with the exact correspondence between the momentum and ladder operators, Eq. (33), is significantly more complex. Now one can apply the commutator relationships, Eq. (13), and to derive Heisenberg EOM for the linear triatomic.

Following a procedure that is similar to the steps taken in deriving the EOM for the single Morse oscillator, we obtain the following set of coupled differential equations for the linear triatomic

\[ \frac{d}{dt} (\hat{K}_u^0(t)) = \frac{i \omega}{2\nu} \left( (\hat{K}_u^0(t)) + (\hat{K}_v^0(t))((\hat{K}_u^0(t)) - (\hat{K}_v^0(t))) \right), \]

\[ \frac{d}{dt} (\hat{K}_v^0(t)) = -\frac{i \omega}{\nu} \left( 2(\hat{K}_v^0(t))(\hat{K}_v^0(t)) + \frac{\mu}{M} (\hat{K}_v^0(t))((\hat{K}_v^0(t)) \right. \]

\[ \left. - (\hat{K}_v^0(t))) \right), \]

\[ \frac{d}{dt} (\hat{K}_u^0(t)) = \frac{i \omega}{2\nu} \left( (\hat{K}_u^0(t)) + (\hat{K}_v^0(t))((\hat{K}_u^0(t)) - (\hat{K}_u^0(t))) \right), \]

\[ \frac{d}{dt} (\hat{K}_v^0(t)) = -\frac{i \omega}{\nu} \left( 2(\hat{K}_v^0(t))(\hat{K}_u^0(t)) + \frac{\mu}{M} (\hat{K}_v^0(t))((\hat{K}_u^0(t)) \right. \]

\[ \left. - (\hat{K}_u^0(t))) \right), \]

\[ \frac{d}{dt} (\hat{K}_u^0(t)) = \frac{i \omega}{\nu} \left( 2(\hat{K}_u^0(t))(\hat{K}_u^0(t)) - \frac{\mu}{M} (\hat{K}_u^0(t))((\hat{K}_u^0(t)) \right. \]

\[ \left. - (\hat{K}_u^0(t))) \right). \]

It should be noted that in the above set of equations the expectation values of \( \hat{K}_{uv}^0 \) are no longer constants of motion, in contrast to the single Morse oscillator. They evolve as energy flows from one mode to the other. Therefore, the
above differential equations are nonlinear. They cannot be readily solved by analytic methods and must be propagated numerically. Nevertheless, further progress can be made by analytic techniques.

The EOM for \( \langle \dot{K}^{\alpha\nu}_0 \rangle \) can be rewritten in terms of momenta and coordinates as

\[
\frac{d\langle \dot{K}^{\alpha\nu}_0 (t) \rangle}{dt} = \frac{\beta^2 \nu}{2M} p_{\alpha\nu},
\]

(56)

where \( C \) is the mass ratio

\[
C = \frac{\mu}{M}.
\]

(60)

and \( \gamma \) is defined in Eq. (27). The solutions of these equations are derived in Appendix. The exact correspondence between the position-momentum and ladder operators, Eq. (33), gives

\[
\frac{1}{y(t)} = \sin \gamma t \left( \frac{p_y(0)}{2 \beta \hbar} y(0) - \frac{p_y(0)}{2 \beta \hbar} y(0) \right)
\]

\[
+ \sin \gamma t \left( \frac{1 - C}{2 \beta \hbar} p_y(0) y(0) + \frac{p_y(0)}{y(0)} \right)
\]

\[
+ \frac{1}{2} \cos \gamma t \left( \frac{1}{y(0)} - \frac{1}{y(0)} \right)
\]

\[
+ \frac{1}{2} \cos \gamma t \left( \frac{1}{y(0)} + \frac{1}{y(0)} \right) + \frac{\nu(1 - \cos \gamma \nu t)}{(2s + 1)(2s - 1)},
\]

(61)

The harmonic-like correspondence, Eq. (40), gives

\[
\frac{z^{\alpha\nu}(t)}{\beta} = \sin \gamma t \left( \frac{1 + C}{2 \mu \omega} (p_{\alpha\nu}(0) - p_{\alpha\nu}(0)) \right)
\]

\[
+ \sin \gamma t \left( \frac{1 - C}{2 \mu \omega} (p_{\alpha\nu}(0) + p_{\alpha\nu}(0)) + \frac{1}{2} \cos \gamma t (z^{\alpha\nu}(0) - z^{\alpha\nu}(0)) \right)
\]

\[
- z^{\alpha\nu}(0) + \frac{1}{2} \cos \gamma t (z^{\alpha\nu}(0) + z^{\alpha\nu}(0)),
\]

(62)
where \( z'' = 1 - e^{2\beta z} \) and similarly for \( z'' \). The frequency terms \( \gamma_1 \) and \( \gamma_2 \) are
\[
\gamma_1 = \sqrt{C + 2} \gamma, \\
\gamma_2 = \sqrt{1 - C} \gamma.
\]
(63)
Both solutions, Eqs. (61) and (62), reduce in the appropriate limit to the EOM for the linear triatomic with the atoms interacting by harmonic potentials.

III. RESULTS AND DISCUSSION

The Morse oscillator is used extensively in literature and examples to choose from abound.1-15,49-52 Here, we consider two cases for the single Morse oscillator and one example of coupled Morse oscillators.

A. O–H stretch

The first example is the O–H stretch of water, as represented in the SPC-F potential,1 which is widely used in physical-chemical modeling of bulk water. The potential includes both harmonic and anharmonic descriptions of the O–H stretching motion. We consider the more accurate anharmonic version represented by a Morse potential of the form given in Eq. (1). The two parameters of the Morse potential are \( V_0 = 0.708 \) mdyn Å and \( \beta = 2.567 \) Å\(^{-1}\). Knowing the reduced mass of the O–H stretch allows us to calculate the parameter \( \nu \), Eq. (5), as \( \nu = 34.7547 \). It should be noted that there exist only 16 bound states for this Morse potential. Therefore, even at high energies the system is far from the classical limit, where a large number of bound states is required. In spite of this, the classical dynamics generated by the SPC-F potential is regarded as a faithful representation of the O–H motion of water.1

The exact classical-mechanical evolution was generated numerically using the fifth-order Runge–Kutta algorithm. The numerical results were compared to both exact and approximate analytic formulas, Eqs. (36) and (42), respectively, as well as to the harmonic oscillator approximation with the frequency determined by the curvature of the Morse potential at the bottom of the well. Three separate initial conditions were considered. The initial potential energy was set to the minimum, and the initial kinetic energy was varied from near the harmonic limit to far from the harmonic limit. Figures 1(a)–1(c) shows the results for the initial kinetic energies of \( h\omega \), \( 3h\omega \), and \( 7h\omega \), respectively. As expected, Eq. (36) gives the exact result for all initial conditions chosen, while the harmonic-like approximation, Eq. (42), shows a substantial improvement over the harmonic oscillator description.

B. Xe–Xe dimer

Next, we investigate an example with a larger value of \( \nu \), bringing the system closer to the classical limit. For this example we choose the Morse potential used in Ref. 5 to model clusters of xenon atoms. In present, we consider two xenon atoms interacting through the Morse potential. Ref. 5 gives the following parameters for the potential, Eq. (1): \( V_0 = 3.05 \times 10^{-21} \) J and \( \beta = 2.439 \) nm\(^{-1}\). Given the reduced mass of Xenon, these parameters correspond to \( \nu = 283.5729 \). There are 141 bound states for this system, and it is expected to be much closer to the classical limit than the first example.

As before, three cases are considered with the initial potential energy set to the minimum for all three. Figures 1(d)–1(f) shows the results for the initial kinetic energies of \( h\omega \), \( 3h\omega \), and \( 50h\omega \), respectively. These initial kinetic energies correspond to the average thermal energies at 3, 60, and 150 K. Equation (36) gives the exact results for this example. Both the harmonic oscillator approximation and the harmonic-like solution, Eq. (42), fail for the high energy case due to the large anharmonicity accessible near the dissociation limit. Nevertheless, the harmonic-like approximation provided by Eq. (42) shows a substantial improvement over the true harmonic description.

C. Linear triatomic

Next, consider two coupled Morse oscillators representing a linear triatomic molecule. For this example, the system is taken to be far into the classical limit with the following Morse parameters \( V_0 = 1250 \) and \( \beta = 0.0003 \). The reduced masses are \( \mu = 0.75 \) and \( M = 3 \), Eq. (50). The units are such...
that $h=1$. The preceding parameters lead to values of $\nu$ = 5000 and $\omega$ = 1. Three specific cases for the initial conditions are considered. These are the antisymmetric stretch, the symmetric stretch and a mixed stretching mode, where all of the initial kinetic energy is put into one of the Morse potentials. The approximate analytic solutions shown in Figs. 2–4 are obtained using Eq. (61) and harmonic-like Eq. (62).

Figure 2 gives the evolution of one of the coordinates for the antisymmetric stretching motion of the triatomic. The initial conditions are $p_u(0) = p_v(0)$, and not $p_u(0) = -p_v(0)$ as might be intuitively expected. This arises from the relationship expressed in Eq. (47). The initial conditions for the coordinates $u(0)$ and $v(0)$ are chosen to be at their minima for all examples. Four values for the initial momenta are chosen, $p_u(0) = p_v(0) = -1, -10, -20, -30$ in parts (a)–(d) of Fig. 2, respectively. Since the time evolution of $u(t)$ and $v(t)$ will give identical results, only $u(t)$ is shown. The exact numerical data for the classical dynamics of the triatomic (solid line) are compared to the results from Eq. (61) (long dashed) and harmonic-like Eq. (62) (short dashed), as well as to the evolution of two coupled harmonic oscillators with the frequency given by the curvature at the bottom of the Morse potential (dashed-dotted). Equation (61) is exact for the antisymmetric stretch. The harmonic-like approximation, Eq. (62), shows significant improvement over the coupled harmonic oscillators. All examples converge to the appropriate harmonic limit, as illustrated in Fig. 2(a).

Figure 3 illustrates the symmetric stretch. The approximation made in Eq. (59) no longer holds away from the harmonic limit for the symmetric stretch, as it did for the antisymmetric stretch, and the $\langle K_q \rangle$ terms are not constants of motion. Therefore, the defined effective frequencies, Eqs. (27) and (63), and the values of $s$ will change over time, and Eq. (61) will not be exact away from the harmonic limit. This is indeed the case, as seen in parts (b) and (d)–(f) of Fig. 3. However, both Eqs. (61) and (62) show a significant improvement over the straight harmonic approximation. The results are good in part because the fluctuations of the effective time-dependent frequency have a tendency to average out over time.

Figure 4 represents a situation where one degree of freedom is given an initial kinetic energy, while the other degree of freedom starts out with no kinetic energy. In this case, the time evolution of both coordinates $u(t)$, parts (a)–(c), and $v(t)$, parts (d)–(f), are shown. As in the case for the symmet-
ric stretch, we expect the approximation made in Eq. (59) to fail away from the harmonic limit. \( \langle K_0 \rangle \), \( s \) and the effective frequencies are no longer constants with time. Parts (a) and (c) of Fig. 4 show that the appropriate behavior in the harmonic limit is obtained. Parts (b,c,d,f) indicate that the approximations break down when the energy is increased, as expected. The analytic results reported for the symmetric and mixed cases, Figs. 3 and 4, can be improved further by going beyond the approximations made in Eqs. (61) and (62) and solving Eq. (57) directly.

**IV. CONCLUSIONS**

The current paper presented the first application of the QHD approach to chemical systems described by the Morse raising and lowering operators, thereby extending the earlier studies performed with the ordinary harmonic operators. The second order QHD EOM for the Morse oscillator were derived and an analytic solution to these equations was found. The first-order QHD closure gave classical dynamics of the Morse oscillator and the analytic solutions to the classical dynamics.

The Morse potential was represented in terms of the ladder operators, which satisfy the commutator relations for the SU(2) group. While other types of raising and lowering operators can also be used to represent the Morse dynamics\textsuperscript{24,30,31}, the SU(2) operators provide a concise representation that is particularly useful within the QHD framework, since it limits both the number and the order of the QHD variables that are required in order to capture quantum-mechanical effects. The SU(2) operators lead to a faster converging QHD series compared to other operators for two reasons. First, the SU(2) operators form a closed algebra. Even though this algebra does not include the Morse Hamiltonian, Eq. (16), and as a result the QHD EOM form an infinite hierarchy, the terms of the SU(2) hierarchy tend to close partially and to branch less than terms based on other operators. Second, the Morse Hamiltonian itself has a very simple form in the SU(2) representation, Eq. (16). Therefore, the Heisenberg commutators that give rise to EOM for the expectation values are also simple and contain few terms. In comparison, the operators defined in Refs. 24, 30, and 31 were introduced with molecular and spectroscopic applications in mind. For instance, the operators of Ref. 24 give exact matrix elements for the optical transition dipole moments involving the Morse momentum operator. Therefore, a QHD hierarchy involving these alternative Morse operators would be particularly useful for a semiclassical spectroscopic analysis.

The evolution of the ladder operators was considered in the Heisenberg representation. The exact quantum dynamics of the system can be found with an infinite set of coupled differential equations. In order to allow for useful analytic solutions they must be decoupled. We applied QHD closures to decouple the EOM for the lower-order operators from those for the higher-order variables. The resulting approximate EOM could be solved analytically in a closed form. The accuracy of the approximate solutions compared to the full quantum result depended on the level at which the QHD approximation is taken. This work considered the first and second-order QHD approximations. The first-order approach is equivalent to classical dynamics. Therefore, our semiclassical approach allowed us to derive closed analytic solutions for the classical dynamics of the Morse oscillator. It should be noted that the semiclassical results obtained in this work are applicable to the bound region of the Morse potential and, in general, cannot be used in the dissociative region.

The reported analyses were performed using the Morse ladder operators, which can be related exactly to the position and momentum operators. The exact relationship between the ladder and position-momentum operators is fairly complex. A simpler, approximate relationship, which becomes exact near the harmonic limit, can be used instead. The EOM obtained using this approximate harmonic-like relationship are simple and significantly outperform the straightforward harmonic approximation. Both the accurate and simpler relationships between the ladder and position-momentum operators lead to EOM that conserve the total energy and contain other constants of motion originating from the conservation of \( \langle K_0 \rangle \) in Eq. (23).

The semiclassical analytic expressions for the dynamics of the Morse oscillator were illustrated with two realistic systems, including the O–H stretch of water and the Xe–Xe
dimer. The simple, harmonic-like approximation provided substantial improvements over the true harmonic description, while the full solution of the first-order equations gave the exact closed form of the classical dynamics.

Next, the semiclassical approach was applied to coupled Morse oscillators. The system consisted of three particles. The two identical outside particles formed a linear chain with the middle particle and interacted with the middle particle through Morse potentials. Expressing the Hamiltonian using the Morse ladder operators, we derived analytic first-order EOM. Because the \( \hat{K}_0 \) ladder operator was no longer a constant of motion for the coupled system, in contrast to the single Morse oscillator, the first-order QHD closure gave nonlinear EOM. Close to the harmonic limit it was possible to treat the expectation value of \( \hat{K}_0 \) as a constant, reducing the number of differential equations from six to four and making them linear. This set of differential equations was solved analytically, generating a closed form solution for the approximate classical dynamics of two coupled Morse oscillators.

Using the exact and approximate correspondence between the Morse ladder operators and the position-momentum variables, we compared the semiclassical expressions for the coupled Morse oscillators with the exact numerical results and the harmonic limit. Three sets of initial conditions were considered, including the symmetric stretch, the antisymmetric stretch and a mixed mode. The exact operator correspondence produced an exact analytic expression for the classical dynamics of the antisymmetric stretch. The harmonic-like correspondence showed a significant improvement over the harmonic description. The symmetric and mixed modes were described approximately. Since \( \hat{K}_0 \) is time dependent for the symmetric stretch and the mixed mode, the semiclassical solutions deviated from the exact numerical answer away from harmonic limit. In this case, the results obtained using the harmonic-like correspondence between the ladder and position-momentum operators were of the same quality as the results obtained using the exact correspondence.

The classical-like analytic solutions for the dynamics of the one and two-dimensional Morse oscillators can be used to simplify numerical simulations of multidimensional systems. For instance, the fast motions of the OH and CH bonds are often described by Morse potentials. In a complex molecular system involving multiple time scales, the evolution of these bonds create numerical bottlenecks and limit the size of the integration time-step. The analytic solutions of the Morse problem can be used to eliminate the need to propagate the fast motions numerically and to allow one to increase the time step and extend the simulation to longer times. In such cases, the exact and approximate analytic solution of the classical-mechanical dynamics of the Morse oscillator, Eqs. (36) and (42) will depend parametrically on the coordinates of the slower modes. Additionally, zero-point energy and other quantum-mechanical effects associated with the OH and CH motions can be incorporated into numerical simulation using the analytic solutions (22) of the second-order QHD equations.

Quantum effects in the Morse oscillator dynamics were captured with the second-order approximation. The number of the second-order QHD Eq. (21) is only twice that of the classical mechanics, Eq. (23). It is straightforward to extend the technique to higher order. The general approach introduced and advocated in this work allows one to study quantum-mechanical effects in the Morse oscillator dynamics at little computational cost.

ACKNOWLEDGMENTS

Multiple and fruitful discussions with Yuriy Pereverzev are greatly appreciated. The research was supported by grants from the NSF under Grant No. CHE-0701517 and ACS-PRF 46772-AC6.

APPENDIX: SOLUTIONS FOR THE LINEAR TRIATOMIC

Here, we obtain solutions to Eq. (59), which was derived in Sec. II E for the linear triatomic molecule represented by coupled Morse oscillators. The system of linear differential Eq. (59) for the expectation values of the ladder operators can be solved by standard techniques, for instance by finding the appropriate eigenvalues and eigenvectors. For simplicity, we drop the expectation value notation \( \langle \cdots \rangle \), since all terms have been decoupled to the first order. The expectation values evolve according to

\[
\hat{K}_0(t) = \frac{1}{8} \left( \frac{e^{i\gamma_4 t} - e^{-i\gamma_4 t}}{\sqrt{C + 1}} \right) \left( \hat{K}_0^a(0)(C + 2) - \hat{K}_0^a(0)C - \hat{K}_0^a(0) \right) \\
\times (C + 2) + \hat{K}_0^a(0)(2 - C) + 2(\hat{K}_0^a(0))e^{i\gamma_4 t} + 2(\hat{K}_0^a(0))e^{-i\gamma_4 t} + e^{i\gamma_4 t} + e^{-i\gamma_4 t} \right),
\]

\[
\hat{K}_0(t) = \frac{1}{8} \left( \frac{e^{i\gamma_4 t} - e^{-i\gamma_4 t}}{\sqrt{C + 1}} \right) \left( \hat{K}_0^a(0)C - \hat{K}_0^a(0)(C + 2) \\
- \hat{K}_0^a(0)C + \hat{K}_0^a(0)(C + 2) \right) - \frac{e^{i\gamma_4 t} - e^{-i\gamma_4 t}}{\sqrt{1 - C}} \left( \hat{K}_0^a(0)C \\
+ \hat{K}_0^a(0)(2 - C) + \hat{K}_0^a(0)C + \hat{K}_0^a(0)(2 - C) \right) \\
+ 2(\hat{K}_0^a(0) - \hat{K}_0^a(0))e^{i\gamma_4 t} + 2(\hat{K}_0^a(0) - \hat{K}_0^a(0))e^{-i\gamma_4 t} + \hat{K}_0^a(0))e^{i\gamma_4 t} + e^{-i\gamma_4 t} \right),
\]

\[
\hat{K}_0(t) = \frac{1}{8} \left( \frac{e^{i\gamma_4 t} - e^{-i\gamma_4 t}}{\sqrt{C + 1}} \right) \left( \hat{K}_0^a(0)(C + 2) + \hat{K}_0^a(0)C + \hat{K}_0^a(0) \right) \\
\times (C + 2) - \hat{K}_0^a(0)(C + 2) + \hat{K}_0^a(0)(2 - C) \\
+ \hat{K}_0^a(0)C + \hat{K}_0^a(0)(2 - C) + \hat{K}_0^a(0)C + 2(\hat{K}_0^a(0))e^{i\gamma_4 t} + 2(\hat{K}_0^a(0))e^{-i\gamma_4 t} + e^{i\gamma_4 t} + e^{-i\gamma_4 t} \right),
\]
\[
\begin{align*}
\hat{K}_c(t) &= \frac{1}{8} \left( \frac{e^{i\gamma_1 t} - e^{-i\gamma_2 t}}{\sqrt{C + 1}} (\hat{K}_c^+(0) + \hat{K}_c^-(0) + \hat{K}_c^+(0)(C + 2) + \hat{K}_c^-(0)(C + 2)) \right. \\
&+ \hat{K}_c^+(0)(C - \hat{K}_c^-(0))(C + 2) - \frac{e^{i\gamma_1 t} - e^{-i\gamma_2 t}}{\sqrt{1 - C}} (\hat{K}_c^+(0)C + \hat{K}_c^-(0)(C + 2)) \\
&+ \hat{K}_c^+(0)(2 - C) + \hat{K}_c^-(0)(C + 2 - C) \right) \\
&+ 2(\hat{K}_c^+(0) - \hat{K}_c^-(0)) e^{i\gamma_1 t} + e^{i\gamma_2 t} + 2\hat{K}_c^-(0) \\
&+ \hat{K}_c^+(0)) (e^{i\gamma_1 t} + e^{i\gamma_2 t}) \right), \\
\end{align*}
\]

(A1)

where \( C \) is given by Eq. (60), and \( \gamma_1, \gamma_2 \) are given by Eq. (63).

In order to obtain the time dependence in the position-momentum representation, we can relate the coordinate variables to the Morse raising and lowering operators using either the exact expression, Eq. (33), or the much simpler harmonic-like approximation, Eq. (40). The latter is more appropriate in the limits used for deriving the analytic form of Eq. (A1) and gives rise to fairly simple expressions compared to the much more complex form of the expressions obtained using Eq. (33).

Starting with Eq. (A1) and using Eq. (33), we find the time dependence of \( y^{(t)} \)

\[
\frac{1}{y^{(t)}} = \frac{1}{4s\beta t} \sin \gamma_1 t \left[ \frac{p_{s}(0)}{y^{(t)}(0)} - \frac{p_{s+1}(0)}{y^{(t)}(0)} \right] \\
\times \left[ C \left( \frac{(2s + 1)\sqrt{s + 1} + (2s - 1)\sqrt{s - 1}}{2(2s + 1)(2s - 1)\sqrt{s(s - 1)}} \right) + 2 \right] \\
+ \frac{1}{4s\beta t} \sin \gamma_2 t \left[ \frac{p_{s+1}(0)}{y^{(t)}(0)} - \frac{p_{s}(0)}{y^{(t)}(0)} \right] \\
\times \left[ 2 - C \left( \frac{(2s + 1)\sqrt{s + 1} + (2s - 1)\sqrt{s - 1}}{2(2s + 1)(2s - 1)\sqrt{s(s - 1)}} \right) \right] \\
+ 2\cos \gamma_1 t \left( \frac{1}{y^{(t)}(0)} - \frac{1}{y^{(t)}(0)} \right) + \frac{1}{2} \cos \gamma_2 t \left( \frac{1}{y^{(t)}(0)} \right) \\
+ \frac{1}{y^{(t)}(0)} + \frac{\nu(1 - \cos \gamma_2 t)}{(2s + 1)(2s - 1)} .
\]

(A2)

This expression can be further simplified by noticing that the following term rapidly approaches its limit when \( s \gg 1 \)

\[
\frac{((2s + 1)\sqrt{s + 1} + (2s - 1)\sqrt{s - 1})}{2(2s + 1)(2s - 1)\sqrt{s(s - 1)}} \approx 2.
\]

(A3)

This allows us to rewrite Eq. (A2) in its final form, Eq. (61), as seen in Sec. II E. The EOM for the harmonic-like limit are found in a similar fashion by starting with Eq. (A1) and using Eq. (40) to relate the position-momentum variables to the raising and lowering operators. After simplification we obtain Eq. (62) for the harmonic-like limit.