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Operator-based derivation of the wavefunctions of the Morse potential

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Abstract

The Morse potential is an important problem to examine due to its applications in describing vibrations and bond breaking in molecules. It also shares some properties with the simpler harmonic oscillator, at the same time displaying differences, allowing for an interesting contrast to its well-studied counterpart. The solution of the Morse potential is not usually taught in a quantum mechanics class, since using differential equations makes it very tedious. Here, we illustrate how to solve the Morse potential using the Schrödinger factorization method. This operator method is a powerful tool to find the energy eigenvalues, eigenstates, and wavefunctions without using differential equations in position space, allowing us to solve more problems without requiring a discussion of hypergeometric or confluent hypergeometric functions.

Keywords: morse oscillator, physics education, anharmonic oscillator, exactly solvable model

1. Introduction

Quantum mechanics is usually taught using a position representation where energy eigenfunctions are found by solving the time-independent Schrödinger equation as a differential equation. Students often find this work challenging because they need to learn the series

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solution method. Furthermore, it is not clear how useful it is to teach this technique, as modern research rarely uses the Frobenius method.

Another way to teach quantum mechanics is to use ladder operators to elegantly find the eigenvalues and eigenstates of the harmonic oscillator. This operator-based approach can be extended to other exactly solvable problems. In 1940, Schrödinger developed the factorization method [1–4] to solve these problems using operator-based methods. This approach was re-energized in the 1980's by Witten's development of supersymmetric quantum mechanics and the classification of shape-invariant potentials [5–9].

The Morse potential [10] plays an important role in molecular physics and chemistry because it includes anharmonic effects on vibrations and provides a more realistic description of diatomic molecules than the simpler harmonic oscillator. For example, bond breaking, which is a fundamental process for describing chemical reactions, can be approximated by the anharmonic oscillator model, while it cannot be described using the harmonic approximation. The Morse potential is also key in finding the transition matrix elements for rovibrational spectra.

The solution of the Morse potential problem can be carried out using differential equations, but the analysis is rather tedious, so it is not often taught. It has also been solved in supersymmetric quantum mechanics using the Lie algebra of the ladder operators [11–13], but this is also likely to be complicated for most students and it does not determine the wavefunctions. However, the energy eigenvalues of the bound states of the Morse potential, in fact, can be determined through a straightforward algebraic factorization of the Hamiltonian [14].

Here, we first review the standard Schrödinger factorization method for the energy eigenvalues and eigenstates, and then we show how to generalize a recent operator-based approach to determine the wavefunctions as well. We will find that these energy eigenstates involve associated Laguerre polynomials, which are represented in the following way as a Rodrigues formula:

$$L_n^{(\alpha)}(y) = \frac{y^{-\alpha}\mathrm{e}^{y}}{n!} \cdot \frac{\mathrm{d}^n}{\mathrm{d}y^n}(y^{n+\alpha}\mathrm{e}^{-y}). \tag{1}$$

Interestingly, our work discovers a different form of the Rodrigues formula for the wavefunction of the Morse potential, as we discuss further below.

The remainder of the paper is organized as follows: In section 2, we review the standard Schrödinger factorization method, while section 3 and section 4 discuss the derivation of the energy eigenvalues and energy eigenstates of the Morse potential problem. We also apply the operator-form of a Rodrigues formula to derive the wavefunctions. Section 5, provides some tips for how to include these ideas in a graduate-level quantum mechanics class. Finally, a summary is given in section 6.

2. Review of Schrödinger factorization method

In the Schrödinger factorization method, which works for nearly all exactly solvable single-particle quantum mechanics problems, we start a factorization chain by factorizing the Hamiltonian $\hat{H}$ with potential $V(\hat{x})$ into a positive-semidefinite form via

$$\hat{H} = \frac{\hat{p}^2}{2M} + V(\hat{x}) = \frac{\hat{p}^2}{2M} + V_0(\hat{x}) = \hat{A}_0^\dagger \hat{A}_0 + E_0 = \hat{H}_0, \tag{2}$$

where potentials in the factorization chain are indexed by n and denoted V_n, with $V_0 = V$ the initial potential in the factorization chain. Similarly, the energies E_n in the factorization at each step of the chain, are the eigenenergies of the original Hamiltonian $\hat{H} = \hat{H}_0$. $\hat{A}_0^\dagger$ and $\hat{A}_0$ are Hermitian conjugate ladder operators of the form

$$\hat{A}_n = \frac{1}{\sqrt{2M}}(\hat{p} - \mathrm{i}\hbar k_n W_n(k_n'\hat{x})) \tag{3}$$

with a real-valued superpotential W_n (which is determined in the process of solving the factorization chain) and wavenumbers k_n and k_n' which are also determined at each step of the factorization method. The wavenumber k_n, with dimensions of inverse length, is used to ensure the term added to the momentum operator has the same dimensions as momentum in the ladder operators, while the wavenumber k_n', also with dimensions of inverse length, is used to ensure the function W_n has a dimensionless argument. While the $\hat{A}_n$ and $\hat{A}_n^\dagger$ operators are called ladder operators, they do not raise or lower the energy eigenvalues for the general case, but instead they are used to construct the energy eigenstates of the Hamiltonians in the factorization chain. Explicit values for all of these objects will be given later, as we work to concretely solve for the factorization chain of the Morse potential. The ladder operators take this form, because the Hamiltonian is quadratic in $\hat{p}$ and has no linear terms in momentum. The factorized form of the Hamiltonian in equation (2) is a positive-semidefinite form, because $\langle\psi|\hat{H}_0|\psi\rangle = \|\hat{A}_0|\psi\rangle\|^2 + E_0$, for arbitrary normalized states $|\psi\rangle$. This implies that if a physical state $|\phi_0\rangle$ exists that satisfies the so-called subsidiary condition, given by $\hat{A}_0|\phi_0\rangle = 0$, then, it is the ground state and the ground-state energy is E_0. Note that this behavior holds for the factorization of the simple harmonic oscillator as well, although it is not often described in this way, and the conventional ladder operators there are rescaled from the ones used here. For example, Ikenberry [15] discusses the operator methods for the harmonic oscillator similar to what we did here in his section 11.4.

To find the first excited state of $\hat{H}$, we must form the next step in the factorization chain in the following way. We define the first auxiliary Hamiltonian $\hat{H}_1$ by reversing the order of the ladder operators $\hat{A}_0^\dagger$ and $\hat{A}_0$, while using the same energy E_0:

$$\hat{H}_1 = \hat{A}_0\hat{A}_0^\dagger + E_0 = \hat{H}_0 + [\hat{A}_0, \hat{A}_0^\dagger] = \frac{\hat{p}^2}{2M} + V_0(\hat{x}) + [\hat{A}_0, \hat{A}_0^\dagger] = \frac{\hat{p}^2}{2M} + V_1(\hat{x}), \tag{4}$$

where $V_1(\hat{x}) = V_0(\hat{x}) + [\hat{A}_0, \hat{A}_0^\dagger]$, which generally is a different function than the potential V_0 in the original Hamltonian $\hat{H}_0$ (concrete examples will be given later). Next, we factorize this new Hamiltonian in the standard form, given by

$$\hat{H}_1 = \hat{A}_1^\dagger\hat{A}_1 + E_1 \tag{5}$$

with a new superpotential W_1 included in $\hat{A}_1$ given by equation (3) with $n = 1$. The first auxiliary Hamiltonian ground state is determined by the subsidiary condition $\hat{A}_1|\phi_1\rangle = 0$. We then continue in the same fashion to determine additional steps in the chain. New auxiliary Hamiltonians and their ground states are found by repeating this procedure. We have

$$\hat{H}_n = \hat{A}_{n-1}\hat{A}_{n-1}^\dagger + E_{n-1} = \frac{\hat{p}^2}{2M} + V_n(\hat{x}) = \hat{A}_n^\dagger\hat{A}_n + E_n, \tag{6}$$

and

$$\hat{A}_n|\phi_n\rangle = 0. \tag{7}$$

In order to be able to carry out the factorizations analytically, we require that the superpotentials all have the same functional form, with only the numerical parameters in them varying from one Hamiltonian to another. This is the key requirement to have an analytically solvable problem. When this occurs, the original Hamiltonian is said to have a shape-invariant potential. All exactly solvable potentials in quantum mechanics are shape-invariant potentials, including the Morse potential.

The definitions of the factorization chain lead to the intertwining relation between the auxiliary Hamiltonians and ladder operators, given by

$$\hat{H}_n\hat{A}_n^\dagger = (\hat{A}_n^\dagger\hat{A}_n + E_n)\hat{A}_n^\dagger = \hat{A}_n^\dagger(\hat{A}_n\hat{A}_n^\dagger + E_n) = \hat{A}_n^\dagger\hat{H}_{n+1}, \tag{8}$$

that is when a Hamiltonian is moved past its raising operator, from left to right, its index increases by one. From the intertwining relation, we can find the excited energy eigenstates of $\hat{H}_0$. We claim that the nth energy eigenstate of $\hat{H}_0$ is given by the state

$$|\psi_n\rangle = C_n\hat{A}_0^\dagger\hat{A}_1^\dagger\hat{A}_2^\dagger \cdots \hat{A}_{n-1}^\dagger|\phi_n\rangle, \tag{9}$$

where C_n is the normalization coefficient and $|\phi_n\rangle$ is the ground state wavefunction of the nth auxiliary Hamiltonian $\hat{H}_n$ (satisfying $\hat{H}_n|\phi_n\rangle = E_n|\phi_n\rangle$). This is shown by acting $\hat{H}_0$ onto the state $|\psi_n\rangle$ and using the intertwining relation to move the Hamiltonian to the right. We find

$$\begin{aligned}\hat{H}_0|\psi_n\rangle &= C_n\hat{H}_0\hat{A}_0^\dagger\hat{A}_1^\dagger\hat{A}_2^\dagger \cdots \hat{A}_{n-1}^\dagger|\phi_n\rangle = C_n\hat{A}_0^\dagger\hat{H}_1\hat{A}_1^\dagger\hat{A}_2^\dagger \cdots \hat{A}_{n-1}^\dagger|\phi_n\rangle\\ &= C_n\hat{A}_0^\dagger\hat{A}_1^\dagger\hat{H}_2\hat{A}_2^\dagger \cdots \hat{A}_{n-1}^\dagger|\phi_n\rangle = C_n\hat{A}_0^\dagger\hat{A}_1^\dagger\hat{A}_2^\dagger \cdots \hat{A}_{n-1}^\dagger\hat{H}_n|\phi_n\rangle\\ &= E_nC_n\hat{A}_0^\dagger\hat{A}_1^\dagger\hat{A}_2^\dagger \cdots \hat{A}_{n-1}^\dagger|\phi_n\rangle = E_n|\psi_n\rangle.\end{aligned} \tag{10}$$

Hence, $|\psi_n\rangle$ is an eigenstate with energy E_n of the original Hamiltonian $\hat{H}$. To find the normalization constant, we calculate $\langle\psi_n|\psi_n\rangle$ by replacing $\hat{A}_0\hat{A}_0^\dagger$ by $\hat{H}_1 - E_0$ and then moving the auxiliary Hamiltonian to the right as follows:

$$\begin{aligned}\langle\psi_n|\psi_n\rangle &= |C_n|^2\langle\phi_n|\hat{A}_n \cdots \hat{A}_1\hat{A}_0\hat{A}_0^\dagger\hat{A}_1^\dagger \cdots \hat{A}_n^\dagger|\phi_n\rangle\\ &= |C_n|^2\langle\phi_n|\hat{A}_n \cdots \hat{A}_1(\hat{H}_1 - E_0)\hat{A}_1^\dagger \cdots \hat{A}_n^\dagger|\phi_n\rangle\\ &= |C_n|^2\langle\phi_n|\hat{A}_n \cdots \hat{A}_1\hat{A}_1^\dagger(\hat{H}_2 - E_0) \cdots \hat{A}_n^\dagger|\phi_n\rangle\\ &= |C_n|^2\langle\phi_n|\hat{A}_n \cdots \hat{A}_1\hat{A}_1^\dagger \cdots \hat{A}_n^\dagger(\hat{H}_n - E_0)|\phi_n\rangle\\ &= |C_n|^2(E_n - E_0)\langle\phi_n|\hat{A}_n \cdots \hat{A}_1\hat{A}_1^\dagger \cdots \hat{A}_n^\dagger|\phi_n\rangle.\end{aligned} \tag{11}$$

This has removed the two innermost operators and replaced them by the difference of two energies. Repeating this procedure to remove each pair of lowering and raising operators, we obtain

$$|C_n| = \frac{1}{\sqrt{(E_n - E_0)(E_n - E_1) \cdots (E_n - E_{n-1})}}. \tag{12}$$

In addition to the original Hamiltonian, the factorization chain creates a series of auxiliary Hamiltonians. Each auxiliary Hamiltonian $\hat{H}_n$ shares all the eigenvalues with the previous one $\hat{H}_{n-1}$ except for the ground state given by $\hat{E}_{n-1}$. So, the spectra of the factorization chain can be represented as in figure 1. To verify this, we can follow the previous discussion to see that the lth excited state of $\hat{H}_{n-l}$ is given by

$$|\phi_{n-l}^{(l)}\rangle = C_{n-l}^{(l)}\hat{A}_{n-l}^\dagger\hat{A}_{n-l+1}^\dagger \cdots \hat{A}_{n-1}^\dagger|\phi_n\rangle, \tag{13}$$

where we use the (l) superscript to denote the lth excited state. By acting $\hat{H}_{n-l}$ onto $|\phi_{n-l}^{(l)}\rangle$ and using intertwining, we can immediately show it is an eigenstate of $\hat{H}_{n-l}$ with eigenvalue E_n. Similarly, finding the norm of the state and using the same approach as we did above, shows us that

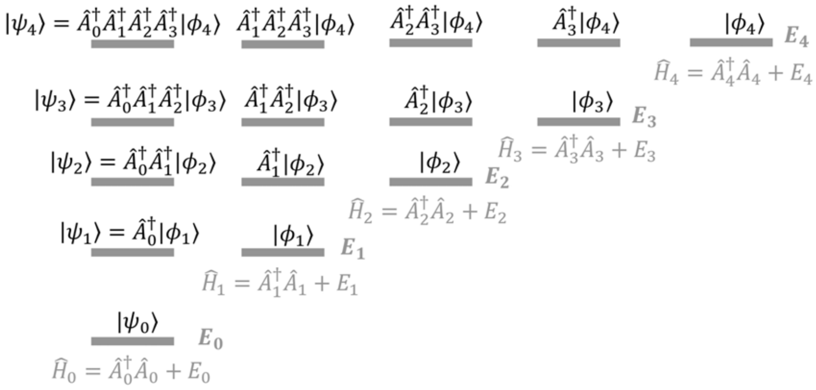

Figure 1. Factorization chain spectra, energy eigenstates, and auxiliary Hamiltonians. The initial Hamiltonian $\hat{H}$ is denoted as $\hat{H}_0$ to clarify that it is the initial Hamiltonian in the factorization chain and its excited states, with energies $\{E_0, E_1, \cdots\}$ are depicted in the first column and labeled with $|\psi_i\rangle$ to distinguish them from the auxiliary ground states labeled by $|\phi_i\rangle$. The eigenstates (unnormalized) are formed by acting a string of raising operators from 0 to $n-1$ to the nth auxiliary ground state. Moving to the right, each subsequent column corresponds to an auxiliary Hamiltonian with a different potential. They share the same energies with the previous Hamiltonian to the left, except for the lowest energy, which is not shared. When developing the Rodrigues formula, we use a recurrence relation that moves us from right to left along a horizontal row of the chain.

$$C_{n-l}^{(l)} = \frac{1}{\sqrt{(E_n - E_{n-l})(E_n - E_{n-l+1})\cdots(E_n - E_{n-1})}}. \tag{14}$$

In this way, we can immediately see that the spectra of the factorization chain show degeneracy across all Hamiltonians in a given row. The number of these Hamiltonians that have degenerate energy eigenvalues increases as n increases.

This approach appears quite different from the standard ladder operator approach of the harmonic oscillator, but it is actually the same. The key point to notice is that for the conventional harmonic oscillator all of the ladder operators are the same $\hat{A}_i = \hat{A}$ and are independent of the index, as are all auxiliary ground states. This allows the ladder operators to be used to move up and down the spectrum. One can solve the Morse potential using operators that raise or lower the energy eigenvalue [16, 17], but that approach is different from how we proceed here and those operators are different from the ones used to form the factorization chain.

The factorization process requires solving nonlinear equations, as we will see below. When this occurs, there often is more than one solution. In order to determine the correct factorization, we must have that $k_n W_n(k_n' x)$ is positive for $x \to +\infty$ and is negative for $x \to -\infty$ to guarantee the auxiliary ground state is normalizable. Note that we are working with a real-valued function here, rather than an operator, to enforce the required condition for normalizability of the wavefunction. We will see how we use this fact later. The position-space wavefunction is then given by

$$\psi_n(x) = \langle x|\psi_n\rangle, \tag{15}$$

with $|x\rangle$ the position eigenstate, which satisfies $\hat{x}|x\rangle = x|x\rangle$, and can be expressed as $|x\rangle = \exp(-\mathrm{i}x\hat{p}/\hbar)|0_x\rangle$, with $\hat{x}|0_x\rangle = 0$ the position eigenstate at the origin of the position axis. Instead of using a differential equation approach, we will calculate the wavefunctions by using a generalized operator form of the Rodrigues formula. The general procedure was worked out in [18]. It involves five steps:

(i) Rewrite the raising operators as similarity transformations:

$$\hat{A}_n^\dagger = \frac{1}{\sqrt{2M}} \hat{O}_n \, \hat{p} \, \hat{O}_n^{-1}; \tag{16}$$

(ii) Use the subsidiary condition and the nth auxiliary ground state $|\phi_n\rangle$ to construct a state annihilated by $\hat{p}$. This state allows us to add $\hat{p}$ acting on it to any expression without changing it;
(iii) Employ this 'add-zero' strategy to convert the string of raising operators into a set of nested commutators;
(iv) Find a recurrence relation for the nested commutators as a function of n; and
(v) Employ the operator-form of the Rodrigues formula to solve the recurrence relation of the product of raising operators as a function of the position operators only.

This is a fully algebraic procedure that does not require solving any differential equations.

Note that there are other ways to proceed that employ the Rodrigues formula or related methods. The most direct link is with the Laplace method solution [19, 20], which derives the Rodrigues formula from evaluating a multiple pole in the process of determining the solution via contour integration. This ends up being a bit different from approaches that employ the Laplace transform to solve the problem [21, 22], which is a second alternative.

In the next section, we find the energy eigenvalues, ladder operators, and energy eigenstates of the Morse potential, using the procedures outlined here.

3. Energy eigenvalues of the Morse potential

The one-dimensional Morse potential describes the stretching of a diatomic molecule and is given by

$$V(\hat{\tilde{x}}) = D_\mathrm{e}(\mathrm{e}^{-2a(\hat{\tilde{x}}-x_\mathrm{e})} - 2\mathrm{e}^{-a(\hat{\tilde{x}}-x_\mathrm{e})}) = D_\mathrm{e}(1 - \mathrm{e}^{-a(\hat{\tilde{x}}-x_\mathrm{e})})^2 - D_\mathrm{e}, \tag{17}$$

where D_e is the depth of the potential and is related to the dissociation energy, $\hat{\tilde{x}}$ is the distance between two atoms, x_e is the equilibrium bond length, and a is an inverse-length parameter that controls the curvature of the potential, see figure 2. Expressing the Morse potential this way in terms of $\hat{\tilde{x}}$ is a common practice in Chemistry. This potential represents an approximation to the anharmonic potential of a molecule as it is stretched that is much more accurate than the simple harmonic oscillator does. The potential rises rapidly as we squeeze the molecule to a length less than the equilibrium separation given by x_e due to the strong repulsion between the ion cores. As we pull the molecule apart, the potential comes back to zero more slowly, representing the long-range nature of the screened Coulomb force. In Physics, it is more convenient to introduce the operator $\hat{x} = \hat{\tilde{x}} - x_\mathrm{e}$ as we now do—the oscillator then has its equilibrium position at the origin of the $\hat{x}$ variable.

With a little trial and error, we find the superpotential must take the form $W_n(k_n'x) = -\mathrm{e}^{-ax} + \lambda_n$, with $\lambda_n > 0$, for the Morse potential; the superpotential is positive as $x \to +\infty$ and negative as $x \to -\infty$ as required for normalizability. One can see that we have $k_n' = a$ independent of n for the Morse potential and the explicit value for λ_n is yet to be determined. The lowering operator $\hat{A}_n$ and the raising operator $\hat{A}_n^\dagger$ can then be constructed as

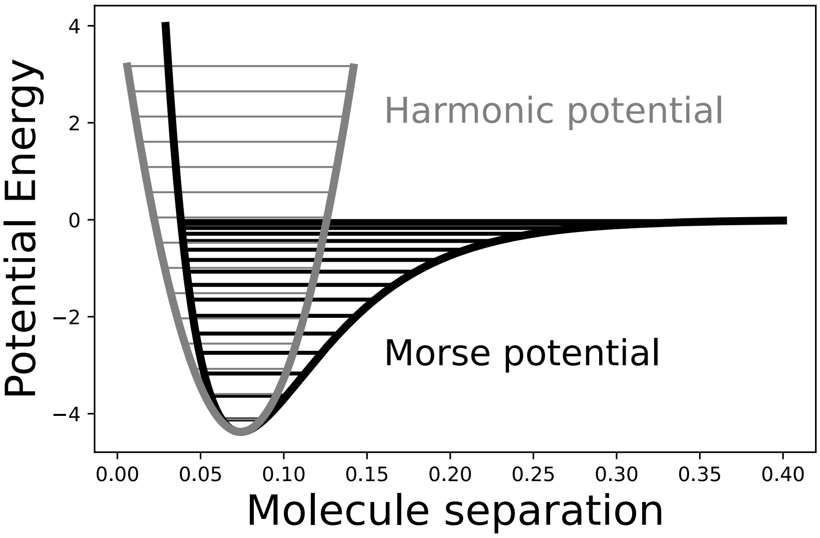

Figure 2. Morse potential (black) and best fit harmonic potential (gray) plotted with respect to $\bar{x}$, illustrating the energy levels with horizontal lines. The lowest-lying energy levels line up well, but then as we approach $E = 0$, the Morse potential energies pile-up near $E = 0$, while the harmonic oscillator ones remain evenly spaced. The depth of the potential is D_e and the parameter a controls the curvature near the minimum. The plot shifts the potential out by the equilibrium separation x_e to be more representative of the application to a molecule. Note that while the Morse potential allows for negative $\bar{x}$ values, which are physically forbidden, the probability of being in the negative $\bar{x}$ region is exceedingly small for all bound-state energy eigenstates.

$$\hat{A}_n = \frac{1}{\sqrt{2\mu}}(\hat{p} - \mathrm{i}\sqrt{2\mu D_\mathrm{e}}(-\mathrm{e}^{-a\hat{x}} + \lambda_n)) \tag{18}$$

where μ is the reduced mass of the diatomic molecule, and $\hat{A}_n^\dagger$ is the Hermitian conjugate of $\hat{A}_n$; the choice $\hbar k_n = \sqrt{2\mu D_\mathrm{e}}$ follows because there is only one way to generate the $\mathrm{e}^{-2a\hat{x}}$ term, which fixes that term; note that k_n is also independent of n. Following the procedure for constructing the factorization chain, we next compute $\hat{A}_{n-1}\hat{A}_{n-1}^\dagger$, which gives us

$$\hat{A}_{n-1}\hat{A}_{n-1}^\dagger = \frac{\hat{p}^2}{2\mu} + D_\mathrm{e}\mathrm{e}^{-2a\hat{x}} - \left(2D_\mathrm{e}\lambda_{n-1} - \frac{\hbar a\sqrt{D_\mathrm{e}}}{\sqrt{2\mu}}\right)\mathrm{e}^{-a\hat{x}} + D_\mathrm{e}\lambda_{n-1}^2 = \hat{H}_n - E_{n-1} \tag{19}$$

and then we must refactorize to find $\hat{A}_n^\dagger\hat{A}_n$, which gives us

$$\hat{A}_n^\dagger\hat{A}_n = \frac{\hat{p}^2}{2\mu} + D_\mathrm{e}\mathrm{e}^{-2a\hat{x}} - \left(2D_\mathrm{e}\lambda_n + \frac{\hbar a\sqrt{D_\mathrm{e}}}{\sqrt{2\mu}}\right)\mathrm{e}^{-a\hat{x}} + D_\mathrm{e}\lambda_n^2 = \hat{H}_n - E_n. \tag{20}$$

The coefficients of the $\mathrm{e}^{-a\hat{x}}$ term must be the same, so, we have

$$\lambda_n = \lambda_{n-1} - \frac{\hbar a}{\sqrt{2\mu D_\mathrm{e}}}, \tag{21}$$

which can be iterated to give us

$$\lambda_n = \lambda_0 - \frac{n\hbar a}{\sqrt{2\mu D_\mathrm{e}}}, \tag{22}$$

concretely determining its value. We finally find λ_0 by using equation (20) with the initial Morse potential $V_0(\hat{x})$ expressed in terms of $\hat{x}$. This gives us

$$\lambda_0 = 1 - \frac{\hbar a}{2\sqrt{2\mu D_\mathrm{e}}}, \tag{23}$$

and then we find that

$$\lambda_n = 1 - \frac{(n+\frac{1}{2})\hbar a}{\sqrt{2\mu D_\mathrm{e}}}. \tag{24}$$

The energy is given by $E_n = -D_\mathrm{e}\lambda_n^2$ or

$$E_n = -D_\mathrm{e}\left(1 - \frac{(n+\frac{1}{2})\hbar a}{\sqrt{2\mu D_\mathrm{e}}}\right)^2 = -D_\mathrm{e} + (n+\frac{1}{2})\hbar a\sqrt{\frac{2D_\mathrm{e}}{\mu}} - \left(n+\frac{1}{2}\right)^2\frac{\hbar^2 a^2}{2\mu}. \tag{25}$$

This energy can be thought of as a displacement of the origin by $-D_\mathrm{e}$ plus a harmonic oscillator energy with an effective frequency of $\omega_\mathrm{eff} = a\sqrt{2D_\mathrm{e}/\mu}$ plus an anharmonic correction given by $\left(n+\frac{1}{2}\right)^2\hbar^2a^2/2\mu$.

Note that the coefficient of the $\mathrm{e}^{-a\hat{x}}$ term must be negative, otherwise there cannot be a bound state, because the auxiliary potential would have no minimum. This tells us that we must have $n < \sqrt{2\mu D_\mathrm{e}}/\hbar a$. But, we have another restriction, which is that we must have $E_n < 0$ for a bound state, because the Morse potential approaches 0 as $x \rightarrow 0$, so the maximal value for n occurs when the energy first vanishes. If we think of n as a continuous variable, then the energy first vanishes when

$$n = \frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar a} - \frac{1}{2}, \tag{26}$$

as shown in the first equality in equation (25), which means the maximal n value allowed is when n is the largest integer smaller than the right hand side of equation (26).

4. Energy eigenstates of the Morse potential

The energy eigenstates are given in equations (9) and (12). The wavefunction is, of course,

$$\psi_n(x) = \langle x|\psi_n\rangle, \tag{27}$$

with $|x\rangle$ the position eigenstate at position x.

Our first step to finding the wavefunction is to rewrite the raising operator as a similarity transformation of the momentum operator. Recall the Hadamard lemma, given by

$$\mathrm{e}^{\hat{A}}\hat{B}\mathrm{e}^{-\hat{A}} = \hat{B} + [\hat{A}, \hat{B}] + \frac{1}{2!}[\hat{A}, [\hat{A}, \hat{B}]] + \frac{1}{3!}[\hat{A}, [\hat{A}, [\hat{A}, \hat{B}]]] + \cdots, \tag{28}$$

where each subsequent term is an increasingly nested commutator with $\hat{A}$ and divided by $n!$. Note that when evaluating nested commutators, it is most efficient to evaluate them from the inside first and then move outward with each step. There are two cases of the Hadamard lemma that we need. The first is

$$\mathrm{e}^{\alpha\hat{x}}\hat{p}\mathrm{e}^{-\alpha\hat{x}} = \hat{p} + \alpha[\hat{x}, \hat{p}] + \frac{\alpha^2}{2}[\hat{x}, [\hat{x}, \hat{p}]] + \cdots = \hat{p} + \mathrm{i}\hbar\alpha, \tag{29}$$

because a constant commutes with everything. The second is

$$\mathrm{e}^{\beta\mathrm{e}^{-a\hat{x}}}\hat{p}\mathrm{e}^{-\beta\mathrm{e}^{-a\hat{x}}} = \hat{p} + \beta[\mathrm{e}^{-a\hat{x}}, \hat{p}] + \frac{\beta^2}{2}[\mathrm{e}^{-a\hat{x}}, [\mathrm{e}^{-a\hat{x}}, \hat{p}]] + \cdots = \hat{p} - \mathrm{i}\hbar a\beta\mathrm{e}^{-a\hat{x}}, \tag{30}$$

because $\hat{x}$ commutes with a function of $\hat{x}$. So, we have that

$$\begin{aligned}
\hat{A}_n^\dagger &= \frac{1}{\sqrt{2\mu}}(\hat{p} + \mathrm{i}\sqrt{2\mu D_\mathrm{e}}(-\mathrm{e}^{-a\hat{x}} + \lambda_n)) \\
&= \frac{1}{\sqrt{2\mu}}\mathrm{e}^{\frac{\sqrt{2\mu D_\mathrm{e}}\lambda_n\hat{x}}{\hbar}}\mathrm{e}^{\frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar a}\mathrm{e}^{-a\hat{x}}}\hat{p}\mathrm{e}^{-\frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar a}\mathrm{e}^{-a\hat{x}}}\mathrm{e}^{-\frac{\sqrt{2\mu D_\mathrm{e}}\lambda_n\hat{x}}{\hbar}} \\
&= \frac{1}{\sqrt{2\mu}}\mathrm{e}^{\left(\frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar} - (n+\frac{1}{2})a\right)\hat{x} + \frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar a}\mathrm{e}^{-a\hat{x}}}\hat{p}\mathrm{e}^{-\left(\frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar} - (n+\frac{1}{2})a\right)\hat{x} - \frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar a}\mathrm{e}^{-a\hat{x}}}.
\end{aligned} \tag{31}$$

Our goal is to find a recurrence relation to re-express the product of raising operators as a polynomial of exponentials of position operators. This can always be done, because when the momentum operator acts on an auxiliary ground state, it is replaced by an exponential plus a constant, and commutators of momentum with exponentials yield exponentials. The procedure to determine the polynomial can be quite tedious, so finding a recurrence relation allows us to solve all problems at once in a simpler way.

The recurrence relation we need to work out moves horizontally along a constant energy row of the factorization chain, as opposed to running along a vertical column. This is because we want the innermost term in the commutator to be the same for all recurrences (which will become clear soon). Hence, when we form the product of the raising operators, for a general state in the nth row, we find that

$$\begin{aligned}
|\phi_{n-l}^{(l)}\rangle = C_{n-l}^{(l)}&\left(\frac{1}{\sqrt{2\mu}}\right)^l \mathrm{e}^{\left(\frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar} - (n-l+\frac{1}{2})a\right)\hat{x} + \frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar a}\mathrm{e}^{-a\hat{x}}}(\hat{p}\mathrm{e}^{-a\hat{x}})^l \\
&\times \mathrm{e}^{-\left(\frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar} - (n+\frac{1}{2})a\right)\hat{x} - \frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar a}\mathrm{e}^{-a\hat{x}}}|\phi_n\rangle,
\end{aligned} \tag{32}$$

because the intermediate factors nearly cancel, leaving behind just $\mathrm{e}^{-a\hat{x}}$. Note that this requires removing a factor of $\mathrm{e}^{-a\hat{x}}$ and associating it with the $\hat{p}$ in the last factor on the right.

Our next step is to find the state annihilated by $\hat{p}$. To do this, we start with the subsidiary condition for the nth auxiliary Hamiltonian, which gives us

$$\hat{A}_n|\phi_n\rangle = 0 \qquad \Rightarrow \qquad \hat{p}\mathrm{e}^{\left(\frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar} - \left(n+\frac{1}{2}\right)a\right)\hat{x} + \frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar a}\mathrm{e}^{-a\hat{x}}}|\phi_n\rangle = 0. \tag{33}$$

We define

$$\hat{B}_n = \left(\frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar} - \left(n + \frac{1}{2}\right)a\right)\hat{x} + \frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar a}\mathrm{e}^{-a\hat{x}}, \tag{34}$$

to simplify the expressions that follow.

We start by examining the first factor of $\hat{p}\mathrm{e}^{-a\hat{x}}$ in equation (32), which can be expressed as

$$\begin{aligned}\hat{p}\mathrm{e}^{-a\hat{x}}\mathrm{e}^{-\hat{B}_n}|\phi_n\rangle &= \hat{p}\mathrm{e}^{-a\hat{x}}\mathrm{e}^{-2\hat{B}_n}\mathrm{e}^{\hat{B}_n}|\phi_n\rangle \\ &= (\hat{p}\mathrm{e}^{-a\hat{x}}\mathrm{e}^{-2\hat{B}_n} - \mathrm{e}^{-a\hat{x}}\mathrm{e}^{-2\hat{B}_n}\hat{p})\mathrm{e}^{\hat{B}_n}|\phi_n\rangle \\ &= [\hat{p},\, \mathrm{e}^{-a\hat{x}}\mathrm{e}^{-2\hat{B}_n}]\mathrm{e}^{\hat{B}_n}|\phi_n\rangle,\end{aligned} \tag{35}$$

because the second term in the second line vanishes due to the momentum operator annihilating the state to the right of it. This allows us to convert the momentum operator acting on a state into a commutator of the momentum operator acting on the state. We can then repeat the procedure $l - 1$ more times to find that

$$|\phi_{n-l}^{(l)}\rangle = C_{n-l}^{(l)}\left(\frac{1}{\sqrt{2\mu}}\right)^{l}\mathrm{e}^{\hat{B}_l}[\hat{p},\, \mathrm{e}^{-a\hat{x}}[\hat{p},\, \mathrm{e}^{-a\hat{x}}[\cdots[\hat{p},\, \mathrm{e}^{-a\hat{x}}\mathrm{e}^{-2\hat{B}_n}]\cdots]]]_l\mathrm{e}^{\hat{B}_n}|\phi_n\rangle, \tag{36}$$

which has l multiple nested commutators. Because the commutator of $\hat{p}$ with a function of $\hat{x}$ will be another function of $\hat{x}$, we can move the rightmost $\mathrm{e}^{\hat{B}_n}$ operator to the left. Next, because the Leibniz rule for commutators says that

$$\mathrm{e}^{-a\hat{x}}[\hat{p}, f(\hat{x})] + [\mathrm{e}^{-a\hat{x}}, f(\hat{x})]\hat{p} = [\mathrm{e}^{-a\hat{x}}\hat{p}, f(\hat{x})], \tag{37}$$

and because the second commutator on the left hand side is zero, we can move the $\mathrm{e}^{-a\hat{x}}$ terms to the right into each adjacent nested commutator, to lie next to the $\hat{p}$ operator on the left, or

$$|\phi_{n-l}^{(l)}\rangle = C_{n-l}^{(l)}\left(\frac{1}{\sqrt{2\mu}}\right)^{l}\mathrm{e}^{\hat{B}_l+\hat{B}_n}\mathrm{e}^{a\hat{x}}[\mathrm{e}^{-a\hat{x}}\hat{p},\, [\mathrm{e}^{-a\hat{x}}\hat{p},\, [\cdots,[\mathrm{e}^{-a\hat{x}}\hat{p},\, \mathrm{e}^{-a\hat{x}}\mathrm{e}^{-2\hat{B}_n}]\cdots]]]_l|\phi_n\rangle. \tag{38}$$

We can then rearrange the quantum state to be

$$\begin{aligned}|\phi_{n-l}^{(l)}\rangle = C_{n-l}^{(l)}&\left(\frac{\mathrm{i}\hbar a}{\sqrt{2\mu}}\right)^{l}\mathrm{e}^{-(2n+l)a\hat{x}+\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}(a\hat{x}+\mathrm{e}^{-a\hat{x}})} \\ &\times\left[\frac{\mathrm{e}^{-a\hat{x}}}{\mathrm{i}\hbar a}\hat{p},\, \left[\frac{\mathrm{e}^{-a\hat{x}}}{\mathrm{i}\hbar a}\hat{p}, \left[\cdots, \left[\frac{\mathrm{e}^{-a\hat{x}}}{\mathrm{i}\hbar a}\hat{p},\, \mathrm{e}^{2na\hat{x}-\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}(a\hat{x}+\mathrm{e}^{-a\hat{x}})}\right]\cdots\right]\right]\right]_l|\phi_n\rangle.\end{aligned} \tag{39}$$

This equation resembles the Rodrigues formula in equation (1), if we recall that the momentum operator is represented by $-\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}x}$ in position space. But, unlike the standard Rodrigues formula, where the derivative is taken l times in a row, here, we have an extra factor of e^{-ax} to the left of each derivative, which makes it a different form (we will not explicitly work out the full differential form, as we do not need it for our work).

The claim is that the operators multiplying the auxiliary Hamiltonian ground state are equal to a Laguerre polynomial of exponentials multiplied by exponentials and exponentials of exponentials. To verify this, we examine the first few cases concretely, and then prove the general result via induction. So, when $l = 1$, we have that the nested commutators satisfy

$$\begin{aligned}&\left[\frac{\mathrm{e}^{-a\hat{x}}}{\mathrm{i}\hbar a}\hat{p},\, \mathrm{e}^{2na\hat{x}-\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}(a\hat{x}+\mathrm{e}^{-a\hat{x}})}\right] \\ &= \left(-2n + \frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}(1 - \mathrm{e}^{-a\hat{x}})\right)\mathrm{e}^{(2n-1)a\hat{x}-\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}(a\hat{x}+\mathrm{e}^{-a\hat{x}})}.\end{aligned} \tag{40}$$

The first associated Laguerre polynomial is given by $L_1^{(\alpha)}(y) = -y + \alpha + 1$, which tells us that

$$y = \frac{2\sqrt{2\mu D_{\mathrm{e}}}}{\hbar a}\mathrm{e}^{-a\hat{x}} \tag{41}$$

and

$$\alpha_n = -(2n+1) + \frac{2\sqrt{2\mu D_{\mathrm{e}}}}{\hbar a} \qquad (l = 1). \tag{42}$$

Next, we compute the second nested commutator, with $l = 2$, to find that

$$\begin{aligned}
&\left[\frac{\mathrm{e}^{-a\hat{x}}}{\mathrm{i}\hbar a}\hat{p},\left[\frac{\mathrm{e}^{-a\hat{x}}}{\mathrm{i}\hbar a}\hat{p},\ \mathrm{e}^{2na\hat{x}-\frac{2\sqrt{2\mu D_{\mathrm{e}}}}{\hbar a}(a\hat{x}+\mathrm{e}^{-a\hat{x}})}\right]\right]\\
&=\left[\frac{\mathrm{e}^{-a\hat{x}}}{\mathrm{i}\hbar a}\hat{p},\left(-2n+\frac{2\sqrt{2\mu D_{\mathrm{e}}}}{\hbar a}(1-\mathrm{e}^{-a\hat{x}})\right)\mathrm{e}^{(2n-1)a\hat{x}-\frac{2\sqrt{2\mu D_{\mathrm{e}}}}{\hbar a}(a\hat{x}+\mathrm{e}^{-a\hat{x}})}\right]\\
&=\left(2n(2n-1)+\frac{2\sqrt{2\mu D_{\mathrm{e}}}}{\hbar a}(-(4n-1)+2(2n-1)\mathrm{e}^{-a\hat{x}})\right.\\
&\qquad\left.+\frac{8\mu D_{\mathrm{e}}}{\hbar^2 a^2}(1-2\mathrm{e}^{-a\hat{x}}+\mathrm{e}^{-2a\hat{x}})\right)\mathrm{e}^{(2n-2)a\hat{x}-\frac{2\sqrt{2\mu D_{\mathrm{e}}}}{\hbar a}(a\hat{x}+\mathrm{e}^{-a\hat{x}})}.
\end{aligned} \tag{43}$$

Now, we have $L_2^{(\alpha)}(y) = \frac{1}{2}(y^2 - 2(\alpha+2)y + (\alpha+1)(\alpha+2))$. Comparing to equation (43), we find that we have the same y as in equation (41), and the same α as in equation (42), so they appear to be independent of l.

This is now sufficient for us to come up with the induction hypothesis, which is that

$$\begin{aligned}
&\left[\frac{\mathrm{e}^{-a\hat{x}}}{\mathrm{i}\hbar a}\hat{p},\left[\frac{\mathrm{e}^{-a\hat{x}}}{\mathrm{i}\hbar a}\hat{p},\left[\cdots,\left[\frac{\mathrm{e}^{-a\hat{x}}}{\mathrm{i}\hbar a}\hat{p},\ \mathrm{e}^{2na\hat{x}-\frac{2\sqrt{2\mu D_{\mathrm{e}}}}{\hbar a}(a\hat{x}+\mathrm{e}^{-a\hat{x}})}\right]\cdots\right]\right]\right]_l\\
&=l!L_l^{(\alpha_n)}\left(\frac{2\sqrt{2\mu D_{\mathrm{e}}}}{\hbar a}\mathrm{e}^{-a\hat{x}}\right)\mathrm{e}^{\left(2n-l\right)a\hat{x}-\frac{2\sqrt{2\mu D_{\mathrm{e}}}}{\hbar a}(a\hat{x}+\mathrm{e}^{-a\hat{x}})}.
\end{aligned} \tag{44}$$

We verify this general result by assuming it holds for all values up to l, and then prove it holds for $l + 1$. We have already established that it does hold for $l = 1$ and $l = 2$. Writing it down for $l + 1$ and using the result for l then gives us

$$\begin{aligned}
&\left[\frac{\mathrm{e}^{-a\hat{x}}}{\mathrm{i}\hbar a}\hat{p},\left[\frac{\mathrm{e}^{-a\hat{x}}}{\mathrm{i}\hbar a}\hat{p},\left[\cdots,\left[\frac{\mathrm{e}^{-a\hat{x}}}{\mathrm{i}\hbar a}\hat{p},\ \mathrm{e}^{2na\hat{x}-\frac{2\sqrt{2\mu D_{\mathrm{e}}}}{\hbar a}(a\hat{x}+\mathrm{e}^{-a\hat{x}})}\right]\cdots\right]\right]\right]_{l+1}\\
&=\left[\frac{\mathrm{e}^{-a\hat{x}}}{\mathrm{i}\hbar a}\hat{p},\ l!L_l^{(\alpha_n)}\left(\frac{2\sqrt{2\mu D_{\mathrm{e}}}}{\hbar a}\mathrm{e}^{-a\hat{x}}\right)\mathrm{e}^{\left(2n-l\right)a\hat{x}-\frac{2\sqrt{2\mu D_{\mathrm{e}}}}{\hbar a}(a\hat{x}+\mathrm{e}^{-a\hat{x}})}\right].
\end{aligned} \tag{45}$$

We will use the Leibniz rule to evaluate the commutator. The commutator of the exponential is easy to work out, as we have done this before. The commutator of the associated Laguerre polynomial is more complicated. We have

$$\frac{1}{\mathrm{i}\hbar a}\left[\hat{p},\,L_l^{(\alpha_n)}\left(\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}\mathrm{e}^{-a\hat{x}}\right)\right]=\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}\mathrm{e}^{-a\hat{x}}L_l^{(\alpha_n)\prime}\left(\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}\mathrm{e}^{-a\hat{x}}\right),\tag{46}$$

where the prime indicates the derivative of the associated Laguerre polynomial. Now, the associated Laguerre polynomials satisfy a simple derivative rule, given by

$$L_l^{(\alpha)\prime}(y)=-L_{l-1}^{(\alpha+1)}(y).\tag{47}$$

Next, we use the associated Laguerre polynomial recurrence relations to re-express our results as follows:

$$\begin{aligned}-L_{l-1}^{(\alpha+1)}(y)&=L_l^{(\alpha)}(y)-L_l^{(\alpha+1)}(y)\\&=\frac{l}{y}L_l^{(\alpha)}(y)-\frac{l+\alpha}{y}L_{l-1}^{(\alpha)}(y).\end{aligned}\tag{48}$$

This now allows us to compute the commutator. We find

$$\begin{aligned}&\left[\frac{\mathrm{e}^{-a\hat{x}}}{\mathrm{i}\hbar a}\hat{p},\left[\frac{\mathrm{e}^{-a\hat{x}}}{\mathrm{i}\hbar a}\hat{p},\left[\cdots,\left[\frac{\mathrm{e}^{-a\hat{x}}}{\mathrm{i}\hbar a}\hat{p},\,\mathrm{e}^{2na\hat{x}-\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}(a\hat{x}+\mathrm{e}^{-a\hat{x}})}\right]\cdots\right]\right]\right]_{l+1}\\&=l!\left(\left(2l+1+\alpha_n-\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}\mathrm{e}^{-a\hat{x}}\right)L_l^{(\alpha_n)}\left(\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}\mathrm{e}^{-a\hat{x}}\right)\right.\\&\quad\left.-(l+\alpha_n)L_{l-1}^{(\alpha_n)}\left(\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}\mathrm{e}^{-a\hat{x}}\right)\right)\mathrm{e}^{\left(2n-l-1\right)a\hat{x}-\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}(a\hat{x}+\mathrm{e}^{-a\hat{x}})}\end{aligned}\tag{49}$$

Now, we need to use our final recurrence relation for the associated Laguerre polynomials, which is

$$(2l+1+\alpha-y)L_l^{(\alpha)}(y)-(l+\alpha)L_{l-1}^{(\alpha)}(y)=(l+1)L_{l+1}^{(\alpha)}(y).\tag{50}$$

This shows that the term in the parenthesis on the right hand side of equation (49) is equal to $(l+1)L_{l+1}^{(\alpha_n)}(y)$, which is what is needed to complete the proof by induction. Hence, we have shown that equation (44) holds. The associated Laguerre polynomial recurrence relations used here can be found in [23].

The state we are interested in is the one with $l=n$. Noting thar $|\phi_0^{(n)}\rangle$ is the same as $|\psi_n\rangle$ and that $C_0^{(n)}=C_n$, we now find that the wavefunction can be written as

$$\begin{aligned}\psi_n(x)=\langle x|\psi_n\rangle&=C_n\left(\frac{\mathrm{i}\hbar a}{\sqrt{2\mu}}\right)^n n!\,\mathrm{e}^{-2nax}L_n^{(\alpha_n)}\left(\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}\mathrm{e}^{-a\hat{x}}\right)\langle x|\phi_n\rangle\\&=(\mathrm{i}^n)\sqrt{n!}\sqrt{\frac{\Gamma\left(\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}-2n\right)}{\Gamma\left(\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}-n\right)}}\,\mathrm{e}^{-2nax}L_n^{(\alpha_n)}\left(\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}\mathrm{e}^{-a\hat{x}}\right)\phi_n(x),\end{aligned}\tag{51}$$

after working out the constant C_n using the fact that

$$\begin{aligned}E_n-E_m&=(n-m)\frac{\hbar a}{\mu}\sqrt{2\mu D_\mathrm{e}}+(n-m)(m+n+1)\frac{\hbar^2a^2}{2\mu}\\&=\frac{\hbar^2a^2}{2\mu}(n-m)\left(\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}-n-m-1\right).\end{aligned}\tag{52}$$

Here, $\Gamma(z)$ is the gamma function. Note that the nth auxiliary Hamiltonian ground state $\phi_n(x)$ must be normalized in this expression.

To calculate $\phi_n(x)$ we use the fact that $\hat{p}$ annihilates $\mathrm{e}^{\hat{B}_n}|\phi_n\rangle$, as follows: First, we introduce a factor of $1 = \mathrm{e}^{-\hat{B}_n}\mathrm{e}^{\hat{B}_n}$ to the left of $|\phi_n\rangle$ and evaluate $\mathrm{e}^{-\hat{B}_n}$ against the position bra $\langle x|$ to find that

$$\phi_n(x) = \langle x|\phi_n\rangle = \langle x|\mathrm{e}^{-\hat{B}_n}\mathrm{e}^{\hat{B}_n}|\phi_n\rangle = \mathrm{e}^{-\left(\frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar a}-n-\frac{1}{2}\right)ax}\mathrm{e}^{-\frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar a}\mathrm{e}^{-ax}}\langle x|\mathrm{e}^{\hat{B}_n}|\phi_n\rangle. \tag{53}$$

Next, we use the fact that the position bra can be re-expressed as the translation of the position state at the origin to the position x via $\langle x|=\langle 0_x|\mathrm{e}^{\frac{i}{\hbar}x\hat{p}}$. Then, because the $\hat{p}$ operator annihilates $\mathrm{e}^{\hat{B}_n}|\phi_n\rangle$, the translation operator can be replaced by 1 after acting on the state to its right. Then, the $\mathrm{e}^{\hat{B}_n}$ operator can act to the left against the position state at the origin, replacing $\hat{x}$ by 0. We finally find that

$$\phi_n(x) = \mathrm{e}^{-\left(\frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar a}-n-\frac{1}{2}\right)ax}\mathrm{e}^{-\frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar a}(\mathrm{e}^{-ax}-1)}\langle 0_x|\phi_n\rangle. \tag{54}$$

The factor $\langle 0_x|\phi_n\rangle$ is the value of the wavefunction at the origin, which is our normalization constant. To determine it, we need to evaluate the following integral:

$$\begin{aligned}1 &= |\langle 0_x|\phi_n\rangle|^2\int_{-\infty}^{\infty}\mathrm{d}x\ \mathrm{e}^{-\left(\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}-2n-1\right)ax}\mathrm{e}^{-\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}(\mathrm{e}^{-ax}-1)}\\ &= |\langle 0_x|\phi_n\rangle|^2\mathrm{e}^{\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}}\frac{1}{a}\left(\frac{\hbar a}{2\sqrt{2\mu D_\mathrm{e}}}\right)^{\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}-2n-1}\Gamma\left(\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}-2n-1\right),\end{aligned} \tag{55}$$

and solve for $\langle 0_x|\phi_n\rangle$.

Putting everything together, we obtain the final formula for the nth excited state of the Morse potential is given by

$$\begin{aligned}\psi_n(x) = &\sqrt{\frac{an!\left(\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}-2n-1\right)}{\Gamma\left(\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}-n\right)}}\left(\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}\mathrm{e}^{-ax}\right)^{\frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar a}-n-\frac{1}{2}}\\ &\times L_n^{\left(\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}-2n-1\right)}\left(\frac{2\sqrt{2\mu D_\mathrm{e}}}{\hbar a}\mathrm{e}^{-a\hat{x}}\right)\mathrm{e}^{-\frac{\sqrt{2\mu D_\mathrm{e}}}{\hbar a}\mathrm{e}^{-ax}}\end{aligned} \tag{56}$$

where we removed a factor of i^n, because it is a global phase factor. This is the standard result for the wavefunction of the Morse potential. Recall that when working with it for a molecule, we replace $x \rightarrow \bar{x} - x_\mathrm{e}$, with x_e the equilibrium separation of the molecule.

In figure 3, we plot the first four probability distributions for a harmonic oscillator that fits the Morse potential and the first six for the Morse potential. While the ground state is nearly identical (both in energy and in the probability distribution) for the two potentials, they rapidly differ for higher levels. This is the reason why the Morse potential is a much better approximation to the molecular potential for fitting vibrations than the harmonic oscillator,

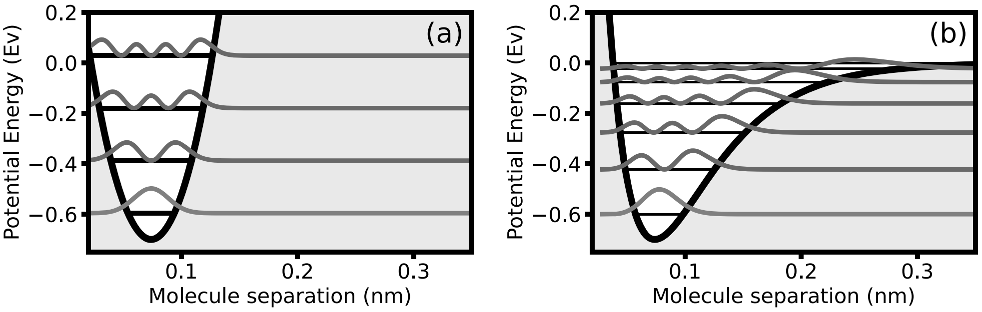

Figure 3. (a) Harmonic oscillator probability distributions for the first four eigenstates and (b) Morse probability distributions for the first six eigenstates a potential that has 7 vibrational states. The harmonic oscillator is set to fit the curvature of the Morse potential at its minimum and displaced downward in energy to coincide with the minimum. The gray region is the forbidden region. Note how the higher-n Morse probability distributions become more and more asymmetric, with long tails stretching to the right and how the harmonic oscillator energy levels differ significantly for larger n.

5. Pedagogical ideas for working with students

In this section, we present some ideas of activities that students can do who are working with this material. The first one is that we can approximate the Morse potential near its minimum by a quadratic potential by simply performing a Taylor series expansion about $x = 0$. Have the students determine the frequency of the harmonic oscillator and compare the energies of the harmonic oscillator with the corresponding harmonic oscillator energy. How different are these energies at the last allowed bound state of the Morse potential?

A second example, is to have the students look at real experimental data for vibrational energy levels of diatomic molecules. One can have them fit the spectra, which correspond to energy-level differences, to determine the parameters of the Morse potential that fits the molecule best. They can then count the number of bound states and see how that compares to the total number of bound states for the molecule.

The parameter D_e is called the dissociation energy in the Morse potential, as it is supposed to represent the energy needed to dissociate the molecule from its ground state. But this estimate is too high. The true dissociation energy is the $|E_0|$. Have students write an essay about how they can use the experimental dissociation energy and molecular spectroscopy to fit all of the parameters of the Morse potential.

Finally, one can also ask students to work through different parts of the derivation, such as determining C_n or finding the normalization constant for $\phi_n(x)$. Once the wavefunctions are found, have students plot them out and discuss their behavior, as compared to those of the simple harmonic oscillator.

6. Summary

Quantum mechanics has many exactly solvable problems, but we only show the students a small subset of them. One of the reasons why is that the conventional Frobenius method for solving differential equations becomes very tedious for these other exactly solvable problems, so they are often not covered. This is a pity, because there are lots of interesting results about these systems that should be discussed with students to help them connect the formal ideas of quantum mechanics to experiment.

In this work, we showed an alternative way to solve the Morse potential problem, avoiding the use of differential equations completely and instead working with operators in a representation-independent fashion. This approach illustrates how we can solve exactly solvable problems using the factorization method and the hidden structure of the factorization chain, which is not known to many students. It also allows us to find the wavefunctions in a straightforward way, which is more concrete than differential equation based approaches.

We hope that instructors will consider using these ideas in graduate-level quantum mechanics classes to show how theory is connected to experiment and to add more exactly solvable solutions into the classroom than just the particle in a box, delta function potentials, the harmonic oscillator and the Coulomb problem. Additionally, teaching the operator method prepares students for the language of second quantization. Consequently, exposing students early on to the operator-based language helps them to develop mastery of both operator algebras and differential equations, which allows them to advance faster in future more advanced topics.

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Data availability statement

No new data were created or analysed in this study.

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