Morse potential on a quantum computer and supersymmetric quantum mechanics

Joshua A. Apanavicius[1] and Michael D. McGuigan[2]
[1)] *Department of Physics, Indiana University, Bloomington, IN 47405*
[2)] *Computational Science Initiative, Brookhaven National Laboratory, Upton, NY 11973*

(Dated: 27 September 2020)

In this paper we discuss the Morse potential on a quantum computer. The Morse potential is useful to describe diatomic molecules and has a finite number of bound states which can be measured through spectroscopy. It is also a example of an exactly soluble potential using super-symmetric quantum mechanics. Using the super-symmetric quantum mechanics formalism one can derive a hierarchy of Hamiltonians such that the ground state of the next rung on the hierarchy yields the first excited state of the Hamiltonian below it. Using this method one can determine all the states of the Morse potential by calculating all the ground states of the sequence of Hamiltonians in the hierarchy. We use IBM's Quantum Information Software Kit (QISKit) together with the Variational Quantum Eigensolver (VQE) algorithm to calculate all the ground state energies of the sequence of Hamiltonians and find agreement with the exact expression for the bound state energies of the Morse Potential. We analyze different variational forms, Hamiltonian mappings and optimizers to study the numerical effect on the calculations. Finally we discuss the application of a direct variational calculation of excited states for the Morse potential.

I. INTRODUCTION

The Morse potential was introduced in 1929[1] to describe the bound state energies of diatomic molecules. The potential also serves as an example of an exactly soluble model in that one can analytically determine all the eigenstates and eigenvalues. The exact solvablity can be traced back to it's relation to super-symmetric quantum mechanics (SusyQM), definition of ladder operators and a set of Hamiltonians that are related by a change of parameters in the potential. The use of VQE has been shown to be an efficient quantum algorithm for the calculation of ground state energies on noisy intermediate scale quantum computers. Having an exact solution for the Morse potential gives us an excellent point of comparison and allows us to see what level of accuracy can be achieved on current quantum computing hardware and software.

This paper will serve as an introduction to the calculation of bound states using the hierarchy of Hamiltonian method as well as a study of the Morse potential on a quantum computer. First we will go over the theoretical underpinnings of the VQE algorithm by introducing the Variational method from which the VQE algorithm originated from. We will work through an example of calculating the ground state energy of the heavily studied anharmonic oscillator with the variational method. Then we will go over the relation of the Morse potential to supersymmetric quantum mechanics, discuss the hierarchy of Hamiltonians approach for the Morse potential and how this can be used to calculate all the bound states, and give the exact solutions to the Morse potential's bound states. Next we discuss the calculation of the bound states for the Morse potential using the VQE algorithm and compare our results to the exact calculation. We discuss various parameters involved with running VQE such as variational forms, optimizers, quantum circuit depth, and number of shots (measurements) that are used in the calculation. Finally, we will end with a brief overview of the main results from this research and try to give an outline of the issues we faced and give insights for future research in this area.

II. METHODS

A. The Variational Method

In many instances the eigenvalue problem is impossible to solve exactly. This is one of the reasons the anharmonic oscillator and Morse potential were chosen for this study, they fall into the rare class of exactly solvable equations. However, many approximation methods exist that can give very accurate results. One very powerful approximation is the variational method. It is an approximation that guarantees to find an upper bound for the ground state energy E_0 encoded in the Hamiltonian H within the state ψ. The variational method can be seen as a way to construct a function $E(\psi)$, where $E(\psi)$ is the mean value of the energy in the state $|\psi\rangle$, which is easily computed using the following relation:[2]

$$E_0 \leqslant \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \equiv E(\psi) \tag{1}$$

The variational method is powerful because it can give an accurate idea of the ground state energy of essentially any system by constructing a simple function that in reality does nothing more than calculate two integrals on a random wave function. When compared to solving a set of differential equations, the complexity pales in comparison.

1. *Example: The Anharmonic Oscillator*

The Anharmonic Oscillator has a potential of the form

$$V(x) = \lambda x^4 \tag{2}$$

where λ is a constant. Meaning the Hamiltonian is of the form:

$$H = p^2 + \lambda x^4 \tag{3}$$

The first step in the variational method is to choose a trial wave function that we hope best represents the actual wave function. Unfortunately this boils down to a complete guess, but we can still get very accurate results with some reasoning. We expect the following with regards to the ground state: it will have even parity, no nodes, peak at $x = 0$ (so as to minimize $V(x)$), and vanish as $|x| \to \infty$. A trial wave function that has all of these properties with the added nicety of being easy to integrate and differentiate is a Gaussian of the form:

$$\psi(x,\alpha) = e^{-\alpha x^2/2}$$

where α is a free parameter. Therefore, the energy function $E(\psi)$ as a function of α is:

$$E(\alpha) = \frac{\int e^{-\alpha x^2/2}(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \lambda x^4)e^{-\alpha x^2/2}dx}{\int e^{-\alpha x^2/2}dx}$$

$$E(\alpha) = \frac{\hbar^2\alpha}{4m} + \frac{3\lambda}{4\alpha^2}$$

Our goal is to find E_0, which means we need to find the minimum of $E(\alpha)$. To do this we simply differentiate $E(\alpha)$, set it equal to 0, and solve for α

$$\frac{dE}{d\alpha} = \frac{\hbar^2}{4m} - \frac{3\lambda}{2\alpha^3} = 0 \implies \alpha_0 = \left(\frac{6m\lambda}{\hbar^2}\right)^{1/3}$$

α_0 corresponds to the minimum of the energy function, which is:

$$E(\alpha_0) = \frac{3}{8}\left(\frac{6\hbar^4\lambda}{m^2}\right)^{1/3}$$

We know for a fact that the ground state energy of the anharmonic oscillator is roughly 1.06 eV. Using units such that $\hbar = 1$ $\lambda = 1$, along with $m = \frac{1}{2}$ and plug them into $E(\alpha_0)$, we get 1.08. With the agreed upon value being 1.06, the variational method gives an approximation within 3% of the actual value without having to solve any differential equations. We will now apply this method algorithmically using VQE.[2]

B. VQE Workflow

The Variational Quantum Eigensolver is a hybrid classical/quantum algorithm that iteratively calculates the expectation value of Hamiltonians ($\langle H \rangle$) in many different predetermined quantum states in many quantum modules on a Quantum Processin Unit (QPU). The expectation values are then averaged and optimized on classical CPUs before starting the process over again. An overview of this algorithm is shown in Figure 1.

C. Workflow

The general workflow for running VQE is as follows: First, generate a Hamiltonian in the form of a text file for each energy level in each basis. This is done in Wolfram Mathematica because it is very easy to represent complex mathematical formulas in. Mathematica also has powerful Eigensolvers that we use to further check the exact values of the energy levels. Next, we load the Mathematica generated text file representation of each Hamiltonian into QISKit and run the VQE. QISKit also has a classical eigensolver that we use as the value for the optimizers to aim for.

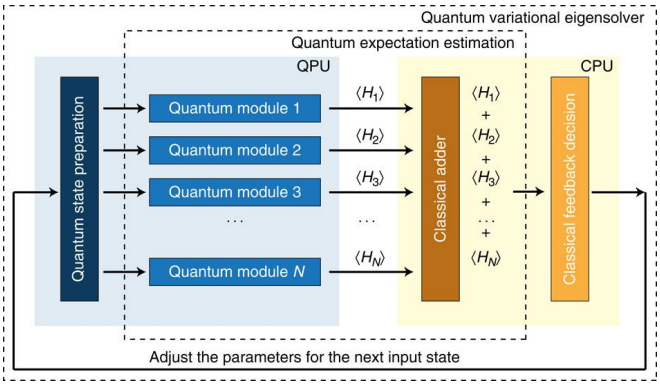

FIG. 1. The Variational Quantum Eigensolver architecture: **Algorithm 1:** Previously prepared quantum states are fed into quantum modules to compute $\langle H_i \rangle$, where H_i is any given term in the sum defining H. The results are passed to the CPU which computes $\langle H_i \rangle$. **Algorithm 2:** Determines the new state parameters by running a classical minimization algorithm on the CPU to find $\langle H \rangle$ and inputs this into the QPU.[3]

D. QISKit VQE Parameters

The VQE algorithim has a number of parameters that can greatly effect the outcome of the calculation. The main parameters of interest are:

- Variational Form
- Initial state
- Optimizer
- Depth
- Number of shots
- Number of qubits

we will breifly go through each to explain what they are.

1. *Variational Form*

Trial wave function, ψ, that is dependent on a certain number of parameters.

2. *Initial State*

The initial state of the variational form.

3. Optimizer

The optimizers in QISKit optimize the parameters for the trial wave function in an attempt to find the minimum (ground state) of the wave function. QISKit has many optimizers at its disposal, but we will use the following:

- Simultaneous Perturbation Stochastic Approximation (SPSA)
- Constrained Optimization BY Linear Approximation (COBYLA) - A numerical optimization method for constrained problems where the derivative of the objective function is not known.
- Limited-memory Broyden-Fletcher-Goldfarb-Shanno Bound (L-BFGS-B) - An iterative method for solving unconstrained, non-linear optimization problems, but approximates BFGS using a limited amount of computer memory.
- Sequential Least SQuares Programming (SLSQP) - Minimizes a function of several variables with any combination of bounds, equality and inequality constraints.

4. Depth

The length of the longest path from the input of the circuit to the output.

5. Shots

The number of measurements for each iteration.

6. Number of qubits

The number of qubits determines the size of the position and momentum operators. n qubits correspond to a matrix of size 2^n. We primarily used four qubits, making all of our operators 16×16 in size.

E. The Morse Potential

In its relation to supersymmetric quantum mechanics the Morse potential is written as:

$$V_-(x,A) = e^{-2x} - (2A+1)e^{-x} + A^2 \tag{4}$$

with A given by the Morse parameter. This potential is shown in Fig. 2 for $A = 5$.

To make the connection with supersymmetric quantum mechanics we write the minus and plus partner potential as:

$$\begin{aligned} V_-(x) &= W(x)^2 - W'(x) \\ V_+(x) &= W(x)^2 + W'(x) \end{aligned} \tag{5}$$

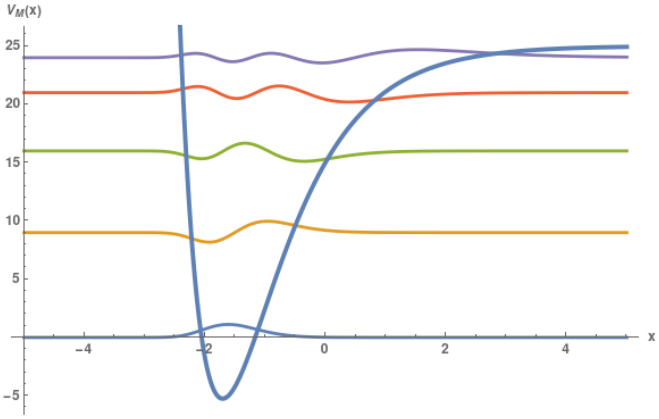

FIG. 2. Morse potential for $A = 5$ with five bound state energies $0, 9, 16, 21, 24$

where the superpotential $W(x)$ is given by:

$$W(x) = A - e^{-x}$$

so that the plus partner potential is given by:

$$V_+(x,A) = e^{-2x} - (2A-1)e^{-x} + A^2$$

The partner Hamiltonians are:

$$\begin{aligned} H_- &= p^2 + V_-(x) = p^2 + W(x)^2 - W'(x) \\ H_+ &= p^2 + V_+(x) = W(x)^2 + W'(x) \end{aligned} \tag{6}$$

where we have set $2m = 1$. The ladder operators are given by:

$$\begin{aligned} a &= ip + W(x) = ip + A - e^{-x} \\ a^\dagger &= -ip + W(x) = -ip + A - e^{-x} \end{aligned} \tag{7}$$

Then the partner Hamiltonians can be realized as:

$$\begin{aligned} H_- &= a^\dagger a \\ H_+ &= aa^\dagger \end{aligned} \tag{8}$$

One can then form a hierarchy of Hamiltonians as $H_i = p^2 + V_i(x)$ where:

$$\begin{aligned} V_0(x) &= V_-(x,A) \\ V_1(x) &= V_+(x,A) \\ V_2(x) &= V_+(x,A-1) + 2A - 1 \\ V_3(x) &= V_+(x,A-2) + 4A - 4 \\ V_4(x) &= V_+(x,A-3) + 6A - 9 \end{aligned} \tag{9}$$

These are plotted in Fig. 3 Exact solutions to the Schrodinger equation can be obtained using the ladder operators for the Morse potential. The expressions are given by: with eigenfunctions:

$$\psi_n^-(x) = e^{-x(A-n)} e^{-e^{-x}} L_n^{(2A-2n)}(2e^{-x}) \tag{10}$$

with $L_n^{(k)}(y)$ the associated Laguerre polynomials. with bound state energies:

$$E_n = A^2 - (A-n)^2 \tag{11}$$

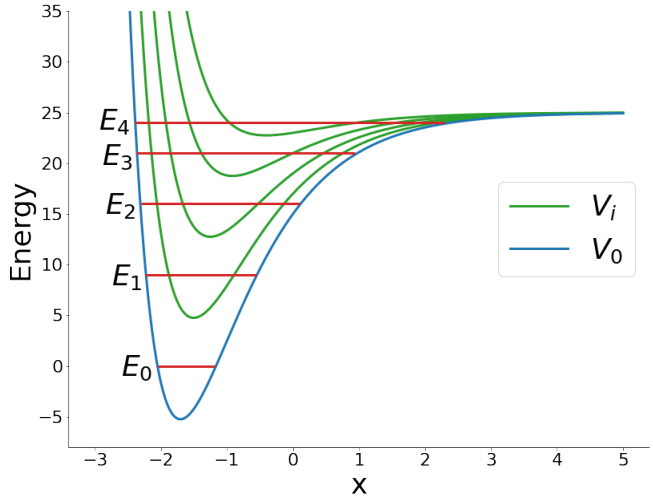

FIG. 3. Hierarchy of Hamiltonians associated with the Morse potential for $A = 5$. Each horizontal line represents an energy level given by equation 11

For $A = 5$ these are given by:

$$E_0 = 0 \tag{12}$$
$$E_1 = 9 \tag{13}$$
$$E_2 = 16 \tag{14}$$
$$E_3 = 21 \tag{15}$$
$$E_4 = 24$$

which correspond to the energy levels of the Morse potential shown in Fig. 3

III. CALCULATION OF MORSE POTENTIAL BOUND STATE ENERGIES USING THE VQE

Before one can set up the calculation to compute ground state energies using the VQE we need to perform a Hamiltonian mapping in terms of qubits. The first step is to represent the Hamiltonian as a $N \times N$ matrix using a discrete quantum mechanics approximation to the quantum mechanical operators which would be infinite dimensional for bosonic observables. In this paper we will explore three different types of discrete Hamiltonians and compare the results from each.

A. Gaussian or Simple Harmonic Oscillator basis

This is a very useful basis based on the matrix treatment of the simple harmonic oscillator which is sparse in representing the position and momentum operator. For the position operator we have:

$$X_{osc} = \begin{bmatrix} 0 & \sqrt{1} & 0 & \cdots & 0 \\ \sqrt{1} & 0 & \sqrt{2} & \cdots & 0 \\ 0 & \sqrt{2} & \ddots & \ddots & 0 \\ 0 & 0 & \ddots & 0 & \sqrt{N-1} \\ 0 & 0 & \cdots & \sqrt{N-1} & 0 \end{bmatrix} \tag{16}$$

while for the momentum operator we have:

$$P_{osc} = \frac{i}{2} \begin{bmatrix} 0 & -\sqrt{1} & 0 & \cdots & 0 \\ \sqrt{1} & 0 & -\sqrt{2} & \cdots & 0 \\ 0 & \sqrt{2} & \ddots & \ddots & 0 \\ 0 & 0 & \ddots & 0 & -\sqrt{N-1} \\ 0 & 0 & \cdots & \sqrt{N-1} & 0 \end{bmatrix} \tag{17}$$

The Morse Hamiltonian H_- is then

$$H_- = P_{osc}^2 + Exp(-2X_{osc}) - (2A+1)Exp(-X_{osc}) + A^2 I \tag{18}$$

where Exp refers to the Matrix exponential and I is the $N \times N$ identity matrix.

B. Position basis

In the position basis the position matrix is diagonal but the momentum matrix is dense and constructed from the position operator using a Sylvester matrix F. In the position basis the position matrix is:

$$(X_{pos})_{j,k} = \sqrt{\frac{2\pi}{4N}}(2j - (N+1))\delta_{j,k} \tag{19}$$

and the momentum matrix is:

$$P_{pos} = F^{\dagger} X_{pos} F$$

where

$$F_{j,k} = \frac{1}{\sqrt{N}} e^{\frac{2\pi i}{4N}(2j-(N+1))(2k-(N+1))}$$

The Morse Hamiltonian is formed from

$$H_- = P_{pos}^2 + e^{(-2X_{pos})} - (2A+1)e^{(-X_{pos})} + A^2 I \tag{20}$$

but in this case the matrix exponential is very simple as it is the exponential of a diagonal matrix.

C. Finite difference basis

This type of basis arises when differential equations are rewritten in terms of finite difference equations. In this case the position operator is again diagonal but the momentum operator, although not diagonal, is still sparse. In the finite difference basis the position matrix is:

$$(X_{fd})_{j,k} = \sqrt{\frac{1}{2N}}(2j - (N+1))\delta_{j,k}$$

and the momentum-squared matrix is:

$$P_{fd}^2 = \frac{N}{2}\begin{bmatrix} 2 & -1 & 0 & \cdots & 0 \\ -1 & 2 & -1 & \cdots & 0 \\ 0 & -1 & \ddots & \ddots & 0 \\ 0 & 0 & \ddots & 2 & -1 \\ 0 & 0 & \cdots & -1 & 2 \end{bmatrix} \quad (21)$$

The Morse Hamiltonian is then:

$$H_- = P_{fd}^2 + Exp(-2X_{fd}) - (2A+1)Exp(-X_{fd}) + A^2 I \quad (22)$$

IV. RESULTS

We first go through the results found from the Mathematica scripts used to generate the text file Hamiltonians that were fed into our QISKit simulations. The we go through all of the simulations that were ran on either a local qasm simulator from QISKit or the IBMQ qasm simulator. We find that the IBMQ simulator performs orders of magnitude better than the local qasm simulator.

A. Morse Potential

1. *Mathematica*

BASIS	STATE	ENERGY	MATHEMATICA	% ERROR
Position	E_0	0	-0.00302	0.0121
	E_1	9	8.86163	1.5374
	E_2	16	16.0054	0.0338
	E_3	21	21.0028	0.0133
	E_4	24	23.9999	0.0004
Oscillator	E_0	0	0.09977	0.3991
	E_1	9	9.4035	4.4833
	E_2	16	15.8266	1.0838
	E_3	21	20.9531	0.2233
	E_4	24	24.0026	0.0108
Finite Difference	E_0	0	0.41809	1.6724
	E_1	9	8.90641	1.0399
	E_2	16	16.4100	2.5625
	E_3	21	21.3636	1.7314
	E_4	24	23.9884	0.0483

TABLE I. Results from Mathematica's implementation of an eigensolver

2. *IBMQ qasm simulator*

The results outlined in Table III where obtained using IBM's QASM simulator that was accessed through the IBM Quantum experience API. Note only the position basis was ran because we ran into connectivity issues with the API and could not run the other Hamiltonians.

State	Variational Form	Optimizer	Depth	# of Shots	# of qubits
E_0	RY	SPSA	20	1000	3
E_1	RY	SPSA	10	1000	3

TABLE II. Simulation Parameters for Table III

BASIS	STATE	ENERGY	VQE	% ERROR
Position	E_0	0	1.0653	19.5962
	E_1	9	8.3889	0.9589

TABLE III. Results from IBMQ qasm Simulator

Figures 4 and 5 visualize how the optimizer converges to the minimul eigenvalue for these two runs IBMQ's qasm simulator:

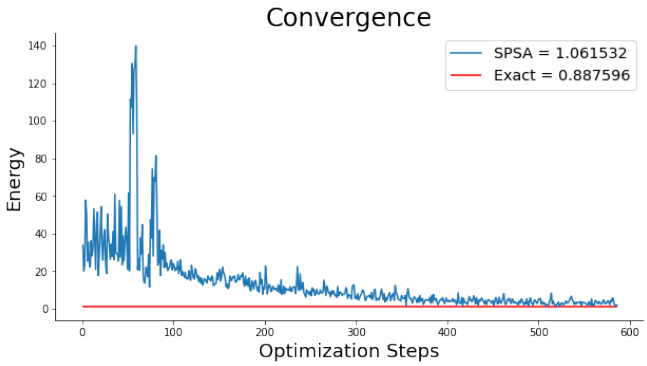

FIG. 4. Ground state VQE calculation for the Morse potential

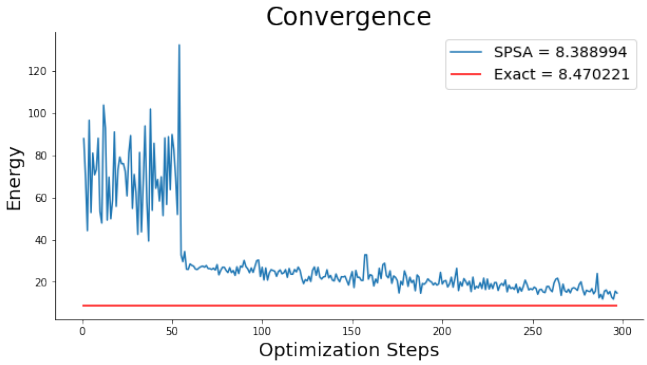

FIG. 5. First excited state VQE calculation for the Morse potential

3. *Local qasm simulator*

All of the simulations outlined below were ran on the QASM simulator from QISKit with the following parameters:

Variational Form	Optimizer	Depth	# of Shots	# of qubits
RY	SPSA	20	8000	4

TABLE IV. Simulation parameters for Table V

BASIS	STATE	ENERGY	VQE	% ERROR
Position	E_0	0	34.2388	1.13e+06
	E_1	9	26.6279	200.485
	E_2	16	27.01	68.76
	E_3	21	23.0975	9.9736
	E_4	24	29.7551	23.98
Oscillator	E_0	0	229.237	229661
	E_1	9	1972.98	20881.3
	E_2	16	-306.793	2038.47
	E_3	21	2311.86	10933.5
	E_4	24	2695.41	11129.6
Finite Difference	E_0	0	29.2759	6902.3
	E_1	9	662.993	7343.99
	E_2	16	155.684	848.71
	E_3	21	2027	9388.1
	E_4	24	30.3296	26.4346

TABLE V. Results for local qasm simulator

V. CONCLUSION

We successfully implemented the hierarchy of Hamiltonian method to calculate the first two bound states of the Morse potential using the VQE algorithm on IBM's qasm simulator. We were able to run VQE on the first five energy states on a local qasm simulator, but the results were much worse.

In section two we went over the main parameters involved with running VQE. However, there are many more options and settings that have yet to be explored. This is mainly due to run times being on the order of hours, sometimes days for a single run on local simulators. For example, we found that in some instances increasing the depth up to 50 can yield very good results, but the simulation took almost three days to complete. At some point we want to deploy this on a real quantum computer, which at the moment would be subjected to queuing as they are public machines, which further increases an already long run time. As previously mentioned, all VQE algorithms were ran on classical machines simulating the nature of quantum computers. In the future we hope to run everything on real quantum hardware. We also hope to take a deeper dive into noise and error mitigation as that is the current bottleneck in the quantum computing realm. All code used to run the simulations discussed in this paper can be found at the following GitHub repository: github.com/japanavi/morse_vqe

VI. ACKNOWLEDGMENTS

I would like to thank my mentor Michael McGuigan for his continual encouragement, support, and collaboration throughout this project. I would also like to thank Brookhaven National Laboratory for hosting my stay and allowing me to pursue this interesting project. This project was supported in part by the U.S. Department of Energy, Office of Science, Office of Workforce Development for Teachers and Scientists (WDTS) under the Science Undergraduate Laboratory Internships Program (SULI).

VII. REFERENCES

[1] P. M. Morse, "Diatomic Molecules According to the Wave Mechanics. 2. Vibrational Levels," Phys. Rev. **34**, 57 (1929). doi:10.1103/PhysRev.34.57

[2] Shankar, R., 1994. Principles Of Quantum Mechanics. 1st ed. Plenum, pp.439-445.

[3] A. Peruzzo, J. McClean, P. Shadbolt, M. Yung, X. Zhou, P. Love, A. Aspuru-Guzik, J. O'Brien, "A variational eigenvalue solver on a quantum processor", arXiv:1304.3061

[4] A. Bordoni, "Systematic calculation of molecular spectra through a complete Morse expansion".

[5] I. Cooper, "An integrated approach to ladder and shift operators for the Morse oscillator, radial Coulomb and radial oscillator potentials", J. Phys. A: Math. Gen. 26, 1601 (1993).

[6] G. Junker, P. Roy, "Supersymmetric construction of exactly solvable potentials and nonlinear algebras", Physics of atomic nuclei 61, 1736 (1998).

[7] M. Arik, M. Baykal, A. Baykal, "Factorization method for d-dimensional isotropic harmonic oscillator and the generalized Laguerre polynomials", arxiv:0808.2289

[8] M. Berrondo, A. Palma,J. Loez-BonillA, "Matrix elements for the Morse potential using ladder operators", Int.J.Quant.Chem. 31, 243 (1987).

[9] E. Fidiani, Modeling of diatomic molecules using the Morse potential and the Verlet algorithm, AIP Conference Proceeding 1719, 030001 (2016)