Morse potential energy spectra through the variational method and supersymmetry

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Abstract
The Variational Method is applied within the context of Supersymmetric Quantum Mechanics to provide information about the energy and eigenfunction of the lowest levels of a Hamiltonian. The approach is illustrated by the case of the Morse potential applied to several diatomic molecules and the results are compared with established results.

I. Introduction
Two decades ago Supersymmetric Quantum Mechanics, SQM, was born as a simplest case of field theory in the study of SUSY breaking mechanism of higher dimensional quantum field theories, developed to unify the four fundamental interactions in nature, namely the electroweak, strong and gravitational interactions. So far, SQM has been extensively used to explore different aspects of non-relativistic quantum mechanical systems (see, for instance, [1]-[2] and references therein). The new algebraic method is specially good to treat analytically solvable potential problems, [3], [4]. Nevertheless, the approximation methods have shown to be of great interest to provide new results in potential problems. In this context, one has recently suggested that the variational method could be applied within the formalism of SQM, [5]-[7]. This approach has already been successfully applied to the Hulthén potential, [7]. Here the technique is applied to the Morse potential, one of the most successful models to represent the states of diatomic molecules, [8], [9]. The results are shown to be in good agreement with the numerical data and results from the other approximation techniques.

The formalism of variational method can be found in several text books of quantum mechanics, (see for instance [10]); it can be used to obtain the approximate energy spectra of potentials, in particular, the ground-state. The approach consists in using the trial wave-function $\Psi(r)$ that depends of a number of parameters and in

1PACS No. 31.15.Q, 11.30.P
2Work supported in part by CNPq
varying these parameters in the expression for the expectation value of the energy

\[ E = \frac{\int \psi^* H \psi \, dr}{\int |\psi|^2 \, dr} \]  

(1)

where \( H \) is the Hamiltonian of the system. The variational parameters in \( \psi \) are varied until the expectation value of the energy is minimum. This value is an upper limit of the energy level. Usually this method is applied only to get the ground state energy, although it can be applied to get the energy of the excited states as well.

Thus the central point of the variational method approach is the obtention of the trial wavefunction. At this crucial point the superalgebra is used to obtain this function. In what follows, we briefly review the main principles of SQM and introduce the variational method. The case of angular momentum \( l = 0 \), which is exactly solvable, is explicitly evaluated from SQM formalism in order to get the hierarchy. We then apply the variational scheme to the Morse potential for different values of \( l \) and for various diatomic molecules and compare the results with known results from other numerical methods, \([11],[12]\).

II. Supersymmetric Quantum Mechanics

In SQM, \([1]-[7]\), for \( N = 2 \) we have two nilpotent operators, \( Q \) and \( Q^+ \), that satisfy the algebra

\[ \{Q, Q^+\} = H_{SS} \quad ; \quad Q^2 = Q^{+2} = 0, \]  

(2)

where \( H_{SS} \) is the supersymmetric Hamiltonian. This algebra can be realized as

\[ Q = \begin{pmatrix} 0 & 0 \\ A^- & 0 \end{pmatrix}, \quad Q^+ = \begin{pmatrix} 0 & A^+ \\ 0 & 0 \end{pmatrix} \]  

(3)

where \( A^\pm \) are bosonic operators. With this realization the supersymmetric Hamiltonian \( H_{SS} \) is given by

\[ H_{SS} = \begin{pmatrix} A^+ A^- & 0 \\ 0 & A^- A^+ \end{pmatrix} = \begin{pmatrix} H^+ & 0 \\ 0 & H^- \end{pmatrix}. \]  

(4)

\( H^\pm \) are called supersymmetric partner Hamiltonians and share the same spectra, apart from the nondegenerate ground state. Using the super-algebra a given Hamiltonian can be factorized in terms of the bosonic operators. In \( \hbar = c = 1 \) units, it is given by

\[ H_1 = -\frac{1}{2} \frac{d^2}{dr^2} + V_1(r) = A_1^+ A_1^- + E_0^{(1)} \]  

(5)

where \( E_0^{(1)} \) is the lowest eigenvalue and the function \( V_1(r) \) includes the barrier potential term. The bosonic operators are defined by

\[ A_1^\pm = \frac{1}{\sqrt{2}} \left( \mp \frac{d}{dr} + W_1(r) \right) \]  

(6)
where the superpotential $W_1(r)$ satisfies the Riccati equation

$$W_1^2 - W_1' = 2V_1(r) - 2E_0^{(1)}.$$  

(7)

The eigenfunction for the lowest state is related to the superpotential $W$ as

$$\Psi_0^{(1)}(r) = Nexp(-\int_0^r W_1(\bar{r})d\bar{r}).$$  

(8)

Now it is possible to construct the supersymmetric partner Hamiltonian,

$$H_2 = A_1^+ A_1^- + E_0^{(1)} = -\frac{1}{2} \frac{d^2}{dr^2} + \frac{1}{2} (W_1^2 + W_1') + E_0^{(1)}.$$  

(9)

If one factorizes $H_2$ in terms of a new pair of bosonic operators, $A_2^\pm$ one gets,

$$H_2 = A_2^+ A_2^- + E_0^{(2)} = -\frac{1}{2} \frac{d^2}{dr^2} + \frac{1}{2} (W_2^2 - W_2') + E_0^{(2)}.$$  

(10)

where $E_0^{(2)}$ is the lowest eigenvalue of $H_2$ and $W_2$ satisfy the Riccati equation,

$$W_2^2 - W_2' = 2V_2(r) - 2E_0^{(2)}.$$  

(11)

Thus a whole hierarchy of Hamiltonians can be constructed, with simple relations connecting the eigenvalues and eigenfunctions of the $n$-members, $[1], [13]-[15]$

$$H_n = A_n^+ A_n^- + E_0^{(n)}$$  

(12)

$$A_n^\pm = \frac{1}{\sqrt{2}} \left( \mp \frac{d}{dr} + W_n(r) \right)$$  

(13)

$$\Psi_n^{(1)} = A_1^+ A_2^+ ... \psi_0^{(n+1)} \quad E_n^{(1)} = E_0^{(n+1)}$$  

(14)

$$\Psi_0^{(1)}(r) = Nexp(-\int_0^r W_1(\bar{r})d\bar{r}).$$  

(15)

In this work our interest is in the ground-state eigenfunction, to apply the variational method. As shown above, in SQM formalism the ground state eigenfunction can be determined from the superpotential $W(r)$, which satisfies the Riccati equation, eq.(7). Usually, if the potential is not exactly solvable, it is easier to determine an approximation for the superpotential in eq.(7) than an eigenfunction that satisfies the Schroedinger equation for the original Hamiltonian. Thus we make an ansatz in the superpotential based in the superalgebra information in order to evaluate the trial wavefunction that minimizes the expectation value of the energy, eq.(1). This formalism is applied to the Morse potential.

III. The Morse Potential
For the diatomic system, the three dimensional Morse oscillator can be written as,

\[ V_M = D(e^{-2a(r-r_e)} - 2e^{-a(r-r_e)}) \]  \hspace{1cm} (16)

where \( D \) is the dissociation energy, \( r_e \) is the equilibrium internuclear distance and \( a \) is the range parameter. We rewrite the original Schroedinger equation \( H\Psi = E\Psi \) in terms of a new variable \( y \),

\[
\left(-\frac{d^2}{dy^2} + \frac{l(l+1)}{y^2} + \lambda^2(e^{-2(y-y_e)} - 2e^{-(y-y_e)})\right)\Psi(y) = \epsilon\Psi(y) \]  \hspace{1cm} (17)

where \( y = ar \) and the constants are set like

\[ y_e = ar_e, \quad \lambda^2 = \frac{2mD}{a^2\hbar^2}, \quad E = \epsilon\hbar^2a^2 \]  \hspace{1cm} (18)

and the parameter \( m \) is the reduced mass of the molecule.

**Case \( l = 0 \)**

In this case the Schroedinger equation is exactly solvable and therefore the hierarchy of Hamiltonians can be constructed. For this case the Schroedinger equation is reduced to the form

\[
\left(-\frac{d^2}{dy^2} + \lambda^2(e^{-2(y-y_e)} - 2e^{-(y-y_e)})\right)\Psi(y) = \epsilon\Psi(y) \]  \hspace{1cm} (19)

The associated Riccati equation is then

\[ W_1^2 - W_1' + \epsilon_0^{(1)} = V_1(y) \] \hspace{1cm} (20)

with

\[ V_1(y) = \lambda^2(e^{-2(y-y_e)} - 2e^{-(y-y_e)}) \] \hspace{1cm} (21)

whose solution is given by

\[ W_1(y) = -\lambda e^{-(y-y_e)} + (\lambda - 1/2) \] \hspace{1cm} (22)

and the ground-state energy is

\[ \epsilon_0^{(1)} = -(\lambda - 1/2)^2 \] \hspace{1cm} (23)

To find the second member of the super-family we solve the equation

\[ W_2^2 + W_2' + \epsilon_0^{(1)} = V_2(r) \] \hspace{1cm} (24)

We then find that the superpartner is given by

\[ W_2(y) = -\lambda e^{-(y-y_e)} + (\lambda - 3/2) \] \hspace{1cm} (25)
and the ground-state energy is
\[ \epsilon_0^{(2)} = -(\lambda - 3/2)^2. \]  

(26)

The process of factorization can be continued and the whole hierarchy can be evaluated. The result is
\[
V_{n+1}(y) = \lambda^2 (e^{-2(y-y_e)} - 2e^{-(y-y_e)}) + 2n\lambda e^{-(y-y_e)} \\
W_{n+1}(y) = -\lambda e^{-(y-y_e)} + (\lambda - \frac{2n + 1}{2}) \\
\epsilon_0^{(n+1)} = -(\lambda - \frac{2n + 1}{2})^2.
\]

(27)

Case \( l \neq 0 \)
In this case an analytical exact solution cannot be determined. Nevertheless, based in the above arguments on how to obtain the trial wavefunction, we make the following ansatz for the superpotential
\[
W_1(y) = -\lambda e^{-(y-y_e)} - \frac{(l + 1)}{y} + C.
\]

(28)

The first term is taken from the one-dimensional Morse superpotential, case of \( l = 0 \), eq.(22), [16]. The knowledge of the second term comes from the study of three-dimensional potentials, (see, for instance, assyntotically linear potential, [17], and the truncated Coulomb potential, [18]). The \( c \)-number \( C \) will be taken as the variational parameter in the trial wavefunction.

The eigenfunction obtained from eq. (8) is then
\[
\Psi(y) \propto e^{-\lambda e^{-(y-y_e)}} y^{l+1} e^{-Cy}.
\]

(29)

Using this expression as a trial wavefunction in the variational method we change the parameter \( C \) by the variational parameter \( \mu \), i.e.,
\[
\Psi_\mu = \Psi(y, C = \mu) \propto e^{-\lambda e^{-(y-y_e)}} y^{l+1} e^{-\mu y}.
\]

(30)

The energy is then obtained by minimisation of the energy expectation value with respect to \( \mu \). Thus, the equation to be minimised is
\[
E_\mu = \int_0^{\infty} \Psi_\mu(y) [-\frac{d^2}{dy^2} + \lambda^2 (e^{-2(y-y_e)} - 2e^{-(y-y_e)}) + \frac{l(l+1)}{y^2}] \Psi_\mu(y) dy \\
\int_0^{\infty} \Psi_\mu(y)^2 dy.
\]

(31)

We have used this expression to minimize the energy expectation value of various molecules: \( H_2, HCl, CO \) and \( LiH \). The explicit values of the energy for \( n = 0 \) and different values of \( l \) are shown, for known values of their respective potential parameters, [19]: \( D, a, r_e \) and \( m \).
**Table 1.** Energy eigenvalues (in eV) for different values of \( l \) for \( H_2 \) molecule, with \( D = 4.7446eV, a = 1.9426\AA^{-1}, r_e = 0, 7416\AA \) and \( m = 0, 50391amu \). Comparison is made with results from ref.[12].

| \( l \) | Variational results | Shifted \( 1/N \) expansion results | Modified shifted \( 1/N \) expansion results | Exact Numerical expansion results |
|---|---|---|---|---|
| 0 | -4.4758 | -4.4749 | -4.4760 | -4.4759 |
| 5 | -4.2563 | -4.2589 | -4.2592 | -4.2589 |
| 10 | -3.7187 | -3.7247 | -3.7252 | -3.7242 |
| 15 | -2.9578 | -2.9663 | -2.9670 | -2.9654 |
| 20 | -2.0735 | -2.0839 | -2.0846 | -2.0826 |

**Table 2.** Energy eigenvalues (in eV) for different values of \( l \) for \( HCl \) molecule, with \( D = 37255cm^{-1}, a = 1.8677\AA^{-1}, r_e = 1.2746\AA \) and \( m = 0.9801045amu \). Comparison is made with results from ref.[11].

| \( l \) | Variational results | Shifted \( 1/N \) expansion results | Modified shifted \( 1/N \) expansion results |
|---|---|---|---|
| 0 | -4.4360 | -4.4352 | -4.4355 |
| 5 | -4.3971 | -4.3967 | -4.3968 |
| 10 | -4.2940 | -4.2939 | -4.2940 |

**Table 3.** Energy eigenvalues (in eV) for different values of \( l \) for \( CO \) molecule, with \( D = 90540cm^{-1}, a = 2.2994\AA^{-1}, r_e = 1.1283\AA \) and \( m = 6.8606719amu \). Comparison is made with results from ref.[11].

| \( l \) | Variational results | Shifted \( 1/N \) expansion results | Modified shifted \( 1/N \) expansion results |
|---|---|---|---|
| 0 | -11.093 | -11.091 | -11.092 |
| 5 | -11.085 | -11.084 | -11.084 |
| 10 | -11.066 | -11.065 | -11.065 |

**Table 4.** Energy eigenvalues (in eV) for different values of \( l \) for \( LiH \) molecule, with \( D = 20287cm^{-1}, a = 1.1280\AA^{-1}, r_e = 1.5956\AA \) and \( m = 0.8801221amu \). Comparison is made with results from ref.[11].
### Variational results

|       | Variational results | Shifted 1/N expansion results | Modified shifted 1/N expansion results |
|-------|---------------------|-------------------------------|----------------------------------------|
| 0     | -2.4291             | -2.4278                       | -2.4280                                 |
| 5     | -2.4014             | -2.3999                       | -2.4000                                 |
| 10    | -2.3287             | -2.3261                       | -2.3261                                 |

We stress that in fact we are dealing with an effective potential $V_{eff}$ that satisfies Riccati equation, i.e.,

$$V_{eff}(y) = \bar{W}_1^2 - \bar{W}_1' + E(\bar{\mu}) \quad (32)$$

where $\bar{W}_1 = W_1(\bar{\mu})$ is given by eq. (28) and $\bar{\mu}$ is the parameter that minimises the energy of eq. (31). It is given by

$$V_{eff} = -\lambda e^{-(y-y_e)} + \left(-\lambda e^{-(y-y_e)} + \mu - \frac{l+1}{y}\right)^2 - \frac{l+1}{y} + E(\bar{\mu}) \quad (33)$$

The plots of both $V_{eff}$ and $V_M$ (plus the potential barrier term) in the same graph for $l = 5$ are shown below. The upper curve corresponds to $V_{eff}$. We notice that for low energies the effective potential is quite similar to the real Morse potential and this is why our results are in such a good agreement with the other results.

![Potential](image.png)

**Figure 1**: Plot of $V_M$ plus the potential barrier term and $V_{eff}$.

### IV. Conclusions
The SQM formalism was used to explore the Morse potential. The hierarchy of Hamiltonians was evaluated for the case of angular momentum \( l = 0 \), for which the Morse potential is exactly solvable.

We have shown a new approach through the application of the variational method with the SQM formalism to evaluate the eigenvalues of the Morse oscillator for different values of the angular momentum \( l \). The determination of the trial wave function motivated by SQM was made by an ansatz in the superpotential. The application of the method for diatomic molecules indicated that the values obtained are in very good agreement with shifted large-\( N \) technique results, (SLNT), modified large-\( N \) technique results (SLNT) and numerical data.

We conclude that the conception of the trial wavefunction through the superpotential is a simple and good alternative procedure that enables to evaluate the energy eigenvalues with a reasonable accuracy. This is not a priori obvious and it suggests that it is a suitable method to treat other potentials.

**Acknowledgements**
The authors would like to thank Prof. U. P. Sukhatme for reading the manuscript.

**References**

[1] F. Cooper, A. Khare and U. P. Sukhatme, Phys. Rep. 251 (1995) 267

[2] R. W. Haymaker and A. R. Rau, Am. J. Phys. 54 (1986) 928

[3] L. Gedenshtein and I. V. Krive, So. Phys. Usp. 28 (1985) 645

[4] E. Drigo Filho and R. M. Ricotta, [hep-th 9904038](https://arxiv.org/abs/9904038)

[5] E. Gozzi, M. Reuter and W. D. Thacker, Phys. Lett. A183 (1993) 29

[6] F. Cooper, J. Dawson and H. Shepard, Phys. Lett. 187A (1994) 140

[7] E. Drigo Filho and R. M. Ricotta, Mod. Phys. Lett. A10 (1995) 1613

[8] I. L. Cooper, J. Phys. Chem. A 102 (1998) 9565

[9] D. A. Mazziotti, Chem. Phys. Lett. 299 (1999) 473

[10] L. I. Schiff, *Quantum Mechanics*, McGraw-Hill Book Co., NY, 1968

[11] M. Bag, M. M. Panja, R. Dutt and Y. P. Varshni, Phys. Rev. A46 (1992) 6059

[12] D. A. Morales, Chem. Phys. Lett. 161 (1989) 253

[13] C. V. Sukumar, J. Phys. A: Math. Gen. 18 (1985) L57

[14] C. V. Sukumar, J. Phys. A: Math. Gen. 18 (1985) 2917

[15] E. Drigo Filho and R. M. Ricotta, Mod. Phys. Lett. A14 (1989) 2283
[16] E. Drigo Filho, J. Phys. A: Math. Gen. 21 (1988) L1025
[17] E. Drigo Filho, Mod. Phys. Lett. A11 (1996) 207
[18] E. Drigo Filho, Mod. Phys. Lett. A9 (1994) 411
[19] Y. P. Varshni, Can. J. Chem. 66 (1988) 763