Vibrational ground state energy for confined molecules

Elso Drigo Filho and Josimar Fernando da Silva
Universidade Estadual Paulista (UNESP), Instituto de Biociencias, Letras e Ciencias Exatas, Campus Sao Jose do Rio Preto
E-mail: elso.drigo@unesp.br

Abstract. The ground state vibrational energies for three confined diatomic molecules (nitrogen, lithium and NaH) are determined by using the variational method. The approach proposed allows us to build trial eigenfunctions based on wave functions obtained from the supersymmetric quantum mechanics formalism. The Morse potential is used to simulate the molecular bound and the confinement is analyzed by introducing two barriers with the minimum of the potential inside this region. The methodology adopted was successfully used previously to describe the hydrogen molecule. The conclusion from these results is that the approach can be extended for other diatomic molecules.

1. Introduction
Quantum confined systems have several applications in different branches of physics as, for example, in high pressure systems, semiconductors and nanostructures. In this context, different mathematical approaches have been used [1].

The confinement of quantum particles and systems can involve different objects such as electrons, atoms or molecules. The main interest of the present work is to compute the ground state vibrational energy for three confined diatomic molecules, specifically, the lithium (Li₂) and nitrogen (N₂) homonuclear molecules and the sodium hydride (NaH) heteronuclear molecule. Usually, the energy of diatomic molecules can be separated into three parts which have origins in different kind of motions. The physical behavior of these spectra is related as electronic excitations, vibrations and rotations [2].

The vibrational energy, which is our focus here, is computed using a phenomenological potential. In this work the Morse potential is used to simulate the vibrational interaction between the atoms in the molecule [2, 3, 4] and the variational method is used to determine the ground state energies. Thus, trial eigenfunctions need to be introduced for each problem.

In the approach used here, these functions are built from the formalism of Supersymmetric Quantum Mechanics (SUSYQM) by the choice of an appropriate superpotential. This methodology has been successful used for several unconfined [5, 6, 7, 8, 9] and confined quantum systems [10, 11, 12, 13]. Specifically, the hydrogen molecule was studied by introducing a maximum and a minimum radius of confinement [13]. The maximum radius fixes the maximum volume accessible to the system and the minimum radius determines how close the atoms can be in the molecule. The results presented here were obtained by using this approach.
2. Methodology

The time-independent Schrödinger equation for a non-relativistic three-dimensional quantum system can be written as:

\[-\hbar^2 \frac{d^2}{dr^2} \Psi(r) + V_{\text{eff}}(r) \Psi(r) = E \Psi(r),\]

where the symbols have the usual meaning, \(\hbar\) is the Planck constant divided by \(2\pi\) and \(m\) is the reduced mass. The effective potential \((V_{\text{eff}}(r))\) is the original potential plus the barrier of potential term, which is proportional to \(\frac{l(l+1)}{r^2}\), \(l\) is the quantum number of the angular moment.

In general, solving Schrödinger equation (1) is not a trivial task and so approximate methods need to be used, such as the variational method [10, 11]. In this approach, a trial eigenfunction is used to determine the expected value of energy for the system being analyzed. The variational principle assures that the value obtained is greater than the true energy eigenvalue. Therefore, considering only the radial coordinate, it can be written:

\[\frac{\int \Psi^*_r \hat{H} \Psi_r dV}{\int \Psi^*_r \Psi_r dV} \geq E_{\text{exact}},\]

where \(\hat{H}\) represents the Hamiltonian operator of the problem, \(E\) is the energy eigenvalue of the studied state and \(\Psi_r\) is the chosen trial function. It is important to express that if the function \(\Psi_r\) is similar to the real wave function, the obtained expected value will be close to the real value of \(E\). It is possible to improve the efficiency of the method by introducing a set of parameters (\(\gamma\)), the variational parameters, that permit to minimize the expected value of energy. The molecular bond is strongly directed and, in the case analyzed in this work, it is adopted \(l = 0\). Thus, in the calculations made the system is considered one-dimensional. It is also important to emphasize that the challenge of this method consists on determining an appropriate trial wave function [14].

The formalism of SUSYQM is adopted to obtain a wave function adequate to the problem studied. In this way, it is appropriate to remember some aspects of the formalism of the SUSYQM. The supersymmetric formalism starting from the factorized Hamiltonian [5, 6, 7, 8, 9, 10, 11, 12]:

\[-\frac{d}{dr} + W(r) \left( \frac{d}{dr} + W(r) \right) \Psi(r) = 0,\]

for simplicity, we adopt \(\hbar = 2m = 1\). The function \(w(r)\) is called as superpotential. By using equations (1) and (3) we obtain the following Riccati equation:

\[-\frac{dW(r)}{dr} + W^2(r) = V_{\text{eff}}(r) - E.\]

The \(E\) corresponds to the ground state energy and the eigenfunction \(\Psi(r)\) is determined by:

\[\Psi(r) \propto e^{-\int W(r) dr}.\]

Thus, when the Riccati equation (4) is solved, the wave function to the ground state can be obtained from equation (5). However, if it is not possible to obtain an exact solution, it is still possible to search for an approximate solution for the superpotential. This solution generates a wave function through equation (5) that supplies an appropriate trial function for the variational method.

For the confined case, the introduction of an additional term in the superpotential is necessary. This term is \(\frac{1}{(R_{\text{max}} - r)}\), where \(R_{\text{max}}\) is the confinement radius. This new term creates, in the
original potential, an infinity barrier when \( r \to R_{\text{max}} \), which is responsible for the trapping of the system. As the confinement needs to be inserted in large and small values of the variable, a second confinement term was inserted in the equation and this term is \(-\frac{1}{(r-R_{\text{min}})}\), where \( R_{\text{min}} \) is the minimum confinement radius. This term provides a second infinity barrier for small values of \( r \). Therefore, the resulting superpotential is:

\[
W_{\text{con}}(r) = W_{\text{ncon}}(r) + \frac{1}{(R_{\text{max}} - r)} - \frac{1}{(r - R_{\text{min}})}.
\]  

(6)

The \( W_{\text{ncon}}(r) \) is the superpotential for the unconfined potential and \( W_{\text{con}}(r) \) is the superpotential for the confined case. The last two terms correspond to the confinement for large and small values for the coordinate.

3. Diatomic Molecules

The vibrations of diatomic molecules can be described by Morse potential [15, 4] and it can be written as [16]:

\[
V_M(r) = D_e \left( e^{-2a(r-r_e)} - 2e^{a(r-r_e)} \right),
\]  

(7)

where \( D_e \) is the dissociation energy, \( r_e \) is the equilibrium internuclear distance and \( a \) is one parameter related to the vibrational frequency of a diatomic molecule.

Rewriting the three-dimensional Schrödinger equation for the Morse potential in terms of a new variable \( x = ar \) and replacing the original wave function, \( \Psi(r) \), by \( \Psi(r) = \frac{\phi(x)}{r} \) gives [12]:

\[
\frac{-\hbar^2}{2m} \frac{d^2 \phi(x)}{dx^2} + 3 \lambda^2 \left[ e^{-2(x-x_e)} + 2e^{-(x-x_e)} \right] \phi(x) + \frac{l(l+1)\phi(x)}{x^2} = \epsilon \phi(x),
\]  

(8)

where the constants are \( \lambda^2 = \frac{2mD_e}{\hbar^2} \), \( \epsilon = \frac{2mE}{\hbar^2} \), \( x_e = ar_e \) and \( m \) represents the reduced mass of the molecule. Thus, the Hamiltonian operator for a system described by the Morse potential added to the potential barrier is:

\[
\hat{H}(x) = -\frac{d^2}{dx^2} + \lambda^2 \left[ e^{-2(x-x_e)} + 2e^{-(x-x_e)} \right] + \frac{l(l+1)}{x^2}.
\]  

(9)

The problem involving the unconfined Morse potential had already been treated using of the variational method associated to SUSYQM [6]. In this case, the suggested superpotential is:

\[
W_{M_{\text{ncon}}}(x) = -\lambda e^{-(x-x_e)} - \frac{(l+1)}{x} + \gamma,
\]  

(10)

where \( \gamma \) is used as a variational parameter. If the superpotential for the unconfined system is known, then one obtains the superpotential for the confined system by using the prescription given in equation (6) [12]. In this case, the complete superpotential is given by:

\[
W_{M_{\text{con}}}(x) = -\lambda e^{-(x-x_e)} - \frac{(l+1)}{x} + \gamma + \frac{1}{(x - X_{\text{max}})} - \frac{1}{(x - X_{\text{min}})}
\]  

(11)

where \( X_{\text{max}} = aR_{\text{max}} \) and \( X_{\text{min}} = aR_{\text{min}} \) corresponding to the maximum and minimum distances of the cavity in which the system is inserted.

According to equation (5), when the superpotential for confined system is used (equation (10)) the trial wave function to be used in the variational method is:

\[
\phi_{M\gamma}(x) \propto x^{(l+1)}(X_{\text{max}} - x)(x - X_{\text{min}})e^{-\lambda e^{-(x-x_e)} + \gamma x}
\]  

(12)
In this approach the suggested trial function, equation (12), depends on one variational parameter, $\gamma$. Thus, the variational energy is obtained through the minimization of the expected energy value related to this parameter. The expression of energy for the system is given by:

$$
\epsilon = \frac{\int_{X_{\text{min}}}^{X_{\text{max}}} \phi_{M\gamma}^*(x) \left\{ -\frac{d^2}{dx^2} + \lambda^2 \left[ e^{-2(x-x_e)} - 2e^{-(x-x_e)} \right] + \frac{l(l+1)}{x^2} \right\} \phi_{M\gamma}(x) dx}{\int_{X_{\text{min}}}^{X_{\text{max}}} |\phi_{M\gamma}(x)|^2 dx}.
$$

(13)

The numerical result is obtained by minimizing this function with respect to the variational parameter, $\frac{\partial \epsilon}{\partial \gamma} = 0$.

4. Results

Using the approach described here, the ground state energy for the $N_2$, $Li_2$ and $NaH$ molecules were computed. The first step is to identify the Morse parameters for these molecules. The parameters used here are obtained from reference [4] and they are presented in Table 1. As usual, $a_0$ is the Bohr radius.

Table 1. Morse potential parameters [4] for calculating the ground state energy of $N_2$, $NaH$ and $Li_2$.

| Molecule | $D_e$ (hartree) | $\omega_e$ (hartree) | $a$ ($a_0^{-1}$) | $r_e$ ($a_0$) |
|----------|----------------|----------------------|----------------|-------------|
| $N_2$    | 0.364006       | 0.010746436          | 1.42308        | 2.074352218 |
| $NaH$    | 0.072901       | 0.005358706          | 0.58879        | 3.569692392 |
| $Li_2$   | 0.039276       | 0.001601187          | 0.45440        | 5.051804485 |

The energy eigenvalues are obtained by the minimization of equation (13) with respect to the variational parameter $\gamma$ and using the values showed in Table 1. The numerical results are presented in Table 2. In this table, energy eigenvalues for the difference between the minimum and the maximum values of the radial coordinate, $\Delta r = R_{\text{max}} - R_{\text{min}}$, are shown. The value of $l$ is fixed as equal to zero. As expected, for large values of $\Delta r$, the energy eigenvalues tend to be equal to the value obtained for the unconfined case.

Table 2. Ground state energy of $N_2$, $NaH$ and $Li_2$ for $l = 0$ and different sizes of confined cavity ($\Delta r$).

| Molecule | $E(\Delta r = 0.2a_0)$ | $E(\Delta r = 0.8a_0)$ | $E(\Delta r = 2.0a_0)$ | $E(\Delta r = 4.0a_0)$ |
|----------|------------------------|------------------------|------------------------|------------------------|
| $N_2$    | -0.35277               | -0.35577               | -0.35789               | -0.35788               |
| $NaH$    | -0.00219               | -0.06787               | -0.07017               | -0.07024               |
| $Li_2$   | -0.01961               | -0.03785               | -0.03846               | -0.03848               |
As expected, for large values of $\Delta r$, the energy eigenvalues approximate the value of the ground state obtained for the unconfined case, i.e., they approach the depth of the well [4]. This can be seen by comparing the eigenvalues module presented in the last column of Table 2 with the values of $D_e$ shown in the second column of Table 1.

5. Conclusions
The treatment proposed has proved to be a good alternative approach to study the Schrödinger equation. In particular, for confined systems as, for instance, the confined Morse potential. This approach, originally proposed to study hydrogen molecule [12], can be extended to more complex systems. In this work, it was extended to other homonuclear molecules and to one heteronuclear molecule, i.e. the lithium (Li$_2$) and nitrogen (N$_2$) homonuclear molecules and sodium hydride (NaH) heteronuclear molecule. Numerical results obtained for the ground state energy eigenvalues (Table 2) are consistent with others present in the literature. In particular, for unconfined systems, the results for the value of the confinement radii ($\Delta = 4$ a$_0$) are close to the depth of the well ($-D_e$). In general, the energy increases as the confinement radius decreases. This can be understood as a direct result of the confinement and the increase of the kinetic energy of the system. This latter effect is the result of spatial constraint and an increase in linear momentum as a consequence of the uncertainty principle.

As a final note, it is important to emphasize that the inclusion of the terms $\frac{1}{(R_{\text{max}}-r)}$ and $-\frac{1}{(r-R_{\text{min}})}$ in the superpotential shows to be efficient to describe systems near the minimum of the potential. This result reinforces the approach used here and suggests that it could be an effective procedure to use for other confined systems.

Acknowledgements
The authors would like to thank the Brazilian agencies FAPESP (Proc. No. 2018/12984-9) and CAPES, for their partial support of this work.

References
[1] Sabin J and Brandas E J 2009 Advances in quantum chemistry: theory of confined quantum systems-part one (Academic Press)
[2] Levine I N, Busch D H and Shull H 2000 Quantum chemistry (Prentice Hall Upper Saddle River, NJ)
[3] Morse P M 1929 Diatomic molecules according to the wave mechanics. ii. vibrational levels Physical Review 34(1) 57
[4] Varshni Y 1988 Approximations for the inner branch of potential curves of diatomic molecules Canadian journal of chemistry 66(4) 763–766
[5] Borges G R P, de Souza Dutra A, Drigo E and Ruggiero J R 2003 Variational method for excited states from supersymmetric techniques Canadian Journal of Physics 81(11) 1283–1291
[6] Filho E D and Ricotta R M 2000 Morse potential energy spectra through the variational method and supersymmetry Physics Letters A 269(5-6) 269–276
[7] Filho E D and Ricotta R M 1995 Supersymmetry, variational method and Hulthén potential Modern Physics Letters A 10(22) 1613–1618
[8] Cooper F, Dawson J and Shepard H 1994 SUSY-based variational method for the anharmonic oscillator Physics Letters A 187(2) 140–144
[9] Gozzi E, Reuter M and Thacker W 1993 Variational methods via supersymmetric techniques Physics Letters A 183(1) 29–32
[10] Filho E D and Ricotta R M 2002 Supersymmetric variational energies for the confined coulomb system Physics Letters A 299(2-3) 137–143
[11] Filho E D and Ricotta R M 2003 Supersymmetric variational energies of 3d confined potentials Physics Letters A 320(2-3) 95–102
[12] Silva F R and Filho E D 2010 A new type of confinement for the morse potential Chemical Physics Letters 498(1-3) 198–202
[13] Silva F R and Filho E D 2010 Confined Lennard–Jones Potential: A variational treatment Modern Physics Letters A 25(08) 641–648
[14] I S L 1968 *Quantum Mechanics* (McGraw-Hill) ISBN 978-0070856431
[15] Atkins P, Depaula J and Keeler J 2018 *Atkins’ Physical Chemistry* (Oxford University Press) ISBN 0198769865
[16] Zhang L Z, Xiong Y, Cheng P, Tang G Q and Liao D Z 2002 Molecular orbital confinement of a schiff base molecule in the nanoporous channels of MCM-41 host *Chemical Physics Letters* **358**(3-4) 278–283