

# On the variational solution of morphed molecular potential in a diatomic molecule

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**Abstract** The general one-dimensional potential energy function, including centrifugal distortion, for a diatomic molecule is morphed with a series of Morse-like functions for each of the rotational quantum numbers  $J$ . For each of the morphed potential, explicit formulae for the matrix elements of the complete energy matrix, on the basis of the solutions of the one-dimensional harmonic oscillator, are given and these may be used in connection with the variational procedure to solve the corresponding vibrational Schrödinger equation. From the set of vibrational levels  $\{E_{vJ}\}$ ,  $J = 0, 1, 2, \dots$  the ro-vibrational transitions can be deduced.

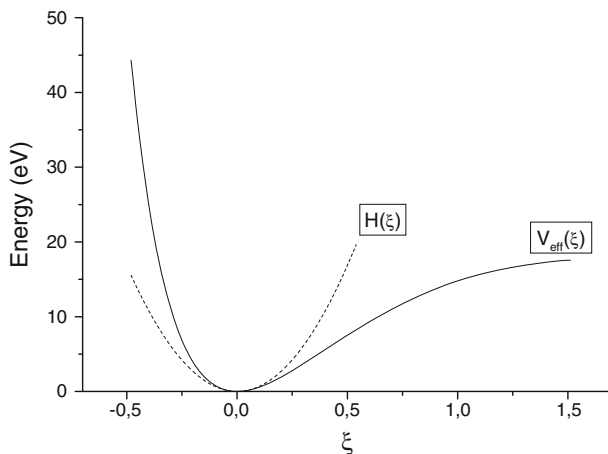
**Keywords** Morphing · Morse-like potential · Matrix elements

## 1 Introduction

In this work, we present closed formulae for the computation of energy matrix elements, to be used in a variational approach to solve the vibrational Schrödinger equation of a rotating oscillator (i.e. a diatomic molecule). There, the internuclear distance  $X$  varies subjected to the centrifugal distortion and the potential energy  $V(x)$  is the general (Morse-shaped) molecular potential, either of experimental nature or theoretically calculated from some ab initio method, for a non-rotating molecule, which in general cannot be represented by a single Morse function but instead, by a rather complex analytical curve which nevertheless resembles the Morse function. The Schrödinger

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**Fig. 1** The Morse-like potential energy curve  $V(\xi)$  (solid) and the harmonic potential  $H(\xi)$  (dotted)

equation for a distorted rotating oscillator is of the form:

$$\left\{ -\frac{\hbar^2}{2\mu} \nabla^2 + V_{eff}(x) \right\} \Psi(x) = E \Psi(x) \tag{1}$$

where  $V_0(x)$  is the electronic energy of a non-rotating molecule and the effective potential

$$V_{eff} = V^0(x) + \frac{\hbar^2 J(J + 1)}{2\mu x^2} \tag{2}$$

changes with increasing values of the rotational quantum number  $J$ .

The basis set, chosen for the variational procedure, consists of a complete set of eigenfunctions of the harmonic oscillator, centered at the origin. Together with choosing the basis set, and for generality purposes, it is convenient make Eq. (1) dimensionless. In order to do this, we define the harmonic potential, which will give raise to the basis set, by computing the curvature  $\mathbf{K}$  of  $V^0(x)$  (i.e. the second derivative) at the origin and rewrite both terms in the potential energy function of Eq. (2) in terms of the dimensionless variable  $\xi = \sqrt{\alpha}x$ , where  $\alpha = \frac{\sqrt{\mathbf{K}}\mu}{\hbar}$  and  $\mu$  being the reduced mass. Both potentials have the same curvature at the origin as shown in Fig. 1.

The most convenient variational basis set, and simpler to treat, is then the set of eigenfunctions of the dimensionless harmonic oscillator centered at the origin, these functions are:

$$\Psi_n(\xi) = \sqrt{\frac{1}{\sqrt{\pi} n! 2^n}} H_n(\xi) e^{-\frac{\xi^2}{2}} \quad n = 0, 1, 2, \dots \tag{3}$$

or in terms of the original variable

$$\Psi_n(x) = \sqrt{\frac{1}{n! 2^n}} \sqrt{\frac{\alpha}{\pi}} H_n(x) e^{-\frac{\alpha x^2}{2}} \quad n = 0, 1, 2, \dots \quad (4)$$

There, energies are measured in units of  $\hbar\omega = \hbar\sqrt{\frac{k}{\mu}}$

Equation (1) now takes the dimensionless form:

$$\left\{ -\frac{1}{2} \nabla_{\xi}^2 + V_{eff}^*(\xi) \right\} \Psi(\xi) = E * \Psi(\xi)$$

For simplicity and without loss of generality, we assume the minimum of the potential energy function located at  $\xi = 0$ , this condition can always be accomplished by a simple change in variable. Although the minimum of  $V_{eff}^*(\xi)$  is shifted with increasing values of the rotational quantum number  $J$ , its position is completely irrelevant for the determination of vibrational energy levels. This is not the case for the value of energy at the minimum.

## 2 Morphed potentials

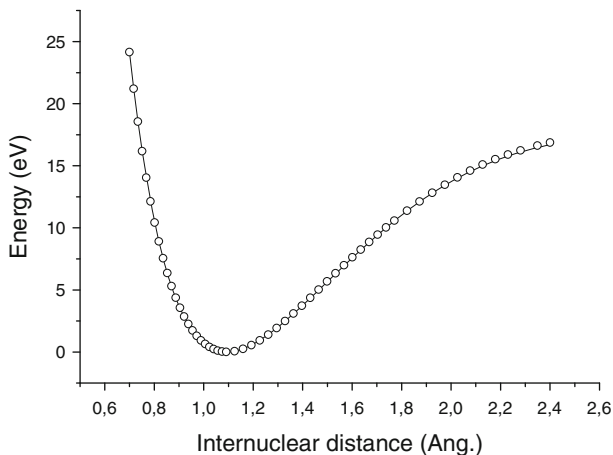
The description of potential energy surfaces (PES) for a diatomic molecule has been customarily given by the two-parameter Morse Potential. Even though for which there is an analytical solution of Eq. (1), it does not generally fit the experimental or *ab-initio* PES. A much better description is obtained by a generalized exponential function [1–4] centered at the origin such as:

$$V(r) = \sum_{k=2}^{k=m} A_k (1 - e^{-\alpha r})^k \quad (5a)$$

which can be “morphed” to almost exactly reproduce the experimental or theoretical PES. We find in the literature, that the value of  $m$ , the number of functions used for morphing, does not exceed 4 or 5 and the method of solving Eq. (1) is the approximate reduced potential method (RPC)[4]. In this work, we have developed the necessary methodology to use this expansion with larger values of  $m$  (10 or more depending of the need) and then solving Eq. (1) variationally over a very large basis set of  $N$  ( $N \geq 100$ ) of Harmonic Oscillator (HO) wave functions, which were defined above.

Figure 2 depicts an example of the morphing of an experimental potential energy curve as a function of the internuclear distance for a diatomic molecule. The experimental points were computed using an *ab initio* method with the sole purpose of generating the Morse-shaped curve. The solid line in that figure, represents the morphed potential computed using Eq. (5a) with  $m = 8$ .

The effective potential, generated for different rotational quantum numbers  $J$ , is then morphed by mean of an expansion of an adequate number of Morse-like exponential



**Fig. 2** Experimental potential energy curve (circles) versus internuclear distance for a diatomic molecule. The solid line corresponds to the morphed potential as obtained with Eq. (5a)

functions, i.e. a least square fitting of the type [13]:

$$V_{eff}^*(\xi) = \sum_{k=0}^{k=m} A_k (1 - e^{-\alpha\xi})^k \tag{5b}$$

where  $A_k$  and  $\alpha$  are optimization parameters. Upon simplification Eq. (5b) becomes

$$V_{eff}^*(\xi) = \sum_{k=0}^{k=m} \left\{ \sum_{j=0}^{j=m-k} \binom{k+j}{j} A_{k+j} \right\} e^{-\alpha k \xi} \tag{6}$$

### 3 Energy matrix elements

In view of Eq. (6), the scaled dimensionless molecular potential, we have derived the necessary expressions to analytically compute the Hamiltonian matrix elements within the basis of the harmonic oscillator eigenfunctions of Eq. (3). These are as follows:

#### 3.1 Kinetic energy

To evaluate the matrix elements for the kinetic energy operator  $\hat{T}$ , we make use of the Hermite differential equation [7–9] in the form

$$\frac{d^2}{d\xi^2} \left( H_n(\xi) e^{-\frac{\xi^2}{2}} \right) + (2n - \xi^2 + 1) H_n(\xi) e^{-\frac{\xi^2}{2}} = 0 \tag{7}$$

and due to the hermiticity of  $\hat{T}$ , we find:

$$\left\langle \Psi_k(\xi) \left| \frac{-1}{2} \frac{d^2}{d\xi^2} \right| \Psi_l(\xi) \right\rangle = \frac{-1}{2\sqrt{\pi}l!2^l} \left\{ \left\langle H_k(\xi) e^{-\frac{\xi^2}{2}} \left| \xi^2 \right| H_l(\xi) e^{-\frac{\xi^2}{2}} \right\rangle - (2l+1)\delta_{kl} \right\} \quad (8)$$

The integrals in the right hand side of Eq. (8) are already known [8–12]

$$\left\langle H_k(\xi) e^{-\frac{\xi^2}{2}} \left| \xi^2 \right| H_l(\xi) e^{-\frac{\xi^2}{2}} \right\rangle = \begin{cases} \frac{1}{2}\sqrt{l(l-1)} & l = k - 2 \\ \frac{1}{2}(2l + 1) & l = k \\ \frac{1}{2}\sqrt{(l+1)(l+2)} & l = k + 2 \\ 0 & \text{otherwise} \end{cases} \quad (9)$$

nevertheless, we have derived [13] a more simple and convenient way to compute these matrix elements

$$\left\langle H_k(\xi) e^{-\frac{\xi^2}{2}} \left| \frac{d^2}{d\xi^2} \right| H_l(\xi) e^{-\frac{\xi^2}{2}} \right\rangle = \begin{cases} -\frac{1}{2}(2k+1) & l = k \\ \sqrt{\frac{\binom{M}{2}}{2}} & l = k \pm 2 \quad M = \text{biggest between } (k, l) \\ 0 & \text{Otherwise} \end{cases} \quad (10)$$

### 3.2 Potential energy

From Eq. (6), it is seen that the potential energy operator can be written as a series of exponential in terms in the form

$$V_{eff}^*(\xi) = \sum_{r=0}^{r=m} B_r e^{-\alpha r \xi} \quad (11)$$

where the  $B_r$  coefficients are merely constants. Then, the matrix elements  $V_{kl}$  of the potential energy operator is a sum of terms of the type:

$$V_{kl} = \sum_{r=0}^{r=m} B_r \frac{1}{\sqrt{\pi k!l!2^{k+l}}} \int_{-\infty}^{+\infty} H_k(\xi) e^{-(\alpha r \xi + \xi^2)} H_l(\xi) d\xi = \sum_{r=0}^{r=m} B_r \langle k | e^{-\alpha r \xi} | l \rangle \quad (12)$$

In Eq. (12), for simplicity we have dropped the dimensionless superscript (\*) and “effective” labels in the potential energy matrix elements. To evaluate these integrals we have derived the following closed expressions:

### 3.3 Diagonal terms

These terms are simpler to evaluate and reduce to:

$$\langle k | e^{-a\xi} | k \rangle = e^{\frac{a^2}{4}} \sum_{j=0}^{j=k} \frac{\binom{k}{j}}{2^j j!} a^{2j} \quad (13)$$

### 3.4 Off-diagonal terms

For  $k < l$  we have:

$$\langle k | e^{-a\xi} | l \rangle = \frac{e^{\frac{a^2}{4}}}{\sqrt{2^k k!} \sqrt{2^l l!}} \sum_{j=0}^{j=k} \left[ (-a)^{|l-k|+2j} \binom{k}{j} 2^{k-j} \times \begin{cases} \prod_{m=(l-k+j+1)}^{m=l} m & \text{if } j \neq k \\ 1 & \text{if } j = k \end{cases} \right] \quad (14)$$

For  $l < k$  reverse the indexes.

These integrals are readily programmed in a computer code. The next step is the solution of the secular equation  $|H_{kl} - E\delta_{kl}| = 0$  since the basis set is already orthonormal.

### 3.5 Ro-vibrational levels

To obtain ro-vibrational levels, we solve variationally Eq. (1) for a parametric value of the rotational quantum number  $J$  and a set  $\{E_n\}$  ( $n = 0, 1, 2, \dots$ ) of energy levels is obtained. Repeating this procedure for  $J = 0, 1, 2, \dots$ , a manifold of ro-vibrational energy levels, for  $\{E_n\}_J$  is obtained.

From this set of values, we have shown in a previous work [5,6] that the transitions energies, between ro-vibrational energy levels, can then be computed by subtracting the appropriate energy levels in agreement with the selection rules  $\Delta J = 0, \pm 1$  and  $\Delta n = \pm 1$ .

## References

1. B.A. McElmurry, R.R. Lucchese, J.W. Bevan, S.P. Belov, I.I. Leonov, Chem. Phys. Lett. **407**, 40 (2005)
2. C.S. Esteves, H.C.B. de Oliveira, L. Ribeiro, R. Gargano, K.C. Mundim, Chem. Phys. Lett. **427**, 10 (2006)
3. F. Wanga, C. Yang, Z. Zhu, J. Mol. Struct. (Theochem) **684**, 9 (2004)
4. V. Spirko, J. Mol. Spectrosc. **235**, 268 (2006)

5. J.R. Letelier, M.L. Senent, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **65**(5), 1030 (2006)
6. N. Inostroza, J.R. Letelier, M.L. Senent, *J. Mol. Struct. Theochem.* **947**, 40 (2010)
7. R. Liboff, *Introductory Quantum Mechanics*, 4th edn. (Addison Wesley, Reading, 2003)
8. D. Griffiths, *Introduction to Quantum Mechanics*, 2nd edn. (Prentice Hall, Englewood Cliffs, 2004)
9. M. Abramowitz, I. Stegun (eds.), *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables* (Dover, New York, 1965)
10. W.W. Bell, *Special Functions for Scientists and Engineers* (D. van Nostrand Company Ltd, London, 1968)
11. G. 't Hooft, S. Nobbenhuism, *Special Functions and Polynomials* From: <http://www.phys.uu.nl/thoof/lectures/specialfct.pdf>
12. E.W. Weisstein, *Hermite Polynomial*. From: MathWorld, A Wolfram Web Resource <http://mathworld.wolfram.com/HermitePolynomial.html>
13. Some derivations in this paper were performed by using Maple(TM). Maple12. (Maplesoft, a division of Waterloo Maple Inc., Waterloo, Ontario)