

A Comparison of Various Variational Approaches for Solving the One-dimensional Vibrational Schrödinger Equation

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Abstract

In this study, we compare three variational approaches for solving the one-dimensional Schrödinger equation. Particular attention is paid to accurate calculation of the vibrational energy levels lying close to the dissociation limit in bound electronic states of diatomic molecules. The approaches are tested on the ground state of the hydrogen molecule.

1. Introduction

It is not easy nowadays to justify searching for a new approach for solving a one-dimensional Schrödinger equation, particularly that describing molecular vibrations. Besides the well-known perturbative solutions or the models like that by Morse, a number of simple numerical procedures are available. However, the appearance of some special effects, like large-amplitude vibrations in “floppy” molecules, peculiar forms of the potential energy curves, avoided crossings of the potential energy surfaces, the need for compact wave functions in terms

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of expansions in appropriate bases *etc.* has a consequence that this apparently trivial problem is not yet universally solved. This matter illustrates also the fact that a more than modest contribution, meanwhile thirty years old [1], of one of the present authors (M.P.) in which a comparison of several methods for solution of the vibrational Schrödinger equation based on *ab initio* computed potential energy curves was carried out, belongs to the most cited of his papers. In this study, two variational approaches were discussed. The first one was based on the polynomial representation of the potential energy curve and the use of the eigenfunctions of a one-dimensional harmonic oscillator as the basis for matrix representation of the Hamiltonian. This approach has later been refined and the accuracy of the corresponding results for vibrational energy levels and wave functions was explicitly demonstrated in Ref. [2]. However, this method cannot describe properly the levels close to the dissociation limit (of e.g. diatomic molecules), because the polynomial representing the potential energy curve tends to (+ or -) infinity at large values of the vibrational coordinate, instead of asymptotically approaching the energy of separated atoms. This fact motivated the alternative use of trigonometric functions (Fourier series) for representing the potential energy curves and also the vibrational basis functions [3–6]. Such an approach can be applied not only in cases when the potential energy function is periodic, but also when such periodicity does not exist; in the latter case one can define an artificial periodicity, provided that it does not obscure the real physical situation. While removing the problem of false representation of the dissociation limit, this approach has, however, several drawbacks. Accurate fitting of some particular forms of the potential energy functions (typically of those resembling exponential functions) to trigonometric series is not easy, relatively large basis sets have to be used (see, e.g. [6]) to achieve high numerical accuracy of the results (particularly for the wave functions), *etc.* For these reasons, we introduce in the present study a third approach that seems to overcome the drawbacks of the two above mentioned. It should be stressed that all three methods can be applied not only to handle the vibrations in diatomic molecules, but also in a very common case when a multidimensional vibrational problem can be in a good approximation reduced to an effectively one-dimensional problem.

Of course, there are many alternative ways for solution of the one-dimensional Schrödinger equation. Here we wish to mention only several studies recently published in the present journal [7-12]. For a more detailed overview the reader is referred to the references cited in these papers.

The present paper is organized as follows: In Section 2 we briefly describe the three approaches for solving the vibrational Schrödinger equation. In Section 3. we apply them to compute the vibrational energy levels in the ground electronic state of the hydrogen molecule. In these computations the very accurate potential energy curve calculated by Kolos and Wolniewicz [13] is employed. This section involves brief concluding remarks.

2. Method

In the present paper we deal with the one-dimensional Schrödinger equation,

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + V(x) \right] \Psi(x) = E\Psi(x), \quad (1)$$

$$-\infty \leq x \leq \infty,$$

where μ is the reduced mass, and $V(x)$ an appropriate function representing the potential energy for vibrations of molecular nuclei. In this section we describe three variational approaches for solving Eq. 1.

2.1. Polynomial approach

The potential energy is assumed to be of the form

$$V = \sum_{k=0}^K c_k x^k. \quad (2)$$

c_k are the expansion coefficients obtained by fitting the *ab initio* computed electronic energies in the framework of the Born–Oppenheimer approximation, V_1, V_2, \dots, V_N , to the function (2) by means of the least squares procedure. It is convenient to rewrite (2) as

$$V = c_0 + c_1 x + \frac{1}{2} k x^2 + \left(c_2 - \frac{1}{2} k \right) x^2 + c_3 x^3 + \dots + c_K x^K. \quad (3)$$

The Hamiltonian in the Schrödinger equation (1) can now be written in the form

$$\hat{H} = \hat{H}_0 + \hat{V}', \quad (4)$$

where

$$\hat{H}_0 \equiv -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} k x^2, \quad (5)$$

and

$$\hat{V}' \equiv c_0 + c_1 x + \left(c_2 - \frac{1}{2} k \right) x^2 + c_3 x^3 + \dots + c_K x^K. \quad (6)$$

The (orthonormal) basis functions for the representation of the Hamiltonian (4) are taken in the form of eigenfunctions of the one-dimensional harmonic oscillator with the reduced mass μ and the conveniently chosen “force constant” k ,

$$\psi_n(x) = \sqrt{\frac{\alpha}{\pi} \frac{1}{2^n n!}} \cdot H_n(\sqrt{\alpha} x) \cdot \exp\left(-\frac{1}{2} \alpha x^2\right), \quad (7)$$

where $\alpha = \sqrt{k\mu}/\hbar$, and H_n represents the n -th Hermite polynomial. The matrix elements of the operator \hat{H}_0 are

$$(H_0)_{nm} \equiv \int_{-\infty}^{\infty} \psi_m^*(x) \hat{H}_0 \psi_n(x) dx = \left(n + \frac{1}{2} \right) \hbar \omega \cdot \delta_{n,m}, \quad (8)$$

with $\omega \equiv \sqrt{k/\mu}$. The part \hat{V}' of the Hamiltonian only involves the terms x^k . The corresponding matrix elements can be easily calculated by using the formulae

$$x_{mm} \equiv \int_{-\infty}^{\infty} \psi_m^*(x) \hat{x} \psi_n(x) dx = \sqrt{\frac{m+1}{2\alpha}} \cdot \delta_{n,m+1} + \sqrt{\frac{m}{2\alpha}} \cdot \delta_{n,m-1} \quad (9)$$

and

$$x H_n(\sqrt{\alpha} x) = \frac{1}{2\sqrt{\alpha}} H_{n+1}(\sqrt{\alpha} x) + \frac{n}{\sqrt{\alpha}} H_{n-1}(\sqrt{\alpha} x). \quad (10)$$

2.2. Fourier approach

This approach may be used when the potential energy curve has certain periodicity (as e.g. for torsional vibrations) or if some artificial periodicity is properly *defined*. Let r be a real vibrational coordinate (e.g. the bond length in a diatomic molecule). Choosing for “the period” some length L covering the complete range of physically relevant variations of r , we define a new variable ϕ as

$$\phi \equiv \frac{\pi}{L} r. \quad (11)$$

The potential energy function is then expressed in the form

$$V = \sum_{k=0}^K c_k \cos\left(k \frac{\pi}{L} r\right) \equiv \sum_{k=0}^K c_k \cos(k\phi). \quad (12)$$

The application of the least squares procedure leads to the optimal expansion coefficients. Depending on the concrete situation, we can use as the basis functions for the representation of the Hamiltonian either cos or sin functions in $n\phi$, or both of them. In the former case the orthonormalized basis functions are

$$\begin{aligned}\psi_n(r) &= N_n \cos\left(n \frac{\pi}{L} r\right) = N_n \cos(n\phi), \\ N_0 &= \frac{1}{\sqrt{2L}}, \\ N_n &= \frac{1}{\sqrt{L}}, \quad n = 1, 2, \dots, N.\end{aligned}\tag{13}$$

The kinetic energy operator is

$$\hat{T} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} \equiv -\frac{\hbar^2}{2\mu} \left(\frac{\pi}{L}\right)^2 \frac{d^2}{d\phi^2},\tag{14}$$

and its matrix has only diagonal elements,

$$T_{mn} = \int_{-L}^L \psi_m^*(r) \hat{T} \psi_n(r) dr = \frac{\hbar^2}{2\mu} \left(n \frac{\pi}{L}\right)^2 \cdot \delta_{n,m}\tag{15}$$

The elements of the potential energy matrix are

$$\begin{aligned}V_{mn} &\equiv \int_{-L}^L \psi_m^*(r) \hat{V} \psi_n(r) dr = \sum_{k=0}^K c_k N_m N_n \int_{-L}^L \cos\left(m \frac{\pi}{L} r\right) \cos\left(k \frac{\pi}{L} r\right) \cos\left(n \frac{\pi}{L} r\right) dr = \\ &= \frac{c_k}{2} (\delta_{m-n,k} + \delta_{m-n,-k} + \delta_{m+n,-k} + \delta_{m+n,k})\end{aligned}\tag{16}$$

The sin basis consists of the functions

$$\psi_n = \frac{1}{\sqrt{L}} \sin\left(n \frac{\pi}{L} r\right) = \frac{1}{\sqrt{L}} \sin(n\phi).\tag{17}$$

The matrix elements of the potential energy part of the Hamiltonian are

$$\begin{aligned}
 V_{mn} &\equiv \int_{-L}^L \psi_m^*(r) \hat{V} \psi_n(r) dr = \frac{1}{L} \sum_{k=0}^K V_k \int_{-L}^L \sin\left(m \frac{\pi}{L} r\right) \cos\left(k \frac{\pi}{L} r\right) \sin\left(n \frac{\pi}{L} r\right) dr = \\
 &= \frac{1}{2} (\delta_{m-n,k} + \delta_{m-n,k} - \delta_{m+n,-k} - \delta_{m+n,-k}) = \frac{1}{2} (\delta_{m-n,k} + \delta_{m-n,k} - \delta_{m+n,-k}).
 \end{aligned} \tag{18}$$

2.3. “New” approach

For the reasons that will be explained in Chapter 3, it is convenient to generalize the Polynomial approach assuming the potential energy function is of the form

$$V = \sum_{k=0}^K c_k x^k \exp(-\beta x^2). \tag{19}$$

β is a suitably chosen parameter. For $\beta = 0$ this approach reduced to the Polynomial one. The expansion coefficients are obtained by solving the system of equations

$$\begin{pmatrix} \sum_{i=1}^N \exp(-2\beta x_i^2) & \sum_{i=1}^N x_i \exp(-2\beta x_i^2) & \sum_{i=1}^N x_i^2 \exp(-2\beta x_i^2) & \dots & \sum_{i=1}^N x_i^K \exp(-2\beta x_i^2) \\ \sum_{i=1}^N x_i \exp(-2\beta x_i^2) & \sum_{i=1}^N x_i^2 \exp(-2\beta x_i^2) & \sum_{i=1}^N x_i^3 \exp(-2\beta x_i^2) & \dots & \sum_{i=1}^N x_i^{K+1} \exp(-2\beta x_i^2) \\ \sum_{i=1}^N x_i^2 \exp(-2\beta x_i^2) & \sum_{i=1}^N x_i^3 \exp(-2\beta x_i^2) & \sum_{i=1}^N x_i^4 \exp(-2\beta x_i^2) & \dots & \sum_{i=1}^N x_i^{K+2} \exp(-2\beta x_i^2) \\ \dots & \dots & \dots & \dots & \dots \\ \sum_{i=1}^N x_i^K \exp(-2\beta x_i^2) & \sum_{i=1}^N x_i^{K+1} \exp(-2\beta x_i^2) & \sum_{i=1}^N x_i^{K+2} \exp(-2\beta x_i^2) & \dots & \sum_{i=1}^N x_i^{2K} \exp(-2\beta x_i^2) \end{pmatrix} \begin{pmatrix} V_0 \\ V_1 \\ V_2 \\ \dots \\ V_K \end{pmatrix} =$$

$$= \begin{pmatrix} \sum_{i=1}^N \exp(-\beta x_i^2) E_i \\ \sum_{i=1}^N x_i \exp(-\beta x_i^2) E_i \\ \sum_{i=1}^N x_i^2 \exp(-\beta x_i^2) E_i \\ \dots \\ \sum_{i=1}^N x_i^K \exp(-\beta x_i^2) E_i \end{pmatrix}. \tag{20}$$

All integrals needed for computation of the elements of the Hamiltonian matrix can be obtained by means of the formulae

$$\begin{aligned} \int_{-\infty}^{\infty} \exp(-\alpha x^2) dx &= \sqrt{\frac{\pi}{\alpha}}; \\ \int_{-\infty}^{\infty} x^n \exp(-\alpha x^2) dx &= \frac{\sqrt{\pi} (n-1)!}{2^{n-1} \left(\frac{n}{2}-1\right)! \alpha^{\frac{n+1}{2}}}, \quad n \geq 2 \end{aligned} \quad (21)$$

(n is even integer). The basis functions are chosen in the form

$$\psi_n(x) = N_n x^n \exp\left(-\frac{1}{2} \alpha x^2\right) = \sqrt{\frac{2^{2n-1} (n-1)! \alpha^{n+1/2}}{\sqrt{\pi} (2n-1)!}} x^n \exp\left(-\frac{1}{2} \alpha x^2\right). \quad (22)$$

($N_0 = \sqrt[4]{\alpha/\pi}$). These basis functions are normalized, but not mutually orthogonal. The elements of the overlap matrix are

$$\begin{aligned} S_{mn} &\equiv \int_{-\infty}^{\infty} \psi_m^*(x) \psi_n(x) dx = N_m N_n \int_{-\infty}^{\infty} x^{m+n} \exp(-\alpha x^2) dx = \\ &= N_m N_n \sqrt{\frac{\pi}{\alpha^{m+n+1}}} \frac{(m+n-1)!}{2^{m+n-1} \left(\frac{m+n}{2}-1\right)!} = \sqrt{\frac{(m-1)!(n-1)!}{(2m-1)!(2n-1)!}} \frac{(m+n-1)!}{\left(\frac{m+n}{2}-1\right)!}. \end{aligned} \quad (23)$$

($m+n$ is even; the special case is $S_{00} = 1$). The elements of the kinetic energy matrix are

$$\begin{aligned} T_{mn} &\equiv -\frac{\hbar^2}{2\mu} \int_{-\infty}^{\infty} \psi_m^*(x) \frac{d^2}{dx^2} \psi_n(x) dx = \\ &= -\frac{\hbar^2}{2\mu} N_m N_n \left[n(n-1) \int_{-\infty}^{\infty} x^{m+n-2} \exp(-\alpha x^2) dx - \right. \\ &\quad \left. - (2n+1)\alpha \int_{-\infty}^{\infty} x^{m+n} \exp(-\alpha x^2) dx + \alpha^2 \int_{-\infty}^{\infty} x^{m+n+2} \exp(-\alpha x^2) dx \right], \end{aligned} \quad (24)$$

and the potential energy is represented by the matrix with the elements

$$\begin{aligned}
 V_{mn} &\equiv \sum_{k=1}^K V_k \int_{-\infty}^{\infty} \psi_m^*(x) x^k \exp(-\beta x^2) \psi_n(x) dx = N_m N_n \sum_{k=1}^K V_k \int_{-\infty}^{\infty} x^{m+n+k} \exp[-(\alpha + \beta)x^2] dx = \\
 &= N_m N_n \sum_{k=1}^K V_k \sqrt{\frac{\pi}{(\alpha + \beta)^{m+n+k+1}}} \frac{(m+n+k-1)!}{2^{m+n+k-1} \left(\frac{m+n+k}{2} - 1\right)!} = \\
 &\sum_{k=1}^K V_k \sqrt{\frac{(m-1)!(n-1)! \alpha^{m+n+1}}{(2m-1)!(2n-1)!(\alpha + \beta)^{m+n+k+1}}} \frac{(m+n+k-1)!}{2^k \left(\frac{m+n+k}{2} - 1\right)!}.
 \end{aligned} \tag{25}$$

($m+n+k$ is even).

3. Results and Discussion

As a concrete example we apply Eq. 1 for calculating the vibrational energy levels of the H_2 molecule. It is well known that the “radial” part of the nuclear Schrödinger equation for diatomic molecules has the form [14]

$$\frac{1}{r^2} \frac{d}{dr} \left[r^2 \frac{dR(r)}{dr} \right] + \left\{ -\frac{J(J+1)}{r^2} + \frac{2\mu}{\hbar^2} [E - U(r)] \right\} R(r) = 0, \tag{26}$$

i.e. it involves the radial coordinate r defined in the range $0 \leq r \leq \infty$; J is the rotational quantum number ($J = 0, 1, 2, \dots$), and $U(r)$ is the potential energy for vibrational motions. Eq. 26 may be simplified by the substitution $R(r) = S(r)/r$, which for the case $J = 0$ leads to the equation

$$\begin{aligned}
 &\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + U(r) \right] S(r) = ES(r), \\
 &0 \leq r \leq \infty,
 \end{aligned} \tag{27}$$

In bound electronic states, the potential energy $U(r)$ has a minimum value at some equilibrium

internuclear distance r_e . Introducing the new coordinate $\xi \equiv r - r_0$, we transform Eq. 27 into

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{d\xi^2} + U(\xi) \right] S'(\xi) = ES'(\xi), \quad (28)$$

$$-r_e \leq \xi \leq \infty.$$

Since U rises rapidly when $r \rightarrow 0$, i.e. for $\xi \rightarrow -r_e$, we can safely replace the real boundary condition $\lim_{\xi \rightarrow -r_e} S' = 0$ by $\lim_{\xi \rightarrow -\infty} S' = 0$, i.e. to define the coordinate ξ in the range $-\infty \leq \xi \leq \infty$. Renaming ξ as x , we bring Eq. 27 to the form of Eq. 1.

In Table 1 are presented the results of calculations of the vibrational levels in the ground electronic state of the H_2 molecule. We employ the potential energy curve pointwise calculated by Kolos and Wolniewicz [13].

Table 1. Vibrational levels of the ground electronic state of the H_2 molecule. $-5 \leq V \leq 5$

v	Exact	Polynomial				Fourier		Present		
		$r_0=1.4$	$r_0=1.4$	$r_0=2.0$	$r_0=1.4$	sin	cos	$r_0=1.4$	$r_0=2.5$	$r_0=2.0$
		$\alpha=17$	$\alpha=10$	$\alpha=10$	$\alpha=10$			$\alpha=10$	$\alpha=10$	$\alpha=10$
		$\beta=0$	$\beta=0$	$\beta=0$	$\beta=0$			$\beta=1$	$\beta=1$	$\beta=1$
		$V \leq 10$	$V \leq 10$	$V \leq 10$	$0.9 \leq V \leq 2.4$	$-5 \leq V \leq 5$		$V \leq 10$		
0	0	0	0	0	0	0	0	0	0	0
1	4162	4198	4198	4140	4162	4162	4162	4156	4161	4162
2	8089	8114	8114	8058	8089	8090	8090	8098	8090	8090
3	11785	11786	11786	11757	11786	11785	11785	11777	11786	11786
4	15254	15236	15236	15235	15258	15253	15253	15249	15254	15256
5	18496	18476	18475	18489	18533	18495	18495	18508	18497	18497
6	21511	21509	21502	21510	21696	21508	21508	21547	21512	21511
7	24294	24385	24307	24294	24899	24289	24289	24301	24295	24294
8	26838	27318	26874	26832	28267	26832	26832	26848	26843	26837
9	29131	30578	29197	29117	31850	29123	29123	29188	29162	29130
10	31158	34265	31409	31141	35656	31146	31146	31432	31175	31159
11	32894	38379	33801	32912	39692	32880	32879	33959	32916	32924
12	34308	42907	36597	34584	43924	34314	34271	36837	34367	34603

In the second column of Table 1 are displayed the energies of thirteen discrete vibrational levels, obtained by an exact numerical solution of the Schrödinger equation, as given in Ref. [15]. The results of the present calculations are shown in columns three to eleven. We employ generally all the potential energy points computed in Ref. [13] (80 points), except of those for very small internuclear distances ($r < 0.75$ bohr), corresponding to energies very high compared to that of the dissociation limit (-1.0 hartree). Omitting these points we substantially facilitate the fitting of the potential curve, without influencing the accuracy of the discrete energy levels to be computed. All the energy levels in Table 1 are given with respect to the lowest-lying one ($E = 0$).

The columns three to six contain the results obtained by the Polynomial approach. That means that the potential energy curve is represented by a polynomial expansion and the vibrational basis function are the eigenfunctions of an appropriately chosen harmonic oscillator. As already stated, our new approach (denoted by “Present” in Table 1) collapses into the Polynomial one when the value of the parameter β equals zero. In all cases when either of these two approaches are employed, the number of basis functions is 30. The bases of such size ensure the convergence of the results for the lowest thirteen vibrational levels. The number of terms in the potential energy expansions is 21 (except in computations of the energy levels given in the sixth column, where it is 11).

The results displayed in the third column are generated by the most straightforward application of the Polynomial approach. The parameter α , determining the form of the vibrational basis functions, is chosen to be 17.3 bohr^{-2} . This value is obtained as $\alpha = \sqrt{k\mu} / \hbar$, where k is the harmonic force constant for the potential energy curve in question, $k = 0.330 \text{ hartree bohr}^{-2}$. The basis functions are centered at the value of $r_0 = 1.401 \text{ bohr}$, being the equilibrium H-H bond length (i.e. the value of the x coordinate at this point is taken to be zero). Note that already the energy difference between the first and the zeroth vibrational level, 4198 cm^{-1} , is significantly above that obtained in the exact treatment. On the other hand, the energy of the level $v = 12$ (42907 cm^{-1}) is very much higher than the exact one (34308 cm^{-1}). Only the levels between $v = 3$ and $v = 6$ agree with the exact results.

These results clearly illustrate the drawbacks of the Polynomial method. The two main sources of the errors are: a) Relatively poor representation of the potential energy curve by a polynomial expansion when the curve is extended up to the dissociation limit. Particularly, each

polynomial expansion tends at $x \rightarrow \infty$ to either $+\infty$ or $-\infty$ instead of approaching the horizontal asymptote. b) The eigenfunctions of the harmonic oscillator representing the quadratic approximation of the real problem are in the vicinity of the equilibrium bond length not “diffuse” enough to ensure correct representation of the large-amplitude vibrations. The second of these problems can partly be removed by using smaller α -values (e.g. $\alpha = 10 \text{ bohr}^{-2}$, fourth column in Table 1). Indeed, in this way an appreciably better agreement with the exact results is obtained for the high-energy part of the spectrum. The results can be further improved by shifting the centers of the basis functions towards the internuclear distances larger than the equilibrium one (fifth column, $r_0 = 2 \text{ bohr}$), aiming to better cover the region approaching the dissociation limit. In this way the calculation error for the level $v = 13$ is reduced to roughly 280 cm^{-1} , and the maximal discrepancy between the results given in the columns two (exact) and five for the levels between $v = 0$ and $v = 10$, i.e. in the energy range larger than 31000 cm^{-1} , does not exceed 30 cm^{-1} . The Polynomial method generates, as expected, very accurate results when the dissociative region is cut off. In the sixth column of Table 1 we give the result obtained in calculations that employ only the part of the potential curve between $r = 0.9$ and $r = 2.4 \text{ bohr}$. In this case the potential energy is represented by 11 expansion terms (up to x^{10}). Since the chosen part of the potential curve involves only five lowest-lying vibrational levels, all other levels presented in the sixth column (separated from the former by a horizontal line) are unrealistic. The reason for that is seen in Fig. 1 (middle part): The polynomial expansion has at $x > 2.4 \text{ bohr}$ a completely different form than the exact potential curve. However, the mentioned five levels practically coincide with the exact ones.

In the last three (ninth, tenth and eleventh) columns of Table 1 are displayed the results generated by means of the new procedure (“Present”). In each case the potential energy curve is scaled such that the dissociation limit corresponds to the zero energy. It is represented by the expansion in $x^k \exp(-\beta \cdot x^2)$ with $\beta = 1 \text{ bohr}^{-2}$ and for three different values of r_0 . The first of them ($r_0 = 1.401 \text{ bohr}$) represents the minimum of the potential curve, and the other two values ($r_0 = 2.0$ and 2.5 bohr) are chosen to ensure better description of higher vibrational levels. The vibrational basis functions are of the form $x^n \exp(-0.5 \cdot \alpha \cdot x^2)$ with $\alpha = 10 \text{ bohr}^{-2}$. The best results are obtained with $r_0 = 2.0 \text{ bohr}$ (last column). The levels between $v = 0$ and $v = 11$ calculated in this way virtually coincide with the exact ones. Only two highest-lying levels, $v =$

11, 12 (separated from the former by a horizontal line) are not accurately computed. This is a consequence of the concrete choice of the functions representing the potential energy curve and the vibrational basis functions (in Fig. 1, top, are displayed the first members of these sets of function, $\exp[-(r-r_0)^2]$ and $\psi_0^2 \propto \exp[-10(r-r_0)^2]$); the choice of the parameters $\beta = 1 \text{ bohr}^{-2}$, $\alpha = 10 \text{ bohr}^{-2}$ is a compromise that ensures proper and most economical description of the levels $v = 0$ to $v = 10$.

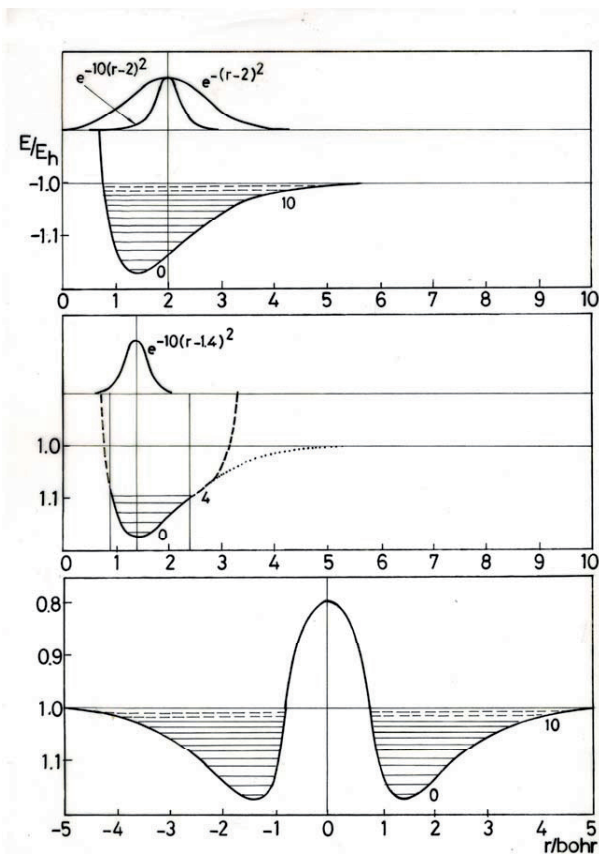


Fig. 1. Bottom: Potential energy curve for the ground electronic state of H_2 and the vibrational levels computed by means of the "New approach". Center: Application of the Polynomial approach. Bottom: Illustration for the use of the Fourier approach.

Finally, in the seventh and the eight column are presented the results obtained by applying the Fourier approach. In this case the potential curve has to be arranged to simulate an artificial periodicity. The choice made in the present study is shown in Fig. 1, bottom. Physically not interesting region of small values for the internuclear distance is replaced by a gaussian-like curve and the dissociation limit is cut off at the value of $r = 5$ bohr, to facilitate the fitting procedure. The results for vibrational energies, obtained by employing 50 expansion terms for the potential energy curve and 50 sin- or cos-type basis functions, are in excellent agreement with the exact ones. All the levels lying below the dissociation limit are artificially double degenerate if both the sin- and cos-vibrational basis functions are used. The splitting starts in the vicinity of the dissociation limit ($v = 11, 12$).

Based on the previous analysis it could be concluded that the Fourier approach is superior to both of the other two proposed. However, it has some disadvantages. As a consequence of the fact that it does not contain any particular feature resembling the vibrational problem, it generally requires relatively large number of expansion terms for the description of both the potential energy curves and wave functions (see e.g. Ref. [6]). Further, artificial small-amplitude oscillatory form of the wave functions makes the computation of some properties (e.g. very small transition moments) inaccurate.

The Fourier approach is, however, very appropriate for handling the problems in which the potential energy curves are really periodic. An important example is the torsional motion, e.g. in B_2H_2 [3] or C_2H_4 [16].

It is hardly possible that the simple and convenient approach denoted in the present study as “New” has not been invented before. However, the sense of the present study is just to show what does (*i.e.* does not) work in handling real one-dimensional molecular vibrations.

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