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A Numerical Method for the Solution of the One-Dimensional Schrödinger Equation

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A numerical method for the calculation of bound states in a one-dimensional potential is suggested, the application of which is very simple and economic. The wavefunctions as well as the potential are approximated by Lagrange interpolation polynomials of the order $2N$. The application of the variational principle yields a $(2N-1)^{\text{th}}$ order eigenvalue problem of the symmetric matrix $\boldsymbol{H}$ derived from the universal matrices $\boldsymbol{T}$ and $\boldsymbol{V}^{(l)}$ $(l=0, 1, \ldots, N)$ and $(2N+1)$ discrete potential values of the actual problem by means of simple matrix algebra. The accuracy of the obtained energies and wavefunctions depends on the parameter N.

The proposed method has been applied to different types of potentials. Using polynomials of the order twenty ($N = 10$), generally the results are quite satisfactory for the states of quantum numbers $n \leqq 4$.

Key words: Numerical solution of the Schrödinger equation – Schrödinger equation, numerical solution of ~

1. Introduction

In consequence of the development of both the numerical *ab initio* and semiempirical methods of quantum chemistry and of the computer facilities, the calculation of potential surfaces for the movement of nuclei in molecules and complexes has become more and more possible. In some cases it is desirable to complete such computations by the calculation of stationary states of the nuclei in these potentials (determination of vibrational frequencies, investigation of vibronic interactions, estimation of proton-transfer rates in the double-well potentials of hydrogen bonds etc.).

The most simple problem in this respect is the calculation of bound states in a one-dimensional potential $v(x)$. Besides the possibility of the numerical integration of the Schrödinger equation using the Runge-Kutta-Merson method [1] some approximate procedures have been described in the literature, e.g. the method of Somorjai and Hornig [2] and the procedure of Stratmann and Seelig [3]. Because of the special approximations of the potential and the wavefunctions the method proposed by Somorjai and Hornig is applicable mainly to oscillator-like problems. Rai and Ladik [4] have used this method for an investigation of the proton vibrations in the double-well potentials of hydrogen bonds. But in this calculation the accuracy of the wavefunctions was poor. Stratmann and Seelig use a finite difference approximation for the Schrödinger equation. They obtain a problem which may be solved iteratively. This method is very convenient for potentials as they occur in the one-dimensional electron gas model of π-electron systems.

In the following we suggest a new method for the numerical solution of the one-dimensional Schrödinger equation which is applicable to potentials, given analytically or numerically. It is assumed that the potential can be approximated by polynomials of not too high order in that range, in which the wavefunctions of the relevant states yield essential contributions. The application of the variational principle to the values of the wavefunction itself (for discrete arguments) results in an algebraic eigenvalue problem of a Hamilton matrix **H**. Due to this procedure any integral calculations are avoided in actual problems. The integrals are contained in some universal matrices which are constants of the procedure.

2. General Formulation

The one-dimensional Schrödinger equation (in atomic units) reads

$$\mathscr{H}\,|\chi_i(x)\rangle = \varepsilon_i\,|\chi_i(x)\rangle \qquad \langle\chi_i|\chi_i\rangle = 1 \tag{1}$$

with the Hamiltonian

$$\mathscr{H} = -\frac{1}{2M}\,\frac{d^2}{dx^2} + v(x) \tag{2}$$

where M denotes the mass of the particle and $v(x)$ means the one-dimensional potential.

In order to approximate the wavefunctions by Lagrange interpolation polynomials, $(2N+1)$ equidistant points x_l $(l=-N, -N+1, \ldots, 0, \ldots, N-1, N)$ are chosen on the x-axis in that range, in which the relevant wavefunctions are essentially different from zero. These x-values are used as arguments of the interpolation. By the appropriate choice of the distance b between two neighbouring arguments x_k and x_{k+1} $(-N \leqq k \leqq N-1)$ the assumption

$$\chi_i(x) = 0 \quad \text{for} \quad x \leqq x_{-N} \quad \text{and} \quad x \geqq x_N \tag{3}$$

can be justified approximately. Since a normalized wavefunction with z nodes cannot be represented by a polynomial of order less than $z+2$ in the range $\{x_{-N} \leqq x \leqq x_N\}$ and surely a higher order is necessary for a proper approximation, the parameter N should be large compared with z, when z is the quantum number of the highest state to be determined.

For the following derivations it is very convenient to substitute

$$\xi = (x - x_0)/b\,. \tag{4}$$

Further, we define the Lagrange polynomials

$$L_k(\xi) = f_{|k|}\,L(\xi)/(\xi - k) \qquad -N \leqq k \leqq N \tag{5}$$

where

$$L(\xi) = \frac{(-1)^N}{(N!)^2}\prod_{i=-N}^{N}(\xi - i)$$

$$f_{|k|} = \begin{cases} 1 & \text{for} \quad k=0 \\ \displaystyle\prod_{i=1}^{|k|}\frac{i-N-1}{i+N} & \phantom{\text{for}} \quad k \neq 0\,. \end{cases}$$

Using these functions for the approximation of the wavefunctions we obtain the interpolation polynomials

$$\chi_i(\xi) = \sum_{l=-N}^{N} \hat{C}_{l,i} L_l(\xi) \tag{6}$$

with the coefficients

$$\hat{C}_{l,i} = \chi_i(l) \,. \tag{7}$$

The boundary conditions following from Eq. (3) read then

$$\hat{C}_{-N,i} = \hat{C}_{N,i} = 0 \,. \tag{8}$$

They imply that all integrals over wavefunctions may be written with finite limits of integration:

$$\frac{1}{b} \int_{-\infty}^{+\infty} dx \ldots = \int_{-N}^{+N} d\xi \ldots \,. \tag{9}$$

The coefficients $\hat{C}_{l,i} (-N+1 \leqq l \leqq N-1)$ are determined by variation. The variational principle which is equivalent to the Schrödinger equation (1) reads

$$\delta \{ \langle \chi_i | \mathscr{H} | \chi_i \rangle - \varepsilon_i (\langle \chi_i | \chi_i \rangle - 1) \} = 0 \tag{10}$$

where ε_i are the Lagrange multipliers with respect to the normalization conditions of the wavefunctions. The execution of the variation yields as Euler equations for the determination of the coefficients $\hat{C}_{l,i}$ (which form the rectangular matrix $\hat{\boldsymbol{C}}$) the common algebraic problem

$$\hat{\boldsymbol{H}} \hat{\boldsymbol{C}} = \boldsymbol{S} \hat{\boldsymbol{C}} \boldsymbol{E} \qquad b \hat{\boldsymbol{C}}^{+} \boldsymbol{S} \hat{\boldsymbol{C}} = \mathbf{1} \tag{11}$$

of the order $2N-1$.

The elements of the symmetrical matrices $\boldsymbol{H}$ and $\boldsymbol{S}$ and the diagonal matrix $\boldsymbol{E}$ are

$$\begin{aligned} \hat{H}_{m,n} &= \int_{-N}^{+N} d\xi \, L_m(\xi) \left\{ -\frac{1}{2Mb^2} \frac{d^2}{d\xi^2} + v(\xi) \right\} L_n(\xi) \\ S_{m,n} &= \int_{-N}^{+N} d\xi \, L_m(\xi) \, L_n(\xi) \\ E_{m,n} &= \varepsilon_m \delta_{m,n} \qquad -(N-1) \leqq m, n \leqq (N-1) \,. \end{aligned} \tag{12}$$

The matrix $\hat{\boldsymbol{H}}$ can be written as a sum of two parts, representing the kinetic and the potential energy, respectively:

$$\hat{\boldsymbol{H}} = \frac{1}{Mb^2} \hat{\boldsymbol{T}} + \hat{\boldsymbol{V}} \,. \tag{13}$$

The matrix $\hat{\boldsymbol{T}}$ depends on N only, being independent of the parameters of the actual problem. In order to avoid integral calculations for the potential term, too, the potential $v(\xi)$ is approximated, in the same way as the wavefunctions (6), by the interpolation polynomials[1]

$$v(\xi) = \sum_{l=-N'}^{N'} v(l) \, L'_l(\xi) \,. \tag{14}$$

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[1] The primes on N and $L_l(\xi)$ mean that the order of the polynomials for the wavefunctions and the order of the polynomial for the approximation of the potential may be different. For the sake of simplicity only, we assume $N' = N$ in the following.

Thus we obtain the matrix $\hat{\boldsymbol{V}}$ of Eq. (13) in the form of a sum

$$\hat{\boldsymbol{V}} = \sum_{l=-N}^{N} v(l)\, \hat{\boldsymbol{V}}^{(l)} \tag{15}$$

where the elements of the N-depending, but otherwise universal matrices $\hat{\boldsymbol{V}}^{(l)}$ are

$$\hat{V}^{(l)}_{m,n} = \int_{-N}^{+N} d\xi\, L_l(\xi)\, L_m(\xi)\, L_n(\xi)\,. \tag{16}$$

With the aid of the partition (13) and the approximation (15) the matrix $\hat{\boldsymbol{H}}$ for an actual potential $v(\xi)$ is derived from the universal matrices $\hat{\boldsymbol{T}}$ and $\hat{\boldsymbol{V}}^{(l)}$ and some actual parameters by means of simple matrix algebra. The actual parameters are the mass M of the particle, the step width b of the interpolation and the $(2N+1)$ potential values $v(l)$, representing the potential function in the interpolation approximation (14).

There exist numerical methods for the solution of the Eq. (11). But a significant simplification results from the reduction of it to the simple eigenvalue problem (with $\boldsymbol{S}=\mathbf{1}$) by an orthogonalization of the basis $\{L_k\}$. Such a transformation allows to apply standard diagonalization procedures which are much more effective.

We use the symmetrical orthogonalization procedure proposed by Löwdin [5]. Multiplication of Eq. (11) from the left by the matrix $\sqrt{b}\,\boldsymbol{S}^{-1/2}$ yields the new equations

$$\boldsymbol{H}\boldsymbol{C} = \boldsymbol{C}\boldsymbol{E} \qquad \boldsymbol{C}^{+}\boldsymbol{C} = \mathbf{1} \tag{17}$$

where the matrices $\boldsymbol{H}$ and $\boldsymbol{C}$ are defined by

$$\begin{aligned} \boldsymbol{H} &= \boldsymbol{S}^{-1/2}\, \hat{\boldsymbol{H}}\, \boldsymbol{S}^{-1/2} \\ \boldsymbol{C} &= \sqrt{b}\, \boldsymbol{S}^{1/2}\, \hat{\boldsymbol{C}}\,. \end{aligned} \tag{18}$$

It should be observed that the transformation (18) of the matrix $\hat{\boldsymbol{H}}$ may be avoided in actual calculations using the universal matrices

$$\begin{aligned} \boldsymbol{T} &= \boldsymbol{S}^{-1/2}\, \hat{\boldsymbol{T}}\, \boldsymbol{S}^{-1/2} \\ \boldsymbol{V}^{(l)} &= \boldsymbol{S}^{-1/2}\, \hat{\boldsymbol{V}}^{(l)}\, \boldsymbol{S}^{-1/2} \end{aligned} \tag{19}$$

instead of $\hat{\boldsymbol{T}}$ and $\hat{\boldsymbol{V}}^{(l)}$. The matrix $\boldsymbol{H}$ reads then

$$\boldsymbol{H} = \frac{1}{Mb^2}\, \boldsymbol{T} + \sum_{l=-N}^{N} v(l)\, \boldsymbol{V}^{(l)}\,. \tag{20}$$

The solution of the eigenvalue problem (17) yields the matrix $\boldsymbol{C}$. The matrix $\hat{\boldsymbol{C}}$ containing the values of the wavefunctions by virtue of Eq. (6) is obtained from the expression

$$\hat{\boldsymbol{C}} = \frac{1}{\sqrt{b}}\, \boldsymbol{S}^{-1/2}\, \boldsymbol{C}\,. \tag{21}$$

Consequently, besides the universal matrices $\boldsymbol{T}$ and $\boldsymbol{V}^{(l)}$ $(l=0, 1, \ldots, N)$[2] we need the matrix $\boldsymbol{S}^{-1/2}$ for actual calculations.

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[2] It will be shown in the next section that the matrix $\boldsymbol{V}^{(-l)}$ is obtained from the matrix $\boldsymbol{V}^{(l)}$ by transposition with respect to the secondary diagonal.

3. Calculation of the Universal Matrices

Because of the universality of the matrices T, $V^{(l)}$, and $S^{-1/2}$ and the relative large computing time which is necessary for their calculation, compared with the time needed for other operations in an actual calculation, it is recommendable to calculate these matrices only once and to hold them on an external storage volume of the computer equipment.

The first step is the calculation of the matrices S, $\hat{T}$ and $\hat{V}^{(l)}$, the elements of which are given by Eqs. (12) and (16). The application of the partial integration technique shows that all occuring integrals may be expressed by the basic integrals

$$\begin{aligned} p_m &= \int_{-N}^{+N} d\xi\, L^2(\xi)/(\xi-m) \\ q_n &= \int_{-N}^{+N} d\xi\, L^3(\xi)/(\xi-n) \qquad -N \leqq m, n \leqq N\,. \end{aligned} \tag{22}$$

These integrals have the symmetry properties

$$\begin{aligned} p_{-m} &= -p_m \\ q_{-n} &= q_n \end{aligned} \tag{23}$$

which can be proved easily using the property $L(-\xi) = -L(\xi)$. Consequently, only $(2N+1)$ integrals must be calculated.

The analytical integration of the integrals (22) is simple. However during the numerical evaluation of the resulting expressions rather serious problems arise due to small differences of large numbers. In order to overcome these difficulties either one has to use a very large word length of the computer or to carry out the integrations numerically. Mostly the latter possibility will be more practicable than the former.

In the following we give the formulas expressing the various matrix elements in terms of the basic integrals. The elements of the matrices S and $\hat{T}$ are

$$S_{m,n} = f_{|m|} f_{|n|} \bar{S}_{m,n} \tag{24}$$

$$\hat{T}_{m,n} = \frac{1}{2} f_{|m|} f_{|n|} \sum_{r(\neq m)=-N}^{+N} \sum_{s(\neq n)=-N}^{+N} \frac{\bar{S}_{r,s} - \bar{S}_{r,n} - \bar{S}_{m,s} + \bar{S}_{m,n}}{(r-m)(s-n)} \tag{25}$$

where

$$\bar{S}_{m,n} = \begin{cases} (p_m - p_n)/(m-n) & \text{for} \quad m \neq n \\ -2 \sum\limits_{r(\neq m)=-N}^{+N} \bar{S}_{m,r} & \qquad\quad m = n\,. \end{cases} \tag{26}$$

With the aid of a matrix M, the elements of which are given by

$$M_{m,n} = \begin{cases} f_{|m|}/(m-n) & \text{for} \quad m \neq n \\ \sum\limits_{r(\neq m)=-N}^{+N} M_{m,r} & \qquad\quad m = n \end{cases} \tag{27}$$

we obtain the expression (25) in the compact matrix form

$$\hat{T} = \tfrac{1}{2} M \bar{S} M^{+}\,. \tag{28}$$

Using the first of the relations (23) we find

$$S_{m,n} = S_{n,m} = S_{-m,-n} \tag{29}$$

$$\hat{T}_{m,n} = \hat{T}_{n,m} = \hat{T}_{-m,-n}\,, \tag{30}$$

i.e. the matrix $\boldsymbol{S}$ as well as the matrix $\hat{\boldsymbol{T}}$ are symmetrical with respect to both diagonals.

The definition of the matrix elements $\hat{V}^{(l)}_{m,n}$ (16) may be written as

$$\hat{V}^{(l)}_{m,n} = f_{|l|} f_{|m|} f_{|n|} \int_{-N}^{+N} d\xi \, \frac{L^3(\xi)}{(\xi - l)(\xi - m)(\xi - n)}\,. \tag{16}$$

In this case the symmetry $L(-\xi) = -L(\xi)$ implies the relations

$$\hat{V}^{(l)}_{m,n} = \hat{V}^{(l)}_{n,m} = \hat{V}^{(m)}_{l,n} = \hat{V}^{(-l)}_{-m,-n} = f_{|l|} f_{|m|} f_{|n|} \hat{V}_{l,m,n} \tag{31}$$

which reduce the number of the different matrix elements considerably. The decomposition to partial fractions and partial integration of the integral (16) yield the following expressions:

$$\begin{aligned}
\hat{V}_{l,m,n} &= \frac{q_l}{(l-m)(l-n)} + \frac{q_m}{(m-l)(m-n)} + \frac{q_n}{(n-l)(n-m)} && (l \neq m \neq n \neq l) \\
\hat{V}_{l,l,n} &= \frac{1}{l-n} \, \frac{q_n - q_l}{l-n} + \frac{3}{2} \sum_{r(\neq l)=-N}^{+N} \frac{q_r - q_l}{l-r} && (l \neq n) \\
\hat{V}_{l,l,l} &= -3 \sum_{r(\neq l)=-N}^{+N} \hat{V}_{l,l,r}\,.
\end{aligned} \tag{32}$$

For the transformation (19) of the matrices $\hat{\boldsymbol{T}}$ and $\hat{\boldsymbol{V}}^{(l)}$ into $\boldsymbol{T}$ and $\boldsymbol{V}^{(l)}$ the matrix $\boldsymbol{S}^{-1/2}$ is required. Since the matrix $\boldsymbol{S}$ is symmetrical and positive definite we obtain the matrix $\boldsymbol{S}^{-1/2}$ conveniently by diagonalization of $\boldsymbol{S}$, i.e. by using the relation

$$\boldsymbol{S}^{-1/2} = \boldsymbol{U}\boldsymbol{D}^{-1/2}\boldsymbol{U}^{+} \tag{33}$$

where $\boldsymbol{U}$ is the unitary matrix of the eigenvectors of $\boldsymbol{S}$, and $\boldsymbol{D}$ the diagonal matrix with the corresponding eigenvalues in its diagonal:

$$\boldsymbol{S}\boldsymbol{U} = \boldsymbol{U}\boldsymbol{D} \qquad \boldsymbol{U}^{+}\boldsymbol{U} = \boldsymbol{U}\boldsymbol{U}^{+} = \boldsymbol{1}\,. \tag{34}$$

Taking into account the symmetry properties (28) of the matrix $\boldsymbol{S}$ one finds an unitary transformation

$$\tilde{\boldsymbol{S}} = \boldsymbol{X}^{-1}\boldsymbol{S}\boldsymbol{X} \tag{35}$$

which brings the matrix $\boldsymbol{S}$ into the block-diagonal form $\tilde{\boldsymbol{S}}$. Due to this transformation the eigenvalue problem (34) of the order $2N-1$ divides into two problems of the orders N and $N-1$, respectively. (For details see the Appendix.)

The matrix $\boldsymbol{S}^{-1/2}$ has the same symmetry as the matrix $\boldsymbol{S}$ (29). Using these properties it can be shown that the transformations (19) do not influence the symmetry relations (30) and (31). The validity of

$$V^{(-l)}_{m,n} = V^{(l)}_{-m,-n} \tag{36}$$

implies that the symmetrical matrices $V^{(l)}$ have to be calculated and storaged for $l=0,1,\ldots,N$ only. The corresponding matrices for negative indices l are obtained by transposition with respect to the secondary diagonal.

Since the integral calculations are partly sensible concerning the numerical accuracy it is useful to have a measure of the accuracy finally reached. The most critical numbers are contained in the matrices $V^{(l)}$. Therefore the relation

$$\sum_{l=-N}^{+N} \boldsymbol{V}^{(l)} = \boldsymbol{1} \tag{37}$$

seems to be a powerful criterium. This identity can be proved formally using the definitions of the matrices $V^{(l)}$. It states that a shift of the zero point of the potential results in shifting of all energy eigenvalues by the same amount.

4. Symmetrical Potentials

If the potential function $v(\xi)$ has the symmetry

$$v(-\xi) = v(\xi), \tag{38}$$

then the solutions of the Schrödinger equation divide into two sets, including the even states ($\chi(-\xi)=\chi(\xi)$) and the odd states ($\chi(-\xi)=-\chi(\xi)$), respectively. This subdivision is reflected by the eigenvalue problem (17), too. Using the relation (36) together with (38) we find that the matrix $\boldsymbol{V}$ has the same symmetry as $\boldsymbol{T}$, i.e. the whole matrix $\boldsymbol{H}$ is symmetrical with regard to both diagonals. Consequently, in this case the matrix $\boldsymbol{H}$ can be block-diagonalized by the transformation

$$\tilde{\boldsymbol{H}} = \boldsymbol{X}^{-1}\boldsymbol{H}\boldsymbol{X} \tag{39}$$

in the same way as the matrix $\boldsymbol{S}$ (35). The first block of the order N provides the even states and the second block of the order $N-1$ the odd ones.

It should be observed that the reduced eigenvalue problem for the odd states is identical with the problem obtained by the application of the not reduced formalism to one half of the interval (e.g. $\xi \geqq 0$), if the order of the polynomials is also halved. The corresponding problem for the even states may be derived by releasing one of the boundary conditions (8). For this reason it is possible to solve problems having the symmetry (38) with higher accuracy than the asymmetrical ones without computation of universal matrices of higher order.

5. Numerical Examples

To visualize the accuracy of the wavefunctions and the energies obtained by the help of the proposed method we present the numerical results of some simple problems which can be solved analytically, and finally the results for a numerically given double-well potential.

In all the computations the parameter value $N=10$ was used, i.e. the wavefunctions and the potentials were approximated by polynomials of the order twenty.

First we give the potentials $v(x)$, the exact energy levels ε_n, the analytical wavefunctions $\chi_n(x)$ and the boundary conditions as well as the step width b of the interpolation used in the numerical computations (all the values in a.u.).

1. Box Potential

$$v(x)=\begin{cases}0 & \text{for} \quad 0\leqq x\leqq 1\\ \infty & \phantom{\text{for}} \quad x<0 \quad \text{and} \quad x>1\end{cases}$$

$$\varepsilon_n=\frac{\pi^2}{2}(n+1)^2 \qquad \chi_n(x)=\sqrt{2}\sin[(n+1)\pi x]$$

$n=0,1,2,\ldots$

boundary conditions: $\chi_i(0)=\chi_i(1)=0$

step width: $b=0.05$.

2. Harmonic Oscillator Potential

$v(x)=x^2/2$

$\varepsilon_n=n+1/2$ $\qquad$ $\chi_n(x)=A_n\exp(-x^2/2)\,H_n(x)$

A_n – normalization constant

$H_n(x)$ – Hermite polynoms

$n=0,1,2,\ldots$

boundary conditions: $\chi_i(-5)=\chi_i(5)=0$

step width: $b=0.5$.

The simplifications due to the symmetry of the box potential and the harmonic oscillator potential, respectively, are not utilized.

3. Morse Potential

$$v(x)=\exp(-2\sqrt{2}x/10)-2\exp(\sqrt{2}x/10)$$

$$\varepsilon_n=-[1-(n+1/2)/10]^2$$

$$\chi_n(x)=A_n\exp(-\eta/2)\,\eta^{s_n}F(-n,2s_n+1,\eta)$$

$\eta=20\exp(-\sqrt{2}x/10) \qquad s_n=10-n-1/2$

A_n – normalization constant

F – confluent hypergeometric function

$n=0,1,2,\ldots$

boundary conditions: $\chi_i(-8.5)=\chi_i(21.5)=0$

step width: $b=1.5$.

4. In the last example the semiempirical Lippincott-Schroeder potential for the proton vibration in the N–H…O hydrogen bond, with an assumed bond length of 3.0 Å, is used. The numerical values of the potential have been taken

Table 1. Comparison of approximate and exact energy eigenvalues ε_n (a.u.)

n	Box potential		Harmonic oscillator potential		Morse potential		Double well potential	
	approx.	exact	approx.	exact	approx.	exact	approx.	R-K-M[a]
0	4.934	4.9348	0.499	0.5	−0.9025	−0.9025	4.91	3.446
1	19.74	19.739	1.500	1.5	−0.7224	−0.7225	18.48	18.429
2	44.41	44.413	2.499	2.5	−0.5622	−0.5625	28.74	28.747
3	78.95	78.957	3.501	3.5	−0.4217	−0.4225	31.39	30.954
4	123.4	123.37	4.503	4.5	−0.3004	−0.3025	41.51	41.465
5	177.6	177.65	5.529	5.5				
6	241.8	241.81	6.541	6.5				
7	315.8	315.83	7.691	7.5				
8	399.7	399.72	8.731	8.5				

[a] Values taken from the calculation of Biczo *et al.* [1] in which the Runge-Kutta-Merson (R-K-M) method has been used.

Table 2. Box potential: comparison of approximate and exact wavefunction $\chi(x)$ (a. u.)

x (a. u.)	$n=0$ approx.	$n=0$ exact	$n=4$ approx.	$n=4$ exact	$n=7$ approx.	$n=7$ exact	$n=8$ approx.	$n=8$ exact
0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.05	0.221	0.221	−1.000	−1.0	−1.345	−1.345	−1.397	−1.397
0.10	0.437	0.437	−1.414	−1.414	−0.831	−0.831	−0.436	−0.437
0.15	0.642	0.642	−1.000	−1.0	0.831	0.831	1.259	1.260
0.20	0.831	0.831	0.000	0.0	1.345	1.345	0.831	0.831
0.25	1.000	1.0	1.000	1.0	0.001	0.0	−1.000	−1.0
0.30	1.144	1.144	1.414	1.414	−1.346	−1.345	−1.146	−1.144
0.35	1.260	1.260	1.000	1.0	−0.831	−0.831	0.644	0.642
0.40	1.345	1.345	0.000	0.0	0.832	0.831	1.344	1.345
0.45	1.397	1.397	−1.000	−1.0	1.344	1.345	−0.222	−0.221
0.50	1.414	1.414	−1.414	−1.414	0.000	0.0	−1.412	−1.414

from the paper of Biczo *et al.* [1] and are given in the first column of Table 5. The mass $M = 1836$ a.u., the step width $b = 0.09$ Å $= 0.1701$ a.u. and the boundary conditions $\chi_i(0.6\,\text{Å}) = \chi_i(2.4\,\text{Å}) = 0$ (the origin of the x-axis lies in the nitrogen nucleus) are the further input parameters of this computation.

The Table 1 shows the energy levels ε_n obtained numerically in the four cases. For comparison the corresponding exact values are noticed, too (with exception of the last column).

The discrete values of the wavefunctions belonging to the first three examples are given in the Tables 2, 3, and 4. Because of the symmetry of both the box potential and the harmonic oscillator potential in these cases the tabulation includes only the values for one half of the interval taken into consideration. For the double-well potential the wavefunctions are summarized in the Table 5. No exact wavefunctions are available in this case.

The accuracy of the wavefunctions and the energies is determined mainly by the relation of the order of the Lagrange polynomials (i.e. the parameter N) to the

Table 3. Harmonic oscillator potential: comparison of approximate and exact wavefunctions $\chi(x)$ (a. u.)

x	$n=0$		$n=1$		$n=2$		$n=3$	
(a. u.)	approx.	exact	approx.	exact	approx.	exact	approx.	exact
0.0	0.751	0.751	0.000	0.0	−0.529	−0.531	0.000	0.0
0.5	0.663	0.663	0.468	0.469	−0.235	−0.234	0.470	0.478
1.0	0.455	0.456	0.645	0.644	0.322	0.322	0.270	0.263
1.5	0.243	0.244	0.517	0.517	0.605	0.604	−0.316	−0.317
2.0	0.102	0.102	0.287	0.288	0.502	0.503	−0.593	−0.587
2.5	0.033	0.033	0.117	0.117	0.269	0.268	−0.449	−0.453
3.0	0.008	0.008	0.035	0.035	0.100	0.100	−0.220	−0.217
3.5	0.002	0.002	0.008	0.008	0.027	0.027	−0.070	−0.075
4.0	0.000	0.000	0.001	0.001	0.006	0.006	−0.018	−0.017
4.5	0.000	0.000	0.000	0.000	0.001	0.001	−0.001	−0.003
5.0	0.0	0.000	0.0	0.000	0.0	0.000	0.0	−0.000

Table 4. Morse potential: comparison of approximate and exact wavefunctions $\chi(x)$ (a. u.)

x	$n=0$		$n=1$		$n=2$		$n=3$	
(a. u.)	approx.	exact	approx.	exact	approx.	exact	approx.	exact
− 8.5	0.0	0.000	0.0	−0.000	0.0	0.000	0.0	−0.000
− 7.0	0.000	0.000	−0.001	−0.001	−0.000	0.001	0.001	−0.002
− 5.5	0.006	0.006	−0.016	−0.015	0.027	0.026	−0.038	−0.037
− 4.0	0.052	0.052	−0.104	−0.105	0.153	0.154	−0.194	−0.189
− 2.5	0.202	0.201	−0.308	−0.305	0.335	0.331	−0.300	−0.295
− 1.0	0.410	0.412	−0.368	−0.371	0.168	0.174	0.029	0.019
0.5	0.493	0.495	−0.070	−0.069	−0.228	−0.238	0.259	0.276
2.0	0.391	0.391	0.311	0.314	−0.267	−0.266	−0.022	−0.035
3.5	0.220	0.220	0.434	0.432	0.096	0.105	−0.291	−0.299
5.0	0.094	0.094	0.319	0.320	0.387	0.381	−0.098	−0.079
6.5	0.033	0.032	0.166	0.166	0.380	0.377	0.267	0.266
8.0	0.009	0.009	0.070	0.068	0.239	0.241	0.397	0.390
9.5	0.002	0.002	0.022	0.023	0.123	0.118	0.313	0.317
11.0	0.001	0.000	0.007	0.007	0.047	0.048	0.194	0.188
12.5	−0.000	0.000	0.003	0.002	0.014	0.017	0.095	0.092
14.0	0.000	0.000	−0.001	0.000	0.008	0.005	0.036	0.039
15.5	0.000	0.000	0.001	0.000	−0.001	0.001	0.019	0.015
17.0	−0.000	0.000	−0.000	0.000	0.002	0.000	0.003	0.005
18.5	0.000	0.000	0.000	0.000	−0.001	0.000	0.003	0.002
20.0	0.000	0.000	−0.001	0.000	0.002	0.000	−0.002	0.000
21.5	0.0	0.000	0.0	0.000	0.0	0.000	0.0	0.000

number of nodes of the state considered. As expected it decreases with increasing quantum numbers. Of course the accuracy depends also on the fulfilment of the boundary conditions. For a given N the definition of the boundaries implies the step width b. Generally this means that an optimal choice of the boundaries exists for each state separately. Therefore a compromise is necessary which depends on the question whether higher states are of interest or not. In the examples, values of b being optimal for the fifth state were taken. Only in the case of the box

Table 5. Double well potential: potential $v(x)$ (10^{-3} a.u.) and the approximate wavefunctions $\chi(x)$ (a.u.)

x	Potential	Wavefunctions				
(Å)	$v(x)$	$n=0$	$n=1$	$n=2$	$n=3$	$n=4$
0.6	138.00	0.0	0.0	0.0	0.0	0.0
0.69	87.49	0.001	−0.005	−0.001	0.065	0.006
0.78	47.35	0.070	−0.195	−0.004	0.393	0.040
0.87	17.78	0.434	−0.937	−0.011	1.257	0.076
0.96	1.58	1.285	−1.319	−0.009	0.359	−0.028
1.05	− 1.75	1.651	0.122	0.015	−0.971	−0.037
1.14	4.92	1.081	1.385	−0.001	−0.001	0.069
1.23	17.18	0.364	1.079	−0.022	1.354	−0.003
1.32	31.05	0.069	0.343	−0.070	1.064	−0.116
1.41	42.89	0.021	0.075	0.000	0.286	−0.086
1.50	50.66	−0.003	0.027	0.003	0.103	−0.081
1.59	52.86	−0.003	−0.010	0.021	0.054	−0.174
1.68	49.15	0.006	0.004	0.075	−0.043	−0.423
1.77	40.94	−0.004	0.006	0.303	0.033	−1.040
1.86	30.78	−0.001	−0.010	0.922	0.030	−1.415
1.95	23.10	0.006	0.008	1.583	−0.037	−0.382
2.04	23.58	−0.005	0.000	1.438	0.061	1.133
2.13	37.07	0.002	−0.002	0.589	0.007	1.025
2.22	64.90	−0.002	0.001	0.104	0.009	0.250
2.31	106.69	0.003	0.002	0.003	−0.019	0.020
2.40	162.29	0.0	0.0	0.0	0.0	0.0

potential the boundary conditions hold exactly and the results are satisfactory for higher quantum numbers, too.

For the double-well potential, the large deviation of our ground-state energy from that of Biczo *et al.* is caused by the latter calculation, which may be shown by a simple estimation. Surprisingly in a few cases the numerical energies are somewhat below the exact values. Probably this effect is induced by the propagation of small numerical errors of the universal matrices and may be avoided by using a higher precision in the corresponding part of the calculation. On the contrary, the small oscillations of the wavefunctions leading to additional nodes (especially in the case of the double-well potential) are an inevitable consequence of the approximation by polynomials.

The calculations have been carried out by the help of FORTRAN IV programs written for the IBM 360/40 computer. The computing time for the universal matrices was 40 min approximately while one actual problem was solved in less than 10 sec. The method of Givens and Householder has been used for the matrix diagonalizations.

6. Conclusions

The proposed method has been proved to be useful for the approximate determination of bound states of not too high quantum numbers in an one-dimensional potential. Very short computing time is required to obtain the energy levels as well as the wavefunctions.

The latter aspect qualifies the method for applications in the frame of iterative procedures. The problem of the vibrations of protons in a coupled system of hydrogen bonds is treated as an example in a following paper.

Appendix

We use the polynomials $L_k(\xi)$ $(k = -N+1, -N+2, \ldots, N-1)$ given by Eq. (5) as a basis for the matrix representation of the reflection group of the one-dimensional space. This group consists of the two operations: $\mathscr{E}$ (identity) and $\mathscr{I}$ (reflection through the origin). Their application to the basis functions yields

$$\begin{aligned} &\mathscr{E}\, L_k(\xi) = L_k(\xi) \\ &\mathscr{I}\, L_k(\xi) = L_k(-\xi) = L_{-k}(\xi)\,, \end{aligned} \tag{A.1}$$

i.e. the group is represented by the $(2N-1)^{\mathrm{th}}$ order matrices

$$\begin{aligned} A(\mathscr{E}) &= \mathbf{1} \\ A(\mathscr{I}) &= \boldsymbol{P} \end{aligned} \tag{A.2}$$

where the idempotent matrix $\boldsymbol{P}$ has the elements $P_{m,n} = \delta_{-m,n}$. This representation is reducible. Since we have two matrices only, the unitary transformation matrix $\boldsymbol{X}$ which reduces the representation is found easily by diagonalization of the matrix $\boldsymbol{P}$. Due to its idempotency the matrix $\boldsymbol{P}$ has the two degenerate eigenvalues $+1$ and -1, corresponding to the two irreducible representations

$$\begin{pmatrix} A_1(\mathscr{E}) = 1 \\ A_1(\mathscr{I}) = 1 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} A_2(\mathscr{E}) = 1 \\ A_2(\mathscr{I}) = -1 \end{pmatrix}, \tag{A.3}$$

respectively, and the matrix of its normalized eigenvectors may be written as

$$\boldsymbol{X} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & & & & & & -1 \\ & \ddots & & 0 & & \iddots & \\ & & 1 & & -1 & & \\ & 0 & & \sqrt{2} & & 0 & \\ & & 1 & & 1 & & \\ & \iddots & & 0 & & \ddots & \\ 1 & & & & & & 1 \end{pmatrix}. \tag{A.4}$$

This means that a matrix $\boldsymbol{G}$ with the elements

$$G_{m,n} = \int\limits_{-N}^{+N} d\xi\, L_m(\xi)\, \mathscr{G}\, L_n(\xi)\,, \tag{A.5}$$

where $\mathscr{G}$ is a arbitrary operator commuting with $\mathscr{I}$, can be block-diagonalized by the transformation

$$\boldsymbol{G} = \boldsymbol{X}^{-1} \boldsymbol{G} \boldsymbol{X}\,. \tag{A.6}$$

The blocks of the orders N and $(N-1)$ correspond to the two irreducible representations of the one-dimensional reflection group and combine even and odd functions separately.

It can be shown that for each Hermitian operator $\mathscr{G}$ the relations

$$G_{m,n} = G_{n,m} = G_{-m,-n} \tag{A.7}$$

hold. Thus we see that the relations (29) and (30) as well as the possibility to block-diagonalize the matrix $\boldsymbol{S}$ and the matrix $\boldsymbol{H}$ [Eqs. (35) and (39)] are induced by the commutability of the operators 1, $d^2/d\xi^2$ and $v(\xi) = v(-\xi)$ with the operator $\mathscr{I}$.

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