Multipoint Wronskian Method Applied on Model Potentials and Numerical Potential of Triplet H_2

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The multipoint Wronskian method is applied to one-dimensional vibrational eigenvalue problems with two different potential functions. Systematic ways of selecting points are discussed. The errors introduced by interpolation methods and the effect of including higher derivatives of the potential are analyzed.

Key words: Vibrational eigenvalue equation, Wronskian method, Numerical potentials.

Introduction

One of the most interesting areas of chemical physics is the solution of eigenvalue equations for the vibrational motion of small molecules. The ever-popular subject of "chaos in quantum chemistry" requires a thorough understanding of the eigenvalue spectra of model systems. It has been shown that inaccurate calculations may cause even qualitatively incorrect results [1]. On the other hand the vibrational motion of the "real" systems such as diatomic or three-atomic molecules may pose different problems so that even the low-lying states may be difficult to compute accurately [2, 3]. Hence it is understandable that we still have to search for new methods of solving such eigenvalue problems of small dimensions.

The earlier methods of solutions for vibrational potentials of diatomic molecules were mostly based on variations of the Cooley algorithm [4, 5]. These methods were shown to be very reliable for one-dimensional equations. However there is only a small number of applications to the higher systems [6] due to the high cost of computations. On the other hand, the analytical methods can be applied in a variety of problems, but a preliminary modification is necessary for efficient applications. The most common approach is the Rayleigh-Ritz variational method, in which the wavefunction is written as a linear combination of some pre-determined basis functions. Then the unknown coefficients are optimized such that the energy expectation value is minimum. Here the choice of the basis function is very critical [7]. It is clear that any basis set would produce very accurate results if a sufficiently large number of functions can be employed (provided that they form a complete basis). However, in practice this may not be always possible since it is very expensive to carry out large matrix operations. Then one has to find a basis set which has a fast convergence behaviour. The other criterion for the selection of basis functions is the relative ease of the computation of the variational integrals. The standard methods employ functions whose integrals are somewhat simple to generate and construct the largest possible matrices to solve for the eigenvalues.

Recently a quasi-variational method was proposed by Demiralp [8] and generalized by one of us [9]. The Wronskian method also employs a linear combination of basis functions as the trial solution. The main differences from the standard techniques is the fact that no integrals are required. The only requirement is that functions should be differentiable. Since this is much easier to fulfill then the integrability condition, it provides a great freedom for the selection of basis functions. In this work we continue our analysis of the Wronskian method for several model and real systems. Our aim is to work with cases where detailed studies are available so that the advantages and the limitations of the method are clarified.

Method

The following discussion is for one-dimensional problems, but generalization to many-dimensional

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cases is trivial. The eigenvalue equation is

$$H\Psi = E\Psi . \tag{1}$$

Here E is the constant eigenvalue corresponding to the exact wavefunction. A functional form has to be defined for the approximate solutions

$$\mu(x) = \frac{H\Psi(x)}{\Psi(x)} . \tag{2}$$

For the exact solution, E is infinitely differentiable, and all derivatives with respect to the coordinate are zero. As this cannot be satisfied by $\mu(x)$, we may impose the condition that only a finite number of derivatives at a given point in the coordinate space should be zero.

$$\left[\frac{\mathrm{d}^k \mu(x)}{\mathrm{d}x^k}\right]_{x=x_0} = 0 , \quad k = 1, 2, \ldots, n . \tag{3}$$

This is the original formulation of Demiralp, and it focusses only on a single point of the potential curve. If the potential curve has rapidly changing characteristics, then it may be more efficient to apply the above conditions over a range rather than a single point [9],

$$\left[\frac{\mathrm{d}^k \mu(x)}{\mathrm{d}x^k}\right]_{x=x_i} = 0 , \quad \begin{array}{l} i = 1, 2, \ldots, n_p \quad \text{and} \\ k = 1, 2, \ldots, n_c , \end{array} \tag{4}$$

where n_p and n_c are the numbers of points and conditions, respectively.

Now we can continue our derivation by expanding the unknown wavefunction as a linear combination of basis functions:

$$\Psi(x) = \sum_{p=1} C_p \, \Phi_p(x) . \tag{5}$$

After differentiating $H\Psi = E\Psi$ (k times):

$$\left[\frac{\mathrm{d}^k}{\mathrm{d}x^k} \sum_{p=1} C_p H\Phi_p\right]_{x=x_i} = \sum_{p=1} C_p \sum_{l=0} \binom{k}{l} \left[\frac{\mathrm{d}^l \mu}{\mathrm{d}x^l}\right]_{x=x_i} \left[\frac{\mathrm{d}^{k-l}}{\mathrm{d}x^{k-l}} \Phi_p\right]_{x=x_i} \tag{6}$$

applying conditions (4), we obtain

$$\sum_{p=1} C_p \left[\frac{\mathrm{d}^k}{\mathrm{d}x^k} (H\Phi_p)\right]_{x=x_i} = \sum_{p=1} C_p \, \mu \left[\frac{\mathrm{d}^k}{\mathrm{d}x^k} \Phi_p\right]_{x=x_i} . \tag{7}$$

The final form of the equations can be written as

$$\mathbf{AC} = \mu \mathbf{BC} \tag{8}$$

with

$$A_{mp} = \left[\frac{\mathrm{d}^k}{\mathrm{d}x^k} (H\Phi_p)\right]_{x=x_i} , \quad B_{mp} = \left[\frac{\mathrm{d}^k}{\mathrm{d}x^k} \Phi_p\right]_{x=x_i} , \tag{9}$$

where $m = ((i-1)(n_c+1)) + k + 1$ in our formulation. Equation (8) is a generalized eigenvalue problem for an unsymmetric operator and can be solved by standard techniques.

Calculations

The purpose of this report is two-fold. We would like to develop some non-manual way of selecting points to be enforced for (4). We are also interested in the effect of including higher derivatives of $\mu(x)$ on the quality of results. To clarify this point, one should note that numerical solutions of vibrational eigenvalue problems as well as variational ones are obtained by computing only the values of the potential but not of its derivatives. In contrast, the Wronskian method requires the computation of derivatives of the potential, hence it should produce higher quality results. From ab-initio data it is relatively easy to obtain the first derivative with respect to internuclear distance by virtue of the virial theorem. However, higher derivatives are in general computed by numerical procedures which introduce additional errors. Therefore one must find an optimum range of derivatives to be computed provided they are analytically available.

In order to test the applicability of the method we choose two different potentials. As an analytical function we use the Kratzer-Fues potential [10, 11]. This function can be used to describe the interaction potential of a diatomic molecule, it has a regular singularity at the origin and its analytical solution can be obtained in terms of generalized Laguerre polynomials [12],

$$V(x) = V_0 \left(\frac{a^2}{x^2} - \frac{2a}{x}\right) \quad \begin{array}{l} \text{with } V_0 = 25.0 \text{ a.u. and} \\ \qquad a = \ 1.0 \text{ a.u.} \end{array} \tag{10}$$

Basis functions are chosen as exponential functions of the form

$$\Phi_p = x^{p+s-1} e^{-\alpha x} . \tag{11}$$

By setting $s = 1/2(1 + (1 + 8V_0 a)^{1/2})$ and $\alpha = 2V_0 a/s$ we observe that Φ_0 corresponds to the exact ground state, and then we can analyze the higher vibrational eigenfunctions.

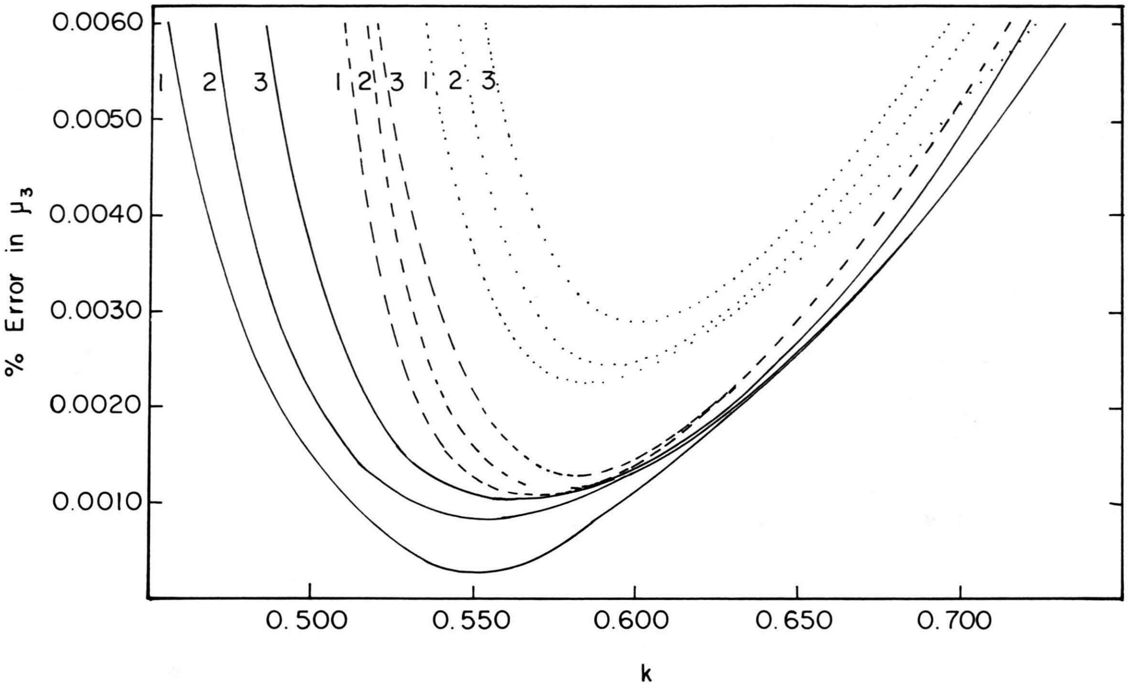

Fig. 1. Percent errors in μ_3 of the Kratzer-Fues potential as a function of the parameter k of (12). —— Gaussian abscissas; – – – Chebyshev abscissas; · · · · evenly spaced points. **1**: six points, **2**: four points and **3**: three points.

Our second test potential is the numerical abinitio data of Kolos and Wolniewicz [13] on the $^3\Sigma_g$ excited state of H_2. It is composed of 42 points between 1.0 a.u. and 10.0 a.u. of distance. Accurate numerical solutions of it are available for comparison purposes. The basis set for this potential is formed from harmonic oscillator eigenfunctions. Its nonlinear parameter is chosen by fitting a harmonic oscillator around the minimum.

Since the Kratzer-Fues potential is an analytical potential and infinitely differentiable, we may analyze the point-selection problem alone, as all derivatives are computed analytically. A systematic way of determining the range for (4) and the distribution of points within this range is reached by defining a parameter k:

$$k = -\frac{V(x)}{V_0} = (1-2x)/x^2. \tag{12}$$

The solution of (12) gives the range as

$$x_{1,2} = \frac{1 \mp \sqrt{1-k}}{k}. \tag{13}$$

The Wronskian method can be considered analogous to numerical integration procedures since they are also based on the computation of some functional forms at selected points. Therefore we choose the points for (4) either equidistantly as in Simpson integration or by appropriately scaled abscissas of Gaussian and Chebyshev quadratures. In Fig. 1 the percent errors of the third eigenvalue are plotted against k for different methods with 3, 4, and 6 point calculations. The final matrix equations are all of dimension $12 \cdot 12$. That is if (4) is enforced on 2 points then up to 5th derivatives of $\mu(x)$ have to be computed. In case of the 6-point calculation only the first derivatives and functional values of $\mu(x)$ are used to set up **A** and **B** matrices of (8), (9).

The best results are obtained by using a Gauss quadrature-type selection of points and working in the region around $k = 0.5$, which corresponds to half the dissociation energy. This result is not unexpected. The points which lie either close to dissociation or those for very short internuclear distances do not contribute to lower eigenvalues. On the other hand, the

Table 1. Percent errors in the eigenvalues of the numerical potential (a.u.).

Point selection	$n=1$	$n=2$	$n=3$	$n=4$
k = 25 Gauss				
Generated points:				
Polyn. interpol. deg. 2	0.750	0.552	3.140	5.392
Polyn. interpol. deg. 3	0.590	0.532	0.659	6.747
Polyn. interpol. deg. 4	0.525	0.467	0.865	6.995
6 points from [13]	0.000	0.001	0.024	0.130

accumulation of points around the minimum poses numerical problems. In particular the rows of Wronskian matrices for higher derivatives tend to be very similar, causing the matrices to be highly singular. In that case the number of eigenvalues in real plane becomes very small. The unexpected result is the somewhat negative effect of higher derivatives. From Fig. 1 it is clear that including higher derivatives improves eigenfunctions only when applied on a large number of points. This shows that the multi-point Wronskian method is more powerful than the original single-point version. This explains the success of local energy methods which are similarly based on properties of eigenfunctions at different regions of coordinate space. Based on results of the Kratzer-Fues problem we can conclude that a weighted distribution of points around the minimum of the potential coupled with restriction on a small number of derivatives produces the best results.

In the numerical potential we are faced by a different type of problem. Since the potential is given in a tabulated form, either some of these points should be used for (4), or some sort of interpolation must be employed to find the values of the potential and/or its derivatives. A systematic selection of points from ab-initio tables cannot be done as they usually concentrate on certain regions of the coordinate space. In order to compare, we choose two sets of points. The first one consists of 6 points which are obtained by Gauss quadrature for $k=0.25$ and the second set is obtained from ab-initio data at $R=1.4$, 1.6, 1.8, 2.1, 2.2, and 2.6 a.u. These points are not optimized but rather they represent both sides of the minimum without being very close to each other. In both cases, (8) is solved by including the first derivatives of $\mu(x)$ only. In Table 1, percent errors of the first 4 eigenvalues are given. Polynomial interpolations of order 2, 3, and 4 are used for the quadrature-generated points. The large differences in the quality of the results clearly show the effect of interpolation. Other interpolation schemes, like spline, Bessel methods or employing polynomials fitted to the first derivatives of the potential, also produce inconsistent results. For quantum-mechanically generated points the exact first derivatives are available, so possible errors only stem from using finite basis sets. This widely varied range of results suggests that the standard methods of solutions of vibrational problems such as basis-set of numerical variational approaches may be strongly influenced by the interpolation techniques used.

In conclusion, we have observed that the multi-point Wronskian method can be applied even in case of singular potentials. Analogous to numerical integration methods, Gauss quadrature can be used for systematic selection of points for analytical potentials. In case of numerical potentials, the main problem seems to be the errors coming from interpolation techniques. But this is not inherent to the Wronskian method only, as the variational methods also behave erratically due to different interpolation methods used [14].

[1] E. Yurtsever and J. Brickmann, Phys. Rev. **A38,** 1027 (1988).
[2] S. Carter and N. C. Handy, Mol. Phys. **47,** 1445 (1982).
[3] G. D. Carney, L. L. Sprandel, and C. W. Kern, Adv. Chem. Phys. 37, 305 (1978).
[4] J. W. Cooley, Math. Comput. **15,** 363 (1961).
[5] F. L. Tobin and J. Hinze, J. Chem. Phys. **63,** 1034 (1975).
[6] J. W. Neuberger and D. W. Noid, Chem. Phys. Lett. **104,** 1 (1984).
[7] E. Yurtsever, Z. Naturforsch. **43a,** 745 (1988).
[8] M. Demiralp, Intern. J. Quant. Chem. **29,** 221 (1986).
[9] E. Yurtsever, Chem. Phys. Lett. **141,** 386 (1987).
[10] A. Kratzer, Z. Phys. **3,** 289 (1920); Ann. Phys. **67,** 127 (1922).
[11] E. Fues, Ann. Phys. **80,** 367 (1926).
[12] J. D. Stetter and R. A. Shatas, Intern. J. Quant. Chem. **5,** 227 (1971).
[13] W. Kolos and L. Wolniewicz, J. Chem. Phys. **48,** 3672 (1968).
[14] E. Yurtsever and M. Pehlivan, Proc. Symp. Numerical Analysis **1985,** 271.