39. *Numerical Solution of an Unharmonic Oscillator Eigenvalue Problem by Milne's Method*

By Hiroshi EZAWA,*) Koichi NAKAMURA,*)
and Yoshitaka YAMAMOTO**)

(Comm. by Takahiko YAMANOUCHI, M. J. A., Feb. 12, 1970)

1. In this note, we shall briefly report on our numerical solution of the quantum mechanical eigenvalue problem,

$$\mathcal{H}u_n(x)=\lambda_n u_n(x), \qquad (u_n \in L_2(-\infty, \infty), n=0, 1, 2, \cdots) \tag{1}$$

with the Hamiltonian,

$$\mathcal{H}=-\frac{d^2}{dx^2}+V(x), \qquad V(x)=-\nu x^2+x^4, \tag{2}$$

where ν is a parameter taking on either positive or negative values. One recognizes immediately that perturbation approach from the harmonic oscillator case cannot be useful even if there were a small parameter in front of the term x^4; when $\nu<0$ the perturbation series diverges! We have encountered the Hamiltonian (2) in our lattice space formulation of the $\lambda\phi^4$ field theory,[1] where the condition of mass-renormalization requires a large positive ν. The Hamiltonian of the same type has been studied by many authors in connection with the inversion vibration of NH_3 molecule[2] and the hydrogen-bonded solids; the 20-parameter variation calculation of Somorjai and Hornig[3] is perhaps the most elaborate, but on the one hand the precision they could obtain for eigenvalues was not high enough for our purpose (see Table below) and on the other they did not give the matrix elements due possibly to the limitation of the variation method.

2. In order to solve the eigenvalue problem (1), one normally attempts to connect smoothly the two solutions of the differential equation $(\mathcal{H}-\lambda)u(x)=0$, one started from $x=+\infty$ and the other from $x=-\infty$ (or from $x=0$ when the potential $V(x)$ is symmetric as ours is) by choosing appropriate value for λ on trial and error basis.

In our present problem, however, we have to determine the eigenvalues very accurately, in particular for the case of large $\nu>0$ because, due to the fact that the potential $V(x)$ is W-shaped having two deep valleys, the eigenvalue spectrum gets a doublet structure; the narrower the spacing becomes the larger the ν one takes.

We used the method proposed by W. E. Milne[4] in 1930; it is best

*) Department of Physics, Gakushuin University.
**) Department of Physics, University of Tokyo.

suited for our purpose because it provides us with a function $N(\lambda)$ that has the following nice properties:—

(N1) It takes on integer values when and only when λ equals one of the eigenvalues λ_n. Moreover,

$$N(\lambda_n)=n+1, \qquad (n=0,1,2,\cdots). \tag{3}$$

(N2) It increases monotonically with λ.

Imagine how sensitive $N(\lambda)$ is to the small variation of λ in the region of the doublet spectrum!

3. Here, we shall present a brief account of Milne's method, since the proof for (N1) and (N2) is not given in Milne's paper.[4] Let $z(x;\lambda)=v_1(x)+iv_2(x)$ be a solution to the differential equation $(\mathcal{H}-\lambda)z=0$ satisfying the initial condition,

$$v_k(x)=\delta_{k1} \quad \text{and} \quad \dot{v}_k(x)=\delta_{k2} \quad \text{at} \quad x=0, \tag{4}$$

where the dot signifies d/dx and δ_{kj} is the Kronecker symbol. We assume generally that $V(x)$ is such that at least one of the v_k's diverges "exponentially" as $x\to\pm\infty$. Now, put the polar form of z as

$$z(x;\lambda)=w(x;\lambda)\exp[i\theta(x;\lambda)], \qquad \theta(0;\lambda)=0. \tag{5}$$

Obviously, z^* gives another solution independent of z ($*$ means complex conjugate), the Wronskian being $z^*\dot{z}-\dot{z}^*z=2i$, which implies $\dot{\theta}=w^{-2}$, or in other words,

$$\theta(x;\lambda)=\int_0^x w(x';\lambda)^{-2}dx'. \tag{6}$$

The function $N(\lambda)$ which we mentioned in the last section is then defined as $\pi^{-1}[\theta(\infty;\lambda)-\theta(-\infty;\lambda)]$, or

$$N(\lambda)=\frac{1}{\pi}\int_{-\infty}^{\infty} w(x';\lambda)^{-2}dx'. \tag{7}$$

In order to prove the property (N1), we put λ equal to an eigenvalue λ_n and write the general solution to the differential equation $(\mathcal{H}-\lambda_n)u=0$ as

$$u(x;\lambda_n)=w(x;\lambda_n)\sin[\theta(x;\lambda_n)-\alpha], \tag{8}$$

where α is an arbitrary real constant. Suppose that this is an eigenfunction, then one must have

$$u(\pm\infty;\lambda_n)=0. \tag{9}$$

But, $w(\pm\infty;\lambda_n)=\infty$ because, due to our assumption, one of the v_k's at least diverges exponentially as $x\to\pm\infty$. Therefore, it is necessary that $\theta(\infty;\lambda_n)-\alpha=n_1\pi$ and $\theta(-\infty;\lambda_n)-\alpha=n_2\pi$ with $n_k=$ integer or zero. Eliminating α one finds

$$N(\lambda_n)=\text{integer}. \tag{10}$$

Conversely, if (10) is satisfied, then one can choose α such that one has for $x>0$,

$$|\sin[\theta(x;\lambda_n)-\alpha]|\leqq\int_x^{\infty} w(x';\lambda_n)^{-2}dx',$$

and at the same time a similar inequality for $x<0$. But, $w(x';\lambda_n)$

increases exponentially, say as $x\to\infty$, so that

$$\int_x^\infty w(x';\lambda_n)^{-2}dx'=\int_x^\infty x'^2 w(x';\lambda_n)^{-2}\cdot(dx'/x'^2)<x\cdot w(x;\lambda_n)^{-2}$$

for sufficiently large x. With similar bound for $x\to-\infty$, one can conclude that

$$|u(x;\lambda_n)|<\text{const. } x/w(x;\lambda_n), \tag{11}$$

which guarantees the boundary condition (9). Thus the first half of (N1) is established.

We note that (8) can be written as

$$u(x;\lambda_n)=w(x;\lambda_n)\sin\left[\int_{-\infty}^x w(x';\lambda_n)^{-2}dx'\right], \tag{12}$$

which tells us that the integer n in (3) is nothing but the number of nodes $u(x;\lambda_n)$ has in $(-\infty,\infty)$. This proves the second half of (N1). One sees from (12) that $N(\lambda_{n+1})>N(\lambda_n)$ for $\lambda_{n+1}>\lambda_n$, a special case of (N2).

In order to prove (N2) for general λ, one starts with the derivative of (6),

$$\frac{\partial\theta(x;\lambda)}{\partial\lambda}=-\int_0^x\left[\frac{\partial z}{\partial\lambda}z^*+z\frac{\partial z^*}{\partial\lambda}\right]w^{-4}dx' \tag{13}$$

On the other hand, differentiation of $(\mathcal{H}-\lambda)\,z(x;\lambda)=0$ with respect to λ gives a differential equation for $\partial z/\partial\lambda$, that is

$$(\mathcal{H}-\lambda)[\partial z/\partial\lambda]=z, \tag{14}$$

which can be solved by the standard variation-of-constant method to give

$$\frac{\partial z(x')}{\partial\lambda}=\frac{i}{2}\left[z(x')\int_0^{x'}|z(x'')|^2\,dx''-z^*(x')\int_0^{x'}z(x'')^2dx''\right]; \tag{15}$$

the parameter λ in $z(x;\lambda)$ is suppressed. Now, substitute (15) into (13), change the order of integration and finally carry out the x'-integration by the help of the differential form of (6), i.e., $dx'/w^2=d\theta(x';\lambda)$, then one gets

$$\frac{\partial\theta(x;\lambda)}{\partial\lambda}=\int_0^x dx''w(x'';\lambda)^2\sin^2[\theta(x;\lambda)-\theta(x'';\lambda)], \tag{16}$$

which leads immediately to (N2). This completes the proof.

4. In practice, the function $N(\lambda)$ can be constructed in the following way. One uses $(\mathcal{H}-\lambda)z=0$ to obtain a differential equation for $w(x;\lambda)$, that is:

$$\left[\frac{d^2}{dx^2}+\lambda-V(x)\right]w+\frac{1}{w^3}=0. \tag{17a}$$

The initial conditions are obtained from (4):

$$w=1 \quad\text{and}\quad \dot{w}=0 \quad\text{at}\quad x=0. \tag{17b}$$

Substituting the solution w into (7), one gets the function $N(\lambda)$.

5. We used IBM 360 (i) to solve (17) for trial values of λ by the

Milne method for the numerical solution of differential equation,[5] (ii) to compute $N(\lambda)$ by Simpson's 1/3-rule and (iii) to repeat interpolations and extrapolations to find $\lambda=\lambda_n$ that satisfies (3) to the desired precision. The results are summarized in Fig. 1. The following Table gives a comparison of our results with Somorjai-Hornig's.[3] Various estimates of errors indicate that the last digits (printed in the smaller letters) may involve errors at most ± 5.

The calculation of matrix elements with the wave function (8) was not so straightforward as one might expect, because a very small error in λ_n could cause a very rapid rise of the tail of (8). We chose to tame

Table I

n	λ_n	
	S-M's	Ours
0	−4.436	$-4.436\ 8_6$
1	−4.349	$-4.349\ 8_4$
2	0.022	$0.024\ 2_2$
3	1.56	$1.567\ 1_4$
4	4.83	$4.831\ 2_2$
5	8.26	$8.275\ _8$
6	12.2	$12.202\ _7$
7	16.5	$16.477\ _9$
8	21.1	

An example of the comparison between Somorjai-Hornig's (S-M's) eigenvalues and ours. The last digits of our eigenvalues may involve errors at most ± 5.

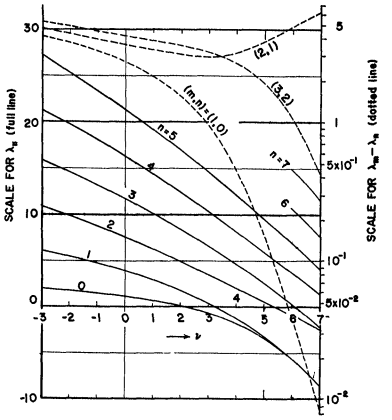

Fig. 1. The eigenvalues (full line) and their spacings (dotted line). From the curves for $\lambda_1-\lambda_0$ and $\lambda_3-\lambda_2$ we can see how the doublet structure sets in.

such tails by replacing them by the WKB asymptotes. Our results for $\langle m|x|n\rangle$ are shown in Fig. 2.

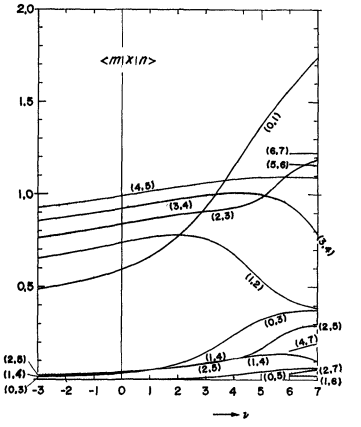

Fig. 2. The matrix elements of x between the eigenstates u_m and u_n. The bracket (4, 5), for instance, means $m=4$, $n=5$.

We computed also the matrix elements, $\langle m|x^2|n\rangle$ and $\langle m|x^3|n\rangle$, which enabled us to check the degree of precision by using various sum rules. Our matrix elements are thus proved to have three to five significant figures.

We wish to thank Prof. T. Yamanouchi for his encouragement. Thanks are also due to Dr. J. Arafune for interesting discussions.

References

1) H. Ezawa: Commun. Math. Phys., **8**, 261 (1968); **9**, 38 (1968).
H. Ezawa, K. Nakamura, and Y. Yamamoto: Nuovo Cimento, **54**A, 512 (1968).
2) See for instance,
G. Herzberg: Molecular Spectra and Molecular Structure, P. 221. Van Nostrand, Princeton (1964).
3) R. L. Somorjai and D. F. Hornig: J. Chem. Phys., **36**, 1980 (1962).
4) W. E. Milne: Phys. Rev., **35**, 863 (1930).
5) S. Moriguchi and M. Takada: Suchi Keisan-Ho, Part II. Iwanami, Tokyo (1958).