NUMERICAL SOLUTION OF NONHARMONIC PROBLEM — A MODIFIED METHOD*

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The least squares method which obtains the best numerical parameters used in the solution of the nonharmonic potential problem is proposed.

Discussion of polyatomic molecule vibrations is based on the use of the following potential function

$$V(x) = \sum_{i=2}^{M} a_i(x-x_0)^i. \tag{1}$$

A special case of this potential function is a harmonic potential obtained from it when $M = 2$. Solution of the Schrödinger equation with the potential function given by Eq. (1) is carried out by a variation method [1–2] with the trial function of the form

$$\Psi(x) = \sum_{i=0}^{N-1} c_i \Phi_i^0(x), \tag{2}$$

where $\Phi_i^0(x)$ is a solution of the harmonic problem. Using the expansion given by Eq. (2), matrix elements of the nonharmonic Hamiltonian are easy to obtain [1].

The main difficulty in application of this method [5] is the choice of adequate parameters for frequency and equilibrium position for the basic harmonic problem. Optimal choice of the parameters should asure a fast convergence of the expansion (2).

It was shown [1–4] that the convergence of the basis function expansion depends on the values of the parameters, particulary on the value of the harmonic frequency ω_0. Keeping that in mind, Jokisaari and Kauppinen [4] have proposed a method giving the frequency ω_0 of the basic problem. In this method the ω_0 is chosen in such a way that the harmonic potential functon with the force constant creating the ω_0 intersects the potential function of calculated problem in a selected energy level. This method requires

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knowledge about one of the energy levels of the problem under consideration. Using this method, the convergence of the solution is obtained for $N = 40-60$, but the method does not define exactly the intersection point in which the best convergence is reached.

In order to obtain a better convergence for the solution it is possible to use another method to determine values of the parameters. In general the harmonic potential function can be described as

$$V(x) = \tfrac{1}{2}kx^2 + lx + r, \tag{3}$$

where $k = \mu\omega_0^2$ and μ is the reduced mass of the problem. The equilibrium position of the oscillation is given by $x_0 = -\frac{l}{k}$. A general feature of the proposed method is that the curve which is given by the Eq. (3) fits the potential function of the calculated problem, particulary the potential function given by Eq. (1), this fitting being performed by the use of the least squares method. The procedure determines the values of the k, l, r parameters and thus the values of the frequency and equilibrium position.

The calculation of Somorjai and Horning [3] is carried out as an ilustrative example. We have calculated the vibrational energies for three kinds of double minimum potential functions: symmetrical V_1, slightly asymmetrical V_6 and strongly asymmetrical V_{11} (see [3] for details). In all cases the best results were obtained if the harmonic potential curve was fitted as far as the point in which the anharmonic potential function has a value of

TABLE I

Vibrational energies of the symmetrical potential function

Level	(a)	(b)	(c)	(d)
0	2894.9	2894.7	2894.7	2895.3
1	2902.5	2902.3	2902.3	2902.9
2	7834.0	7832.3	7832.3	7833.9
3	8202.2	8201.0	8201.0	8205.8
4	11254.1	11246.1	11246.1	11253.7
5	13339.0	13332.5	13332.4	13346.2

All energies are in cm^{-1}, relative to the deeper minimum of the potential. Potential V_1, $x_0 = 0.0$ Å.
(a) $\omega_0 = 1868\ cm^{-1}$ (used by [3]), $N = 20$
(b) $\omega_0 = 4000\ cm^{-1}$ (obtained by presented method), $N = 20$
(c) $\omega_0 = 4000\ cm^{-1}$ (obtained by presented method), $N = 40$
(d) $\omega_0 = 1700\ cm^{-1}$ (obtained by Jokisaari and Kauppinen method), $N = 20$.

about fifteen barrier heights. The results for the symmetrical potential function are gathered in Table I, in which, for comparison, the results obtained by Somorjai and Horning as well as those obtained the use of the Jokisaari and Kauppinen method are shown. In Table II, the results for the asymmetrical potential functions for the parameters obtained by Somorjai and Horning and those obtained in the presented method are compared.

TABLE II

Vibrational energies of the asymmetrical potential functions

Level	(a)	(b)	(c)	(d)
0	2890.0	2889.8	1805.6	1804.9
1	3102.1	3101.9	5055.3	5051.3
2	7875.8	7874.1	7410.7	7401.7
3	8286.7	8285.8	8641.6	8626.6
4	11294.3	11286.6	10364.9	10319.4
5	13390.5	13384.2	12373.9	12277.4

All energies are in cm^{-1}, relative to the deeper minimum of the potential.
(a) potential V_6, $\omega_0 = 1868\,cm^{-1}$, $x_0 = 0.0$ Å (used by [3]), $N = 20$
(b) potential V_6, $\omega_0 = 4200\,cm^{-1}$. $x_0 = -0.0023$ Å (obtained by presented method), $N = 20$
(c) potential V_{11}, $\omega_0 = 1040\,cm^{-1}$, $x_0 = 0.0$ Å (used by [3]), $N = 20$
(d) potential V_{11}, $\omega_0 = 3200\,cm^{-1}$, $x_0 = -0.18$ Å (obtained by presented method), $N = 20$.

The presented results show that the proposed method based on the least squares fitting of the harmonic potential function given by Eq. (3) to the nonharmonic potential function leads to the parameters which guarantee the fast convergence of the basis function expansion.

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