On a Flexible Double Minimum Potential

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The Gauss-perturbed harmonic oscillator, a customary double minimum potential of molecular spectroscopy, is made more flexible by addition of a term $a_4 \cdot \exp(-\gamma_4 X^4)$. The matrix elements of the additional term are calculated in the harmonic oscillator basis in terms of parabolic cylinder functions. A sum rule for matrix elements serves as an independent numerical control. The eigenvalues can be given by straightforward diagonalization of the Hamilton-matrix. In addition, upper and lower bounds are given for the partition function.

1. Introduction

Double minimum potentials are common in molecular spectroscopy for torsional and ring puckering vibrational modes. For proton transfer in biophysics and for the theory of absorption on surfaces they serve as reasonable model potentials. Simple analytical double minimum potential functions are, therefore, necessary. The following model potentials are used customarily.

$$\text{A)} \quad V = \hbar\,\Omega\left\{-\tfrac{1}{2}X^2 + \sum_{k=2} f_{2k}\,X^{2k}\right\}, \qquad (1)$$

$$f_{2k} > 0\,,$$

$$\text{B)} \quad V = \hbar\,\Omega\left\{\tfrac{1}{2}X^2 + \sum_{k=1} \alpha_{2k}\exp(-\gamma_{2k}\,X^{2k})\right\}, \qquad (2)$$

$$\alpha_{2k} \geqq 0,\ \gamma_{2k} \geqq 0$$

where X is a dimensionless normal coordinate. For potential type B only the first term in the sum could be taken into account. These potentials are flexible and can be combined with each other.

Chan and Stelman [1] gave a list of references on various approaches to the double minimum problem and derived eigenvalues for the Gauss-perturbed harmonic oscillator (type B with $k=1$). Further calculations for one dimension were made by Coon, Naugle and McKenzie [2] and for one, two, and three dimensions by Bell [3]. Asymmetric double minimum potentials were treated in several articles by Redding [4] with applications to molecular spectroscopy and proton transfer in organic and biological chemistry.

Analytical solutions of the Schrödinger equation can be obtained for potentials of the Manning [5] or Newton-Thomas [6] type. For arbitrary double minimum potentials, the onedimensional Schrödinger equation can be integrated numerically using the Numerov-Cooley method [4]. A standard technique for analytical potentials is the diagonalization of the Hamilton-matrix in a finite basis. Matrix elements of powers of X can be calculated easily using analytical or operator methods and, therefore, the inclusion of higher terms in potential type A is straightforward. In contrast, the exponential functions of the higher terms of potential type B raise difficulties. In the present note we shall generalize the exponential perturbation type by inclusion of the $k=2$ term.

For practical purposes the additional term

$$V_4 = \hbar\,\Omega\,\alpha_4\exp(-\gamma_4\,X^4) \qquad (3)$$

should have the following properties:

a) it should influence barrier shape and barrier height making the potential more flexible,
b) the matrix elements should be given in the harmonic oscillator basis in terms of well known functions,
c) a linear recursion formula should exist to make the set-up of the Hamilton-matrix easy.

These conditions are fulfilled.

This article is limited to a general discussion of the potential, and to the calculation of eigenvalues and of upper and lower bounds to the partition function. Applications to actual molecules are postponed to another paper where various potential forms for spectra of molecules with double minimum potentials will be compared. Experimental spectra of molecules with double minimum potentials are discussed extensively, not only in the original articles, but also in an excellent monograph [5]. We, therefore, avoid a duplication of references and refer to this review.

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2. Properties of V_4

2.1. Shape of the Potential

Let us first consider the potential type B without the Gauss-term ($\alpha_2 = 0$):

$$V_I = \hbar\,\Omega\{\tfrac{1}{2}X^2 + \alpha_4 \exp(-\gamma_4 X^4)\}\,. \qquad (4)$$

It is entirely different in behaviour from the Gauss-perturbed potential. The latter has a double minimum structure whatever the values of the constants $\alpha_2 > 0$, $\gamma_2 > 0$ may be. In contrast, for the potential V_I different situations exist which can be characterized by means of the equation

$$1 - 4\alpha_4\gamma_4 X^2 \exp(-\gamma_4 X^4) = 0\,. \qquad (5)$$

This equation can have no, two, or four real solutions. In connection with double minimum problems the first two cases are not interesting as they correspond to potentials with only one minimum at $X = 0$. We concentrate on cases where Eq. (5) has four real solutions and the potential V_I has three minima. As is shown in Fig. 1, this triple minimum structure can be very pronounced. But for other values of the constants α_4, γ_4 the minimum at $X = 0$ can be very shallow and, though this minimum never vanishes exactly, the potential can have an almost true double minimum structure. Examples are shown in Figure 2.

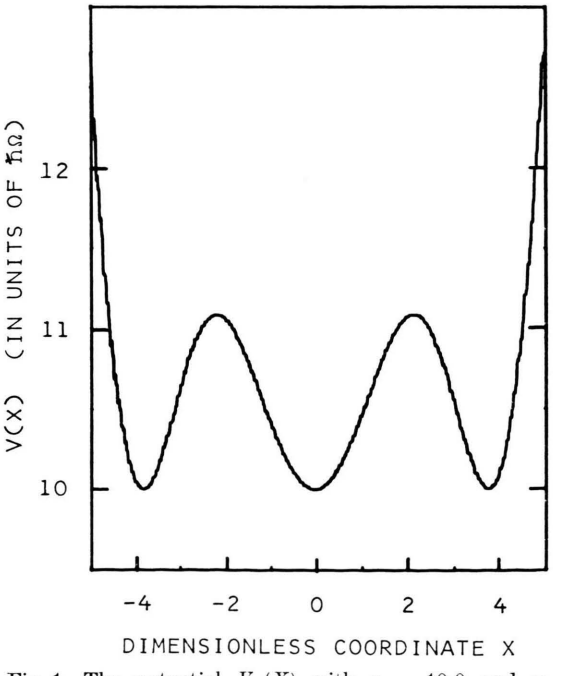

Fig. 1. The potential $V_I(X)$ with $\alpha_4 = 10.0$ and $\gamma_4 = 0.00613$.

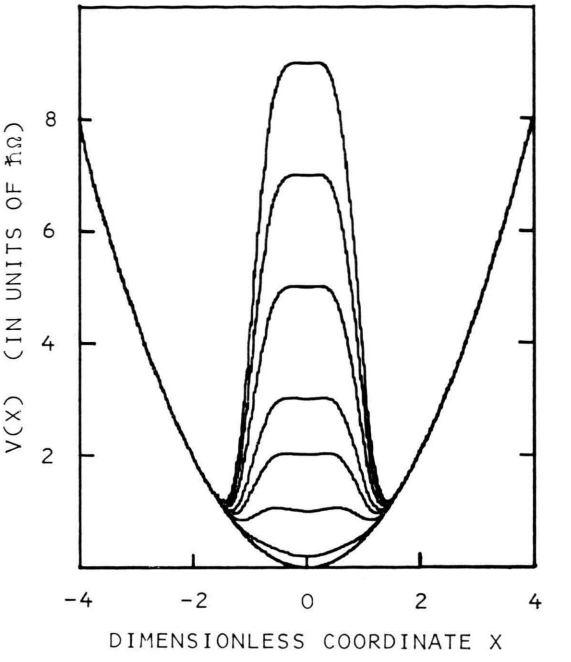

Fig. 2. The potential $V_I(X)$ for several values of α_4: 0.0, 0.2, 1.0, 2.0, 3.0, 5.0, 7.0, 9.0. $\gamma_4 = 1.0$ in all cases.

If we consider the potential type B with non-zero values for both α_2 and α_4,

$$V_{II} = \hbar\,\Omega\{\tfrac{1}{2}X^2 + \alpha_2 \exp(-\gamma_2 X^2) + \alpha_4 \exp(-\gamma_4 X^4)\}\,, \qquad (6)$$

the situation is more complicated. Examples where V_{II} is a true double minimum potential are shown in Figure 3. As is shown for a special case in Fig. 4, barrier shape and barrier height are influenced considerably by the values of α_2 and α_4.

2.2 Calculation of Matrix Elements

Matrix elements are calculated in the harmonic oscillator basis in the coordinate representation. For

$$\hat{H}_0 = \tfrac{1}{2}\hbar\,\Omega(\hat{P}^2 + \hat{X}^2) \qquad (7)$$

the eigenfunctions are

$$\psi_n = (\sqrt{\pi}\,2^n\,n!)^{-1/2} \exp(-X^2/2)\,H_n(X) \qquad (8)$$

where the $H_n(X)$ are the Hermite polynomials. As $\exp(-\gamma_4 X^4)$ is an even function, only matrix elements $\langle n|\exp(-\gamma_4 \hat{X}^4)|m\rangle$ with $(n+m)$ even can be different from zero. If the Hermite polynomials are written explicitly in powers of X, these matrix elements are obtained as a sum of integrals

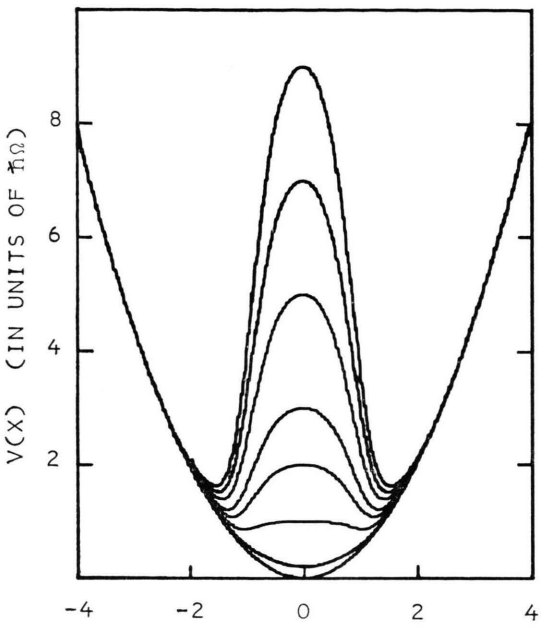

Fig. 3. The full potential $V_{II}(X)$ for several values of $\alpha_2 = \alpha_4$: 0.0, 0.1, 0.5, 1.0, 1.5, 2.5, 3.5, 4.5. $\gamma_2 = \gamma_4 = 1.0$ in all cases.

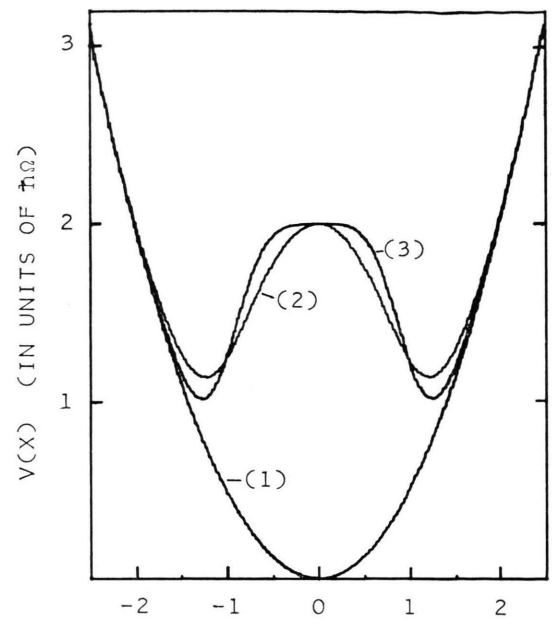

Fig. 4. The harmonic potential (1), and the full potential $V_{II}(X)$ with $\gamma_2 = \gamma_4 = 1.0$ and a constant value $\alpha_2 + \alpha_4 = 2.0$: (2) $\alpha_2 = 1.5$; $\alpha_4 = 0.5$; (3) $\alpha_2 = 0.5$, $\alpha_4 = 1.5$.

of the form

$$I_{2k} = 2\int_0^\infty X^{2k} \exp(-X^2 - \gamma_4 X^4)\, dX\,. \qquad (9)$$

By the substitution $X^2 \to t$ this integral becomes

$$I_{2k} = \int_0^\infty t^{k-1/2} \exp(-t - \gamma_4 t^2)\, dt \qquad (10)$$

and this Laplace transform can be taken from integral tables [7]:

$$I_{2k} = (2\gamma_4)^{-(2k+1)/4}\, \Gamma(k + 1/2) \cdot \exp(1/8\gamma_4)\, D_{-k-1/2}(1/\sqrt{2\gamma_4})\,. \qquad (11)$$

$\Gamma(v)$ is the gamma-function and $D_{-v}(z)$ is a parabolic cylinder function. The relevant formulae for $D_{-v}(z)$ are given in detail by Magnus, Oberhettinger, and Soni [7], but in many cases tabulated values can be used [8]. Five point Lagrange interpolation of the tables gives accurate values of the parabolic cylinder functions. A recurrence relation further simplifies the calculations:

$$D_{v+1}(z) - z D_v(z) + v D_{v-1}(z) = 0\,. \qquad (12)$$

Thus the matrix elements can be calculated in principle from the following formula

$$\langle n | \exp(-\gamma_4 \hat{X}^4) | m \rangle = (n!\, m!/2^{n+m})^{1/2} \exp(1/8\gamma_4) \cdot \sum_{k=0}^{[n/2]} \sum_{l=0}^{[m/2]} (-1)^{k+1} \frac{(n+m-2k-2l)!\, (2\gamma_4)^{-(n+m-2k-2l+1)/4}}{k!\,(n-2k)!\, l!\,(m-2l)!\, [n+m-2k-2l)/2]!}\, D_{-(n+m-2k-2l+1)/2}(1/\sqrt{2\gamma_4})\,. \qquad (13)$$

But for computer calculations the use of recursion relations is more convenient. As was shown by Chan and Stelman [1], a four-term relation can be obtained for any operator $\hat{A}$ which commutes with $\hat{X}$ or $\hat{P}$; from $[\hat{X}, \hat{A}]_- = 0$ follows

$$n^{1/2} \langle n-1 | \hat{A} | m \rangle + (n+1)^{1/2} \langle n+1 | \hat{A} | m \rangle - m^{1/2} \langle n | \hat{A} | m-1 \rangle - (m+1)^{1/2} \langle n | \hat{A} | m+1 \rangle = 0\,. \qquad (14)$$

By this formula $2N-1$ appropiately chosen matrix elements are sufficient to construct a $N \times N$ matrix. To generate the matrix of V_4 row by row, only the first N nonvanishing elements

$$\langle 0 | \exp(-\gamma_4 \hat{X}^4) | 2m \rangle$$

must be calculated from Eq. (13); the elements $\langle 0 | \exp(-\gamma_4 \hat{X}^4) | 2m-1 \rangle$ are zero.

Finally, the matrix obtained in this way can be checked by another formula. With the generating function of the Hermite polynomials one obtains for arbitrary functions $f(X)$

$$e^{-s^2-t^2}\int_{-\infty}^{\infty} f(X)\exp[-X^2+2(s+t)X]\,dX=\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}(\pi\,2^{n+m}/n!\,m!)^{1/2}\langle n|\,f(\hat{X})\,|m\rangle\,s^n\,t^m \tag{15}$$

where s and t are free parameters. With the choice $s=-t$, the power series expansion of $\exp(-2t^2)$, and a comparison of the coefficients of equal powers t^{n+m} the following sum rule results

$$\sum_{k=0}^{2n}(-1)^{n+k}\,n!/[k!\,(2n-k)!]^{1/2}\langle k|\,f(\hat{X})\,|2n-k\rangle=\langle 0|\,f(\hat{X})\,|0\rangle;\quad n=0,1,2,\ldots. \tag{16}$$

3. Exact Bounds to the Partition Function

In a previous article exact bounds to the partition function were derived for oscillators with double minimum potentials [9]. We supplement that article by a brief discussion of exact upper and lower bounds to the partition function of an oscillator with potential V_{II}. For the technique we refer to the article and to a forthcoming paper on analytical bounds to the partition function of a quartic anharmonic oscillator [10].

With

$$\hat{H}_1=\hbar\,\Omega[\alpha_2\exp(-\gamma_2\hat{X}^2)+\alpha_4\exp(-\gamma_4\hat{X}^4)] \tag{17}$$

the Hamiltonian is

$$\hat{H}=\hat{H}_0+\hat{H}_1, \tag{18}$$

where $\hat{H}_0$ is given by Equation (7). A lower bound to the partition function can be calculated by means of the Gibbs-Bogoliubov inequality [11]

$$\begin{aligned}&\mathrm{Tr}\{\exp[-\beta(\hat{H}_0+\hat{H}_1)]\}\geqq q_L\\&\quad=q_0\exp[-\beta\langle\hat{H}_1\rangle_0];\quad\beta=(k_B\,T)^{-1}.\end{aligned} \tag{19}$$

q_0 is the partition function corresponding to $\hat{H}_0$ and $\langle\hat{H}_1\rangle_0$ is the thermal average

$$\begin{aligned}\langle\hat{H}_1\rangle_0&=(1/q_0)\,\mathrm{Tr}\{\exp(-\beta\hat{H}_0)\,\hat{H}_1\}\\&=\frac{\hbar\,\Omega}{q_0}(\alpha_2\,\mathrm{Tr}[\exp\{-\beta\hat{H}_0\}\exp\{-\gamma_2\hat{X}^2\}]\\&\quad+\alpha_4\,\mathrm{Tr}[\exp\{-\beta\hat{H}_0\}\exp\{-\gamma_4\hat{X}^4\}]).\end{aligned} \tag{20}$$

In Ref. [9] only the first trace could be evaluated. But in the meantime, also the solution of the second one — essentially the upper bound to the partition function of a quartic anharmonic oscillator — was possible [10]. Substitution of these results yields

$$\begin{aligned}q_L&=q_0\exp\{-\varepsilon[\alpha_2(1+\gamma_2\,\mu)^{-1/2}\\&\quad+\alpha_4\,R^{1/2}\exp(R^2/4)\,D_{-1/2}(R)]\};\\\varepsilon&=\beta\,\hbar\,\Omega;\quad\mu=\coth(\varepsilon/2);\\R&=(2\gamma_4\,\mu^2)^{-1/2}.\end{aligned} \tag{21}$$

It was also shown in [9] how the bounds to the partition function can be improved by variational methods. As the potential V_{II} is symmetrical, the appropriate variation parameter is a variable frequency ω

$$\begin{aligned}B_L(\omega)=q_0^*\exp\Bigg\{-\varepsilon^*\Bigg[&\frac{1}{4}\,\mu^*\left(\frac{\Omega^2}{\omega^2}-1\right)\\&+\alpha_2\frac{\Omega}{\omega}(1+\gamma_2\,\Omega\,\mu^*/\omega)^{-1/2}\\&+\alpha_4\frac{\Omega}{\omega}R^{*1/2}\exp(R^{*2}/4)\,D_{-1/2}(R^*)\Bigg]\Bigg\}.\end{aligned} \tag{22}$$

The asterisk indicates that the corresponding quantities are functions of ω instead of Ω. The optimal value of ω cannot be given analytically. Therefore, the maximum of $B_L(\omega)$ must be calculated by numerical variation of ω.

An upper bound to the partition function is defined by the Golden-Thompson inequality [11]. In the present case it reads

$$\begin{aligned}&\mathrm{Tr}\{\exp[-\beta(\hat{H}_0+\hat{H}_1)]\}\leqq q_U\\&\quad=\mathrm{Tr}\{\exp(-\beta\hat{H}_0)\exp(-\beta\hat{H}_1)\}\\&\quad=\mathrm{Tr}\{\exp(-\beta\hat{H}_0)\exp[-\varepsilon(\alpha_2\exp\{-\gamma_2\hat{X}^2\}\\&\qquad+\alpha_4\exp\{-\gamma_4\hat{X}^4\})]\}\\&\quad=\sum_{n=0}^{\infty}\frac{(-\varepsilon)^n}{n!}\\&\qquad\cdot\{\alpha_2{}^n\,\mathrm{Tr}[\exp\{-\beta\hat{H}_0\}\exp\{-n\,\gamma_2\hat{X}^2\}]\\&\qquad+\sum_{k=1}^{n}\binom{n}{k}\alpha_2{}^{n-k}\,\alpha_4{}^k\,\mathrm{Tr}[\exp\{-\beta\hat{H}_0\}\\&\qquad\cdot\exp\{-(n-k)\,\gamma_2\hat{X}^2-k\,\gamma_4\hat{X}^4\}]\}.\end{aligned} \tag{23}$$

For these trace expressions we again refer to [10]. The result is

$$\begin{aligned}q_U=q_0\sum_{n=0}^{\infty}\frac{(-\varepsilon)^n}{n!}&\{\alpha_2{}^n(1+n\,\gamma_2\,\mu)^{-1/2}\\&+\sum_{k=1}^{n}\binom{n}{k}\alpha_2{}^{n-k}\,\alpha_4{}^k[R_2/\{1+(n-k)\,\gamma_2\,\mu\}]^{1/2}\\&\cdot\exp(R_2{}^2/4)\,D_{-1/2}(R_2)\};\\R_2=[1+(n-k)\,\gamma_2\,\mu]&/[2k\,\gamma_4\,\mu^2]^{1/2}.\end{aligned} \tag{24}$$

The series converges for every ε and α_2, α_4, γ_2, $\gamma_4 > 0$.

4. Discussion

4.1. Numerical Results

The matrix of V_4 is generated on a digital computer according to Section 2.2. For the contributions of $\exp(-\gamma_2 X^2)$ the formulae given by Chan and Stelman [1] or by Bell [3] can be used. In all cases which we considered the matrix elements are in complete agreement with the sum rule Equation (16). The eigenvalues are calculated by standard matrix diagonalization procedures. Moreover, approximate eigenfunctions can be obtained and so expectation values, e.g. transition moments, are available. The first 10 eigenvalues are obtained with good accuracy using 40 basis functions and double precision arithmetic. Results are shown in Fig. 5 for an oscillator with potential V_I. For a constant value $\gamma_4 = 1$ the first 10 eigenvalues are plotted as a function of α_4. Analogously the eigenvalues of an oscillator with the full potential V_{II} ($\gamma_2 = \gamma_4 = 1$) are plotted as a function of $\alpha_2 = \alpha_4$ in Figure 6. Though the potential shapes are fairly different (compare Figs. 2 and 3) the energy levels

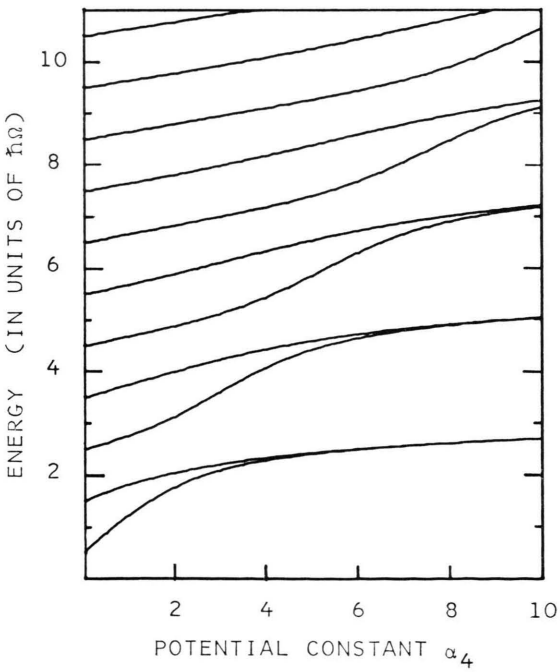

Fig. 5. The first 10 eigenvalues of an oscillator with potential $V_I(X)$, $\gamma_4 = 1.0$, as a function of α_4.

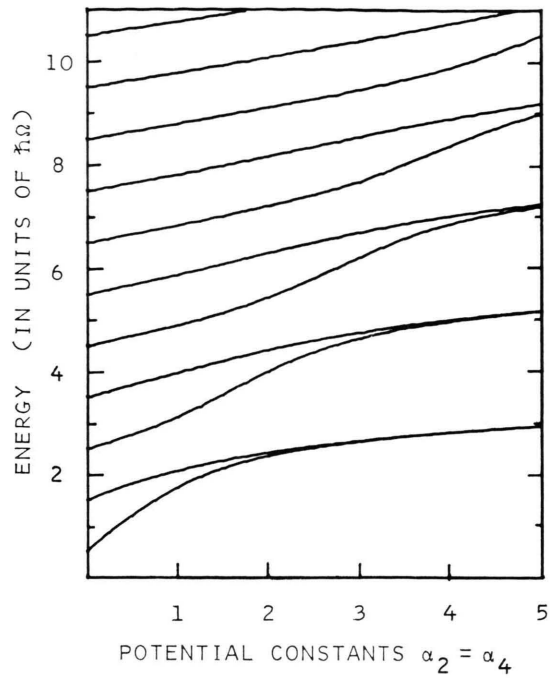

Fig. 6. The first 10 eigenvalues of an oscillator with potential $V_{II}(X)$, $\gamma_2 = \gamma_4 = 1.0$, as a function of $\alpha_2 = \alpha_4$.

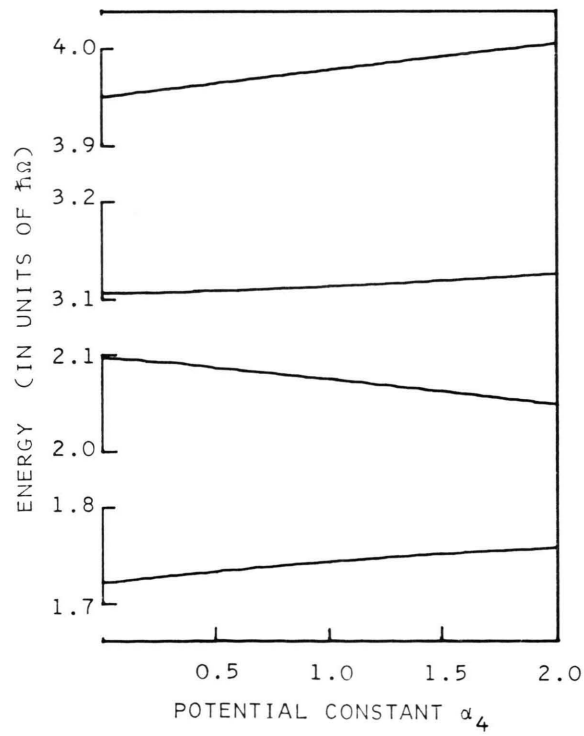

Fig. 7. The first 4 eigenvalues of an oscillator with potential $V_{II}(X)$, $\gamma_2 = \gamma_4 = 1.0$ and $\alpha_2 + \alpha_4 = 2$, as a function of $\alpha_4 = 2 - \alpha_2$.

Table 1. The partition function of an oscillator with potential $V_{II}(X)$ for several values of the reduced temperature $\varepsilon = \beta\hbar\Omega$. q_L = lower bound to the partition function from Eq. (21); $q_L{}^*$ = improved lower bound from Eq. (22); q_{sum} = partition function calculated from the first 10 eigenvalues; q_U = upper bound to the partition function from Equation (24). *I*: $\gamma_2 = \gamma_4 = 1$, $\alpha_2 = 1.5$, $\alpha_4 = 0.5$; II: $\gamma_2 = \gamma_4 = 1$, $\alpha_2 = 0.5$, $\alpha_4 = 1.5$.

	ε	q_L	$q_L{}^*$	q_{sum}	q_U
	0.2	4.420	4.433	3.819	4.467
	0.4	1.787	1.817	1.823	1.869
I	0.6	0.9208	0.9589	1.003	1.017
	0.8	0.5185	0.5576	0.5999	0.6147
	1.0	0.3055	0.3411	0.3765	0.3948
	0.2	4.410	4.424	3.816	4.463
	0.4	1.773	1.805	1.820	1.868
II	0.6	0.9055	0.9470	1.001	1.018
	0.8	0.5042	0.5469	0.5987	0.6176
	1.0	0.2933	0.3321	0.3756	0.3990

are similar in their behaviour. The qualitative behaviour of the energy levels resembles that of the Gauss-perturbed harmonic oscillator given by Chan and Stelman [1]. The influence of the constants α_2, α_4 on the first 4 eigenvalues is shown in Figure 7. For a constant value $\alpha_2 + \alpha_4 = 2$ and for $\gamma_2 = \gamma_4 = 1$ the energy levels and the level spacing differ considerably for different combinations of α_2 and α_4.

Numerical results for the upper and lower bounds to the partition function are given in Table 1. These bounds are similar in behaviour to those for the Gauss-perturbed harmonic oscillator discussed in [9]. Especially at low temperatures ($\triangleq$ great ε-values) the variation of the frequency leads to a strong improvement of the lower bound. The numerical partition function calculated from the first 10 eigenvalues agrees well with the bounds at low temperatures. For small values of ε also higher energy levels become more populated and further Boltzmann-factors must be taken into account. Accordingly, at $\varepsilon = 0.2\, q_{sum}$ is smaller than the exact lower bound.

4.2. *Generalizations of the Potentials*

Plots of the potentials

$$V_{III} = \hbar\Omega\{\tfrac{1}{2}X^2 + \alpha_6 \exp(-\gamma_6 X^6)\}, \quad (25)$$

$$V_{IV} = \hbar\Omega\{\tfrac{1}{2}X^2 + \alpha_8 \exp(-\gamma_8 X^8)\} \quad (26)$$

are shown in Figure 8. Qualitatively the triple minimum structure becomes more pronounced. The calculation of matrix elements in the harmonic oscillator basis in analytical form is no longer

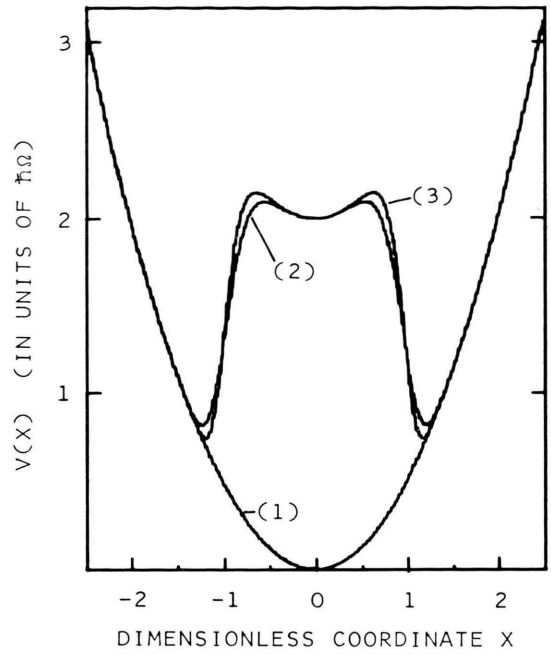

Fig. 8. (1) The harmonic potential. (2) The potential $V_{III}(X)$ with $\alpha_6 = 2.0$ and $\gamma_6 = 1.0$. (3) The potential $V_{IV}(X)$ with $\alpha_8 = 2.0$ and $\gamma_8 = 1.0$.

possible as no Laplace transforms of this type are known. Of course, the integrals can be calculated numerically, but if potentials of this type will be needed, the calculation of eigenvalues and eigenfunctions by numerical integration of the Schrödinger equation seems to be more convenient.

Bell [3] generalized the Gauss-perturbed harmonic oscillator to two and three dimensions by calculating the necessary matrix elements in the two- and three-dimensional harmonic oscillator basis using the (w, l) and the (w, l, m) representation respectively. Analogous calculations could not be performed for the term V_4. Further mathematical work on integrals of the special functions of mathematical physics with $\exp(-\gamma_4 X^4)$ is necessary.

4.3. *Applications of the Results*

As already mentioned in the introduction, we shall apply the potential V_{II} to large amplitude molecular vibrations to investigate the question how good a barrier shape can be extracted from measured vibrational frequencies. Another interesting application are structural phase transitions in solids where mainly double minimum potentials of the quadratic-quartic type have been used. Traces

of exponentials of these operators can be calculated analytically, as was shown in Section 3, so that thermodynamic properties can be given in closed form. The triple minimum potential V_I with a more or less shallow central minimum at $X = 0$ can serve as a model for adsorption at surfaces with flat traps. An application outside molecular physics should be mentioned for completeness. Peres [12] suggested a field theory model of nonlinear coupled oscillators. The elements of the S-matrix are closely related to the matrix elements derived in the text.

5. Conclusion

By inclusion of V_4 we gave a flexible double minimum potential. The eigenvalues can be calculated in the harmonic oscillator basis using Lagrange interpolation of tabulated values of the parabolic cylinder functions and two recursion relations. The matrix elements can be checked by a sum rule. The truncated Hamilton matrix is diagonalized by standard methods. For the calculation of transition integrals or overlap integrals for electronic transitions between double minimum molecular states the truncated harmonic oscillator basis can be used. In cases where the Gauss-perturbed harmonic oscillator gives good agreement with measured low energy levels and disagreement for higher ones the present generalized potential can be applied. Interesting applications of the triple minimum potential V_I may be found outside molecular physics.

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