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ORIGINAL PAPER

Energy spectrum for a modified Rosen-Morse potential solved by proper quantization rule and its thermodynamic properties

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Abstract We apply our recently proposed proper quantization rule, $\int_{x_A}^{x_B} k(x)dx - \int_{x_{0A}}^{x_{0B}} k_0(x)dx = n\pi$, where $k(x) = \sqrt{2M[E - V(x)]}/\hbar$ to obtain the energy spectrum of the modified Rosen-Morse potential. The beauty and symmetry of this proper rule come from its meaning—whenever the number of the nodes of $\phi(x)$ or the number of the nodes of the wave function $\psi(x)$ increases by one, the momentum integral $\int_{x_A}^{x_B} k(x)dx$ will increase by π. Based on this new approach, we present a vibrational high temperature partition function in order to study thermodynamic functions such as the vibrational mean energy U, specific heat C, free energy F and entropy S. It is surprising to note that the specific heat $C(k = 1)$ first increases with β and arrives to the maximum value and then decreases with it. However, it is shown that the entropy $S(k = 1)$ first increases with the deepness of potential well λ and then decreases with it.

Keywords Proper quantization rules · Energy spectrum · Modified Rosen-Morse potential · Partition function

1 Introduction

The exact solutions of quantum systems have been an important research subject and attracted much attention in the development of quantum mechanics since they contain all necessary information of studied quantum systems. To our knowledge, there

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are several main approaches to treat solvable quantum potentials, e.g. the SUSYQM approach [1], the SWKB method [2], the Nikiforov-Uvarov method [3], the factorization formalism [4,5] and exact quantization rule method [6–8]. The latter is the generalization of the Bohr-Sommerfeld quantization rule [9] and the WKB [10–12]. Except for these approaches, the quasilinearization method (QLM) has played an important role in dealing with arbitrary physical potentials numerically [13–20]. Recently, Yin et al. have shown why the SWKB is exact for all shape invariant potentials [21].

The exact quantization rule method is a powerful tool in finding the eigenvalues of all solvable quantum potentials [22–27]. Nevertheless, it involves complicated integral calculations, particularly the calculation of the quantum correction term. To overcome this problem, we have proposed a proper quantization rule [28] and shown its great simplicity and symmetry in comparison with the previous exact quantization rule [29–32]. The purpose of this work is to apply proper quantization rule to obtain the energy levels of modified Rosen-Morse potential and then to study its thermodynamic properties including vibrational mean energy U, specific heat C, free energy F and entropy S as illustrated in Ref. [33]. Such a study was not considered before to our knowledge.

This work is organized as follows. In Sect. 2 we briefly review the proper quantization rule. We apply this method to obtain the energy spectrum of this system in Sect. 3. In Sect. 4 we derive all thermodynamic functions and study their properties. Some concluding remarks are given in Sect. 5.

2 Proper quantization rule

As we know, the one-dimensional Schrödinger equation

$$\frac{d^2}{dx^2}\psi(x) = -\frac{2M}{\hbar^2}[E - V(x)]\psi(x) \tag{1}$$

can be written as a non-linear Riccati equation

$$\frac{d}{dx}\phi(x) = -\frac{2M}{\hbar^2}[E - V(x)] - \phi(x)^2, \tag{2}$$

where $\phi(x) = \psi(x)^{-1}d\psi(x)/dx$ is the logarithmic derivative[1] of wave function $\psi(x)$. For the Schrödinger equation, the phase angle is nothing but the logarithmic derivative $\phi(x)$. It is shown from Eq. (2) that $\phi(x)$ decreases monotonically with respect to x between two turning points, where $E \geq V(x)$. Specifically, as x increases across a node of wave function $\psi(x)$, $\phi(x)$ decreases to $-\infty$, jumps to $+\infty$, and then decreases again. By carefully studying one-dimensional Schrödinger equation, Ma and Xu proposed an exact quantization rule [6,7]

$$\int\limits_{x_A}^{x_B} k(x)dx = N\pi + \int\limits_{x_A}^{x_B} k'(x)\frac{\phi(x)}{\phi'(x)}dx, \tag{3}$$

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[1] As said by Yang in a talk on monopole: “For the Sturm-Liouville problem, the fundamental trick is the definition of a phase angle which is monotonic with respect to the energy. ” [34].

where $k(x) = \sqrt{2M[E - V(x)]}/\hbar$, x_A and x_B two turning points determined by $E = V(x)$. The $N = n + 1$ is the number of zeros of $\phi(x)$ in the region $E \geq V(x)$, and is larger by one than the number n of nodes of wave function $\psi(x)$. From now on, we denote the prime, such as $k'(x)$ and $\phi'(x)$ in above equation, as the first derivative with respect to the argument. The first term $N\pi$ is the contribution from the zeros of $\phi(x)$, and the second is called the quantum correction term. Ma and Xu find that this quantum correction is independent of the number of nodes of wave function. Consequently, it is enough to consider the ground state in calculating quantum correction $Q_0 = \int_{x_A}^{x_B} k_0'(x)\phi_0(x)/\phi_0'(x)dx$.

This methodology can be easily extended to arbitrary dimensional space [27]. It should be pointed out that two integrals in Eq. (3), particularly the calculation of quantum correction term are very difficult and tedious for some physical potentials. To overcome this, we have proposed proper quantization rule [28] as follows:

$$\int_{x_A}^{x_B} k(x)dx - \int_{x_{0A}}^{x_{0B}} k_0(x)dx = (N-1)\pi = n\pi, \tag{4}$$

and

$$\int_{r_A}^{r_B} k(r)dr - \int_{r_{0A}}^{r_{0B}} k_0(r)dr = n\pi. \tag{5}$$

Thus, two integrals involved in the proper quantization rule have same mathematical form. Accordingly, when applying it to calculate the energy levels we only calculate its first integral with respect to $k(x)$, and then replace energy levels E_n by E_0 to obtain the second integral. This will greatly simplify the complicated integral calculations occurred previously [6–8,22–27].

3 Modified Rosen-Morse potential

The modified Rosen-Morse potential is given by [35]

$$V(x) = -\frac{U_0 - U_1 \sinh(\mathrm{x/a})}{\cosh^2(\mathrm{x/a})}. \tag{6}$$

Since $V(x) \to 0$ as $x \to \pm\infty$, the energy E_n of the quantum system, if exists, has to be negative.

Let

$$\begin{aligned} &y = \sinh(x/a), \qquad y \in (-\infty, \infty), \\ &\frac{dy}{dx} = \frac{\sqrt{1+y^2}}{a}, \qquad V(x) = -\frac{U_0 - U_1 y}{1+y^2}. \end{aligned} \tag{7}$$

The non-linear Riccati equation for the ground state is written in a new variable y as

$$\frac{\sqrt{1+y^2}}{a}\frac{d\phi_0(x)}{dy} = -\frac{2M}{\hbar^2}\left[E_0 + \frac{U_0 - U_1 y}{1+y^2}\right] - \phi_0^2(x). \tag{8}$$

Since the logarithmic derivative $\phi_0(x)$ for the ground state has one zero and no pole, it has to take the linear form in y. In addition, in order to meet the term with $\sqrt{1+y^2}$ in the Riccati equation (8), $\phi_0(x)$ can contain an additional factor $(1+y^2)^{-1/2}$, which has no zero in the domain of definition of new variable y

$$\phi_0(y) = -\frac{Ay+B}{a\sqrt{1+y^2}}, \qquad A > 0. \tag{9}$$

Substituting Eq. (9) into Eq. (8), one has

$$-\frac{A-By}{a^2(1+y^2)} = -\frac{2M\left[E_0(1+y^2)+U_0-U_1 y\right]}{\hbar^2(1+y^2)} - \frac{A^2y^2+2ABy+B^2}{a^2(1+y^2)}, \tag{10}$$

from which we find that the ground state energy by solving the non-linear Riccati equation (2) is given by

$$E_0 = -\frac{\hbar^2(G_0-1)^2}{8Ma^2}, \tag{11}$$

where

$$G_0^2 = \frac{1}{2} + \frac{4Ma^2U_0}{\hbar^2} + \left\{\left(\frac{1}{2}+\frac{4Ma^2U_0}{\hbar^2}\right)^2 + \left(\frac{4Ma^2U_1}{\hbar^2}\right)^2\right\}^{1/2}, \tag{12}$$

and two turning points as well as their properties are given by

$$\begin{aligned} y_A &= \sinh(x_A/a) = \frac{-U_1 - \sqrt{U_1^2 - 4E_n(U_0+E_n)}}{2E_n}, \\ y_B &= \sinh(x_B/a) = \frac{-U_1 + \sqrt{U_1^2 - 4E_n(U_0+E_n)}}{2E_n}, \\ y_A + y_B &= U_1/E_n, \qquad y_A y_B = 1 + U_0/E_n. \end{aligned} \tag{13}$$

The momentum $k(x)$ is written as

$$k(x) = \frac{\sqrt{-2ME_n}}{\hbar\sqrt{1+y^2}}\sqrt{(y_B-y)(y-y_A)}. \tag{14}$$

Now, let us calculate the first integral in Eq. (4)

$$\begin{aligned}\int\limits_{x_A}^{x_B} k(x)dx &= \int\limits_{x_A}^{x_B} \frac{1}{\hbar}\sqrt{2M(E-V(x)}dx \\ &= \frac{a\sqrt{-2ME_n}}{\hbar}\int\limits_{y_A}^{y_B} \frac{\sqrt{(y_B-y)(y-y_A)}}{1+y^2}\,dy \\ &= \pi\frac{a\sqrt{-2ME_n}}{\hbar}\left[\frac{1}{2}\left(\sqrt{1+y_A^2}\sqrt{1+y_B^2}-y_Ay_B+1\right)^{1/2}-1\right] \\ &= -\pi\frac{a\sqrt{-2ME_n}}{\hbar}+\frac{a\pi\sqrt{M}}{\hbar}\sqrt{U_0+\sqrt{U_0^2+U_1^2}}.\end{aligned} \tag{15}$$

In the above calculation, the following integral formula was used,

$$\int\limits_a^b \frac{\sqrt{(b-y)(y-a)}}{1+y^2}\,dy = \frac{\pi}{2}\left\{\sqrt{1+a^2}\sqrt{1+b^2}-ab+1\right\}^{1/2}-\pi. \tag{16}$$

By replacing E_n in Eq. (15) by E_0 given in Eq. (11), we obtain

$$\int\limits_{x_{0A}}^{x_{0B}} k_0(x)dx = \frac{\pi}{2}\left[1-G_0+\frac{2a\sqrt{M}}{\hbar}\sqrt{U_0+\sqrt{U_0^2+U_1^2}}\right]. \tag{17}$$

Substituting Eqs. (15) and (17) into Eq. (4) leads to

$$-\pi\left(\frac{a\sqrt{-2E_nM}}{\hbar}-\frac{G_0-1}{2}\right)=n\pi, \tag{18}$$

from which we get the eigenvalues

$$E_n = -\frac{\hbar^2(G_0-2n-1)^2}{8Ma^2}, \quad n=0,1,2,\ldots,<[(G_0-1)/2], \tag{19}$$

where $[f]$ means the largest integer inferior to f.

4 Thermodynamic properties

We now study the thermodynamic properties of this system. For this purpose, it is necessary to obtain the vibrational partition function calculated by

$$Z=\sum_{n=0}^{\lambda}e^{-\beta E_n}, \quad \beta=\frac{1}{kT}, \quad \lambda=\frac{G_0-1}{2}, \tag{20}$$

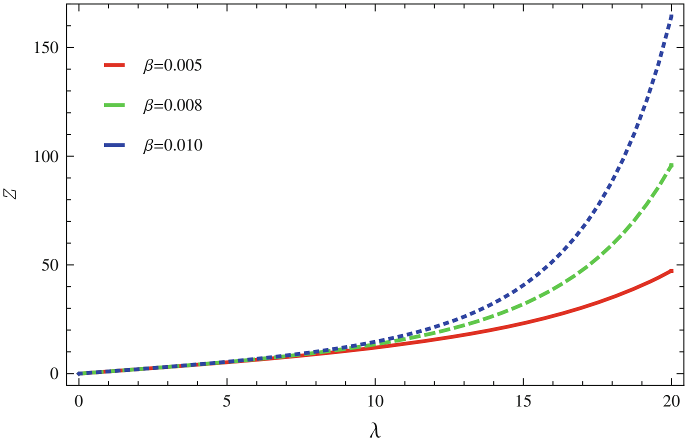

Fig. 1 Vibrational partition function Z as function of α for different β

where k is the Boltzmann factor. Substituting Eq. (19) into Eq. (20) enables us to obtain the following expression

$$Z = \sum_{n=0}^{\lambda} e^{\frac{(\lambda-n)^2}{\alpha^2}}, \quad \alpha = \sqrt{\frac{2M}{\beta}\frac{a}{\hbar}} = \tau/\sqrt{\beta}, \quad \tau = a\sqrt{2M}/\hbar. \tag{21}$$

At high temperature T, for large λ and small β, it can be replaced by the following integral

$$Z = \alpha \int_{0}^{\lambda/\alpha} e^{y^2} dy, \tag{22}$$

where $y = (\lambda - n)/\alpha$. Its exact solution is nothing but the error function [36]

$$\begin{aligned} Z &= \frac{\sqrt{\pi}}{2}\alpha \,\mathrm{Erfi}\left(\frac{\lambda}{\alpha}\right) \\ &= \frac{\sqrt{\pi}}{2}\frac{\tau}{\sqrt{\beta}}\mathrm{Erfi}\left(\frac{\lambda\sqrt{\beta}}{\tau}\right), \end{aligned} \tag{23}$$

which can be used to derive all related thermodynamic functions. For given β and unit τ, the dependences of Z on λ and β are shown in Figs. 1 and 2, respectively. It is found that the Z monotonically increases as λ and β increase.

The vibrational mean energy U can be obtained as

$$\begin{aligned} U &= -\frac{\partial}{\partial\beta}\ln Z \\ &= \frac{1}{2\beta} - \frac{\lambda\, e^{\frac{\lambda^2\beta}{\tau^2}}}{\tau\sqrt{\pi\beta}\,\mathrm{Erfi}\left(\frac{\lambda\sqrt{\beta}}{\tau}\right)}, \end{aligned} \tag{24}$$

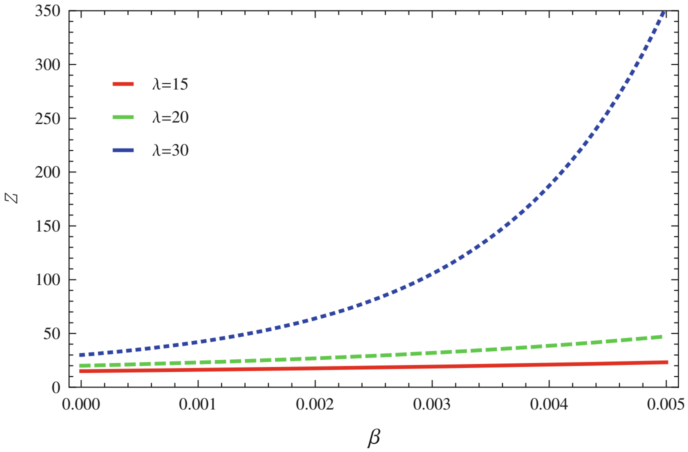

Fig. 2 Vibrational partition function Z as function of β for different λ

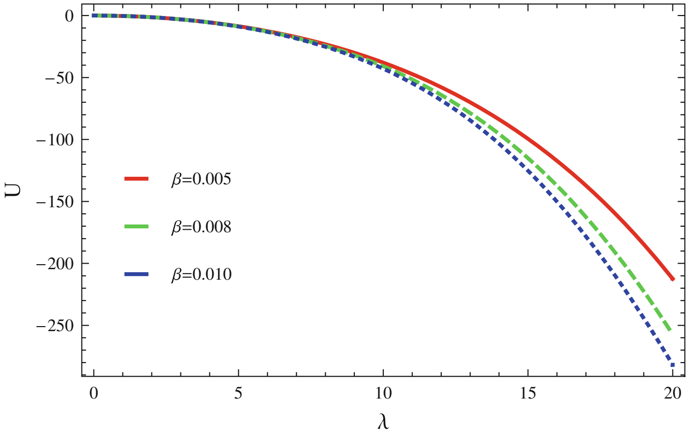

Fig. 3 Vibrational mean energy U as function of λ for different β

which implies that $U = -\lambda^2/(3\tau^2)$ for $\beta \ll 1$. It is shown in Figs. 3 and 4 that the U monotonically decreases with the increasing parameters λ and β.

The vibrational specific heat C is obtained as

$$\begin{aligned} C = & \frac{\partial}{\partial T} U = -k\beta^2 \frac{\partial}{\partial \beta} U \\ = & \frac{1}{2} k \left\{ 1 - \frac{e^{\frac{\lambda^2\beta}{\tau^2}} \lambda\sqrt{\beta} \left[2e^{\frac{\lambda^2\beta}{\tau^2}} \lambda\sqrt{\beta}\tau + \sqrt{\pi}\left(\tau^2 - 2\lambda^2\beta\right) \mathrm{Erfi}\left(\frac{\lambda\sqrt{\beta}}{\tau}\right) \right]}{\pi\tau^3 \mathrm{Erfi}\left(\frac{\lambda\sqrt{\beta}}{\tau}\right)^2} \right\}, \end{aligned} \tag{25}$$

which implies that $C = 0$ for $\beta \ll 1$. It is shown in Fig. 5 that the specific heat C ($k = 1$) increases with the increasing λ. However, the specific heat C first increases with β to the maximum value and then decreases with it as shown in Fig. 6.

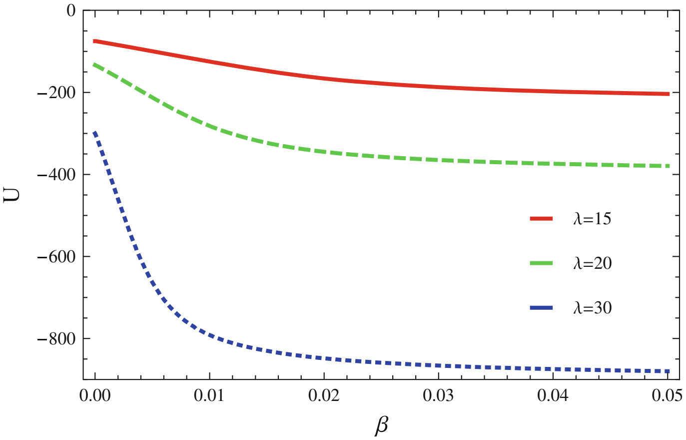

Fig. 4 Vibrational mean energy U as function of β for different λ

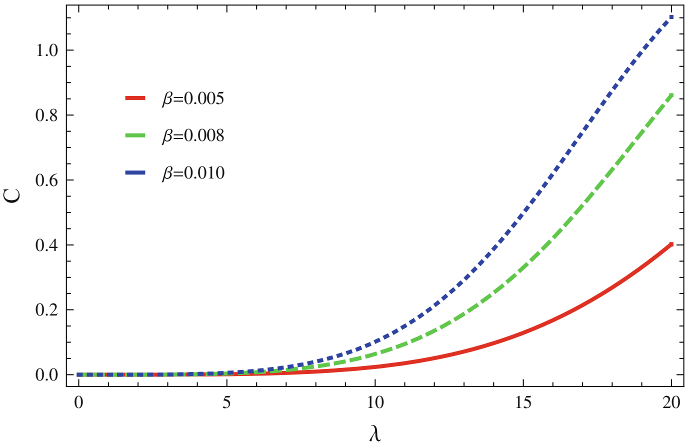

Fig. 5 Vibrational free energy C as function of λ for different β

Let us consider the vibrational free energy F. It can be calculated as

$$\begin{aligned} F = & -\frac{1}{\beta}\ln Z \\ & = -\frac{1}{\beta}\ln\left(\frac{\sqrt{\pi}\,\tau\,\mathrm{Erfi}\left(\frac{\lambda\sqrt{\beta}}{\tau}\right)}{2\sqrt{\beta}}\right). \end{aligned} \tag{26}$$

As shown in Fig. 7, the F decreases monotonically with the increasing parameter λ, while it increases with the parameter β as shown in Fig. 8.

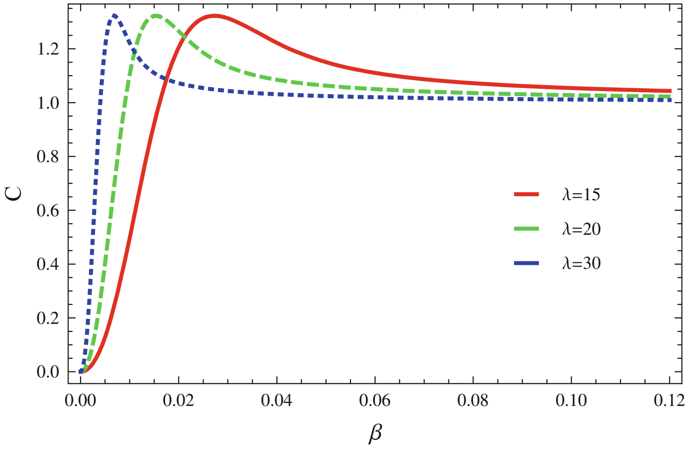

Fig. 6 Vibrational free energy C as function of β for different λ

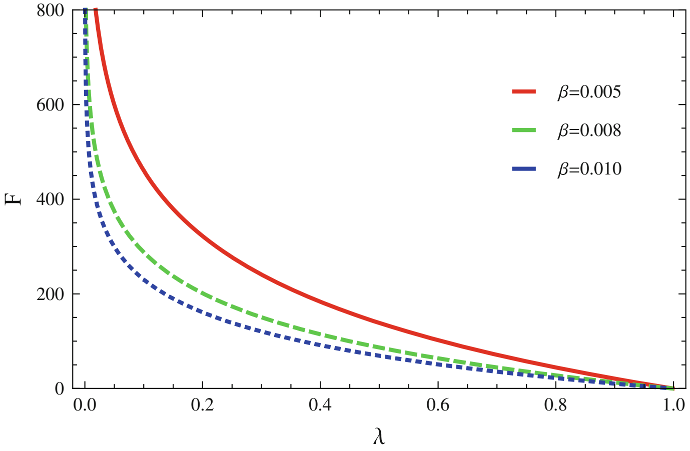

Fig. 7 Vibrational free energy F as function of λ for different β

Finally, we study the vibrational entropy S. It can be obtained by

$$\begin{aligned} S &= k\ln Z + kT\left(\frac{\partial \ln Z}{\partial T}\right)\\ &= k\ln Z - k\beta\left(\frac{\partial \ln Z}{\partial \beta}\right)\\ &= \frac{1}{2}k\left\{-\frac{2e^{\frac{\lambda^2\beta}{\tau^2}}\sqrt{\beta}\lambda}{\sqrt{\pi}\,\tau\,\mathrm{Erfi}\left(\frac{\lambda\sqrt{\beta}}{\tau}\right)} + 2\log\left(\frac{\tau\,\mathrm{Erfi}\left(\frac{\lambda\sqrt{\beta}}{\tau}\right)}{\sqrt{\beta}}\right) + \log\left(\frac{\pi}{4}\right) + 1\right\}. \end{aligned} \tag{27}$$

It is shown in Fig. 9 that the entropy S ($k = 1$) first increases with the λ and then decreases with it. On the other hand, the S decreases with the parameter β as shown in Fig. 10.

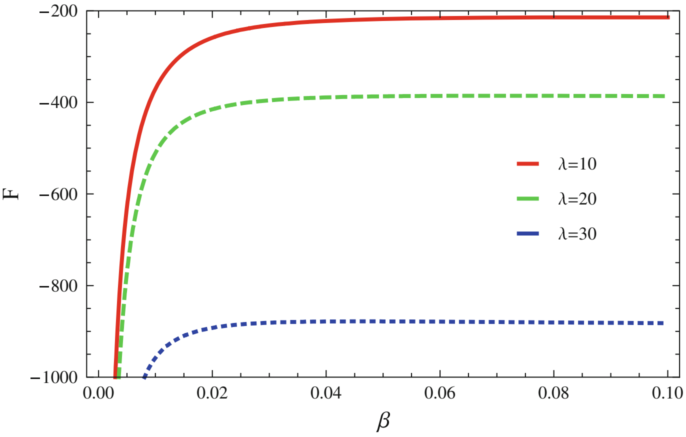

Fig. 8 Vibrational free energy F as function of β for different λ

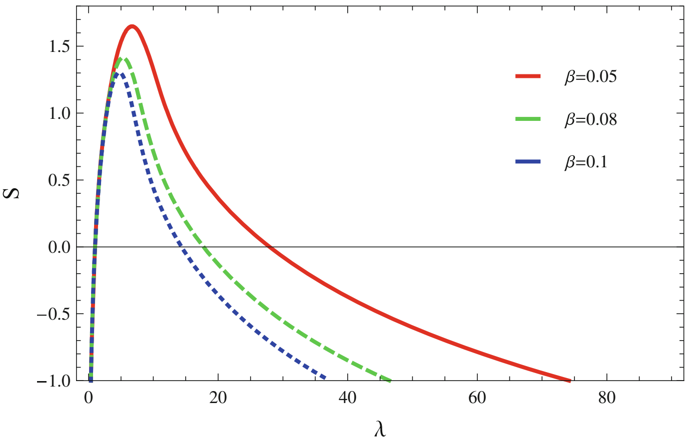

Fig. 9 Vibrational free energy S as function of λ for different β

5 Concluding remarks

We have applied the recently proposed proper quantization rule, $\int_{x_A}^{x_B} k(x)dx - \int_{x_{0A}}^{x_{0B}} k_0(x)dx = n\pi$, where $k(x) = \sqrt{2M[E - V(x)]}/\hbar$ to obtain the energy spectra of the modified Rosen-Morse potential. Its symmetry and simplicity come from its meaning—whenever the number of the nodes of $\phi(x)$ or the number of the nodes of the wave function $\psi(x)$ increases by one, the momentum integral $\int_{x_A}^{x_B} k(x)dx$ will increase by π. The vibrational partition function Z is exactly calculated and used to study thermodynamic functions such as the vibrational mean energy U, specific heat C, free energy F and entropy S. It is found that the specific heat $C(k = 1)$ first increases with β and arrives to the maximum value and then decreases with it.

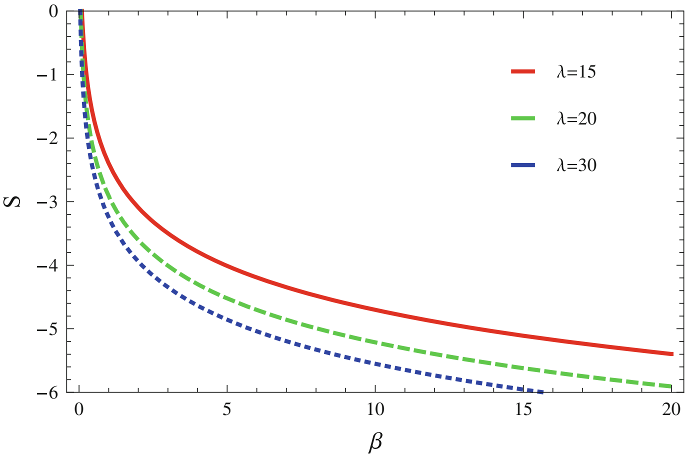

Fig. 10 Vibrational free energy S as function of β for different λ

However, the entropy $S(k = 1)$ first increases with the deepness of potential well λ and then decreases with it.

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