

A Model Effective Mass Quantum Anharmonic Oscillator and Its Thermodynamic Characterization

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Abstract

Using a model anharmonic oscillator with asymptotically decreasing effective mass to study the effect of compositional grading on the quantum mechanical properties of a semiconductor heterostructure, we determine the exact bound states and spectral values of the system. Furthermore, we show that ordering ambiguity only brings about a spectral shift on the quantum anharmonic oscillator with spatially varying effective mass. A study of thermodynamic properties of the system reveals a resonance condition dependent on the magnitude of the anharmonicity parameter. This resonance condition is seen to set a critical value on the said parameter beyond which a complex valued entropy which is discussed, emerges.

Keywords

Ordering Ambiguity, Anharmonicity Parameter, Variable Mass, Anharmonic Oscillator, Thermodynamic Resonance, Complex Entropy, Quantum Harmonic Oscillator

1. Introduction

In material science, the electron effective mass m^* is the mass, it appears to have when probed in the periodic potential of a crystal lattice. The quantum mechanical description of this phenomenon is furnished by the effective mass approximation which is the Schrödinger equation given by:

$$\left[-\frac{\hbar^2}{2m^*} \nabla^2 + U(x) \right] \phi(x) = [E - E_c(r)] \phi(x), \quad (1)$$

wherein $E_c(x)$ is the variable conduction band edge energy, $\phi(r)$ is the envelope function and $U(r)$ some potential energy function which might be due for instance, to an impurity in the crystal. Describing impurities in crystals was the initial purpose of the Effective Mass Theory at its birth in the 1940s [1]. These days, one resorts to it especially in the study of electronic properties of semiconductors [2] [3], quantum wells [4] and quantum dots [5]. In compositionally graded crystals and heterostructures such as $\text{Al}_\delta\text{Ga}_{1-\delta}/\text{GaAs}/\text{Al}_\delta\text{Ga}_{1-\delta}\text{As}$ quantum well (δ being the mole fraction of the Al constituent in the growth direction of the structure), the effective mass becomes position-dependent and the need to do the replacement $m^* \rightarrow m(x)$ arises. However, the quantum kinetic energy operator cannot be expressed as $p^2/2m(x)$ since this structure is obviously non-Hermitian because of the non-vanishing commutator of the momentum and the effective mass operators. Notwithstanding the Hermiticity necessity, an all around characterized quantum kinetic energy operator is relied upon to satisfy various exigencies, for example, Be Galilee Invariant, not prompt infringement of Heisenberg uncertainty rule [6] and guarantee continuity of the envelope function at abrupt interfaces [7].

Ordering these two operators cannot be done in a unique way for a consistent quantum theory with variable mass, reason why one finds a good number of proposals in the literature. O von Roos [8] was the first to propose a generalized Hermitian form as

$$\mathbf{T} = \frac{1}{4} [m^\alpha p m^b p m^\gamma + m^\gamma p m^b p m^\alpha], \quad (2)$$

with the parameters α, b, γ (referred to as ordering ambiguity parameters) constraint by the relation $\alpha + b + \gamma = -1$. One can derive most of the operators proposed in the literature [9] [10] [11] [12] by setting the ambiguity parameters in the von Roos operator.

With this plethora of kinetic energy operators in the literature, the conflict as to which one should be preferred is a long-standing and unresolved one. In an attempt to resolve this issue, Dutra and Almeida [13] used two exactly solved models to propose that exact solutions could be used as a guide towards restricting the possible number of kinetic energy operators at hand. They iterated in a concluding note: "... we did observe that some orderings proposed in the literature lead us to non physically acceptable energies, and could possibly be discarded". In this work, we show in Section 2 that the same methodological framework as used by Dutra and Almeida reveals that the ordering ambiguity parameters only introduce a spectral shift on the system and therefore grants that all possible orderings in the literature are admissible.

The study of thermodynamic properties of physical systems permits for instance to determine system parameters that allow minimum thermodynamic frequency instability such as in quartz resonators [14]. Thermodynamic reson-

ance also finds applications in the detection and destruction of pathogens in human bodies [15] during a flow of high frequency pulsating direct current (PDC), positively polarized, under the condition of electric resonance. It has been shown that the anharmonic oscillator model more accurately predict the thermodynamic properties of molecular vibrations [16]. These promising developments in anharmonic systems is the motivator behind section 3 in which we examine the thermodynamic properties of our model anharmonic oscillator and point out an intricate relationship between the anharmonicity parameter and the ordering ambiguity parameters. Section 3.1 is devoted to discussion of conditions that bring about thermodynamic resonance in the system and concluding remarks are presented in 3.

2. Exactly Solved Model with Position-Dependent Effective Mass

It is note worthy that not all kinetic energy operators seen in the literature are derivable from the von Roos operator. In [13] the authors defined a four term operator that incorporates the the Weyl ordering and the von Roos operator as:

$$\mathbf{T} = \frac{1}{4(a+1)} \left[a \left[\frac{1}{m} p^2 + 2p \frac{1}{m} p + p^2 \frac{1}{m} \right] + m^\alpha p m^b p m^\gamma + m^\gamma p m^b p m^\alpha \right]. \quad (3)$$

Here, the parameter $a \in \{0,1\}$ and the ambiguity parameters are mutually exclusive. Considering the particle in an arbitrary potential $V(x)$, one can construct the Hamiltonian $\mathbf{H} = \mathbf{T} + V(x)$ which can be cast in the form:

$$\mathbf{H} = \frac{1}{2m} p^2 + \frac{i\hbar}{2} \frac{m'}{m^2} p - \frac{\hbar^2}{4(a+1)} \left[(\alpha + \gamma - a) \frac{m''}{m^2} + 2(a - \alpha\gamma - \alpha - \gamma) \frac{m'^2}{m^3} \right] + V(x), \quad (4)$$

where the primes represent differentiation with respect to x . The time-independent Schrödinger equation resulting from the effective Hamiltonian \mathbf{H} expressed as $\mathbf{H}\Psi(x) = E\Psi(x)$ can be re-written with the substitution $\Psi(x) = m^{1/2}\psi(x)$ as

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) - \frac{\hbar^2}{4(a+1)} \left[(\alpha + \gamma + 1) \frac{m''}{m^2} + 2 \left(-\alpha\gamma - \alpha - \gamma + \frac{a-3}{4} \right) \frac{m'^2}{m^3} \right] + \{V(x) - E\} \psi(x) = 0. \quad (5)$$

Equation (5) can be simplified further to

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + \left\{ \left[\eta_1 \frac{m''}{m^2} - \eta_2 \frac{m'^2}{m^3} \right] + V(x) - E \right\} \psi(x) = 0, \\ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + \left\{ \frac{m'^{-\eta_1}}{m^{2-\eta_2}} \left[\frac{m''^{\eta_1}}{m^{\eta_2}} \right] + V(x) - E \right\} \psi(x) = 0, \quad (6)$$

where we have used

$$\begin{aligned}\eta_1 &= -\frac{\hbar^2}{4(a+1)}(\alpha + \gamma + 1), \\ \eta_2 &= \frac{\hbar^2}{2(a+1)}\left(-\alpha\gamma - \alpha - \gamma + \frac{a-3}{4}\right).\end{aligned}\quad (7)$$

Now, for a particle with asymptotically decreasing effective mass

$$m(x) = \frac{m_0}{1 + \lambda x}, \quad (8)$$

in a parabolic confinement potential

$$V(x) = V_0 x^2, \quad (9)$$

Equation (6) takes the form

$$\psi(x) \left(\frac{6a\lambda^2}{m_0} - \frac{4b\lambda^2}{m_0} - E_n + V_0 x^2 \right) - \frac{\hbar^2 (\lambda x + 1)^2 \psi''(x)}{2m_0} = 0. \quad (10)$$

With the transformation

$$\begin{aligned}y &\rightarrow \frac{\sqrt{2m_0 V_0}}{\lambda^2 \hbar} (1 + \lambda x), \\ \psi(x) &\rightarrow (1 + \lambda x)^{\frac{\sqrt{2m_0 V_0}}{\lambda^2 \hbar} - n} e^{-\frac{\sqrt{2m_0 V_0}}{\lambda^2 \hbar} (1 + \lambda x)} \xi(y),\end{aligned}\quad (11)$$

Equation (1) can be transformed to the familiar form

$$y \frac{d^2}{dy^2} \xi + (1 - n - y) \frac{d}{dy} \xi + 2n\xi = 0, \quad (12)$$

after setting

$$-\frac{2m_0(E_n - \rho)}{\hbar^2} + \frac{\sqrt{2m_0 V_0}(2n+1)}{\hbar} - \lambda^2 n(n+1) = 0. \quad (13)$$

Comparing Equation 13 with the confluent hypergeometric differential equation

$$zY'' + (p - z)Y' + qY = 0, \quad (14)$$

that has the confluent hypergeometric functions of the first kind as solutions, *i.e.*

$$Y = A_1 F_1(q, p, z) + BU(q, p, z), \quad (15)$$

it follows that the solutions to Equation (12) are

$$\xi(z) = A_1 F_1(-2n, 1 - n, y) + BU(-2n, 1 - n, y), \quad (16)$$

in the domain $0 \leq y < \infty$ corresponding to $-\frac{1}{\lambda} \leq x < \infty$, where A and B are integral constants. For $A = 0$, the solution reduces to

$$\begin{aligned}\psi_n(x) &= B_n (1 + \lambda x)^{\frac{\sqrt{2m_0 V_0}}{\lambda^2 \hbar} - n} e^{-\frac{\sqrt{2m_0 V_0}}{\lambda^2 \hbar} (1 + \lambda x)} \\ &\times U\left[-2n, 1 - n, \frac{\sqrt{2m_0 V_0}}{\lambda^2 \hbar} (1 + \lambda x)\right],\end{aligned}\quad (17)$$

hence

$$\Psi_n(x) = \frac{B_n}{m_0} (1 + \lambda x)^{\frac{\sqrt{2m_0V_0}}{\hbar\lambda^2} - n + \frac{1}{2}} e^{-\frac{\sqrt{2m_0V_0}}{\lambda^2\hbar}(1+\lambda x)} \times U\left[-2n, 1-n, \frac{\sqrt{2m_0V_0}}{\lambda^2\hbar}(1+\lambda x)\right]. \tag{18}$$

The energy spectrum is obtained from Equation (13) as

$$E_n = (\rho + e_0) + (2e_0 - \delta)n - \delta n^2, \tag{19}$$

where

$$\rho = \frac{\lambda^2}{m_0}(6\eta_1 - 4\eta_2); \quad e_0 = \hbar\sqrt{\frac{2V_0}{m_0}}; \quad \delta = \frac{\hbar^2\lambda^2}{2m_0}. \tag{20}$$

Figure 1 shows a plot of the solutions Equation (18) and Equation (19). The effective potential of the system is a parabola that is sectioned at $x = -\frac{1}{\lambda}$. The hard wall at this location accounts for the nonlinearity of the spectrum in n .

For this exactly solved model, the spectral values are real for all possible values of the ambiguity parameters. Therefore one cannot rely on the admissibility test in [13] (in current use [17] [18] [19]) to discard some orderings from the literature.

3. Thermodynamic Properties of the System

To get an appraisal of the thermodynamic properties of the system, the obvious starting point is the partition function. In the present case, it is given by

$$\begin{aligned} Z &= \sum_{n=0}^{\infty} \exp(-\beta E_n) \\ &= \sum_{n=0}^{\infty} \exp(-\beta(\rho + e_0) + \beta n^2 \delta + n(\beta\delta - 2\beta e_0)) \\ &= e^{-\beta(\rho + e_0)} \sum_{i=0}^{\infty} \sum_{n=0}^{\infty} e^{-n(2\beta e_0 - \beta\delta)} \frac{(\beta\delta n^2)^i}{i!}. \end{aligned} \tag{21}$$

In the last line of Equation (21), we have converted the exponential with argument linear in n to a sum with summation index i . Here $\beta = K_B T$ where K_B is the Boltzmann constant and T the absolute temperature of the system. To evaluate the sum with respect to n , we apply the formula

$$\sum_{m=0}^{\infty} \frac{(cm^2)^g}{g!} e^{-dm} = \frac{\Phi(e^{-d}, -2m, 0)c^g}{g!}, \tag{22}$$

where $\Phi(\cdot)$ is the Lerch transcendent function [20]. This gives

$$Z = e^{-\beta(\rho + e_0)} \sum_{i=0}^{\infty} \frac{(\beta v)^i \Phi(e^{\beta(\delta - 2e_0)}, -2i, 0)}{i!}. \tag{23}$$

For small δ , we neglect terms in δ^2 and higher to obtain

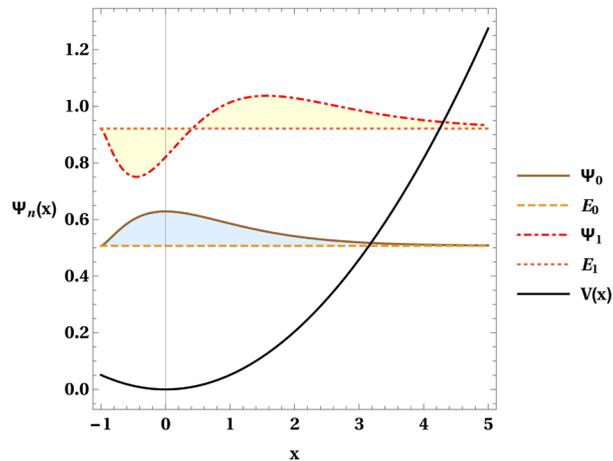


Figure 1. Plot of the potential energy, the first two eigen states and corresponding energy levels. Parameter values used are: $\hbar = m_0 = V_0 = K_B = 1$.

$$Z = \frac{e^{-\beta(\rho+e_0)}}{1 - e^{-\beta(\delta-2e_0)}} + \frac{\beta\delta e^{-\beta(\rho+e_0)} (e^{\beta(\delta-2e_0)} + e^{2\beta(\delta-2e_0)})}{(1 - e^{-\beta(\delta-2e_0)})^3}. \tag{24}$$

It can be seen from Equation (24) that with the substitution of $\lambda = 0$, which translates to $\rho = \delta = 0$, the partition function reduces to that of the linear harmonic oscillator, *i.e.*

$$Z_{\lambda=0} = \frac{e^{-\beta e_0}}{1 - e^{-2\beta e_0}} = \frac{1}{2} \operatorname{csch}(\beta e_0). \tag{25}$$

The Free energy of the system is given by

$$F = -K_B T \log Z$$

$$= -K_B T \log \left(\frac{\beta\delta e^{-\beta(\rho+e_0)} (e^{\beta(\delta-2e_0)} + e^{2\beta(\delta-2e_0)})}{(1 - e^{-\beta(\delta-2e_0)})^3} + \frac{e^{-\beta(\rho+e_0)}}{1 - e^{-\beta(\delta-2e_0)}} \right), \tag{26}$$

its entropy reads

$$S = -\frac{dF}{dT} = \frac{6(\delta - 2e_0)e^{\frac{\delta}{K_B T}}}{e^{\frac{\delta}{K_B T}} - e^{\frac{e_0}{K_B T}}} + \frac{e_0}{T}$$

$$+ K_B \log \left(\frac{e^{-\frac{e_0}{2K_B T}} \left(K_B T \left(e^{\frac{\delta-2e_0}{K_B T}} - 1 \right)^2 + \delta \left(e^{\frac{\delta-2e_0}{K_B T}} + e^{\frac{2(\delta-2e_0)}{TK_B}} \right) \right)}{K_B T \left(1 - e^{\frac{\delta-2e_0}{TK_B}} \right)^3} \right) \tag{27}$$

$$+ \frac{e^{\frac{\delta+e_0}{K_B T}} (K_B T (\delta - 2e_0) + \delta e_0) + e^{\frac{2\delta}{K_B T}} (K_B T (2e_0 - 3\delta) + 2\delta e_0)}{T \left((\delta - 2K_B T) e^{\frac{\delta+e_0}{K_B T}} + e^{\frac{2\delta}{K_B T}} (K_B T + \delta) + K_B T e^{\frac{2e_0}{TK_B}} \right)},$$

and has the shape shown in **Figure 2**.

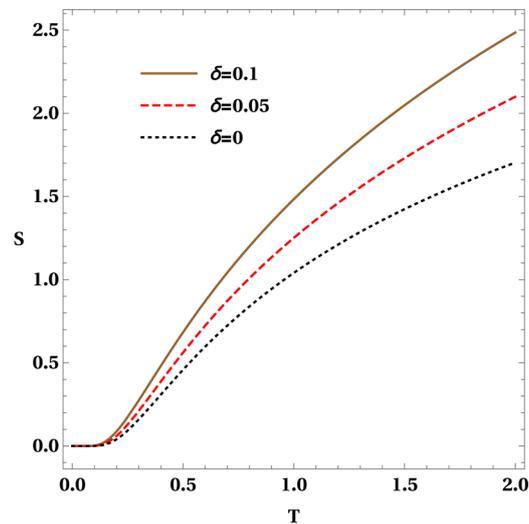


Figure 2. Plot of entropy against system temperature for three values of the nonlinearity parameter. Parameter values used are: $\hbar = m_0 = V_0 = K_B = 1$.

It is easily verified that the entropy reduces to that of the linear harmonic oscillator

$$S = \frac{e_0}{T} \coth\left(\frac{e_0}{K_B T}\right) + K_B \log\left[\frac{1}{2} \operatorname{csch}\left(\frac{e_0}{TK_B}\right)\right], \tag{28}$$

when $\lambda = 0$.

Thermodynamic Resonance

From the result Equation (27), we observe a resonance condition given by

$$\delta = 2e_0, \tag{29}$$

from where a critical value for the anharmonicity parameter can be defined as

$$\lambda_c = \frac{2\sqrt{m_0 e_0}}{\hbar}, \tag{30}$$

for which the entropy reads

$$S = \frac{e_0}{T} + K_B \log[\infty] - K_B. \tag{31}$$

For $\delta < 2e_0$, it is observed that the entropy remains real and tends to increase more rapidly with increase in strength of the anharmonicity as shown in **Figure 2**.

Above the critical value, *i.e.* $\delta > 2e_0$, we observe that the argument of the logarithm in the expression of the entropy becomes negative. The logarithm therefore becomes complex valued. We can separate the real and imaginary parts of the logarithm as follows:

$$K_B \log(\dots) = i\pi K_B \theta[\delta - 2e_0] + K_B \log(|\dots|), \tag{32}$$

where θ is the Heaviside theta function. As such, this leads the entropy to be

expressible as $S = \Re(S) + i\Im(S)$ where

$$\Im(S) = \pi K_B \theta [\delta - 2e_0]. \quad (33)$$

Complex entropy can arise as an extension of the Shannon entropy to classical and nonclassical components of generalized entropy/information descriptors of molecular states in which the real and imaginary parts are provided by the system complex electronic wave-function (quantum probability amplitude) [21]. Complex entropy has been applied in engineering deterministic prediction of outcomes of thermodynamic experiments [22]. In information theory, complex valued information entropy proves useful in the description of directed networks [23]. It also serves a good purpose in explicating energy flows in complex systems [24]. In the present model, complex entropy arises as a consequence of system setting. The result Equation (27) shows that for $\delta > 0$, $S(0) = \infty$. The entropy of the anharmonic oscillator is infinitely large at $T = 0$. **Figure 3** shows a plot of the entropy for $\delta > 2e_0$. While the imaginary part remains constant for all T , the real part exhibits a singularity at $T = 0$ and a minimum which decreases with increasing anharmonicity strength.

4. Discussion of Results

Equation (19) portrays an intricate relationship between the ordering ambiguity and anharmonicity introduced by the position dependence of the effective mass. In fact setting the deformation parameter λ to zero automatically eliminates ordering ambiguity terms from the energy spectrum, reducing the spectrum to the harmonic oscillator spectrum. On the other hand, using the most unambiguous form for the kinetic energy operator in which $\alpha = \gamma = -1/4, b = -1/2$ which returns $\eta_1 = \eta_2 = 0$, the spectrum reduces to that of the harmonic oscillator shifted by an infinite square well like term $\hbar^2 \lambda^2 n^2 / 2m_0$. Here it is apparent that anharmonicity persists in the absence of ordering ambiguity.

We have shown that the effect of position dependence in the effective mass in this oscillator model is the induction of a sort of thermodynamic resonance during which the entropy of the system becomes infinitely large. The resonance condition establishes a threshold on the anharmonicity strength δ_c below which regular evolution of entropy is observed and above which one observes the onset of complex valued entropy. In the latter case, the imaginary part of the entropy has been given the interpretation of the entropy transferred from the system to the environment. This entropy transferred turns out to be a constant πK_B .

Our model exhibits a singularity in the entropy at $T = 0$. This temperature is of course not physically attainable. If instead of T , one looks at the results in terms of $\beta = 1/K_B T$ where heat always flows from a small β (albeit negative) to a bigger one, it turns out that in such an anharmonic oscillator, the system becomes an efficient emitter of heat once the critical anharmonicity λ_c is exceeded.

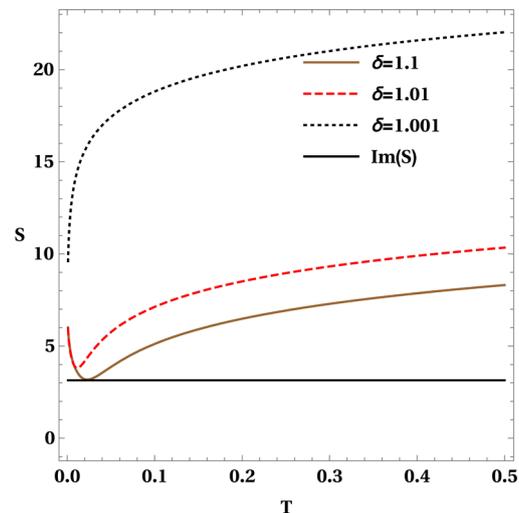


Figure 3. Plot of entropy against temperature for $\delta > 2e_0$. Parameter values used are: $\hbar = m_0 = V_0 = K_b = 1$.

5. Conclusion

Starting with the most general form of the kinetic energy operator for quantum systems with position dependent effective masses, we have shown that the generation of a real spectrum cannot be used to discard some kinetic energy operators from the literature. Using an exactly solved model, of an asymptotically decreasing effective mass system in a parabolic confinement potential, we have shown that the prevalence of ordering ambiguity simply introduces a constant shift in the spectral values of the system. Our results show that anharmonicity introduces a thermodynamic resonance condition in the system, with the onset of a critical value for the anharmonicity parameter beyond which the emitting nature of the system is enhanced. This observation gives a valuable insight for designing semiconductor materials with desired thermodynamic properties

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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