We have developed a theoretical formalism to introduce temperature as a parameter into the framework of non-relativistic quantum mechanics using the laws of classical thermodynamics and the canonical ensemble scheme of statistical mechanics. A self-consistent Hamiltonian has then been constructed for a given quantum many-body system which includes the effect of temperature in the form of correction terms added to the corresponding zero-temperature Hamiltonian of the system. Investigating some quantum mechanical systems with exact zero-temperature solutions including the particle-in-a-box model, the free particle, and the harmonic oscillator within our finite-temperature approach up to the first order of self-consistency has led to temperature-dependent Hamiltonians describing these systems above absolute zero without encountering any physically unacceptable brand of behavior for their wave functions and energy spectra. Results firmly support the view that a quantum mechanical system at a finite temperature behaves as if it is in a zero-temperature excited state.

Keywords Quantum mechanics · Thermodynamics · Statistical mechanics · Temperature-dependent wave function

1 Introduction

Temperature is a collective phenomenon and is only tangible in dealing with macroscopic systems containing as large number of particles as orders of magnitude of the Avogadro’s number [1]. However, statistical mechanics successfully defines the absolute temperature of a given system at the microscopic level in terms of its number of accessible microstates ($\Omega$) as $T = (k_B \partial \ln \Omega(E)/\partial E)^{-1}$ (with $k_B$ the Boltzmann constant and $E$ the total energy), in a similar way as its forerunner, the kinetic theory of gases [2], providing a microscopic expression for instantaneous temperature of the system—$T(t) = [(3N - 6)k_B]^{-1} \sum_{i=1}^{N} m_i v_i^2(t)$, where $m_i$ and $v_i(t)$ are the mass and velocity of particle $i$ at time $t$ respectively, and $N$ is the total number of particles—based on movements of the constituent microscopic corpuscles. As a result, the question that naturally arises is whether it is possible to assign a temperature to a quantum system, or more technically, how do the quantum mechanical properties of a given system evolve at finite temperatures compared to those at absolute zero?

Quantum mechanics, from scratch, has been formulated at absolute zero largely based on the fact that the zero-temperature regime, in its very essence, ignores theoretical complications arising from taking into account the effect of finite temperatures on quantum mechanical systems’ behaviors, providing us with the most fundamental information about the structure of matter at the deepest levels of reality. Moreover, the ground states of systems naturally take place at absolute zero according to the third law of thermodynamics, and the notions of ground or excited states are therefore best described at this lowest possible temperature. Far above absolute zero, the zero-temperature formulation

*Corresponding author
must be seriously modified and revisited because of non-negligible perturbations arising from thermal coupling to the environment.

Historically, studying finite-temperature behaviors of physical systems has been the main subject of thermodynamics, and later on, of statistical mechanics, in which temperature plays a principal role. However, the formulation of quantum statistics as the rewriting of statistical mechanics in terms of operators and wave functions has not yet introduced any new physical idea as such; rather, it has provided us with a highly suited tool for inquiring into typical quantum systems \[1\], without taking the explicit approach of directly constructing the temperature-dependent Hamiltonian and wave function of a given quantum mechanical system. The idea that naturally comes to mind is therefore to develop a theoretical procedure to fit absolute temperature into the formalism of non-relativistic quantum mechanics in order to determine the way the Hamiltonian and wave function of a given quantum many-body system evolve or are modified compared to those at absolute zero when it is thermally coupled to its immediate surroundings.

Such an effort has not yet seriously been spent, therefore, the present work has been devoted to materializing this idea as follows. We first have introduced temperature as a parameter into the Hamiltonian of a classical many-body system using the first and second laws of thermodynamics and the canonical ensemble formalism of statistical mechanics. The language of operators has then been used in order to write down the corresponding quantum mechanical counterpart of the obtained Hamiltonian. We finally apply our procedure to some systems with exact zero-temperature solutions including the particle-in-a-box model \[2\] (as an important prototype to approximate some real physical phenomena such as quantum dots \[3\], biological pigment molecules \[4\], and quantum well lasers \[5\]), the free particle, and the harmonic oscillator (as a useful model for a variety of vibrational phenomena encountered in all branches of physics including classical and quantum mechanics, electrodynamics, statistical mechanics, solid state, atomic, nuclear, and particle physics \[6\]).

2 Basic assumptions

We consider a classical many-body system thermally coupled to a much larger heat reservoir so that the canonical ensemble formalism can indeed be applicable. The many-body system + heat reservoir is also assumed as a single isolated system (with no energy/matter exchange with its environment), while the many-body system itself is considered as a closed one in a way that only energy exchange with the heat reservoir is allowed. We then use the language of operators to construct the quantum mechanical counterpart of the many-body system’s Hamiltonian.

It has long been known that for nanoscale systems, deviations from classical thermodynamics—in which temperature estimations of macroscopic systems in equilibrium are most precise when the related energy fluctuations are large—arise due to their interactions with the environment. Miller and Anders \[9\] have derived a generalized thermodynamic uncertainty relation, which is valid for classical and quantum systems at all coupling strengths via taking into account such interactions within the framework of quantum estimation theory, showing that the non-commutativity between the system’s state and its effective energy operator results in quantum fluctuations that increase temperature uncertainty.

Based on such theoretical issues, the following assumptions has then been made in our present approach: (i) the canonical temperature of the system is treated as a mere parameter (just like time) rather than as an observable; (ii) the system is weakly coupled to its reservoir \[10\] so that the mutual equilibrium state can then be best described by the canonical ensemble; (iii) strength of interactions between the system and reservoir is assumed to be so negligible as the local equilibrium state of the system will accordingly be of the Gibbs form \[13\] \[14\]; and (iv) the internal energy \( U \) can be determined by the bare Hamiltonian of the weakly coupled system \[15\] \[16\]. Rather than devoting us to measuring the temperature itself, here, we try to approximate the behavior of a quantum many-body system at finite temperatures via introducing some correction terms to the corresponding zero-temperature Hamiltonian of the system, demonstrating the effect of temperature and thermal coupling. The associated time-independent Schrödinger equation is then solved in order to calculate the temperature-dependent wave function and energy eigenvalue spectrum.

2.1 Method

Based on the preceding assumptions, the internal energy \( U \) of our classical many-body system is then given by

\[
U = \sum_{i=1}^{N} [T_i + v(\mathbf{r}_i)] + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},
\]

where \( T_i \) and \( v(\mathbf{r}_i) \) are the kinetic and potential energies associated with particle \( i \), the last term denotes interaction between particles \( i \) and \( j \) located at \( \mathbf{r}_i \) and \( \mathbf{r}_j \) (position vectors), respectively, and \( N \) is the total number of constituent particles. From the first law of thermodynamics, and by assuming that no work \( W \) has been done by reservoir on the
system, it follows that
\[ d(U - Q) = dW = 0 \implies U - Q = \text{const.} \equiv E, \]  
(2)
where \( Q \) is the amount of heat absorbed/ transferred from/to the surroundings, and \( E \) is a constant with dimension of energy. Moreover, from the second law of thermodynamics, for a closed system which allows the entry or exit of energy at the equilibrium temperature \( T_{eq} \), change in the entropy \( S \) due to infinitesimal transfer of heat \((dQ)\) is given by
\[ dQ = T_{eq}dS = d(T_{eq}S) \implies Q = T_{eq}S. \]  
(3)
Inserting (1) and (3) in (2), we obtain that
\[ \sum_{i=1}^{N} [T_i + v(r_i)] + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|r_i - r_j|} - T_{eq}S = E. \]  
(4)
Using the canonical-ensemble formula \( A = -k_B T \ln Z(T) \) for the Helmholtz free energy, it follows that
\[ S = - \left( \frac{\partial A}{\partial T} \right)_{N,V} = k_B \left( 1 + T \frac{\partial}{\partial T} \right)_{T=T_{eq}} \ln Z(T), \]  
(5)
where \( Z(T) \) is the canonical partition function of the many-body system. Plugging (5) back into (4) then gives
\[ \sum_{i=1}^{N} [T_i + v(r_i)] + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|r_i - r_j|} - k_B T_{eq} \left( 1 + T \frac{\partial}{\partial T} \right)_{T=T_{eq}} \ln Z(T) = E. \]  
(6)
Using the corresponding quantum mechanical operator \((-\hbar^2/2m)\nabla_i^2\) for the kinetic energy \(T_i\), and by multiplying the both sides of Eq. (6) by the temperature-dependent wave function \(\Psi_{T_{eq}}(r)\), it is obtained that
\[ \left[ \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m} \nabla_i^2 + v(r_i) \right) + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|r_i - r_j|} - k_B T_{eq} \left( 1 + T \frac{\partial}{\partial T} \right)_{T=T_{eq}} \right] \Psi_{T_{eq}}(r) = E \Psi_{T_{eq}}(r), \]  
(7)
where \(\hbar\) is the reduced Planck constant, and \(m_i\) denotes the mass of particle \(i\). We consider Eq. (7) as the generalized time-independent Schrödinger equation of the many-body system at the equilibrium temperature \(T_{eq}\)—the temperature-dependent version can also be simply derived via replacing \(E\) in the right side by its corresponding operator \(\hbar \partial/\partial t\). We also take the approach in that the energy \(E\) is approximated by \((E_{n,0} - \langle E \rangle)_{gs}\), where \(E_{n,0}\) is the corresponding zero-temperature energy of the system associated with the electronic state \(n\), and \((E)_{gs} = \langle E \rangle|_{T_{eq}=0}\) is the canonical-ensemble average of the ground-state energy with \(\langle E \rangle = \sum_i \epsilon_i e^{-\epsilon_i/k_BT_{eq}} / \sum_i e^{-\epsilon_i/k_BT_{eq}} , \beta = 1/k_BT, \) and \(\epsilon_i\) the energy of state \(i\). Irrespective of eliminating electronic states, approximating \(E\) only by its ensemble average results in an overestimation of about \(2(E)\) in energy of the system based on the fact that the temperature-dependent Hamiltonian in the left side of Eq. (7) by its very nature, generates one \(\langle E \rangle\) for any system. Because of the same reason, \(E \approx E_{n,0}\) also gives rise to an overestimation in the ground-state energy, as a result, \(E \approx E_{n,0} - \langle E \rangle_{gs}\) is the best approach. Using the identity \(Z(T) = \text{Tr}(e^{-\beta \hat{H}})\), the Hamiltonian in Eq. (7) then takes the form
\[ \hat{H} = \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m} \nabla_i^2 + v(r_i) \right) + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|r_i - r_j|} - k_B T_{eq} \left( 1 + T \frac{\partial}{\partial T} \right)_{T=T_{eq}} \ln \text{Tr} \left( e^{-\beta \hat{H}} \right). \]  
(8)
The important feature of Eq. (8) is that it is as such a self-consistent Hamiltonian because of \(\hat{H}\) being appeared on the both sides. The more expressive form of Eq. (8) reflecting its self-consistency is therefore
\[ H_I = \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m} \nabla_i^2 + v(r_i) \right) + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|r_i - r_j|} - k_B T_{eq} \left( 1 + T \frac{\partial}{\partial T} \right)_{T=T_{eq}} \ln \text{Tr} \left( e^{-\beta H_{I-1}} \right), \]  
(9)
where \(I\) denotes the order of self-consistency and its minimum value is 1. Starting from \(I = 1\) (giving \(H_0\) on the right side as the corresponding zero-temperature Hamiltonian of the system), any order \(I > 0\) of \(H_I\) is then calculated. For a one-particle system, \(\text{Tr}(e^{-\beta \hat{H}})\) is simply \(\sum_{\text{all states}} e^{-\beta \epsilon_i}\); likewise, for a many-body system consisting \(N\) indistinguishable particles, \(\text{Tr}(e^{-\beta \hat{H}}) = (1/N!) \Pi_{\text{all particles}} \sum_{\text{all states}} e^{-\beta \epsilon_i}\).
3 Results and discussion

3.1 The particle-in-a-box model

Considering a free electron with mass $m$ confined to move inside an infinite, one-dimensional potential well defined by $v(0 \leq x \leq L) = 0$ and $v(0 > x > L) = +\infty$, the first order of self-consistency corresponding with the most dominant term of $e^{-\beta H_{1-1}}$ then gives

$$\text{Tr} \left( e^{-\beta H_{1-1}} \right) |_{T=1} \rightarrow \sum_{\text{all states}} \exp (-\beta H_0) = \sum_{n=1}^{\infty} \exp \left( -\beta \frac{\pi^2 \hbar^2}{2mL^2} n^2 \right), \quad (10)$$

where $\pi^2 \hbar^2 n^2 / 2mL^2 = E_{n,0}$ is the corresponding zero-temperature energy of the system in electronic state $n$. The most dominant term in (10) also associates with the ground state ($n = 1$) of the system at absolute zero. Plugging (10) for $n = 1$ back into (9), and by using the identity $\partial/\partial T = -k_B \beta^2 \partial/\partial \beta$, it is then obtained that

$$H_1 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - k_B T_{eq} \left( 1 - \beta \frac{\partial}{\partial \beta} \right)_{T=T_{eq}} \left( -\beta \frac{\pi^2 \hbar^2}{2mL^2} \right) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - k_B T_{eq} \left( -\frac{\pi^2 \hbar^2}{2mL^2} + \frac{\pi^2 \hbar^2}{2mL^2} \right) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2},$$

which is nothing but the zero-temperature Hamiltonian ($H_0$). We are therefore led to include the second most dominant term ($n = 2$) in expression (10), which accordingly results in

$$H_1 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - k_B T_{eq} \left( 1 - \beta \frac{\partial}{\partial \beta} \right)_{T=T_{eq}} \ln \left( e^{-\pi(\lambda_d/2L)^2} + e^{-4\pi(\lambda_d/2L)^2} \right)$$

$$= H_0 - k_B T_{eq} \ln \left( e^{-\pi(\lambda_d/2L)^2} + e^{-4\pi(\lambda_d/2L)^2} \right) - \langle E \rangle,$$

with $\lambda_d = \hbar / \sqrt{2\pi nk_B T_{eq}}$ the mean thermal wavelength associated with massive, non-interacting particles, and

$$\langle E \rangle = \frac{\pi^2 \hbar^2}{2mL^2} e^{-\pi(\lambda_d/2L)^2} e^{-4\pi(\lambda_d/2L)^2} \text{e}^{-\pi(\lambda_d/2L)^2} e^{-4\pi(\lambda_d/2L)^2}.$$

(11)

From Eq. (11) the time-independent Schrödinger equation to be solved is therefore $H_1 \Psi_{n,T_{eq}}(x) = \langle E_{n,0} - \langle E \rangle \rangle s \Psi_{n,T_{eq}}(x)$, which leads to $H_0 \Psi_{n,T_{eq}}(x) = E_{n,T_{eq}} \Psi_{n,T_{eq}}(x)$. As a result, the energy spectrum of the system at $T_{eq}$ is

$$E_{n,T_{eq}} = \frac{\pi^2 \hbar^2}{2mL^2} n^2 + k_B T_{eq} \ln \left( e^{-\pi(\lambda_d/2L)^2} + e^{-4\pi(\lambda_d/2L)^2} \right) + \langle E \rangle - \langle E \rangle \rangle s,$$

(12)

where, from (11), $\langle E \rangle \rangle s = \lim_{T_{eq} \rightarrow 0} \langle E \rangle = \pi^2 \hbar^2 / 2mL^2$. The second and third terms on the right side of (12) are clearly corrections due to temperature. The temperature-dependent wave function of the system is then

$$\Psi_{n,T_{eq}}(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{\sqrt{2mE_{n,T_{eq}}} x}{\hbar} \right),$$

(13)

which is illustrated in Figure [1] for the first two modes $n = 1$ and 2 at two different temperatures including absolute zero. From the left panel [Figures (1a) and (1c)], it is seen that the wave function (13) reduces to its corresponding zero-temperature counterpart, $\Psi_{n}(x) = \sqrt{2/L} \sin (\pi nx/L)$, in the limit $T_{eq} \rightarrow 0$ as expected. Moreover, these wave functions satisfy Dirichlet boundary conditions ($\Psi_{n,T_{eq}} = 0$ everywhere at the boundaries). However, from the right panel [Figures (1b) and (1d)], it could be inferred that this criterion is violated for $T_{eq} > 0$, and holds only for specific values of the equilibrium temperature. Such an inevitable violation, as such, is a direct consequence of thermal coupling to the heat reservoir and can be considered as a feature (not a drawback) of the system at finite temperatures. The wave function (13), however, is conformed to the criteria of being finite everywhere as well as being square integrable as it is inferred from the diagrams. The behavior of $\langle \Psi_{n,T_{eq}} \rangle^2$ is also exactly in accordance with the related zero-temperature wave functions. For $T_{eq} = 5$ [Figures (1b) and (1d)], the same sinusoidal patterns are observed but with a larger compactness compared to $T_{eq} = 0$ [Figure (1a)], indicating that the effect of temperature manifests itself in the form of zero-temperature excited states. Such a theoretical observation is accepted based on the fact that temperature is indeed an external agitating factor to excite the system into its higher electronic states.
The second term in the right side of Eq. 15 is evidently the correction due to temperature. The wave function is then
\[ \langle \psi | \psi \rangle \]
where
\[ H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \]
has a continuous spectrum \((\pm \beta)\) in the limit \(T \to 0\). For \(k = 0\) at absolute zero [Fig. 2(a)], the Re and Im parts are constant functions with the latter one to be zero at everywhere. However, for \(k = 0\) (vanishing momentum) above absolute zero [Fig. 2(b)] the functions take sinusoidal patterns similar to those of

Figure 1: Shapes of the wave function \(\psi\) for the first two modes \(n = 1, 2\) [(a) and (b)], and those of the associated probability densities \(\left| \psi_{n,T_s} \right|^2\) [(c) and (d)] at \(T_s = 0\) and 5, in a contrasting fashion. The \(x_s = x/L\) and \(T_s = T_{eq}/T_H\) are the scaled position and temperature in Hartree atomic units (\(\hbar = k_B = m = 1\)), respectively. Metric values of the Bohr radius \(a_0\) and \(T_H\) are also \(5.292 \times 10^{-11}\) m and \(3.158 \times 10^5\) K according to CODATA 2018 [17].

3.2 The free particle

For a free quantum mechanical particle with a well-defined linear momentum \(p = \hbar k\), \(k\) being the wave number, we get
\[ \text{Tr} \left( e^{-\beta H_{t-1}} \right) |_{I=1} \to \sum_{\text{all states}} e^{-\beta H_0} \to \int_{-\infty}^{\infty} e^{-\beta p^2/2m} dp = \frac{\sqrt{2m\pi}}{\beta}, \] (14)
where we have used the fact that \(H_0\) has a continuous spectrum \((p^2/2m)\), and does not depend on coordinates. Inserting (14) in (9), and for \(I = 1\), it is obtained that
\[ H_1 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - \frac{1}{\beta} \left( 1 - \beta \frac{\partial}{\partial \beta} \right)_{T=T_{eq}} \ln \frac{2m\beta}{\hbar^2} = H_0 - \langle E \rangle \ln(4\pi m \langle E \rangle) + 1. \]
The time-independent Schrödinger equation \(H_1 \psi_{k,T_{eq}}(x) = (E_{k,0} - \langle E \rangle_{gs}) \psi_{k,T_{eq}}(x)\) then gives
\[ H_0 \psi_{k,T_{eq}}(x) = \left( \frac{\hbar^2}{2m} k^2 + \langle E \rangle \ln(4\pi m \langle E \rangle) + 1 \right) \psi_{k,T_{eq}}(x), \] (15)
where \(\langle E \rangle = k_B T_{eq}/2\), \(\langle E \rangle_{gs} = 0\), and we have used the energy-momentum dispersion relation \(E_{k,0} = \hbar^2 k^2/2m\). The second term in the right side of Eq. (15) is evidently the correction due to temperature. The wave function is then
\[ \psi_{k,T_{eq}}^{\pm}(x) = \exp \left( \pm i \left[ k^2 + \frac{mk_BT_{eq}}{\hbar^2} \ln(2\pi mk_BT_{eq}) + 1 \right]^{1/2} x \right), \] (16)
in which the +/- sign indicates traveling to the right/left. Fig. 2 shows the shapes of the real (Re) and imaginary (Im) parts of \(\psi_{k,T_{eq}}^{\pm}(x)\) for \(k = 0\) and 1 at \(T_s = 0\) and 1. As it is seen from the left panel [Figs. 2(a) and 2(c)], the wave function (16) reduces to its zero-temperature form \(e^{\pm i k x}\) in the limit \(T_{eq} \to 0\). For \(k = 0\) at absolute zero [Fig. 2(a)], the Re and Im parts are constant functions with the latter one to be zero at everywhere. However, for \(k = 0\) (vanishing momentum) above absolute zero [Fig. 2(b)] the functions take sinusoidal patterns similar to those of
Temperature: The ignored factor in quantum mechanics

Figure 2: The real (Re) and imaginary (Im) parts of the wave function \( \psi \) associated with a free particle moving to the right of the \( x \)-axis for the wave numbers \( k = 0 \) and 1 at \( T_s = 0 \) and 1. The \( x/a_0 \) is the scaled position.

zero- or finite-temperature excited states (Figs. 2(c) and 2(d), respectively). That the imaginary part of Fig. 2(b) is a non-zero function is also entirely the effect of temperature. Similar to the particle-in-a-box model, the free particle at finite temperatures behaves as if it is in an excited state but at absolute zero.

3.3 The harmonic oscillator

For a quantum mechanical particle oscillating with an angular frequency \( \omega \) under the influence of the one-dimensional harmonic potential \( m \omega^2 x^2 / 2 \), we have

\[
\text{Tr} \left( e^{-\beta H_{1-1}} \right) |_{T = 1} \rightarrow \sum_{\text{all states}} \exp(-\beta H_0) = \sum_{n=0}^{\infty} \exp \left[ -\beta \left( n + \frac{1}{2} \right) \hbar \omega \right],
\]

where \( (n + 1/2) \hbar \omega = E_{n,0} \). Inserting (17) in (9) then gives

\[
H_1 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2 - \frac{1}{\beta} \left( 1 - \beta \frac{\partial}{\partial \beta} \right)_{T=T_{eq}} \ln \sum_{n=0}^{\infty} e^{-\beta (n+1/2) \hbar \omega}.
\]

Similar to the previous systems, taking into account the most dominant term \( (n = 0) \) of the summation results in \( H_0 \) of the system given by the first two terms of the right side of (18). It, therefore, clearly indicates that if a system is in its ground state, only \( T_{eq} = 0 \) can be inferred, in an exact conformity with the third law of thermodynamics. We accordingly are led to include the second most dominant term, namely \( n = 1 \), in Hamiltonian (18), which gives

\[
H_1 = H_0 - k_B T_{eq} \ln \left( e^{-\hbar \omega / 2 k_B T_{eq}} + e^{-3 \hbar \omega / 2 k_B T_{eq}} \right) - \langle E \rangle,
\]

and

\[
\langle E \rangle = \left( \frac{\hbar \omega}{2} \right) \frac{1 + 3 e^{-\hbar \omega / k_B T_{eq}}}{1 + e^{-3 \hbar \omega / k_B T_{eq}}}.
\]

The time-independent Schrödinger equation \( H_1 \Psi_n,T_{eq}(x) = (E_{n,0} - \langle E \rangle) \Psi_n,T_{eq}(x) \) then leads to \( H_0 \Psi_n,T_{eq}(x) = E_{n,T_{eq}} \Psi_n,T_{eq}(x) \), where

\[
E_{n,T_{eq}} = \hbar \Omega_{n,T_{eq}} = (n + 1/2) \hbar \omega + k_B T_{eq} \ln \left( e^{-\hbar \omega / 2 k_B T_{eq}} + e^{-3 \hbar \omega / 2 k_B T_{eq}} \right) + \langle E \rangle - \langle E \rangle_{gs}
\]
Temperature: The ignored factor in quantum mechanics

Figure 3: The first six modes \( (n = 0 - 5) \) of the wave function (21) at \( T_s = 0, 0.1 \) and 10. That the functions are either even or odd depending on the value of \( n \) at finite temperatures is evident, in the same manner as those at absolute zero.

gives the energy spectrum of the system at finite temperatures, and \( \langle E \rangle_{gs} = \hbar \omega / 2 \). The equivalence depicted in (19) accordingly results in

\[
\Omega_{n,T_{eq}} = n\omega + \frac{k_B T_{eq}}{n} \ln \left( e^{-\hbar \omega / 2k_B T_{eq}} + e^{-3\hbar \omega / 2k_B T_{eq}} \right) + \frac{\omega}{2} \frac{1 + 3e^{-\hbar \omega / k_B T_{eq}}}{1 + e^{-\hbar \omega / k_B T_{eq}}},
\]

which is the generalized, temperature-dependent angular frequency of the system. That the last two terms in the right side of (20) are corrections due to temperature is evident. The wave function of the system is then

\[
\Psi_{n,T_{eq}}(x) = \frac{1}{\sqrt{\sqrt{\pi} n! x_0}} \exp \left( -\frac{x^2}{2x_0^2} \right) \mathcal{H}_n \left( \frac{x}{x_0} \right),
\]

where \( \mathcal{H}_n \) is the Hermite polynomial [18] of degree \( n \), and \( x_0 = \sqrt{\hbar / (m\Omega)} \) defines the length scale of the system. Fig. 3 illustrates the first six modes \( n = 0 - 5 \) of (21) at three different temperatures including absolute zero. As it is seen, the wave function (21) is either even or odd depending on \( n \) not only at absolute zero, but also at finite temperatures. All these functions are also physically acceptable based on the fact that they exhibit both finiteness at everywhere and square integrability. In the limit \( T_{eq} \rightarrow 0 \), the corresponding zero-temperature wave functions are also obtained. Because of the logarithmic factor in (20), the wave function (21) shows an ever-broadening trend from zero to \( T_s = 1 \) at all modes; by contrast, it becomes more contracted compared to \( T_s = 0 \) as temperature rises from \( T_s = 1 \) on, which, in turn, increases \( \Omega \) affecting behavior of the wave function through the factor \( x_0 \). In the same manner as the previous systems, thermal coupling to heat reservoir makes the harmonic oscillator at equilibrium in an electronic state behave as though it is in higher zero-temperature modes of vibration.

4 Conclusions

Using laws of classical thermodynamics and the canonical-ensemble scheme of statistical mechanics, we have developed a formalism to fit absolute temperature as a parameter into the framework of non-relativistic quantum mechanics. A self-consistent Hamiltonian has then been derived which describes the behavior of a given quantum many-body system at finite temperatures in that the effect of temperature mathematically appears in the form of correction terms added to the corresponding ground-state Hamiltonian of the system. Applying our procedure to some quantum mechanical systems with exact zero-temperature solutions including the particle-in-a-box model, the free particle, and
the harmonic oscillator up to the first order of self-consistency has resulted in temperature-dependent Hamiltonians describing their behaviors above absolute zero without encountering any physically unacceptable wave functions or energy spectra. Results verify that a quantum mechanical system at finite temperatures behaves as though it is in its zero-temperature excited states.

References

[1] A. Shekaari and M.R. Abolhassani. Car-Parrinello molecular dynamics study of the melting behaviors of \( n \)-atom \((n = 6, 10)\) graphene quantum dots. Chem. Phys. Lett. 678, 177–185 (2017).
[2] R. Clausius, Über die Art der Bewegung, die wir Wärme nennen, Ann. Phys. (Berlin) 100, 353–379 (1857).
[3] R.K. Pathria and P.D. Beale, Statistical Mechanics, third ed., Butterworth Heinemann, Oxford, 2011.
[4] J.H. Davies, The Physics of Low-Dimensional Semiconductors: An Introduction, sixth reprint ed., Cambridge University Press, 2006.
[5] H.S. Mansur, Quantum dots and nanocomposites, Wiley Interdiscip. Rev. Nanomed. Nanobiotechnol. 2, 113–129 (2010).
[6] R. Phillips, J. Kondev, J. Theriot, H. Garcia, and J. Kondev, Physical Biology of the Cell, second ed., Garland Science, 2012.
[7] L. Chen, Quantum well lasers and their applications, Int. J. High Speed Electron. Syst. 7, 373–381 (1996).
[8] N. Zettili, Quantum Mechanics, Concepts and Applications, second ed., John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom, 2009.
[9] H.J.D. Miller and J. Anders, Energy-temperature uncertainty relation in quantum thermodynamics, Nat. Commun. 9, 2203 (2018).
[10] P. Zanardi, M.G.A. Paris, and L. Campos Venuti, Quantum criticality as a resource for quantum estimation, Phys. Rev. A. 78, 042105 (2008).
[11] T.M. Stace, Quantum limits of thermometry, Phys. Rev. A. 82, 011611(R) (2010).
[12] L.A. Correa, M. Mehboudi, G. Adesso, and A. Sanpera, Individual quantum probes for optimal thermometry, Phys. Rev. Lett. 114, 220405 (2015).
[13] M. Ludwig, K. Hammerer, and F. Marquardt, Entanglement of mechanical oscillators coupled to a nonequilibrium environment, Phys. Rev. A. 82, 012333 (2010).
[14] Y. Subasi, C.H. Fleming, J.M. Taylor, and B.L. Hu, The equilibrium states of open quantum systems in the strong coupling regime, Phys. Rev. E 36, 061132 (2012).
[15] U. Seifert, First and second law of thermodynamics at strong coupling, Phys. Rev. Lett. 116, 020601 (2016).
[16] H.J. Miller and J. Anders, Entropy production and time asymmetry in the presence of strong interactions, Phys. Rev. E 95, 062123 (2017).
[17] The Committee on Data for Science and Technology.
http://www.codata.org/
[18] G.B. Arfken, H.J. Weber, and F.E. Harris, Mathematical Methods for Physicists, seventh ed., Academic Press, 225 Wyman Street, Waltham, MA 02451, USA, 2012, pages 873–879.