The non-relativistic and relativistic quantum theory with temperature

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In this paper, we have proposed the principle of quantum thermodynamics, including energy principle and microcosmic entropy principle, and given the quantum thermodynamics of non-relativistic and relativistic quantum theory, i.e., the temperature-dependent Schrödinger equation, Dirac equation and photon equation. We given the solution for wave function and energy level with temperature. Taking the hydrogen atom as an example, we given the temperature correction to hydrogen atom energy level and wave function.

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1. Introduction

The study of the physical properties of materials, focusing on its thermodynamic properties, is of great interest in condensed matter physics, solid-state physics, and materials science [1, 2]. The classical thermodynamics is built with the concept of equilibrium states. However, it is less clear how equilibrium thermodynamics emerges through the dynamics that follows the principle of quantum mechanics. The behaviour of quantum many-body systems driven out-of-equilibrium is one of the grand challenges of modern physics. The problem is particularly challenging when treating the dynamics of realistic finite-temperature systems, rather than systems evolving from the zero-temperature ground state. Recent development in the field of quantum thermodynamics taking place under nonequilibrium state [3-7]. The quantum thermodynamics which has grown rapidly over the last decade. It is fuelled by recent equilibration experiments [8] in cold atomic and other physical systems, the introduction of new numerical methods [9], and the discovery of fundamental theoretical relationships in non-equilibrium statistical physics and quantum information theory [10-13]. In this paper, we have proposed the principle of quantum thermodynamics, including energy principle and microcosmic entropy principle, and given the quantum thermodynamics of non-relativistic and relativistic quantum theory, i.e., the temperature-dependent Schrödinger equation, Dirac equation and photon equation. We given the solution for wave function and energy level with temperature. Taking the hydrogen atom as an example, we given the temperature correction to hydrogen atom energy level and wave function, which should be tested by experiment.

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2. The principle of quantum thermodynamics

1. Energy Principle: At temperature $T$, the classical total energy $E$ of microcosmic particle is

$$E = \frac{p^2}{2m} + V(r) + TS. \quad (1)$$

Where $\frac{p^2}{2m}$ is particle kinetic energy, $V(r)$ is particle potential energy, $TS$ is called particle thermal potential energy, $T$ is the temperature of particle in the external environment and $S$ is particle microcosmic entropy.

At the $i$–th energy level, the classical microcosmic entropy of particle is

$$S_i = -k_B n_i \ln n_i, \quad (2)$$

where $k_B$ is the Boltzmann constant, $n_i$ is the particle numbers of each state in the $i$–th energy level, and the dimension of $TS$ is the energy dimension.

The Eq. (1) is the classical total energy of particle, it should become operator form in quantum theory, it is

$$\hat{E} = \hat{T} + \hat{V}(r) + T\hat{S}. \quad (3)$$

Where $\hat{E} = i\hbar \frac{\partial}{\partial t}$, $\hat{V}(r) = V(r)$ and $\hat{S}$ is the microcosmic entropy operator of particle.

2. Microcosmic Entropy Principle: The microcosmic entropy operator of particle is

$$\hat{S} = -\frac{i}{2} k_B (T \frac{\partial}{\partial T} + \frac{\partial}{\partial T} T). \quad (4)$$

The Eq. (1) can be explained. In thermodynamics, for the infinitely small processes, the entropy is defined as

$$dS = \frac{dQ}{T}. \quad (5)$$

For the finite processes, there is

$$Q - Q_0 = TS - TS_0. \quad (6)$$

At temperature $T$, when a particle has the microcosmic entropy $S$, it should has the thermal potential energy $Q = TS$. The total energy of particle should be the sum of kinetic energy, potential energy and thermal potential energy, the Eq. (1) is obtained.

The Eq. (4) can be explained. We can prove the following operator relation:

$$\hat{T}^+ = \hat{T} = T, \quad (7)$$

$$(-i \frac{\partial}{\partial T})^+ = -i \frac{\partial}{\partial T} \quad (8)$$

$$[\hat{T}, \frac{\partial}{\partial T}] = -1. \quad (9)$$

With Eqs. (7)-(9), the operator $T(-i \frac{\partial}{\partial T})$ is not hermitian operator, but the operator $\frac{1}{2}[T(-i \frac{\partial}{\partial T}) + (-i \frac{\partial}{\partial T})T]$ is hermitian operator. The microcosmic entropy operator can be written as:
\[ \dot{S} = k_B \frac{1}{2} [T(-i \frac{\partial}{\partial T}) + \frac{T}{2} \frac{\partial}{\partial T}] \]
\[ = -i \frac{k_B}{2} (T \frac{\partial}{\partial T} + \frac{\partial}{\partial T} T). \]  
(10)

The Eq. (4) has been obtained.

3. The Schrödinger equation including temperature

With the canonical quantization, \( E = i \hbar \frac{\partial}{\partial t}, \vec{p} = i \hbar \nabla \), substituting Eq. (4) into (3), we can obtain the Schrödinger equation including temperature

\[ i \hbar \frac{\partial}{\partial t} \psi(\vec{r}, t, T) = \left( -\frac{\hbar^2}{2m} \nabla^2 + V(r) - i \frac{k_B}{2} T \left( \frac{\partial}{\partial T} + \frac{\partial}{\partial T} T \right) \right) \psi(\vec{r}, t, T). \]  
(11)

By separating variables

\[ \psi(\vec{r}, t, T) = \Psi(\vec{r}) f(t) \phi(T), \]  
(12)

substituting Eq. (12) into (11), we obtain

\[ i \hbar \frac{df(t)}{dt} = E_n f(t), \]  
(14)

\[ -\frac{\hbar^2}{2m} \nabla^2 \Psi_n(\vec{r}) + V(r) \Psi_n(\vec{r}) = E_{1n} \Psi_n(\vec{r}), \]  
(15)

\[ -i \frac{k_B}{2} T \left( \frac{\partial}{\partial T} + \frac{\partial}{\partial T} T \right) \phi_n(T) = E_{2n} \phi_n(T), \]  
(16)

where \( E_n = E_{1n} + E_{2n} \), they are the undefined constants. The general solution of Eq. (11) is

\[ \psi(\vec{r}, t, T) = \sum_n C_n \Psi_n(\vec{r}) \phi_n(T) e^{-\frac{i}{\hbar} E_n t}, \]  
(17)

For the Eq. (16), we can obtain the solution

\[ E_{2n} = k_B T_0, \]  
(18)

and

\[ \frac{1}{2} T \left( \frac{\partial}{\partial T} + \frac{\partial}{\partial T} T \right) \phi_n(T) = i \phi_n(T) T_0, \]  
(19)

the solution of Eq. (19) is

\[ \phi_n(T) = A \sqrt{T} e^{-T_0}. \]  
(20)
Where $A$ is the normalization constant, and $T_0$ is the temperature constant.

From the above results, we can give the temperature correction of hydrogen energy level and eigenfunction function, they are

$$E_n = E_{1n} + E_{2n} = -\frac{m_e e^4}{2\hbar^2 n^2} + k_B T_0,$$

and

$$\psi_{nlm}(\vec{r},T) = R_{nl}(r)Y_{lm}(\theta,\varphi)\phi_n(T).$$

From Eqs. (21) and (22), we can find the temperature has effect on the hydrogen atom energy level and wave function, but it has not effect on hydrogen atom spectrum. By the accurate measurement of hydrogen atom ionization energy, we can determine the temperature constant $T_0$.

$$-E_1 = -E_{11} - E_{21} = \frac{\mu e^4}{2m^2} - k_B T_0 = E_{exp},$$

where $\mu$ is the reduced mass of hydrogen atom, $e_s = e(4\pi\varepsilon_0)^{-\frac{1}{2}}$, $E_{exp}$ is the experimental value of the hydrogen atom ionization energy, the temperature constant $T_0$ can be determined by the following formula

$$T_0 = \frac{\mu e^4}{2m^2} - E_{exp}. \tag{24}$$

For the free particle of momentum $\vec{p}$, the plane wave solutions and total energy are

$$\psi(\vec{r}, t, T) = A e^{\frac{i}{\hbar}(\vec{p} \cdot \vec{r} - Et + \frac{T_0 T}{2\hbar})}, \tag{25}$$

$$E = \frac{p^2}{2m} + k_B T_0. \tag{26}$$

When $T_0 \to 0$, it becomes the quantum theory without temperature.

4. The Dirac equation including temperature

In section 3, we have studied the quantum theory with temperature for the low energy non-relativistic particle. In the following, we should consider the high energy relativistic case. As is known to all, Dirac equation describes the particle of spin $\frac{1}{2}$, such as electron, by factorizing Einstein’s dispersion relation, such that the field equation becomes the first order in time derivative [16]. Namely, Dirac factorized the relativistic dispersion relation employing four by four matrices, which is expressed as

$$E^2 - c^2 \vec{p}^2 - m_0^2 c^4 = (E - c\vec{p} \cdot \vec{\alpha} - m_0 c^2 \beta)(E + c\vec{p} \cdot \vec{\alpha} + m_0 c^2 \beta) = 0, \tag{27}$$

thus we get

$$E - c\vec{\alpha} \cdot \vec{p} - m_0 c^2 \beta = 0. \tag{28}$$

By canonical quantization Eq. (28), i.e., $E \rightarrow i\hbar \frac{\partial}{\partial t}$, $\vec{p} \rightarrow -i\hbar \nabla$, we can obtain the Dirac spinor wave equation

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{r},t) = (-i\hbar \vec{\alpha} \cdot \nabla + m_0 c^2 \beta)\psi(\vec{r},t), \tag{29}$$

where $\vec{\alpha}$ and $\beta$ are Dirac matrices, and $\psi(\vec{r},t)$ is spinor wave function, they are

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & i \end{pmatrix}, \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}, \tag{30}$$
\[ \psi(r, t) = \begin{pmatrix} \psi_1(r, t) \\ \psi_2(r, t) \\ \psi_3(r, t) \\ \psi_4(r, t) \end{pmatrix} \] (31)

the Eq. (29) is the Dirac equation without temperature, its plane wave solution is

\[ \psi(r, t) = u(p) \exp^{i(\vec{p} \cdot \vec{r} - \frac{Et}{\hbar})}. \] (32)

Where the energy \( E = \pm \sqrt{m^2c^4 + c^2p^2} \), the \( u(p) \) matrix is

\[ u(p) = \begin{pmatrix} u_1(p) \\ u_2(p) \\ u_3(p) \\ u_4(p) \end{pmatrix} \] (33)

When the particle of spin \( \frac{1}{2} \) at temperature \( T \), we should consider the thermal potential energy \( Q = TS \), the Eq. (27) should be written as

\[ (E - TS)^2 - c^2p^2 - m_0^2c^4 = (E - TS - c\vec{p} \cdot \vec{\alpha} - m_0c^2\beta)(E - TS + c\vec{p} \cdot \vec{\alpha} + m_0c^2\beta) = 0, \] (34)

it is similar to Eq. (29), we obtain the Dirac equation with temperature, it is

\[ i\hbar \frac{\partial}{\partial t} \psi(r, t, T) = (T\hat{S} - ich\vec{\alpha} \cdot \vec{\nabla})\psi(r, t, T), \] (35)

substituting Eq. (10) into (33), we obtain

\[ i\hbar \frac{\partial}{\partial t} \psi(r, t, T) = (-\frac{i}{2}k_B T(T \frac{\partial}{\partial T} + \frac{\partial}{\partial T}T) - ich\vec{\alpha} \cdot \vec{\nabla} + m_0c^2\beta)\psi(r, t, T), \] (36)

by separating variables, we obtain the plane wave solution and energy of Eq. (36), they are

\[ \psi(r, t, T) = u(p) \exp^{i(\vec{p} \cdot \vec{r} - \frac{Et}{\hbar})} \phi(T), \] (37)

\[ E = \pm \sqrt{m^2c^4 + c^2p^2 + k_B T_0}. \] (38)

Where \( \phi(T) = A\sqrt{\frac{1}{T_0}} e^{-\frac{T}{T_0}}. \)

5. The photon quantum theory with and without temperature

With Dirac’s factorization approach, we can obtain the spinor wave equation of free photon. For a photon, its mass \( m_0 = 0 \), Eq. (28) becomes

\[ E - c\vec{\alpha} \cdot \vec{p} = 0. \] (39)

By canonical quantization Eq. (39), we obtain the spinor wave equation of photon

\[ i\hbar \frac{\partial}{\partial t} \psi(r, t) = -ich\vec{\alpha} \cdot \vec{\nabla} \psi(r, t) = H \psi(r, t), \] (40)

where \( H = -ich\vec{\alpha} \cdot \vec{\nabla} \) is Hamiltonian operator, and \( \psi \) is the spinor wave function of photon. For the proper Lorentz group \( L_p \), the irreducibility representations of spin \( s = 1 \) photon are \( D_{10}^{10}, D_{01}^{01} \) and \( D_{\pm}^{\pm} \), respectively, and the dimension numbers of irreducibility representations corresponds to three, three and
four, respectively. We choose the spinor wave function of photon as the basis vector of three dimension irreducibility representation, i.e.

\[
\psi(\vec{r}, t) = \begin{pmatrix}
\psi_1(\vec{r}, t) \\
\psi_2(\vec{r}, t) \\
\psi_3(\vec{r}, t)
\end{pmatrix},
\]

(41)

and the \(\vec{\alpha}\) matrices are denoted by

\[
\alpha_x = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & -i \\
i & 0 & 0
\end{pmatrix}, \quad \alpha_y = \begin{pmatrix}
0 & 0 & i \\
i & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}, \quad \alpha_z = \begin{pmatrix}
0 & -i & 0 \\
i & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}.
\]

(42)

The Eq. (40) is the spinor wave equation of photon without temperature, its plane wave solution and energy are

\[
\psi(\vec{r}, t) = u(\vec{p}) \exp\left[i(\vec{p} \cdot \vec{r} - Et)/\hbar\right],
\]

(43)

\[
E = \hbar \omega,
\]

(44)

where the \(u(p)\) matrix is

\[
u(p) = \begin{pmatrix}
u_1(p) \\
u_2(p) \\
u_3(p)
\end{pmatrix}.
\]

(45)

The detailed theory can see the Appendix A of Ref. [15].

When the photon is in the external environment of temperature \(T\), we should consider the thermal potential energy \(Q = TS\), the Eq. (39) should be written as

\[
E - TS - c\vec{\alpha} \cdot \vec{p} = 0.
\]

(46)

By canonical quantization Eq. (46), we obtain its spinor wave equation

\[
i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t, T) = (-\frac{i}{2} k_B T \frac{\partial}{\partial T} + \frac{\partial}{\partial T} T) - ich\vec{\alpha} \cdot \vec{\nabla})\psi(\vec{r}, t, T),
\]

(47)

the Eq. (47) is the spinor wave equation of photon with temperature, its plane wave solution and energy are

\[
\psi(\vec{r}, t, T) = u(\vec{p}) \exp\left[i(\vec{p} \cdot \vec{r} - Et)/\hbar\right] \phi(T),
\]

(48)

\[
E = \hbar \omega + k_B T_0.
\]

(49)

6. Conclusions

In this paper, we have proposed the Principle of quantum dynamics, i.e., energy Principle and microcosmic Entropy Principle. With the canonical quantization, we obtained the temperature-dependent Schrodinger equation, i.e., finite-temperature quantum thermodynamics equation. By separating variables, we given the eigen solution of quantum thermodynamics equation. Taking the hydrogen atom as an example, we given the correction of temperature to hydrogen atom energy level and wave function. By the accurate measurement of hydrogen atom ionization energy, we can determine the temperature constant \(T_0\). On that basis, we can further study multi-body quantum thermodynamics and finite-temperature quantum field theory.

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