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Temperature-time duality exemplified by Ising magnets and quantum-chemical many electron theory

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Abstract In this work, we first present a detailed analysis of temperature-time duality in the 3D Ising model, by inspecting the resemblance between the density operator in quantum statistical mechanics and the evolution operator in quantum field theory, with the mapping $\beta = (k_B T)^{-1} \rightarrow$ it. We point out that in systems like the 3D Ising model, for the nontrivial topological contributions, the time necessary for the time averaging must be infinite, being comparable with or even much larger than the time of measurement of the physical quantity of interest. The time averaging is equivalent to the temperature averaging. The phase transitions in the parametric plane (β, it) are discussed, and a singularity (a second-order phase transition) is found to occur at the critical time t_c, corresponding to the critical point β_c (i.e, T_c). It is necessary to use the 4-fold integral form for the partition function for the 3D Ising model. The time is needed to construct the (3 + 1)D framework for the quaternionic sequence of Jordan algebras, in order to employ the Jordan-von Neumann-Wigner procedure. We then turn to discuss quite briefly temperature-time duality in quantum-chemical many-electron theory. We find that one can use the known one-dimensional differential equation for the Slater sum S(x, β) to write a corresponding form for the diagonal element of the Feynman propagator, again with the mapping $\beta \rightarrow$ it.

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We have both, in recent work, been involved in the statistical mechanics of many-body assemblies. One of us (ZDZ) [1] has worked on the three-dimensional (3D) Ising model, using a quaternion approach which has more recently found favour with mathematicians [2–4]. The other author has been especially involved in quantum-chemical systems described by density functional theory [5,6]: the reference by March and Howard [7] also being highly relevant to the present work.

In [8], Zhang pointed out that the framework of the statistical mechanics for the 3D Ising magnets should include the time, being in the (3 + 1) dimensional Euclidean spacetime. This argument is based on a fact that the temperature in statistical mechanics is actually the time in quantum field theory [9]. This is because the Euclidean time interval can be consistently identified with $\beta = 1/k_B\, T$. In this work, we first present a detailed analysis of temperature-time duality in the 3D Ising models and then turn to quantum-chemical many electron theory.

In quantum statistical mechanics, one deals with the density operator

$$\rho = e^{-\beta \mathrm{H}} \tag{1}$$

where H is the Hamiltonian of the system, and $\beta = (k_B T)^{-1}$. The partition function is expressed as a sum over the eigenstates of the Hamiltonian

$$Z = \sum_n \mathrm{e}^{-\beta \mathrm{E_n}} = Tr e^{-\beta \mathrm{H}} = Tr\rho \tag{2}$$

with the mapping $\beta \rightarrow$ it, it is easy to see the resemblance between the density operator $\mathrm{e}^{-\beta \mathrm{H}}$ and the evolution operator $\mathrm{e}^{-i\mathrm{Ht}}$, which allows the representation of the density operator as a functional integral and the introduction of the Lagrangian formalism into statistical mechanics. The kernel of the density operator for a single degree of freedom is [10]

$$\rho(x_f, x_i) = \left\langle x_f \left| e^{-\beta H} \right| x_i \right\rangle \tag{3}$$

The path integral is adapted to this kernel by performing the Wick rotation, i.e., substituting $t \rightarrow -i\tau$, where τ is a real variable going from 0 to β. The action $S[x(t)]$ then becomes the Euclidian action $iS_E[\mathrm{x}(\tau)]$. The kernel of the density operator is then represented as

$$\rho(x_f, x_i) = \int_{(x_i, 0)}^{(x_f, \beta)} [dx] \exp\left[-S_E(x)\right] \tag{4}$$

The partition function is then expressed as

$$Z = \int dx \rho(x, x) = \int dx \left\langle x \right| e^{-\beta H} \left| x \right\rangle = \int [dx] \exp\left[-S_E(x)\right] \tag{5}$$

To illustrate clearly the temperature-time duality, we also write down here the probability amplitude $\langle x_f \,|U(t)|\, x_i\rangle$ for the system, initially at a well-defined position x_i, to evolve in a finite time toward the final position x_f. The probability amplitude, i.e., the so-called propagator, in path integration can be written as [10]

$$\langle x_f \,|U(t)|\, x_i\rangle = \int_{(x_i,0)}^{(x_f,t)} [dx] \exp[iS(x)] \tag{6}$$

Here $U(t) = e^{-i\mathrm{H}t}$ is the evolution operator. The resemblance between the density operator and the evolution operator can be clearly seen from the comparison of Eqs. (4) and (6). This indicates that the time t is indeed hidden in the framework of the statistical mechanics for an equilibrium system [8].

The Hamiltonian of the Ising system [1] is

$$\mathrm{H} = -\sum_{\langle ij \rangle} J_{ij} S_i S_j - \sum_i h_i S_i \tag{7}$$

In the standard Ising model, one takes the sum such that $<ij>$ are pairs of nearest neighbors [1]. It is well-known that the Ising model can be mapped into a ϕ^4—scalar field theory (or Landau-Ginzburg model) with effective Hamiltonian as [11]

$$\mathrm{H} = \frac{1}{2}\alpha^2 |\nabla\phi|^2 + \frac{1}{2}\mu^2 |\phi|^2 + \frac{1}{4!}\lambda\left(|\phi|^2\right)^2 - \beta B \cdot \phi \tag{8}$$

and both the models are in the same universality class for the critical phenomena. The partition function of the ϕ^4 model is equal to a sum over the possible configurations of the field ϕ

$$Z = \int [d\phi] \exp[-\beta E(\phi)] = \int [d\phi] \exp\left\{-\int d^d x \left[\frac{1}{2}(\nabla\phi)^2 + \frac{1}{2}r\phi^2 + \frac{1}{4}u\phi^4\right]\right\} \tag{9}$$

for zero field [10]. In Eq. (9), the field φ is rescaled by $\sqrt{\beta}$ while the ϕ^4 coupling u is rescaled by $1/\beta$, so that the inverse temperature β does not explicitly appear [10]. However, it is hidden in the formula above. The partition function of a d-dimensional classical model is entirely analogous to the generating functional of a quantum field in d space-time dimensions in the Euclidian formulism. Changing the temperature amounts to scaling the field φ and modifying the ϕ^4 coupling u. Clearly, in the framework of the quantum field theory, both the time and the temperature are considered, and therefore, both of them should appear in the framework of the statistical mechanics for an equilibrium system, like the 3D Ising model.

In [1], one of us (ZDZ) gives quaternion-based three-dimensional (quantum) models of order-disorder transition and simple orthorhombic Ising lattices, based on Jordan-von Neumann-Wigner procedure. The situation investigated is related to the "quaternionic" sequence of Jordan algebras implied by the fundamental paper of Jordan, von Neumann, and Wigner [12]. Such quaternionic sequence of Jordan algebras can be used to bring Zhang's model to a more elegant form [2–4]. It was recently asserted that critical exponents in some bulk magnetic materials indeed form a 3D Ising universality [13].

In the 3D Ising model, the existence of topological factors makes serious challenge to the validation of the ergodic hypothesis [14], which states that the time average of a quantity over the time evolution of a specific microstate equals the average of the same quantity over some statistical ensemble of microstates at fixed time. Acceptance of the ergodic hypothesis implies that the use of a statistical ensemble is justified provided the time necessary for an efficient sweep of the ensemble by any of its microstates is short enough compared with the time of measurement of the physical quantity of interests [10]. However, it is thought here that in the systems like the 3D Ising model, where the topological contributions to the partition function as well as correlation functions and other physical quantities cannot be negligible, the time necessary for the time averaging must be infinite, being comparable with or even much larger than the time of measurement of the physical quantity of interest. This is because the topological effects are non-local: an efficient sweep of the ensemble by any of its microstates should be infinite since the number of these microstates is infinite (see also [14] for detailed discussion). Therefore, it is necessary to use the 4-fold integral form for the partition function for the 3D Ising model, as derived in [1]. In this way, the time is still included in the framework of quantum statistical mechanics for the time averaging physical quantities an equilibrium system. This framework provides the opportunity for constructing the quaternionic sequence of Jordan algebras, so that the Jordan-von Neumann-Wigner procedure can be employed to deal with the 3D Ising model, as illustrated in [1], also see [2–4].

From discussions above, one asserts that the time averaging should be used in the 3D Ising model and there is temperature-time duality. The time averaging of a function $\phi(x(t,\tau))$ is obtained by evaluating the integral,

$$\langle \phi(x(t,\tau))\rangle = \frac{1}{\Delta t}\int_{t_0}^{t_0+\Delta t} dt\phi(x(t,\tau)) \tag{10}$$

where τ is a real variable going from 0 to β. The experiment is carried out over a period of time $t_0 < t < t_0 + \Delta t$. For the systems like the 3D Ising model where the ergodic hypothesis may be invalid, $\Delta t \to \infty$. With the mapping of $t \leftrightarrow -i\tau$ (or $\tau \leftrightarrow$ it), the time averaging is equivalence to the temperature averaging

$$\langle \phi(x(-i\tau, it))\rangle = \frac{1}{-i\Delta\tau}\int_{-i\tau_0}^{-i\tau_0-i\Delta\tau} d(-i\tau)\phi(x(-i\tau, it)) \tag{11}$$

Performing a transformation of variances ($-\mathrm{i}\tau \rightarrow \tau'$ and $\mathrm{it} \rightarrow t'$), this temperature averaging can be simply written as

$$\left\langle \phi(x(\tau', t')) \right\rangle = \frac{1}{\Delta\tau'} \int_{\tau_0'}^{\tau_0'+\Delta\tau'} d(\tau')\phi(x(\tau', t')) \tag{12}$$

In Eq. (12), the imaginary unit i does not explicitly appear, since it is rescaled by a variance transformation. However, it should be noticed that the temperature averaging is performed somehow in the imaginary parametric space. The temperature-time duality is seen clearly from Eqs. (10) and (12). Next, we would like to discuss briefly the phase transitions in the parametric plane (β, it). Since there is a second-order phase transition at the critical point β_c (i.e, T_c), the temperature-time duality implies that this second order phase transition also occurs at it_c. Namely, with time changing, the system experiences a singularity at initial point ($t' = 0$), corresponding to infinite temperature ($\beta = 0$), and another singularity at the critical time t_c' (actually, it_c, in the imaginary parametric space), corresponding to the critical point β_c (i.e, T_c).

From another point of view, a better justification for the use of statistical ensembles follows from dividing the system into a very large number of mesoscopic parts, each of them large enough to display the complex properties of the whole system. At any instant, each of these mesoscopic subsystems is characterized by its own microstate, but the properties of the whole system are obtained by averaging over all subsystems. Thus the ensemble averaging amounts more to a spatial averaging than to a time averaging [10]. In the 3D Ising model, the global effect of topological terms makes such dividing incorrect, since the complex properties of the whole system cannot be displayed well by any of these mesoscopic subsystems. Only the whole system can display the situation uniquely. Such spatial averaging does not work at all for the 3D Ising model. At the outset, the integrand should be performed in four dimensions, since one needs to take the time average by the integrand in the fourth dimension, as pointed out above [again, see [14] for detailed discussion].

We turn more briefly to quantum chemistry, in the current framework, which uses extensively density functional theory (DFT) to treat molecules and clusters [6]. Current non-relativistic usage is then based on a one-body potential energy $V(\mathbf{r})$ which is written in the form [6]

$$V(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_{xc}(\mathbf{r}) \tag{13}$$

Evidently $V_{ext}(\mathbf{r})$ is fixed by the nuclear framework of the cluster, say, under consideration, while $V_{Hartree}(\mathbf{r})$ is determined solely by its ground-state density $n(\mathbf{r})$, to be generated by the one-body potential $V(\mathbf{r})$ in Eq. (13). But unfortunately the exchange (x)-correlation (c) potential $V_{xc}(\mathbf{r})$ remains unknown to date.

To relate DFT in the above form to statistical mechanics, we can use the complete set of wave functions $\psi_i(\mathbf{r})$ generated by $V(\mathbf{r})$ via the Schrödinger equation, with corresponding eigenvalues ϵ_i, to define the canonical, or equivalently Bloch, density matrix [15] $C(\mathbf{r}, \mathbf{r}', \beta)$; where $\beta = (k_B T)^{-1}$ with k_B as Boltzmann's constant and T

the temperature. Explicitly C is given by [15]

$$C(\mathbf{r}, \mathbf{r}', \beta) = \sum_{alli} \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}) \exp(-\beta \in_i). \tag{14}$$

This matrix C then satisfies the so-called Bloch equation (see [15])

$$\hat{\mathrm{H}}_{\mathbf{r}} C(\mathbf{r}, \mathbf{r}', \beta) = -\frac{\partial C(\mathbf{r}, \mathbf{r}', \beta)}{\partial \beta} \tag{15}$$

where the one-body Hamiltonian $\hat{\mathrm{H}}_r$ in the above DFT framework is given by

$$\hat{\mathrm{H}}_{\mathbf{r}} = -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}) \tag{16}$$

where $V(\mathbf{r})$ has the form (13). In [7], however, it is the diagonal form of $C(\mathbf{r}, \mathbf{r}', \beta)$, denoted below as the Slater sum $S(\mathbf{r}, \beta) \equiv C(\mathbf{r}, \mathbf{r}', \beta)|_{\mathbf{r}'=\mathbf{r}}$, which is the main tool. Then one dimension emerges, having Slater sum $S(\mathrm{x}, \beta)$, as the fully tractable case in DFT, since $S(\mathrm{x}, \beta)$ can be shown to satisfy the partial differential equation (see eg [16])

$$-\frac{\hbar^2}{8m} \frac{\partial^3 S(x, \beta)}{\partial x^3} + \frac{1}{2} \frac{\partial V(x)}{\partial x} S(x, \beta) = -V(x) \frac{\partial S(x, \beta)}{\partial x} - \frac{\partial S(x, \beta)}{\partial x \partial \beta} \tag{17}$$

Of course, since $S(\mathbf{r}, \beta)$ is the diagonal element $\mathbf{r}' = \mathbf{r}$ of the canonical density matrix $C(\mathbf{r}, \mathbf{r}', \beta)$ defined in Eq. (14), we see that in DFT the partition function $Z(\beta)$, defined by

$$Z(\beta) = \sum_{alli} \exp(-\beta \in_i) \tag{18}$$

is evidently given, since the ψ_i's are assumed to be normalized in writing Eq. (14), by

$$Z(\beta) = \int S(\mathbf{r}, \beta) d\mathbf{r} \tag{19}$$

or, in relation to the one-dimensional case satisfying Eq. (17), $Z(\beta) = \int_{-\infty}^{\infty} S(x, \beta) dx$.

To make the above quite concrete, the important area opened up experimentally by DeMarco and Jin [17] of ultracold trapped Fermion vapours, is essentially about harmonic confinement, where experimentally it proves possible to range from a quasi-one-dimensional (1D) trap through a quasi-2D trap to a fully spherical 3D trap. Then, from the early pioneering work of Sondheimer and Wilson [18], the Slater sum for D dimensions for such harmonic confinement is known analytically as (see eg [16]),

with $V(r) = \frac{1}{2}m\omega^2 r^2$;

$$S_D(\mathbf{r}, \beta) = \left(\frac{m\omega}{2\pi\hbar}\right)^{D/2} \left[\frac{1}{\sinh^{D/2}(\beta\hbar\omega)}\right] \exp\left[-\frac{m\omega\mathbf{r}^2}{\hbar}\tanh(\beta\hbar\omega/2)\right] \quad (20)$$

Evidently the D-dimensional partition function $Z_D(\beta)$ is obtained immediately from Eq. (20) by integrating over $\mathbf{r}$.

From Eq. (20) (see eg also [16]: Eq. (A16))

$$\frac{1}{S_D(\mathbf{r}, \beta)} \frac{\partial S_D(\mathbf{r}, \beta)}{\partial \mathbf{r}} = -2\omega\mathbf{r}\tanh(\beta\omega/2) \quad (21)$$

which in the form (21) is evidently independent of the dimensionality D.

Turning to future directions, it is noteworthy that one can use the one-dimensional differential Eq. (17) for $S(x, \beta)$ to write a corresponding form for $S(x, it)$, with the mapping $\beta \rightarrow$ it, this being directly related to the diagonal element of the Feynman propagator [7]. Thus, Eq. (17) becomes for the latter quantity

$$-\frac{\hbar^2}{8m}\frac{\partial^3 S(x,it)}{\partial x^3} + \frac{1}{2}\frac{\partial V(x)}{\partial x}S(x,it) = -V(x)\frac{\partial S(x,it)}{\partial x} - \frac{\partial S(x,it)}{\partial x \partial(it)} \quad (22)$$

In this work, we study the temperature-time duality in the 3D Ising model, by inspecting the resemblance between the density operator in quantum statistical mechanics and the evolution operator in quantum field theory. The concept of the temperature averaging is introduced, which is found to be equivalence to the time averaging, according to the temperature-time duality. The phase transitions in the parametric plane (β, it) are richer than we understood before, and a second order phase transition may occur at the critical time t_c, corresponding to the critical point β_c, in the systems like the 3D Ising model. We emphasize that it is necessary to use the 4-fold integral form for the partition function for the 3D Ising model, to include the time. The integrand of the partition function of the 3D Ising model should be performed in four dimensions, since one needs to take the time average by the integrand in the fourth dimension. This (3 + 1)D framework is necessary for constructing the quaternionic sequence of Jordan algebras, to employ the Jordan-von Neumann-Wigner procedure developed in [1], in order to deal with the 3D Ising model. We then turn to discuss briefly temperature-time duality in quantum-chemical many electron theory and find that one can use the one-dimensional differential equation for $S(x, \beta)$ to write a corresponding form for the diagonal element of the Feynman propagator [7], again with the mapping $\beta \rightarrow it$.

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