Density Function Thermal Scaling and Physical Significance of Shape Functions

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Abstract

The solid-state concept of thermal voltage is used to define a homothetic scaling of the quantum mechanical one-particle reduced density function. This scaling might be used to construct a temperature dependent quantum density. Once defined such scaling, named here as thermal scaling, it is simple to use it with a precise temperature, adapting such scaling matching the associated shape function. The temperature achieving this equality is termed Shape Temperature T_S and, if N is the number of particles of a given quantum object, one can demonstrate that the simple equality: $T_S \approx 12N$ holds. Furthermore, Shape Temperature can be associated to a characteristic Shape Frequency $\nu_S^{\max}$, via Wien's law, which yields equality: $\nu_S^{\max} \approx 0.7N \; THz$, linking number of particles with frequency.

Keywords: Electronic Density Function; Shape Function; Thermal Voltage; Density Function Scaling; Thermal Scaling; Shape Temperature; Shape Frequency

Introduction

The definition of shape functions, as was proposed by Parr and Bartolotti [1] in 1983, corresponds to a simple homothecy of the first order reduced quantum density functions. The homothetic parameter being related to the density function inverse Minkowski norm, which coincides with the inverted number of particles, associated to the quantum object attached to it.

Indeed, as many authors have been using shape functions, see for instance the review [2] and included references, in many theoretical applications like quantum similarity [3,4], such an elementary scaling transformation, when performed on the electronic density function, yields undoubtedly quite an interesting chemical concept.

Among other properties, shape functions possess a unit Minkowski norm and as the attached density functions are definite non-negative functions. Both characteristics are sufficient to accept shape functions as one-electron continuous probability density functions.

The present paper tries to connect shape functions with a recent definition of a general density function homothetic scaling, the so called thermal scaling [5]. Thus, first thermal scaling of density functions will be defined, using an original solid-state concept: The thermal voltage [6].

After this, it is essentially a matter of simple study to deduce how thermal scaling and shape functions might be related. Finally, based on thermal scaling, some

considerations about the physical meaning of the shape functions will be put forward. Essentially the Shape Temperature and the related Shape Frequency will be discussed.

Density and Shape Functions

An electronic first order density function: $\rho(\mathbf{r})$ corresponds to the resultant one electron (or one particle, generally speaking) variable function, resulting from integrating any atomic or molecular quantum object density, the squared module of a quantum wave function, by all the electron coordinates except one particle three-dimensional position.

From now on, this paper will name as Density Function the above defined one electron density function.
According to the considerations developed within quantum similarity, see for example [7-14], an electronic Density or Shape Function might be accepted as the ultimate quantum molecular descriptor. Therefore, a possible connection of Shape Function with the physical world acquires some importance. The Density Function statistical connection will be briefly discussed first, to later introduce the Thermal Scaling.

For a given atomic or molecular structure its first order Density Function: $\rho(\mathbf{r})$ corresponds to a probability Density Function. This probabilistic content can be readily seen, transforming it into a homothetic related Shape Function:

$$\sigma(\mathbf{r}) = N^{-1}\rho(\mathbf{r}), \qquad (1)$$

and this is obtained just scaling by the inverse of the number of electrons N, represented by the Minkowski norm of the Density Function, that is:

$$\langle \rho \rangle = \int_D \rho(\mathbf{r}) \, d\mathbf{r} = N . \qquad (2)$$

Therefore, any Shape Function has a unit Minkowski norm:

$$\langle \sigma \rangle = \int_D \sigma(\mathbf{r}) \, d\mathbf{r} = 1 .$$

Besides, one must recall the important fact that both Density and Shape Functions must be implicitly considered multiplied by the electron charge e. The absence in current literature of this constant is due to the universal use of atomic units, which tacitly suppose:

$$e = 1 \ au.$$

It is also instructive to realize that equation (2) might be written as the expectation value of some one-electron unity operator, which can be defined as follows:

$$\forall \mathbf{r} \in \mathrm{R}^3 : \mathbf{1}(\mathbf{r}) = 1 ,$$

Then, obviously enough, one can write:

$$\langle \mathbf{1} \rangle = \int_D \mathbf{1}(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r} \equiv \langle \rho \rangle = N .$$

Thermal Voltage

It is interesting now to consider the so-called Thermal Voltage: V_T, entering the Shockley equation [6], which can be easily defined as the ratio:

$$V_T = \frac{kT}{e} ;$$

where k is the Boltzmann constant and T the absolute temperature. For typical actual admitted values[1] of e and k, while considering the temperature around 300ºK, one obtains: $V_{300K} = 25.85 \ mV \approx 26 \ mV$.

Moreover, using the Thermal Voltage definition at $300º \, K$:

$\dfrac{k\,300}{e} \approx 26 \ mV$, then one can easily write:

$\dfrac{k}{e} = 0.0862 \left[mV \left(ºK \right)^{-1} \right]$ or the inverse ratio:

$$\frac{e}{k} = 11.6 \left[ºK \left(mV \right)^{-1} \right] \rightarrow \frac{e}{k} \approx 12 \left[ºK \left(mV \right)^{-1} \right]$$

Therefore, one might write a computationally more convenient expression, connecting Temperature and Thermal Voltage, like:

$$V_T = 0.0862 \ T \leftrightarrow V_T^{-1} = 11.6 \ T^{-1} .$$

Although Thermal Voltage is a concept developed and relevant in solid state theory and practice, there seems that nothing forbids its use in quantum chemistry.

Thermal Scaling

Indeed, the presence of the electron charge might preclude definition of a thermally scaled Electron Density ρ_T. This can be performed by using a simple temperature dependent scaling of any Density Function ρ, and considering a scale factor made by the inverse of the Thermal Voltage, as follows:

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[1]e (1.6021766208 E-19 C) and k (1.38064852E-23 J/K) or (8.6173303E-5 eV/K).

$$\rho_T(\mathbf{r}) = V_T^{-1}\rho(\mathbf{r}) = \frac{e}{kT}\rho(\mathbf{r}). \qquad (3)$$

The above equation resembles the exponents entering the Boltzmann energy distribution, and appears in the same fashion, within the diode equation describing the current flow in solid state devices [6]. The expression (3) has been recently used to define a universal quantum QSPR operator [5].

Furthermore, dealing with molecular structures, associated to human biological activity, the temperature to scale any associated quantum Density Function might be chosen within the range of more suitable values between: 309-310ºK, better than 300ºK. Thermal Voltage acquires, if this is the case, the value: $V_{309K} \approx 27\ mV$. Thus, one can write for molecular structures within a biological environment temperature of 36-37ºC a scaled Density Function like:

$$\rho_{309K} \approx \frac{1}{27}\rho = 0.037\rho \approx 0.04\rho.$$

One might also propose the term Thermal Scaling to refer to this kind of homothetic temperature dependent transformation of the Density Function.

It is a straightforward to realize that Thermal Scaling and Shape Function are precisely related, as will be discussed next.

Shape Temperature

One can obtain such proposed relation between Shape Function and Thermal Scaling when answering the question: what might be the (Shape) Temperature associated to a Thermal Scaling, transforming the Density Function into a Shape Function?

As it is usual, equation (2) might be schematically written like: $\langle\rho\rangle = N$ and then equation (1) becomes: $\sigma = N^{-1}\rho$, respectively. One can try to observe the inverse Minkowski norm, which is just coincident with the Minkowski normalization factor, of the Density Function as a Thermal Scaling homothetic parameter and therefore use:

$$N^{-1} = \frac{e}{kT_S} \rightarrow T_S = \frac{e}{k}N \rightarrow T_S = 11.6N \approx 12N. \qquad (4)$$

Therefore, the Shape Temperature T_S, which in an atom or molecule becomes roughly equal to twelve times the number of electrons, corresponds to the Thermal Scaling of the Density Function yielding the Shape Function.

This result of equation (4) means that each electron in an atom or molecule contributes with around 12 ºK to the Shape Temperature.

Atomic Shape Temperature can be alternatively expressed as: $T_S^A \approx 12Z$, being Z the atomic number. Consequently, the range of Shape Temperatures in the atomic number range: $Z \in \{1,100\}$ say, does imply an atomic Shape Temperature range of: $T_Z^A \in \{12,1200\}^o K$.

One can also say that Shape Temperature in a quantum object will suffer a variation of 12 ºK, upon exchanging or augmenting the related system by one electron.

An assorted set of Shape Temperatures, rounded to the 1ºK, follows:

Water: 116 ºK · Benzene: 487 ºK · Naphthalene: 516ºK
XeF$_6$: 1253 ºK · UF$_6$: 1694 ºK · UCl$_6$: 2250 ºK

For linear saturated Hydrocarbons, one can write the Shape Temperature as a linear function of the number of carbon atoms n :

$$T_S(n) = 11.6(6n+2n+2) \approx [93n+23]^o K.$$

Translation from any condensed chemical formula of a molecule into Shape Temperature becomes kind of straightforward computational exercise.

Shape Frequency

Once Shape Temperature becomes well-defined, there it is easy to imagine a relationship with a linearly related frequency. Such a connection can be done directly equating Boltzmann energy with Planck-Einstein energy expression or, perhaps it might be better using Wien's displacement law (see for example Chapter 1 of [15]), describing a peak emission at the optical frequency: v_T^{max}, which can be simply written as:

$$v_T^{max} = \frac{\alpha}{h}kT \approx \left(5.879\times10^{10}\ Hz[^\circ K]^{-1}\right)T = \left(58.79\ GHz[^\circ K]^{-1}\right)T$$

where $\alpha \approx 2.821429$ is a constant, resulting from the deduction of Wien's law and h the Planck constant[2].

Therefore, it is easy to write an expression for the Shape Frequency: v_S^{max}, related to Shape Temperature and thus to the number of electrons present within the related quantum object:

$$v_S^{max} = \frac{\alpha}{h}kT_S = \frac{\alpha}{h}k\left(\frac{e}{k}N\right) = \frac{\alpha e}{h}N \rightarrow$$

$$v_S^{max} \approx 12N \times 5.879\times10^{10}\ Hz = 7.055\ 10^{11}N\ Hz$$

$$\approx 7\times10^{11}N\ Hz = 700N\ GHz = 0.7N\ THz.$$

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[2] $h = 4.135667662\ 10^{-15}\ [eV\ s]$

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Such large frequencies, which can be attributed to any quantum object, when considering the one electron hydrogen atom Shape Frequency, one can see it roughly corresponds to seven times the cosmic microwave background radiation.

A quantum object with 10 electrons, for instance, yields a Shape Frequency of 7 THz, already entering the far infra-red range.

Conclusions

Using Thermal Scaling of the Density Function one can straightforwardly observe that there is a specific temperature, the Shape Temperature T_S, which transforms first order quantum Density Functions into Shape Functions.

This temperature can be simply expressed in terms of the quantum object number of particles N: $T_S \approx 12N$.

From Shape Temperature definition, it is a matter of simple manipulation to obtain, via Wien's law, an associated Shape Frequency, which can be also written in terms of the number of particles. Every electron roughly contributes with $0.7THz$ to the total quantum object Shape Frequency. Then, Shape Functions constitute not only a valuable mathematical concept, adopting the form of a continuous probability density distribution, but can be easily connected with the physical world via the notion of Thermal Voltage. Shape Temperature might be also considered as a collective property, which can be connected to kinetic energy of quantum particle swarms.

From a more general point of view, Thermal Scaling might be seen as the possible association of a given arbitrary temperature to any quantum one-particle density function. Finally, the role of the number of atoms in QSPR discussed several years ago [16], has an obvious relation with the role of the number of particles, as a generator of Shape Temperature or Frequency found in the present work.

The results described here about the basic role of the number of particles in Shape Parameters, provides an independent assessment of the obvious importance of the unavoidable quantum system particle count, into the evaluation of submicroscopic systems expectation values.

Conflict of interests

The author states that there is no conflict of interests in this work.

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