

Quantum-Theoretic Shapes of Constituents of Systems in Various States

Elias P. GYFTOPOULOS
Massachusetts Institute of Technology, Room 24-111
77 Massachusetts Avenue
Cambridge, Massachusetts 02139 - USA
Tel.: 617 253 3804; Fax: 617 258 7437
E-mail: epgyft@aol.com

Michael R. von SPAKOVSKY
Virginia Polytechnic Institute and State University
Energy Management Institute
Department of Mechanical Engineering
Blacksburg, Virginia 24061-0238 - USA
Tel.: 540 231 6684; Fax: 540-231-9100
E-mail: vonspakov@vt.edu

Abstract

In previous publications, it has been shown that entropy is a measure of the quantum-theoretic shape of the constituents of a system. In this paper, we present examples of quantum-theoretic shapes of some systems each consisting of one unit of a single constituent, in either a stable (thermodynamic) equilibrium state or in states that are not stable equilibrium. The systems that we consider are a structureless particle confined in either a linear box or a square box, and a harmonic oscillator of a specified fundamental frequency. In general, we find that the shape of each constituent is "smooth"—without ripples—for each thermodynamic equilibrium state, and oscillatory or rippled for states that are either non-equilibrium or unstable equilibrium.

1. Introduction

In the exposition of thermodynamics by Gyftopoulos and Beretta (1991), entropy is shown to be a nonstatistical property—to have a value at an instant in time independent of statistical probabilities and other times—of the constituents of any system in any state in the same sense that inertial mass is a property of the constituents of any system in any state.

In contrast to the plethora of entropy expressions appearing in various formulations of statistical mechanics, in the unified quantum theory of mechanics and thermodynamics by Hatsopoulos and Gyftopoulos (1976), and in an article by Gyftopoulos and Cubukcu (1997), the entropy of thermodynamics is shown to be represented by one and only one functional of a special quantum

mechanical density operator ρ . A brief discussion of this operator is given in the Appendix.

In many textbooks, the probability density function associated with measurement results of the spatial coordinates of the constituents of a system is interpreted as the spatial shape of the constituents of the system (Leighton, 1959; Brandt and Dahmen, 1995a), and the shape is used to calculate atomic, molecular, and ionic radii (Slater, 1963) as well as explain the formation of various compounds. The probability density function of the spatial coordinates enters also into the evaluation of the entropy S ; and, therefore, we can think of entropy as a measure of the spatial shape of the constituents of a system and, thus, achieve a pictorial visualization of a concept that has been puzzling scientists and engineers for over more than a century.

In what follows, we present examples of quantum-theoretic shapes of some systems, each consisting of one unit of a single constituent in various states, nonequilibrium, equilibrium, and stable (thermodynamic) equilibrium. In general, we find that the shape of each constituent is oscillatory or rippled for states that are either nonequilibrium or unstable equilibrium and smooth—without ripples—for each stable equilibrium state.

2. Particle in a Linear Box

2.1. Energy eigenstates

We consider a structureless particle of mass M confined in a linear box—infinitely deep potential well—extending from $x = -d$ to $x = d$ (Figure 1). The Hamiltonian operator of such a particle is given by the relation

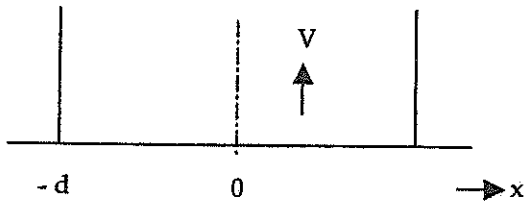


Figure 1. Schematic of a linear box.

$$H = -\frac{\hbar^2}{2M} \frac{d^2}{dx^2} + V(x) \quad (1)$$

where \hbar is Planck's constant divided by 2π , and $V(x)$ the potential energy such that

$$V(x) = \infty \quad \text{for } |x| > d \quad (1a)$$

$$V(x) = 0 \quad \text{for } |x| \leq d \quad (1b)$$

The Hamiltonian operator defines the energy eigenvalue problem

$$H\phi_n(x) = \varepsilon_n \phi_n(x) \quad (2)$$

where ε_n and $\phi_n(x)$ are the n th energy eigenvalue and energy eigenfunction, respectively. We can readily verify that the energy eigenvalues and normalized energy eigenfunctions are given by the relations

$$\varepsilon_n = \frac{\hbar^2 n^2}{8Md^2} \quad \text{for all integer values of } n \quad (3)$$

$$\phi_n(x) = \left(\frac{2}{d}\right)^{0.5} \cos\left(\frac{n\pi x}{d}\right) \quad \text{for } n = 1, 3, \dots \quad (4)$$

$$\phi_n(x) = \left(\frac{2}{d}\right)^{0.5} \sin\left(\frac{n\pi x}{d}\right) \quad \text{for } n = 2, 4, \dots \quad (5)$$

$$\phi_n(x) = 0 \quad \text{for all } n \text{ and } |x| > d \quad (6)$$

and each energy eigenstate has zero value of momentum, that is,

$$\langle p_n \rangle = \int_{-\infty}^{\infty} \phi_n^*(x) \frac{\hbar}{i} \frac{d}{dx} \phi_n(x) dx = 0 \quad (7)$$

where the * indicates the complex conjugate function.

We can use the energy eigenstates to express the probability density function of any state of the particle.

2.2. Nonequilibrium state

We consider a nonequilibrium state—wave packet—having a value of momentum different than zero and a time dependent wave function

$$\psi(x, t) = \sum_{n=1}^{\infty} a_n \phi_n(x) \exp(-i\varepsilon_n t/\hbar) \quad (8)$$

and a shape—probability density function—given by the relation

$$|\psi(x, t)|^2 = \psi^*(x, t) \psi(x, t) \quad (9)$$

It is noteworthy that the wave function can also be written as a density operator ρ . In matrix form and in the energy eigenfunction representation, the k -element of the matrix is given by the relation

$$\rho_{km} = a_k^* \exp(+i\varepsilon_k t/\hbar) a_m \exp(-i\varepsilon_m t/\hbar) \quad \text{for all } k \text{ and } m \quad (10)$$

Moreover, in a representation that has as one of its orthogonal axes $\psi(x, t)$ itself, the density operator

matrix of $\psi(x,t)$ is diagonal and has only one element along the diagonal equal to unity.

A graph of the evolution of the shape of the particle in time is shown in Figure 2. At $t=0$, the wave packet is bell-shaped. Then, it moves toward one wall of the linear box, where it is reflected; and eventually it spreads so widely that it touches both walls simultaneously. Though the shape of the wave packet changes in time, we can easily prove that its entropy is time independent and equal to zero. In general, any shape determined by a wave function has entropy equal to zero (see Appendix).

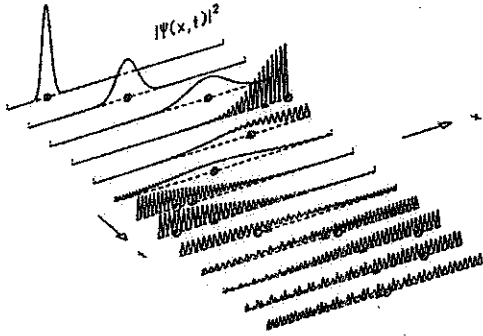


Figure 2. Shape – probability density function – versus time of a particle in a linear box (infinitely deep potential well) in a nonequilibrium state. Arbitrary dimensionless units (Brandt and Dahmen, 1995b).

Other nonequilibrium states correspond to density operators that cannot be represented by wave functions. The entropy of each such state is positive and in general, but not necessarily, increasing spontaneously in time.

2.3. Unstable and stable equilibrium states

In many discussions, the terms equilibrium state and thermodynamic (stable) equilibrium state are used as synonyms. They are not. The former is unstable. To clarify the difference, we consider an equilibrium state that has a density operator matrix, which in the energy representation is diagonal with only three nonzero elements, that is

$$\rho_{22} = 0.1 \quad \rho_{33} = 0.2 \quad \rho_{88} = 0.7 \quad (11)$$

The only three energy eigenvalues that are relevant to this state are

$$\varepsilon_n = h^2 n^2 / 8Md^2 \quad \text{for} \quad n = 2, 3, 8 \quad (12)$$

and the energy E , shape–probability density function $p(x)$ —and entropy are given by the relations

$$\begin{aligned} E &= (h^2 / 8Md^2)(0.1(4) + 0.2(9) + 0.7(64)) \\ &= 47 h^2 / 8Md^2 \end{aligned} \quad (13)$$

$$\begin{aligned} p(x)/(2/d) &= 0.1 \sin^2(2\pi x/d) + 0.2 \cos^2(3\pi x/d) \\ &\quad + 0.7 \sin^2(8\pi x/d) \end{aligned} \quad (14)$$

$$\begin{aligned} S &= -k[0.1 \ln(0.1) + 0.2 \ln(0.2) + 0.7 \ln(0.7)] \\ &= 0.802k \end{aligned} \quad (15)$$

A graph of the shape— $p(x)$ versus x —is shown in Figure 3. The shape is wavy. It is also unstable because a minute perturbation precipitates a spontaneous tendency for the peaks and valleys to proceed to an evening-out evolution and an increase in entropy. The next example illustrates the ultimate result of this evening-out evolution.

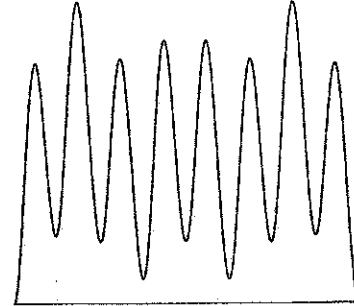


Figure 3 Shape – probability density function versus position – of a particle in a linear box (infinitely deep potential well) in an equilibrium state of energy E (Eq. 13). Arbitrary dimensionless units of the spatial coordinate and the probability density function.

Next, we consider a stable equilibrium state that corresponds to the same energy E (Eq. 13) as that of the equilibrium state just discussed. For such a state, the probability density function is given by the relation

$$\begin{aligned} p(x)/(2Q/d) &= \sum_{n=\text{odd}} \cos^2(n\pi x/d) \exp(-\alpha n^2) \\ &\quad + \sum_{n=\text{even}} \sin^2(n\pi x/d) \exp(-\alpha n^2) \end{aligned} \quad (16)$$

where $Q = \sum_{n=1}^{\infty} \exp(-\alpha n^2)$, $\alpha = h^2 / 8Md^2 kT$, and T is the temperature of the stable equilibrium state.

In thermodynamics, the temperature of a stable equilibrium state is determined solely by its energy. Moreover, for a particle confined in a linear box, $E = kT/2$. Therefore, we have the relations

$$E = 47h^2/8Md^2 = kT/2 \quad (17)$$

$$\alpha = h^2/8Md^2 kT = 1/94 \quad (18)$$

where use has been made of Eq. 13.

A graph of the shape—probability density function versus x —of the particle in the linear box in a stable equilibrium state is shown in Figure 4. For this calculation, we use $\alpha=1/94$, and only 30 terms on the right hand side of Eq. 16. In contrast to the equilibrium state with the same energy (Figure 3), we see that the shape of the stable equilibrium state is uniform almost throughout the entire range of x except near the walls of the linear box where $p(x)$ must reduce to zero.

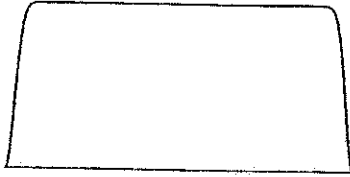


Figure 4 Shape—probability density function versus position—of a particle in a linear box (infinitely deep potential well) in a stable equilibrium state having the same energy E (Eq. 13) as the equilibrium state in Figure 3. Arbitrary dimensionless units of the spatial coordinate and the probability density function.

Upon approximating the sum of the partition function Q for the stable equilibrium state by an integral (Hatsopoulos and Gyftopoulos, 1979), we find that

$$Q = (2\pi Mk Td^2/h^2)^{1/2} = 8.6 \quad (19)$$

$$S = k \ln Q + E/T = 2.65k \quad (20)$$

We see that the entropy of the stable equilibrium state is more than 3.3 times larger than the entropy of the equilibrium state with the same energy.

2.4. Stable equilibrium state

Next, we consider a stable equilibrium state and compute the shape—probability density function $p(x)$ (Eq. 16)—for $\alpha=0.1$, that is, for the same value of Md^2 , a temperature about 10 times smaller than the temperature used for the graph in Figure 4. A graph of this shape with 30 terms on the right hand side of Eq. 16 is shown in Figure 5. Again, we observe that the shape is uniform throughout almost the entire range of values of x , except near the walls of the box.

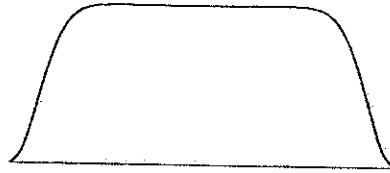


Figure 5. Shape—probability density function versus position—of a particle in a linear box (infinitely deep potential well) in a stable equilibrium state of energy E such that $\alpha=0.1$. Arbitrary dimensionless units of the spatial coordinate and the probability density function.

It is noteworthy that the one-particle results for stable equilibrium states are the basis for the calculation of properties of systems that behave as ideal gases because under such behavior the interactions—internal forces—between the particles are negligible.

3. Particle in a Square Box

3.1. Energy eigenstates

Next, we consider a structureless particle of mass M confined in a square box—two-dimensional, infinitely deep potential well—extending from $x=-d$ to $x=d$, and from $y=-d$ to $y=d$. The Hamiltonian operator of such a particle is given by the relation

$$H = -\frac{\hbar^2}{2M} \frac{d^2}{dx^2} - \frac{\hbar^2}{2M} \frac{d^2}{dy^2} + V(x, y) \quad (21)$$

where

$$V(x, y) = \infty \quad \text{for } |x| > d \text{ and } |y| > d \quad (21a)$$

and

$$V(x, y) = 0 \quad \text{for } |x| \leq d \text{ and } |y| \leq d \quad (21b)$$

The two degrees of freedom x and y are separable, and the quantum probabilities associated with x are not correlated with those associated with y . Therefore, the energy eigenvalues and normalized energy eigenfunctions are given by the relations

$$\varepsilon_{n_x n_y} = h^2(n_x^2 + n_y^2)/8Md^2 \quad (22)$$

$$\varphi_{n_x n_y}(x, y) = \varphi_{n_x}(x) \varphi_{n_y}(y) \quad (23)$$

where $\varphi_{n_x}(x)$ and $\varphi_{n_y}(y)$ are given by Eqs. 4 and 5 for both x and y and for all positive integer values of n_x and n_y . Said differently, each degree of freedom defines a subsystem.

3.2. Unstable and stable equilibrium states

We now consider an equilibrium state such that the energy of each of the two subsystems is given by Eq. 13, the probability density function for the x subsystem by Eq. 14, and the probability density function for the y subsystem by Eq. 14 with x replaced by y .

A graph of the shape—probability density function $p(x, y) = p(x)p(y)$ —is shown in Figure 6. The shape is wavy and unstable because a minute perturbation precipitates the spontaneous tendency for the peaks and valleys to even out. The next example illustrates the ultimate result of this evening-out evolution.

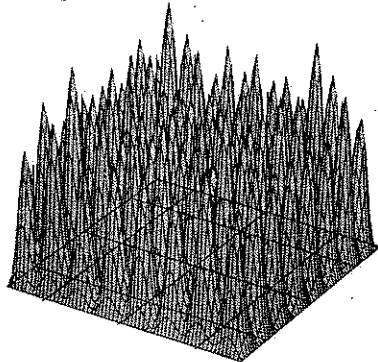


Figure 6. Shape—probability density function versus position—of a particle in a square box (infinitely deep potential well) in an equilibrium state of energy E (Eq. 24). Arbitrary dimensionless units of the two spatial coordinates and the probability density function.

Next, we consider a stable equilibrium state that corresponds to the same energy as that of the

equilibrium state just discussed. In other words, we have that

$$E = \frac{2(47)h^2}{8Md^2} = \frac{94h^2}{8Md^2} = 2(kT/2) \quad (24)$$

$$\alpha = h^2/8Md^2 kT = 1/94 \quad (25)$$

A graph of the shape—probability density function $p(x, y)$ —of the particle in a square box in a stable equilibrium state for $\alpha=1/94$ is shown in Figure 7. In this calculation, we use only 30 terms on the right hand side of Eq. 16 for each degree of freedom. In contrast to the equilibrium state, the shape of the particle in the stable equilibrium state with the same energy as that of the equilibrium state is uniform throughout the square box except near the walls where, as was pointed out earlier, $p(x, y)$ must reduce to zero.

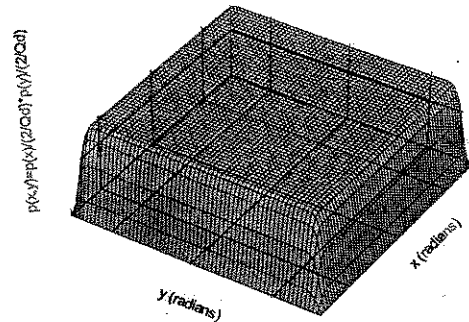


Figure 7. Shape—probability density function versus position—of a particle in a square box (infinitely deep potential well) in a stable equilibrium state of the same energy E as the equilibrium state in Figure 6. Arbitrary dimensionless units of the two spatial coordinates and the probability density function.

4. Harmonic Oscillator

4.1. Energy eigenstates

We consider a structureless particle of mass M that experiences a continuously acting force $F(x)$ which can be thought of as the force of a spring, and which follows Hooke's law

$$F(x) = -kx$$

where the proportionality constant k is the stiffness of the spring. Such a force is called *harmonic*, and the particle a *harmonic oscillator*.

The potential energy stored in the spring is given by the relation

$$V(x) = k x^2 / 2$$

and, therefore, the Hamiltonian operator of the oscillator is

$$H = -\frac{\hbar^2}{2M} \frac{d^2}{dx^2} + \frac{k}{2} x^2 \quad (28)$$

The Hamiltonian operator defines the energy eigenvalue problem

$$H\phi_n(x) = \varepsilon_n \phi_n(x) \quad (29)$$

where ε_n and $\phi_n(x)$ are the n th energy eigenvalue and energy eigenfunction, respectively. Upon introducing the *harmonic oscillation angular frequency*

$$\omega = (k/M)^{1/2} \quad (30)$$

and the dimensionless variable

$$\xi = x/\sigma_0 \quad \text{where} \quad \sigma_0 = (\hbar/M\omega)^{1/2} \quad (31)$$

we can readily verify that the energy eigenstates are such that

$$\varepsilon_n = (n + 1/2) \hbar\omega \quad \text{for} \quad n = 0, 1, 2, \dots \quad (32)$$

$$\phi_n(\xi) = (\sqrt{\pi} 2^n n!)^{-1/2} H_n(\xi) \exp(-\xi^2/2) \quad (33)$$

for $n = 0, 1, 2, \dots$

where $\phi_n(\xi)$ is normalized in ξ , and $H_n(\xi)$ is the n th Hermite polynomial. The eigenfunction $\phi_n(x)$, normalized in x , is

$$\phi_n(x) = (\sigma_0 \sqrt{\pi} 2^n n!)^{-1/2} H_n(x/\sigma_0) \cdot \exp(-x^2/2\sigma_0^2) \quad (34)$$

4.2. Stable equilibrium state

We consider a stable equilibrium state. The shape of the oscillator—probability density function $p(\xi)$ versus the dimensionless position ξ —is given by the relation

$$p(\xi) / [\exp(-\alpha/2) / \sqrt{\pi} Q] = \exp(-\xi^2)$$

$$\cdot \sum_{n=0}^N H_n^2(\xi) \exp(-\alpha n) / 2^n n! \quad (35)^{(27)}$$

where $Q = \sum_{n=0}^{\infty} \exp[-\alpha(n+0.5)]$, and $\alpha = \hbar\omega/kT$.

Graphs of the shapes for $\alpha=0.1$, and $N=5$, 30, and 108 are shown in Figures 8 to 10, respectively. We see that the ripples in Figure 8 are smoothed out as the number of energy eigenstates included in the evaluation of the shape is increased above 30. The shape for $N=108$ represents, to an excellent approximation, a stable equilibrium state, since the values contributed by additional terms for values of N approaching infinity die out exponentially and, thus, negligibly affect the value of the probability density function.

We also calculate the shapes for $\alpha=1$, 10, and 100, and $N=148$. They are shown in Figures 11 to 13, respectively. We see that they are all smooth (without ripples), and conclude that for each of the three cases, $N=148$ is an excellent approximation of the shape of the stable equilibrium state of the harmonic oscillator.



Figure 8 Shape—probability density function versus the dimensionless position ξ —of a harmonic oscillator in an equilibrium state, evaluated for $\alpha=0.1$ and $N=5$ (see text).

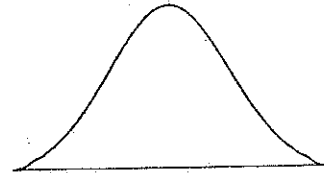


Figure 9 Shape—probability density function versus the dimensionless position ξ —of a harmonic oscillator in an equilibrium state, evaluated for $\alpha=0.1$ and $N=30$ (see text).

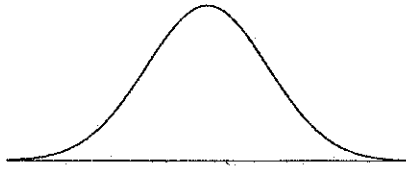


Figure 10 Shape-probability density function versus the dimensionless position ξ —of a harmonic oscillator in a stable equilibrium state, evaluated for $\alpha=0.1$ and $N=108$ (see text).

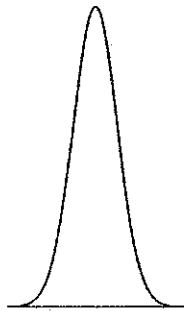


Figure 11 Shape-probability density function versus the dimensionless position ξ —of a harmonic oscillator in a stable equilibrium state, evaluated for $\alpha=1$ and $N=148$ (see text).



Figure 12 Shape-probability density function versus the dimensionless position ξ —of a harmonic oscillator in a stable equilibrium state, evaluated for $\alpha=10$ and $N=148$ (see text).

5. Concluding Remarks

The results and conclusions presented in this paper are based on a unified quantum theory of mechanics and thermodynamics. To illustrate cer-



Figure 13 Shape-probability density function versus the dimensionless position ξ —of a harmonic oscillator in a stable equilibrium state, evaluated for $\alpha=100$ and $N=148$ (see text).

tain fundamental aspects of this theory, we provide graphical illustrations of quantum mechanical shapes—probability density functions with respect to spatial coordinates—of various systems in various states. Admittedly, we have selected very simple examples—one structureless particle confined in a linear box, or in a square box, or by a harmonic oscillator force field—in order to achieve analytically explicit and transparent quantum-theoretic results, and to facilitate the computations. In each case, we find that the shape of nonequilibrium and unstable equilibrium states is rippled (not smooth), whereas for each stable equilibrium state the shape has no ripples (is smooth).

In addition, we find that in each illustration the thermodynamic entropy—a measure of the shape of the state of a system and a fundamental property of matter—increases if the system proceeds spontaneously from a state that is not stable equilibrium to the stable equilibrium state dictated by the second law of thermodynamics. Our examples, thus, provide graphical illustrations of both entropy—a concept, which has puzzled scientists and engineers for over a century—and the cause of irreversibility.

6. Nomenclature

d	distance
E	energy
F	force
\hbar	Planck's constant divided by 2π
h	Planck's constant
H_n	n th Hermite polynomial
H	Hamiltonian operator
k	spring stiffness constant

k	Boltzmann's constant
ℓ	angular momentum quantum number
m	z-component of the angular momentum quantum number
M	mass
n	energy quantum number
p	momentum
p(x)	probability density function in x
Q	partition function
S	thermodynamic entropy
T	thermodynamic temperature
t	time
V	potential energy
x	spatial dimension
y	spatial dimension

Greek Letters

α	given in the paragraph immediately following Eq. 16
α_i	i-th statistical (informational) probability
ϵ_n	n-th energy eigenvalue
ξ	dimensionless variable
ρ	density operator
σ_0	given by Eq. 31
φ_n	n-th energy eigenfunction
ϕ_n	n-th energy eigenfunction normalized in ξ or x
ψ	wave function
ω	harmonic oscillation angular frequency

7. References

- Brandt, S. and Dahmen, H. D., 1995a, "The Picture Book of Quantum Mechanics," Springer-Verlag, New York.
- Brandt, S. and Dahmen, H. D., 1995b, *op.cit.*, p. 106.
- Brandt, S. and Dahmen, H. D., 1995c, *op.cit.*, p. 249.
- Gyftopoulos, E. P. and Beretta, G. P., 1991, "Thermodynamics: Foundations and Applications," Macmillan, New York
- Gyftopoulos, E. P. and Cubukcu, E., 1997, "Entropy: Thermodynamic definition and quantum expression," *Phys Rev. E.*, Vol. 55, No. 4, pp. 3851-3858.
- Hatsopoulos, G. N. and Gyftopoulos, E. P., 1976, "A unified quantum theory of mechanics and thermodynamics. Part I: Postulates," *Foundations of Physics*, Vol. 6, No. 1, pp. 15-31.

Hatsopoulos, G. N. and Gyftopoulos, E. E., 1979 "Thermionic Energy Conversion,, Volume II: Theory, Technology, and Applications," MIT Press, Cambridge, MA, pp. 144-145.

Leighton, R. B., 1959, "Principles of Modern Physics," McGraw-Hill, New York.

Shankar, R. 1994, "Principles of Quantum Mechanics," 2nd Ed., Plenum Press, New York.

Slater, J., 1963, "Quantum Theory of Molecules and Solids," McGraw-Hill, New York.

von Neumann, J., 1995, "Mathematical Foundations of Quantum Mechanics," Princeton University Press, New Jersey.

APPENDIX

The density operator of the unified quantum theory of mechanics and thermodynamics

In many textbooks on quantum mechanics, probabilities associated with measurement results are derived from a normalized wave function $\psi(x)$ or equivalently from either a Dirac ket $|\psi\rangle$ or a projector $|\psi\rangle\langle\psi|$, where x are the spatial coordinates of the constituents of a system, and $\langle\psi|$ is the bra of ket $|\psi\rangle$ (Shankar, 1994). For example, for a system with one degree of spatial freedom x, the probability density function of measurement results of x is given by

$$|\psi(x)|^2 = \langle\psi|x\rangle\langle x|\psi\rangle = \langle x|\psi\rangle^2.$$

In statistical quantum mechanics, probabilities associated with measurement results are derived from a density operator $\rho = \sum_i \alpha_i \rho_i$ which represents a mixture of quantal probabilities derived from projectors $\rho_i = |\psi_i\rangle\langle\psi_i|$ for $i = 1, 2, \dots$ and statistical (informational) probabilities α_i which reflect the lack of information about some or all aspects of the state of a system.

In general, the foundations and theorems of the unified quantum theory of mechanics and thermodynamics differ from those of the ordinary expositions of quantum mechanics and statistical quantum mechanics. Among the many novel concepts and results, two deserve special emphasis for the purposes of this paper. The first is that in contrast to statistical quantum mechanics, a novel concept of the unified quantum theory is that its postulates—quantum-theoretic and thermodynamic—do not apply to density operators that represent mixtures of quantal probabilities derived

from projectors $\rho_i = |\psi_i\rangle\langle\psi_i|$ and statistical (informational) probabilities α_i that reflect the lack of information about some or all aspects of the state of a system. Instead, the unified theory avers that the laws of physics apply only to density operators each of which is construed as the seat of exclusively quantal probabilities, that is, only to operators ρ that can be represented by a homogeneous ensemble of identical systems, identically prepared. A homogeneous ensemble is an ensemble in which the probabilities of results of measurements on any member are represented by the same density operator ρ as those on any other member. Accordingly, experimentally (in contrast to algebraically) the ensemble cannot be decomposed into statistical mixtures of projectors or other non-projector density operators. The concept of a homogeneous ensemble was introduced by von Neumann (1955), but he assumed that it applies only to projectors ($\rho_i = \rho_i^2$), whereas here the concept is extended to all self-adjoint, nonnegative definite, linear, unit trace density operators. Each such operator satisfies the relation $\rho \geq \rho^2$.

The second concept which deserves special emphasis here is that, in contrast to the plethora of expressions for entropy that have been proposed in the scientific literature over the past 140 years, it has been shown that only one conforms with the criteria that must be satisfied by the entropy of thermodynamics, and this expression is (Gyftopoulos and Cubukcu, 1997)

$$S = -k \text{Tr} [\rho \ln \rho] \quad (\text{A-1})$$

where k is Boltzmann's constant, Tr stands for the trace of the operator that follows, and ρ is a density operator which can be represented solely by a homogeneous ensemble. It is noteworthy that, if ρ cannot be represented by a homogeneous ensemble, then $-k \text{Tr} [\rho \ln \rho]$ does not represent the entropy of thermodynamics.

For given values of energy, volume, and amounts of constituents, if ρ is a projector (wave function), then $S=0$; if ρ is not a projector but corresponds to a state which is not stable equilibrium (not thermodynamic equilibrium), then S has a positive value smaller than the largest possible for the given specifications; and if ρ corresponds to the unique stable equilibrium state, then S has the largest value of all the entropies of

the system which share the given values of energy, volume, and amounts of constituents.

To illustrate the fundamental difference between an ensemble that is heterogeneous and one that is homogeneous, we consider the density operator ρ^0 of the electron of a hydrogen atom in a stable equilibrium state. The heterogeneous ensemble would be a combination of sub-ensembles, each of which is specified by one set of values of three quantum numbers: the energy quantum number n , the angular momentum quantum number $0 \leq \ell \leq n-1$, and the z -component of the angular momentum quantum number $-\ell \leq m \leq \ell$. So for $n=3$, there would be nine sub-ensembles because the energy eigenstate is n^2 -fold degenerate. Each of these sub-ensembles has the shape shown in Figure A-1. In contrast, the density operator ρ^0 of

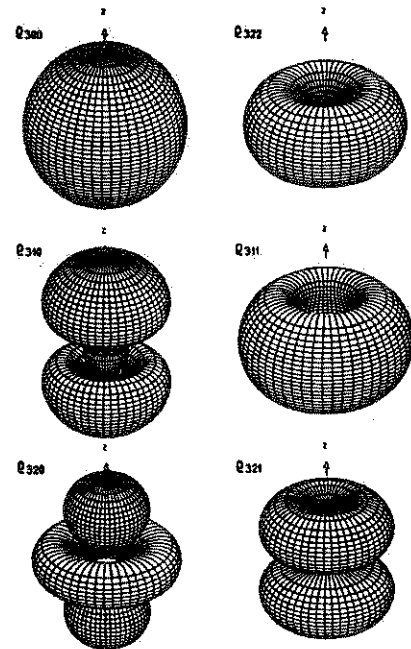


Figure A-1. Heterogeneous sub-ensemble surfaces—shapes—of the constant probability density function $\rho_{3\ell m} = 0.0002$ in full x,y,z -space of the electron in a hydrogen atom in a stable equilibrium state (Brandt and Dahmen, 1995c). The shapes for $m = -1$ and -2 are identical to the ones shown for $m = 1$ and 2 , respectively.

the homogeneous ensemble cannot be in any conceivable way subdivided into sub-ensembles. Each member of the ensemble is described by the same ρ^0 and has a spherical shape as shown in Figure A-2.

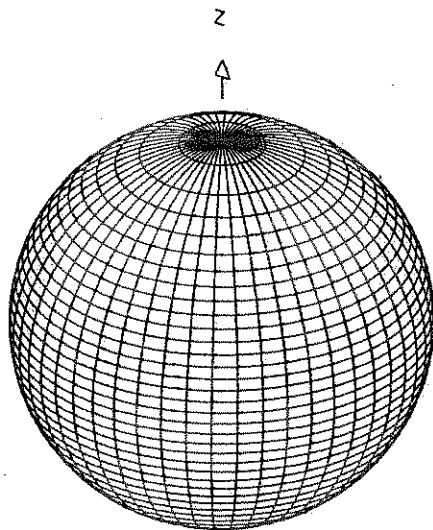


Figure A-2. Homogeneous ensemble member surface—shape—of the constant probability density function in full x,y,z-space of the electron in a hydrogen atom in a stable equilibrium state (arbitrary units).