

SHANNON ENTROPIES FOR ELECTRON POSITION IN HYDROGEN ATOM

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We calculated numerically Shannon's entropies for position of certain quantum states of hydrogen atom and found a phenomenological function for their dependence on the radial quantum number n . Using this function we determined the energy-entropy relation for hydrogen atom and discussed its significance in the interaction of hydrogen atom with photons.

1. Introduction

The determination of the informational parameters of quantum objects has been an important topic in the recent literature of physics, quantum chaos and computers (see e.g. the biography in refs. [1], [2] and [3]). The equivalence of information and negentropy as well as the existence of a linkage between the thermodynamic and information-theoretical entropy threw a new light on the activity of Maxwell's demon [3] and led to formulation of statistical mechanics in terms of information theory [4]. It has been shown already in sixties that the probabilistic interpretation of quantum mechanics forms an appropriate fundament for the application of information theory in quantum mechanics [10]. Due to relation between the physical and information-theoretical entropies via Boltzmann's constant k_B we can ascribe to any quantum object a certain value of its physical entropy $S_{phys} = k_B S_{inf}$ [4]. This makes it possible to consider a quantum object as a thermodynamical system characterized by its energy and entropy and determine the entropy balance also for the interaction of microobjects. If this interaction represents an irreversible process then the entropy balance should be positive otherwise it should be zero. However, the Shannon entropy of a quantum object depends on its state and the chosen observables (position, momentum, etc.) which have often continuous probability distributions and are linked by the quantum mechanical laws. Moreover, the calculation of the Shannon entropies is complicated also by the fact that the integrals representing the Shannon entropy of quantum states cannot be generally evaluated by analytical methods but only numerically. Therefore, it is difficult to find analytically the dependence of Shannon entropies on certain quantum numbers

and one has to find it by some approximative phenomenological formulas. Since the calculation of the complete Shannon entropy for all observables of a real quantum mechanical object would be a huge work we confine ourselves here only to the calculation of the Shannon entropies for the position of a quantum object.

In what follows we calculate numerically the Shannon entropy for localization of electron in real quantum object—the hydrogen atom. We then discuss the results for the emission and absorption of photon by hydrogen atom, a problem which became recently very actual due to new development of quantum optics especially when it became possible to study experimentally a single atom in a cavity interacting with only one radiation mode (for a recent review see, e.g. [7]). Since the hydrogen atom represents a microscopic quantum system which can serve as a component of computer one can, having its information-theoretical characteristics, determine also a fundamental physical limit of computation [9].

Before calculating the information-theoretical entropies of quantum states let us recall the exact definition of information-theoretical entropy as a measure of the probabilistic uncertainty of a stochastic object. This definition is the following [5]: Let \tilde{x} be random variable defined on a stochastic object which takes the different values x_i , $i = 1, 2, \dots, n$, with the probabilities P_i , $i = 1, 2, \dots, n$, i.e. $P(x_i) = P_i$. Let $\mathbf{P} = \{P_1, P_2, \dots, P_n\}$, $\sum P_i = 1$; $P_n \geq 0$, $i = 1, 2, \dots, n$, be the finite probability distribution. The (information-theoretical or Shannon) entropy of any discrete probability distribution is given by the formula [1]

$$H(\mathbf{P}) = H(\tilde{x}) = -\sum P_i \log P_i \quad (1)$$

provided that the series on the right-side-hand converges. The entropy of the continuous random variable \tilde{x} , the probability distribution of which is given by a function of the probability density $p(x)$ has the form [10]

$$H(\tilde{x}_c) = H^{(1)} + H^{(2)} \quad (1a)$$

where $H^{(1)}$ is the so-called differential entropy

$$H^{(1)} = -\int p(x) \log p(x) dx \quad (1b)$$

and $H^{(2)}$ represents the diverging term

$$H^{(2)} = \lim_{\Delta x \rightarrow 0} \log \Delta x \quad (1c)$$

We note that except Shannon's entropy (1) there exists a set of non-standard entropy definitions serving as certain measures of probability uncertainty of stochastic object which are sometimes used also in physics [5].

2. Position entropies of quantum states

The simplest quantum system of two bodies with the Coulomb interaction represents the hydrogen atom. If E is the energy of the electron-proton system then the wave function $\psi(r, \Theta, \varphi)$ of electron is a solution of the Schrödinger equation [6]

$$\left[-\frac{\hbar^2}{2m} \Delta - \frac{e^2}{r} \right] \psi(r, \Theta, \varphi) = E \psi(r, \Theta, \varphi) \quad (a)$$

Carrying out the separation of angular and radial variables the eigenfunctions of (a) for eigenenergies E_n are

$$\psi_{n,l,\lambda}(r, \Theta, \varphi) = X_{n,l} Y_{l,\lambda}^m(\Theta, \varphi),$$

where $X_{n,l}$ are radial functions and $Y_{l,\lambda}$ are the spherical harmonics. n, l and λ is radial (principal), azimuthal and magnetic quantum number, respectively. The probability of finding electron within the volume element, $d\tau$, is $dP = \psi \psi^* d\tau$ and the corresponding probability density

$$p(r, \Theta, \varphi) = \frac{dP}{d\tau} = \psi \psi^*$$

Inserting $p(r, \Theta, \varphi)$ in (1b) we get

$$H_{n,l,\lambda} = -\int |\psi_{n,l,\lambda}|^2 \log |\psi_{n,l,\lambda}|^2 d\tau \quad (2)$$

Since integrals (2) are generally very difficult to evaluate analytically (because of the logarithm in their integrands) we calculated them numerically. To do this for all n, l, λ would be very lengthy work, therefore, we selected only some specific and interesting wave functions with $n = 1, 2, \dots, 10$ and $l = 0$, $\lambda = 0$. Putting $x = r/(na)$ ($a = 0.52 \times 10^{-10}$ m - atom radius), the radial function can be written in the form [8]

$$X_{n,l} = N_{n,l} e^{-x} P_{n,l}(x) \quad (3)$$

where

$$N_{n,l} = \frac{1}{\pi} \left(\frac{1}{na} \right)^{\frac{3}{2}} \quad (4)$$

is the norm and $P_{n,l}(x)$ is the polynomial function

$$P_{n,l}(x) = a_0 + a_1 x + a_2 x^2 + \dots + a_n x^{n-1}$$

The coefficients a_0, a_1, \dots, a_{10} are given in Table I. Inserting the normed radial functions ($l = 0, \lambda = 0$) in (2) we obtain

$$H_n^{(1)} = -\int_0^\infty N^2 e^{-2x} (P_{n,0}(x))^2 \log \left[N^2 e^{-2x} (P_{n,0}(x))^2 \right] x^2 dx \quad (5)$$

Taking into account that

$$\int_0^\infty N^2 e^{-2x} (P_{n,0}(x))^2 \log N^2 x^2 dx = \log N^2$$

Table 1.

m	0	1	2	3	4	5	6	7	8	9	I_n
n	1	1									0.7500
	2	-1									1.2220
	3	-2	2/3								1.4981
	4	-3	2	-1/3							1.6940
	5	-4	4	-4/3	2/15						1.8460
	6	-5	20/3	-10/3	2/3	-2/45					1.9701
	7	-6	10	-20/3	6	-4/5	4/75				2.0751
	8	-7	14	-35/3	14	-14/5	4/3				2.1660
	9	-8	56/3	-46/3	23/3	-46/45	46/315	-1/7			2.2463
	10	-9	24	-28	84/3	-28	16/3	-4/7	23/79380	2/63	2.3180

we have

$$H_n = -\log N^2 + I_n,$$

where

$$I_n = -\int_0^{\infty} e^{-2x} (P_{n,0}(x))^2 \log [e^{-2x} (P_{n,0}(x))^2] x^2 dx. \quad (6)$$

The integrals (6) we calculated numerically with accuracy of 10^{-4} and their values are given in Table 1 in the last column. We see that the higher is the quantum number n the larger is the probability uncertainty in electron location. With (4) equation (5) turns out to be

$$H_n^{(1)} = \log(\pi\alpha^3) + 3 \log n + I_n. \quad (7)$$

I_n represents a discrete function of n which can be well fitted (with accuracy of 1%) by a phenomenological function of the form

$$I_n = a + b \log n, \quad (8)$$

where $a = 0.75$ and $b = 0.681$. Substituting (8) in (7) we get the entropy (1a)

$$H_n = \log(\pi\alpha^3) + 0.75 + 3.681 \log n + H^{(2)} \quad (9)$$

Since the entropy of a continuous random variable always diverges (see (1c)) it is more appropriate to consider only the differences of two entropies because then their diverging terms cancel. We have

$$\Delta H = H_{n+1} - H_n = 3.681 \log \left(\frac{n+1}{n} \right). \quad (10)$$

The difference ΔH is a function only of the corresponding radial quantum number n . If $n \rightarrow \infty$ then $\Delta H \rightarrow 0$ as it should be. In what follows we shall investigate the connection between the entropies of individual quantum states and their corresponding eigenenergies.

3. Energy-entropy relation for quantum states

The eigenenergies of electron in hydrogen atom are $E_n = -A/(n)^2$,

$$A = \frac{me^4}{2\hbar}$$

and the logarithm of the ratio E_n/E_{n+1} is

$$\log \left(\frac{E_n}{E_{n+1}} \right) = 2 \log \left(\frac{n+1}{n} \right) \quad (11)$$

Inserting (11) in (10) we obtain

$$\Delta H = H_{n+1} - H_n = k \log \left(\frac{E_n}{E_{n+1}} \right) = k 2 \log \left(\frac{n+1}{n} \right), \quad (12)$$

where $k=1.840$. Equation (12) represents the energy-position entropy relation of quantum states $|\psi_{n,0,0}\rangle$ for the hydrogen atom.

4. Discussion and some conclusions

When the energy of a hydrogen atom changes from value E_{n+1} to a lower value E_n , then the difference in energy is emitted as a photon of frequency $h\nu = E_{n+1} - E_n$. The corresponding change of position entropy of H-atom, $\Delta H_A = k_B(H_{n+1} - H_n)$, is positive which means that the emission of photon by H-atom is a process in which the uncertainty in electron localization is decreased. Recently, the entropy determination of the quantum state of the emitting atom became important in the connection with the new development of quantum optics which investigates a large variety of quantum phenomena in the interaction of photons with atoms [7]. Especially interesting is the study of a single atom inside a cavity interacting with one cavity radiation mode. As is well known atoms in free space interact with a continuum of radiation modes which causes the irreversible decay of an excited atom. On the other hand, under the special conditions the spontaneous emission of an atom in a cavity can be reversible process. The reversible and irreversible processes differ from each other by their total entropy balance, because for the irreversible processes the entropy balance is positive whereas for the reversible one it is zero. The determination of the energy and entropy balance of a microprocess has some importance also for the description of H-atom as an information sender and receiver as well as the quantum memory and operational component of the computers [9]. Note that there are other measures of the probability uncertainty of a continuous random variable \tilde{x} . Well-known is the measure defined by the formula $S = 1 - \int [\varphi(x)]^2 dx$, where $\varphi(x)$ is the function of the probability density of \tilde{x} . Using the H-atom wave functions we get

$$S_{n1\lambda} = 1 - \int |\psi_{n1\lambda}(r, \Theta, \varphi)|^4 d\tau(r, \Theta, \varphi).$$

The determination of $S_{n1\lambda}$ for H-atom will be the subject of a subsequent paper.

References

- [1] J.J. Halliwell: *Phys. Rev. D* **49** (1993) 2739;
- [2] K.R.W. Jones: *J. Phys. A* **23** (1993) 1247;
- [3] H.S. Leff, A.F. Rex (eds): *Maxwell's demon-entropy, information, computing*, A. Hilger, Bristol, 1990;
- [4] E.T. Jaynes: *Phys. Rev.* **106**, **107** (1957) 620 and 106;
- [5] V. Majerník, B. Mamojka: *Physica Scripta* **44** (1991) 412;
- [6] A. Messiah: *Quantum Mechanics*, Vol.1, Nord-Holland, Amsterdam, 1972;
- [7] G. Rempe: *Contemporary Phys.* **34** (1993) 119;
- [8] W. Weizel: *Electrone, Atome und Moleküle*, Volk und Wissen, Berlin, 1950;
- [9] R. Landauer: *Phys. Scripta* **35** (1987) 88; *Found. Phys.* **16** (1986) 551;
- [10] V. Majerník: *Acta Physica Austriaca* **25** (1967) 243;