Speculation of Quantum Bound State Thermodynamics Part II

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   In Part I we argued that both the first law of thermodynamics dE=TdS-dW and the form S/(-k) = Integral dp dx P(x)P(p) ln{P(x)P(p)} = Integral P(x)ln(P(x)) + Integral P(p) ln(P(p)) may be established at the level of a pure quantum bound state with P(x)=W(x)W(x) and P(p)=a(p)a(p) where W(x)=wavefunction = Sum over p a(p)exp(ipx). We further argued that S=Sp+Sx in order that L, the length of a box with infinite potential walls, should disappear (from S) so that a quantum adiabatic transformation where n=energy level remains constant is isentropic. In fact, we argued that the P(x)ln(P(x)) form follows from this rule and an assumption of additive entropies Sp and Sx. As a result, probability at the pure bound state level is not based on the maximization of entropy as P(x)=W(x)W(x) and P(p) =a(p)a(p) and W(x) follows from the solution of the time-independent Schrodinger equation.
   In this note we examine the case of two level bound state system (analyzed in (1)) to see how the thermodynamic temperature behaves in such a case and examine the maximization of entropy. T is already present in the pure energy state picture (TdS), but for two levels or more, it plays a different role in that P(ei) where ei is the ith energy level becomes a function of T which enters as a Lagrange multiple during the maximization of S with respect to P(ei) with the constraint Sum over i eiP(ei) = Eave. No such maximization of entropy occurs at the pure bound state level. We note, however, that for a quantum adiabatic transformation for a particle in a box with infinite potential walls, P(ei) values must remain constant as L changes. Ei is proportional to 1/LL so a solution is to use ei/T with T is proportional to 1/LL. Thus the parameter T already enters P(ei) in order to ensure that an adiabatic transformation is isentropic.
   In the pure bound state, one was forced to use P(x)P(p)ln(P(x)P(p)) because P(x) is proportional to 1/L and P(p) to L. In other words in the pure state there are two kinds of probabilities (p and x) and one must ensure that L disappears. For the two level system there is only one type of probability which contains ei(L) so this L must be offset within the probability itself i.e. by using T. Thus thermodynamical and statistical mechanical behaviours which seem to be present at the pure quantum bound state level have different features for multiple level systems even though the first law of thermodynamics remains the same as does the form of entropy. What seems to change is the role of T temperature.
   We try to examine these features in this note. In particular we also find that maximization of entropy subject to constant energy which is usually linked to high N scenarios (i.e. factorial calculation in the high N limit) follows from the first law of thermodynamics with dW=0. Thus it holds even for one quantum particle with two energy levels (particle in a box with infinite walls). This, however, makes use of the form E=Sum over i ei P(ei). Such a form does not hold for example for a pure bound state.

Pure Bound State, First Law of Thermodynamics and Shannon's Form of Entropy

   In Part I we argued that both the first law of thermodynamics dE=TdS - dW and Shannon's form of entropy are present in pure bound state quantum mechanics. Furthermore we argued

that at this level, one does not need to think of $P(x) = W(x)W(x)$, $P(p) = a(p)a(p)$ where $W(x)$ = wavefunction = Sum over p $a(p)\exp(ipx)$ in terms of the maximization of entropy with a constraint of constant average energy. It is the time-dependent Schrodinger equation which determines $W(x)$, $a(p)$ and so $P(x)$ and $W(x)$. The Shannon's form appears because one wishes a quantum adiabatic transformation i.e. the changing of L the box size with the energy level kept constant to be isentropic. $P(x)$ is proportional to $1/L$ and $P(p)$ to L. If one wishes to have a function S (entropy) which removes L and is "additive" i.e. separates $P(p)$ and $P(x)$ terms, then a solution is:

$S/(-k) = $ Integral dpdx $P(x)P(p) \ln\{P(x)P(p)\}= $ Integral dp $P(p)\ln(P(p)) + $ Integral dx $P(x)\ln(P(x))$ ((1))

One may note that this Shannon's form is equivalent to an information theory probability term, but information theory relies on large N values. Here that is fine because x and p may take on many values. Thus at the pure bound state level the form of entropy chosen to remove L is mathematically equivalent to an information probability theory picture.

If one changes L adiabatically then $dE=dW$ i.e. one has mechanical work and $dS=0$. $S=Sp(n)+Sx$. S does not depend on L, but depends on n.
Consider jumping from $n=0$ to $n=1$. In such a case L is constant and there is no mechanical work. E is proportional to $1/LL$, however, and dS does not contain L, so one needs a factor proportional to $1/LL$ i.e. T the temperature. Thus the temperature does not play any role in $S=Sp(n)+Sx$. In the next section we see that matters are very different for a two (or multiple) energy level system. In such a case, T is an important part of $P(ei)$, but for the two level system it again provides a $1/LL$ factor. This time, however, that is used to cancel the $1/LL$ from ei i.e. one has a function of ei/T. With L removed, so may have a quantum adiabatic transformation which is isentropic.

Extension to a Two Energy Level System (Particle in a Box With Infinite Potential Walls)

Consider (as in (1)) a system with:

$W(x,t) = a(n=1) \exp(-E1\,t)\,W1(x) + a(n=2)\exp(-E2\,t)\,W2(x)$ ((2))

We assume that the first law of thermodynamics from the pure bound state case holds i.e. $dE=TdS - dW$ and also carry over the Shannon's form of entropy with a probability of $P(ei)P(x)P(p)$ where $i=0$ and 1. We let $g=a(1)a(1)$. Then $a(2)a(2)=1-g$.

$S/(-k) = $ g ln g + (1-g) ln(1-g) + g $(Sp(n)+Sx)$ ((3))

In (1) the effects of the bound state i.e. $Sp(n)+Sx$ are not included. In previous notes we have argued that they should be, but only experimental results may determine if they play a role. We have noted that for n large $Sp(n)$ approaches a constant so one does not expect to see effects in the Maxwell-Boltzmann distribution.

In (1) it is suggested that;

$$dQ = \text{Sum over i} \quad e_i \, d\{a(n)a(n)\} \quad (i=1,2) \quad ((4))$$

Then T temperature is defined through $dQ/T = dS$ ((5)) with S given in terms of Shannon's entropy.

$$Eave = bg \, 4b \, (1-g) \quad ((6)) \text{ where } b= nn/LL \quad (3.14*3.14*hbar*hbar/2m)$$

Using ((4)) and ((5)) one may solve for g and find as in (1):

$$g = 1/\{\exp(3b/T) + 1\} \quad ((7a))$$

If one retains $S=Sp+Sx$ in ((4)) then $g= 1/\{\exp(3b/T)\exp(S) + 1\}$ ((7b))

We point out that the form ((5)) is identical to a maximization of entropy with the constraint of constant average energy even for a two level system i.e.

$$dS + (1/T) \{ e(0) \, dg + e(1) \, d(1-g)) \} = 0 \quad ((8a)) \text{ where } 1/T \text{ is a Lagrange multiplier}$$

Thus already at the two energy level picture- the simplest modification of pure bound states, maximization of entropy may be used to find P(ei) even with S=bound state entropy included.

In fact the maximization of entropy with respect to a constraint follows from the first law of thermodynamics with dW=0. One has:

$$dS - 1/T \, dE = 0 \quad ((8b))$$

((8b)) is precisely a maximization equation. E= Sum over ei P(ei) and dE for dW=0 is dE=Sum over i ei dP(ei). Similarly S may be written as a function of P(ei) and maximized.

This is completely different from the situation for a pure bound state. The fact that ((7a)) and ((7b)) already contain the extra thermodynamic parameter T (temperature) already differs from the bound state picture, but the idea of an adiabatic transformation (change in L with n constant) which is central to the pure bound case is also present in the two level picture. One has P(ei) and ei is proportional to 1/LL. An immediate way to ensure that L disappears so that an adiabatic transformation is isentropic is to replace ei by ei/T where T is proportional to 1/LL. In fact one may directly calculate T for the two level system i.e.

$$T/3b1 = \{ (E/b1) - 4 \} / \{ 1- E/b1) \quad \text{where } E=Eave \text{ and } b1 \text{ is proportional to } 1/LL \quad ((9))$$

Thus T is proportional to b1 and hence 1/LL as already anticipated.

Maximization of Entropy and the Information Theory Probability or Maximum Number of States

  In the previous section we showed that maximization of entropy subject to an energy constraint follows directly from the first law of thermodynamics with dW=0 if E=Sum over i ei P(ei). Thus it holds even for two energy levels. This we argue is interesting because in statistical mechanics large N assumptions are usually made in order to obtain the Shannon's entropy form S/(-k)= Sum over i P(ei) ln(P(ei)). For instance, one may use factorials to count the possible number of arrangements. For large N, the factorial expression yields Shannon's entropy. Alternatively in information theory one considers P(ei) for large N situations for which the expected number of ei appearances is NP(ei). (Consider tossing a coin N times. Only if N is very large does one expect to see half the outcomes as heads and the other half as tails.) Then

Probability = Product over i P(ei) $^{NP(ei)}$

ln(Probability) = Sum over i   NP(ei) ln(P(ei))

Thus in these large N instances maximizing entropy is linked to maximizing arrangements or probability. We argue, however, that no such picture is needed for maximization which follows from the first law of thermodynamics i.e. dE=TdS. This holds even for two levels and one quantum particle. The key, however, is that E=Sum over i eiP(ei). This form does not hold for a pure bound state and so one does not maximize entropy subject to constraints (except for the ground state oscillator) in that case.

Reaction Considerations

   In the above section maximization of entropy with respect to constant average energy led to P(ei) for a two level system. This approach may be applied to an N level system with N very large i.e.

Max: -{Sum over i P(ei) ln(P(ei)) + S(i)P(ei) } + 1/T Sum over i ei P(ei) —->

-1 - ln(P(ei)) - S(i) + 1/T ei = 0 or   P(ei) =   C exp(-ei/T)exp(1+S(i))   ((10))

Here S(i) = Sp(i)+Sx for the bound state. This term is usually not present in the literature as the bound state entropy is not considered there, but as mentioned experimental results need to determine if it should be used. exp(-ei/T) is the Maxwell-Boltzmann distribution.

This distribution may be obtained without any consideration of entropy or its maximization by considering time reversal balance of elastic collisions among the ei state with the assumption that e1 collides with e2 is proportional to P(e1)P(e2). Then:

e1+e2=e3+e4 and P(e1)P(e2)=P(e3)P(e4)

Taking ln of the second equation and linking to the first yields: P(ei)=Cexp(-ei/T) ((11))

We note that in principle a more complicated solution may be found i.e. P(ei) = C exp(-ei/T) exp(-S(i)/T) if   S(1)+S(2)=S(3)+S(4) where S(i) could be the pure state entropy. The pure bound state entropy, however, does not add so simply except in the high n case for which S(i)=constant.

One may note that the reaction picture holds in the two level case. There one has to think in terms of a photon i.e.

E1 + Ephoton = E2   and f(e1)f(photon) = f(e2)

Taking ln of the second equation yields the form exp(-ei/T). For a two body system with n=1 and n=2   e1=b and e2=4b. Thus:

Cexp(-b/T) + Cexp(-4b/T) = 1   or   P(e1)= 1 / {1+ exp(-3b/T)   ((12))

Thus one does not need the idea of maximization of entropy subject to a constraint. An issue arises, however, related to S=Sp(i)+Sx the pure bound state entropy. As seen in ((12)) it is not present. One may "bring it in" i.e. extend exp(-ei/T) to exp(-ei/T)exp(Si/T) if the photon has an extra probability piece such that:

S1 + extra photon entropy = S2   ((13))

This extra photon entropy, however, would affect the Planck distribution it seems which is experimentally verified. Thus one needs to calculate S1 and S2 numerically for a particle in a box with infinite walls to see how large the internal Sp(i) is.

Scattering and exp(-ei/T) Form

   In the above section we have seen that P(ei) depends on an internal parameter T temperature which is not part of P(x) or P(p) in the pure bound state case. If one uses the first law of thermodynamics established at the pure bound state level for a case of no work i.e dE=TdS then it seems that one may establish the form of S in terms of an inverse function of exp(-ei/T). (In the pure bound case it was introduced in order to eliminate L the box length). Consider:

dE= Sum over i   ei df(ei) = T dS

If S is to be written as the average of quantity i.e. $S/(-k) = $ Sum over i f(ei) function(ei/T) from the scattering picture, then one needs ln(f(ei)) where:

f(ei)= exp(-ei/T) / C(T)   ((14))

Then (with k=1)   dE = T d Sum f(ei) (ei/T + ln(C)) or 0= T dln(C)/dT dT - E/T   ((15))

((15)) is in fact the case.

Conclusion

   In particular we argue that the first law of thermodynamics and Shannon's form of entropy follow from considerations of a pure bound state. There is no maximization of Shannon's entropy subject to constraints in order to find probabilities P(x) or P(p). If one considers the next simplest case, i.e. two energy levels (for a particle in a box with infinite potential walls), then one may retain the first law of thermodynamics and Shannon's form. Now E= Sum over i ei P(ei) and for the case of dW=0,   dS-1/T dE = 0. This is precisely of the form of a maximization of entropy subject to constant average energy form with the function P(ei) being varied. Thus we argue that maximization of entropy in order to find the form of P(ei) emerges already for a two level system. This is in contrast to the arguments used to show that Shannon's form appears from factorial arrangement counting schemes with N being very large or from information theory in which NP(ei) is the number of outcomes if N is very large. No assumptions of very large N's are needed, only the form E= Sum over i ei P(ei) and the first law of thermodynamics. The form E=Sum over i ei P(ei) does not hold for a pure bound state and so there is no maximization of entropy in that case. It is interesting to note that the parameter T appears for a pure bound state, but is not part of P(x) and P(p). For the two level system, P(ei) already needs a parameter if it is to stay constant as L changes in a quantum adiabatic transformation. Thus one has P(ei/T) with ei proportional to 1/LL and T also. The statistical behaviour of two state system already differs from the pure bound state, but the first law of thermodynamics and the Shannon's form of entropy are retained.

References

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