

S5: THE THERMODYNAMICS OF PSI

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The little delta used in S4 are called functional variations the influence directly the function f say which may be the argument of another function $g(f)$ inside an integral. Let us begin by giving some elementary rules about the functionals:

$$\begin{aligned}
 \delta(e^{-U}) &= e^{-\delta U} \\
 de^{-U} &= -e^{-U} dU \\
 d(\delta(e^{-U})) &= d(e^{-\delta U}) = -e^{-\delta U} d(\delta(U)) \quad (1) \\
 \delta(d(e^{-U})) &= \delta(e^{-U} dU) = e^{-\delta U} \delta(dU)
 \end{aligned}$$

So, in general $\delta(d()) \neq d(\delta())$ and this is so in our case.

COMPLETING THE ENERGY CONSIDERATIONS USED IN S1 AND THE TALK ABOUT THE VIRIAL THEOREM IN S4

In my article called ‘An extension of Dirac notation and its consequences I had used the following formula (although I had made a typing mistake in the minus sign):

$$-\frac{1}{2} \int \vec{P} \cdot \vec{E} dV = \langle K.E. \rangle \quad (2a)$$

This was extracted from the virial theorem as:

$$\int \vec{r} \cdot \frac{d\vec{F}}{dV} dV = \langle \vec{r} \cdot \vec{F} \rangle \quad (2b)$$

The means are so according to the quantum mechanics formulation. There is another term of the virial theorem though:

$$\int \vec{F} \cdot \frac{d\vec{r}}{dV} dV = -\int |\psi|^2 \nabla U \cdot \frac{d\vec{r}}{d\vec{S}d\vec{r}} d\vec{S}d\vec{r} =$$

$$= -\int |\psi|^2 \frac{dU}{d\vec{r}} \frac{d\vec{r}}{d\vec{S}d\vec{r}} d\vec{S}d\vec{r} = -\int |\psi|^2 dU \quad (2c)$$

But we saw in S3 that :

$$\nabla P = -|\psi|^2 \nabla U = \frac{d\vec{F}}{dV} \implies$$

$$\int \vec{r} \cdot \frac{d\vec{F}}{dV} dV = \langle \vec{r} \cdot \vec{F} \rangle = -2\langle K.E. \rangle = -2\int |\psi|^2 (E - U) dV, \quad (2d)$$

$$\nabla P = \frac{dP}{d\vec{r}} d\vec{r} = r \frac{dP}{dr} = -|\psi|^2 \nabla U d\vec{r} = -|\psi|^2 dU$$

To truly complete the virial theorem we should complete the virial theorem keeping in mind that the force is minus grad(U) times charge :

$$\int -|\psi|^2 \nabla U \cdot \vec{r} dV = \langle \vec{r} \cdot \vec{F} \rangle = \int (\vec{r} \cdot \frac{d\vec{F}}{dV} + \vec{F} \frac{d\vec{r}}{dV}) dV =$$

$$= \int \vec{r} \cdot \nabla P dV - \int |\psi|^2 dU = \int r \frac{dP}{dr} dV - qdU \implies \quad (3)$$

$$\implies r \frac{dP}{dr} dV - eEd(e^{-U/E}) = -r \frac{dP}{dr} dV$$

$$2r \frac{dP}{dr} dV = E \frac{dq}{e} \quad (4)$$

Now, pressure could be homogeneous function of r of the n(th) degree say. In that case the transformation rho->n(rho) gives:

$$\left(r' \frac{dP}{dr'} \right)_{r'=nr} = nr \frac{dP}{dr} = nP \quad (5)$$

In the case of the atom $U=-1/r$ and $(dU/dV)dV$ goes as $(1/r^2)dr$. Then $PdV \approx Fdr \approx dW \approx dU$ should go as $1/r^2 dr$ as well so from eq.4 P should go as $P=1/\rho^4=F/S$ exactly. With the help of eq.4 and eq.5 we get:

$$2n'PdV = 2ndW = \frac{Edq}{e} = \frac{(n+1/2)\hbar\omega_0 dq}{e} \quad (4a)$$

So what is really the charge? Is it an elementary amount of work? And what should explain the thermal currents associated with it? We believe the electron to be an

elementary thermal charge. However eq.4 explains the quantization of Energy for the harmonic oscillator. Towards higher levels pressure goes as $1/(\rho^n)$. Still, we always measure Energy as $\hbar \omega$ times n . Solving eq.4 supposing the units of pressure to be expressed in:

$$\text{Units of } (P) = \frac{\hbar \omega_0}{4N} \quad (4b)$$

For the harmonic oscillator

Now there is always a quantum number associated with Energy and we may solve for the quantum number n' of Pressure.

Solving now for the quantum number n' of pressure we find:

$$2n' = 2n + 1$$

There is no solution to this for integers. So we are left with the solution:

$$2n' = 2n \quad (4c)$$

Plus recognizing the fact that:

$$dU = TdS - PdV = d'Q - PdV \quad (5)$$

The elementary charge must be the electron then, for we may not get lower in energy than that. We have found out in S4 that of course we could add some thermal charge with photons or magnetic fields (raising the entropy $\Delta(S)$) and then the energy could be raised.

Yet there is another picture. Equivalently to changing ψ and thus Pressure we might change the volume and leave Pressure (ψ) the same.

From 2d:

$$\begin{aligned} \int -\bar{r} \frac{dU}{d\bar{r}} \frac{|\psi_1|^2}{N} dV &= \int \frac{|\psi_1|^2}{N} dU(rdS) = -2 \langle K.E. \rangle \\ &= \int \frac{|\psi_1|^2}{N'} dUrdS' + \delta \langle K.E. \rangle = \\ &= \int \frac{|\psi_1|^2}{N'} dUrdS' + \int \hbar \omega_0 \frac{|\psi_1|^2}{N'} dV' \end{aligned} \quad (6)$$

The wave functions cancel and we have, writing for the moment $dV' = r'dS'$:

$$\begin{aligned}
dU \left(\frac{dV}{N} - \frac{dV'}{N'} \right) &= \hbar \omega_0 \frac{dV'}{N'} \implies \\
\implies dU \left(\frac{dV}{N} - \frac{dV'}{N'} - \hbar \omega_0 \frac{dV'}{N' dU} \right) &= 0 \quad (7)
\end{aligned}$$

Now we may check and use the result found in S4:

$$\frac{1}{N} = \frac{1}{N_0} \frac{d(\delta V)}{dV} \quad (8)$$

Where the constant N_0 units we haven't determined yet.

Equations 7 and 8 combine to:

$$dU \left(d(\delta V) - d(\delta V') - \hbar \omega_0 \frac{\delta(dV')}{dU} \right) = 0 \quad (9)$$

Now we might say that there is no change in the volume in considering ψ_1 because we measured it correctly. Then the first term in eq.9 vanishes and we have:

$$\begin{aligned}
dU d(\delta V') &= \hbar \omega_0 \delta(dV') \implies \\
\frac{dU}{N'} dV' &= \hbar \omega_0 \delta(dV') \quad (10)
\end{aligned}$$

Remembering the law for the charge:

$$\begin{aligned}
q &= q_0 e^{-U/E} \implies \\
\frac{dq}{q} &= -\frac{dU}{E} \implies \delta \left(\frac{dq}{q} \right) = -dU \delta \frac{1}{E} = \\
&= -dU / (2n+1) \hbar \omega_0 \quad (11)
\end{aligned}$$

We have the result by combining eq.10,11 :

$$-\frac{\delta \left(\frac{dq}{q} \right) dV'}{N'} = \frac{\delta(dV')}{N_0} \quad (12)$$

Transforming eq.5 and since $dU=0$ (we measure in the same potential alright:

$$\delta \left(\frac{d'Q}{Q_0} \right) = \delta \left(\frac{dq}{q} \right) = \delta \left(\frac{P dV'}{Q_0} \right) \quad (13)$$

Combining eq.12 with eq.13 , using eq.8 we arrive at:

$$\delta(dV') = \frac{\delta(PdV')dV'}{Q_0N'} \implies$$

$$\delta(dV') = \frac{\delta(PdV')d(\delta V')}{Q_0} \quad (14)$$

In order for equation 14 to be correct Pressure should be kept constant and then:

$$n = \frac{Pd(\delta V')}{Q_0} \quad (15)$$

Of course Q_0 is the quantum of energy and dividing $\delta(E)$ by it we have integer again in this representation as well, in general. Pressure remains the same since we used the same representation of ψ_1 . I left out the units for a moment but that should explain the whole result.

$$PdV' = nN'Q_0 \quad (16)$$

Thus we have determined the changed volume as a function of the pressure we kept constant (we chose steady ψ_1 and pressure therefore). Indeed there is the obvious solution (but is it the only one?)

$$\frac{V_1}{V_2} = \frac{N_1}{N_2} \quad (17)$$

We could consider then N as the volume of the system in a way.

Psi = Pounds (per) Square Inch

$$\hbar = \frac{h}{2\pi} = h \text{ bar} . \quad \text{One bar} = 10^5 \text{ N/m}^2 \approx 1 \text{ Atmosphere}$$