Comments on the 'Principle of maximum physical hardness'

In a recent paper, Pearson[1] analyses the proof of Parr and Chattaraj[2] (PC) for the principle of maximum chemical hardness. He argues that the proof is very general and can also be applied to many observables, other than softness. In particular, using the equation (11) of PC (equation (1) below), he claims to prove the principle of maximum physical hardness. Thus two principles are claimed to be true – one of maximum physical hardness, and the other of maximum chemical hardness.

It is the aim of this letter to show that the arguments of Pearson[1] and those of PC[2] are in error. We have already commented[3] on the paper of PC[2] and have given a numerical counterexample, which shows that their proof of the principle of maximum chemical hardness is in error. See also the recent paper of Chattaraj, Liu and Parr[4] which says, 'Recently it has been correctly pointed out[3] that the proof by two of us[2] of the maximum hardness principle is not true in general'. Here we point out why the method adopted by Pearson is incorrect.

As the derivation given by Pearson[1] is based upon that of PC, we consider the arguments given by them. They consider a non-equilibrium ensemble with the distribution $F(\mathbf{r}^N, \mathbf{p}^N)$ and denote the time-dependent expectation value of any observable A by $\bar{A}(t)$. That is, $\bar{A}(t) = \int d\mathbf{r}^N \int d\mathbf{p}^N A(t) F(\mathbf{r}^N, \mathbf{p}^N)$. They claim that for a class of $F(\mathbf{r}^N, \mathbf{p}^N)$,

$$\bar{A}(0) = \langle A \rangle + \langle A \rangle^{-1} \langle (A - \langle A \rangle)^2 \rangle. \qquad (1)$$

Equation (1) is just the equation (5) of Pearson[2] (equation (11) of PC), rewritten in a slightly different manner. A simple argument is enough to convince the reader that this equation cannot be correct. The left hand side of the equation depends on the non-equilibrium ensemble that one chooses while the right hand side has only equilibrium expectation values in it! In fact, the result of PC is valid specifically for the ensemble, $F(\mathbf{r}^N, \mathbf{p}^N) = \langle A \rangle^{-1} A f(\mathbf{r}^N, \mathbf{p}^N)$, where $f(\mathbf{r}^N, \mathbf{p}^N)$ is the distribution function for the equilibrium ensemble, as may be seen from the equation (8) of PC. Calculating $\bar{A}(0)$ with this gives $\bar{A}(0) = \langle A^2 \rangle / \langle A \rangle$, which is equal to the right hand side of the equation (1), thus verifying the equation (1) for just this particular ensemble. But that does not make the result valid for an arbitrary non-equilibrium ensemble. If in the true spirit of linear response theory, one follows the section 8.5 of the book by Chandler[5] and takes the non-equilibrium ensemble to be proportional to $e^{-\beta(H + \Delta H)}$, with H being the Hamiltonian, and $\Delta H = -fA$, where f is an applied field that couples to A, then one obtains

$$\bar{A}(0) = \langle A \rangle + \beta f \langle (A - \langle A \rangle)^2 \rangle. \qquad (11)$$

As one can choose the coupling field f arbitrarily, it is clear that one does not have any inequality of form $\bar{A}(0) \geq \langle A \rangle$, as claimed by Pearson[2]. As the inequality is not valid, one must clearly view the results obtained by Pearson with caution.

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Biobatteries to utilize bioenergy from fruit and vegetable wastes

Biomass and biowastes represent a large potential energy resource that is renewable on a sustained basis[1]. Production of energy from biomass and biowaste resources became globally popular because of decreasing fossil energy supplies and increasing cost and demand for energy, a growing awareness of environmental impact associated with fossil fuel usage as well as surplus global biomass production and potential resource of biowaste produce[2]. Several research studies[3–7] have highlighted production of solid, liquid and gaseous fuels from biomass and agricultural waste produce. In the recent past, generation of electricity from biowaste materials and/or municipal garbage was also made possible by converting the waste materials into biogas which in turn was used for the production of electricity based on the most advanced turbine technology[2].

Although Hwang *et al.*[8] developed the concept of biocells, later led to their preparation using bacterial membranes and platinum–silver electrodes to generate voltage in light[9], attempts to produce electric power directly by electrochemical method from biowaste resources have been limited. Low power dry cells, which are widely used for calculators, wall clocks, video game toys, etc. are now becoming expensive and often non-available in time at village level. Therefore, we have attempted to prepare biobatteries utilizing commonly-available domestic biowaste materials and to use them in low voltage appliances as alternatives to the conventional low power dry cells (batteries).

Ripe banana and orange peels or vegetable scrap, which are thrown as domestic waste (garbage) were collected and macerated into a fine paste without adding water. Pieces of copper and zinc sheets (0.5 mm thickness) were collected from metal scrap merchants. Copper and zinc plates measuring 10 cm^2 (4 cm × 2.5 cm) area were cut and selected as electrodes. Each electrode was connected with a short piece of insulated wire through a small hole made at one end of each electrodes. Electrodes were inserted into about 20 g of paste of fruit or vegetable waste taken in (30 ml) plastic vials. Similarly electrodes were inserted directly into fresh and intact vegetables/fruits used in this study (Table 1) to make biobatteries. Electric potential generated in each battery was measured by multimeter on DC mode. Each biobattery was found to produce a low voltage power measuring 0.5–0.8 V and 0.2–1.4 mA (Table 1). Therefore a number of biobatteries were connected in series to increase the voltage output. Cumulative output of power generated in 2–4 biobatteries prepared with paste of ripened banana fruit peels was applied to wall clocks or calculators or video game toys through suitable connections using insulated electric wire and was found to make them function without using conventional low power dry cells. Life/durability of newly-constructed biobatteries was assessed by measuring output of power generated in biobatteries at regular time intervals over a period of four weeks and/or using them continuously for wall clocks or calculators. It was found that these batteries exhibited potential and were found functional over a substantial period of time (more than four weeks) without changing electrodes or electrolytic medium (Table 2). Further, it was found that performance of biobatteries could be improved by frequent cleaning of electrodes with water and without disturbing electrolytic medium. The results showed that among the electrolytic media tested, the paste of ripened banana fruit peels with copper–zinc electrode combination was found effective for the performance of biobatteries. Studies on the evaluation of factors influencing the performance of biobatteries show that the size and quality of both electrodes and medium of electrolyte are important. Further, studies on chemical analysis of electrolyte viz. the paste of fruit and/or vegetable wastes used in biobatteries would be useful to understand the electrochemical mechanism(s) underlying the production of low voltage power in these biobatteries. However, further work on design and construction of biobatteries with different electrode combinations is needed to make them handy, durable and popular.

Table 1. Output of power generated in biobatteries prepared from different plant materials (fruits and vegetables). Measurements of power generated in each type of biobattery were repeated on batteries which were constructed using fresh samples of the same material and with the same set of electrodes. Data represent the mean ± SD of at least five measurements made on different batteries

	Power output of biobattery	
Material used	Volts	mA
Brinjal	0.60 ± 0.08	0.52 ± 0.08
Cabbage	0.68 ± 0.06	0.24 ± 0.06
Carrot	0.60 ± 0.09	0.21 ± 0.05
Cattle dung (gobar)*	0.66 ± 0.08	0.98 ± 0.16
Lemon (ripened)	0.76 ± 0.05	0.57 ± 0.07
Orange (peels)	0.64 ± 0.12	1.04 ± 0.10
Banana fruit (peels)	0.74 ± 0.05	1.33 ± 0.12
Potato	0.62 ± 0.05	0.72 ± 0.05
Raddish	0.58 ± 0.08	0.69 ± 0.04
Sweet potato	0.56 ± 0.08	0.92 ± 0.06
Tomato (ripened)	0.62 ± 0.12	1.15 ± 0.16
Vegetable scrap**	0.60 ± 0.10	0.96 ± 0.08

*Represent livestock waste biomass.

**Represent vegetable waste biomass from kitchen.

Table 2. Performance and/or durability assessment of biobatteries prepared from peels of ripened banana fruit. Measurements of cumulative output of power generated from three biobatteries which were connected continuously in series to wall clock to make it work were made at weekly intervals over a period of four weeks. Data represent the mean ± SD of three replicated measurements

Time of measurement (weeks)*	Power output	
	Volts	mA
0	1.97 ± 0.15	1.36 ± 0.12
1	1.92 ± 0.11	1.27 ± 0.09
2	1.85 ± 0.09	1.24 ± 0.15
3	1.80 ± 0.10	1.20 ± 0.08
4	1.69 ± 0.12	1.13 ± 0.09

*Weeks after preparation of biobatteries.

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