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A comparison of some efficiency factors in photovoltaics

P T Landsberg†, A De Vos‡ and P Baruch§

† Faculty of Mathemetical Studies, Southampton University, Southampton SO9 5NH, UK

‡ Laboratorium voor Elektronika en Meettechniek, State University of Gent, Belgium

§ Groupe de Physique des Solides, associé au CRNS, Université Paris 7, France

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Abstract. Shockley and Queisser, in their fundamental paper, defined an 'ultimate efficiency' $\eta_{\rm ult}$, as the ratio of electrical output power (assuming the voltage factor and the fill factor to be unity) to the radiative input power (assuming maximum light concentration) in an ideal solar cell.

We here discuss this efficiency factor for a general density of states $g(x)$, where $x = h\nu/kT_{\rm p}$ and $T_{\rm p}$ is the pump temperature. Its maximum with respect to variations of the bandgap $E_{\rm g}$ occurs at a certain value of $E_{\rm g}$, say $E_{\rm g0}$, yielding $\eta_{\rm ult}(x_{\rm g0})$, where $x_{\rm g0} \equiv E_{\rm g0}/kT_{\rm p}$. The efficiency η of a simple solar cell in the presence of surroundings at temperature $T_{\rm s}$ is proportional to $\eta(T_{\rm p}, T_{\rm s}) \boxminus \int_{x_{\rm g}}^{\infty}\{[1/(\exp(x)-1)]-[1/(\exp(((x-v)/T_{\rm s})T_{\rm p})-1)]\}g(x)\,{\rm d}x$. Its maximum with respect to $x_{\rm g}$ and v is $\eta_{\rm max}(T_{\rm p}, T_{\rm s})$. We show here that the Shockley–Queisser efficiency is the same as $\eta_{\rm max}$, provided the ambient is set at absolute zero of temperature: $\eta_{\rm ult}(x_{\rm g0}) = \eta_{\rm max}(T_{\rm p}, 0)$.

Comments are also made on: (i) the possibility of several maxima of $\eta_{\rm ult}(x_{\rm g0})$ for certain appropriately chosen $g(x)$; and (ii) its dependence on the number of dimensions $n = 1, 2, 3, 4, \ldots, \infty$: $29, 39, 44, 48, \ldots, 100\%$, if $g(x)$ is chosen as if due to an n-dimensional cube.

1. Introduction

A widely used and cited method for obtaining an approximate estimate for solar energy conversion is associated with the excellent paper by Shockley and Queisser [1]. Nonetheless we have to point out again, as was done earlier [2], that the method was employed six years earlier by Trivich and Flinn [3], for which they have not received the credit that might have been expected.

In the present paper we make three points:

(i) The approximate procedure of Trivich, Flinn, Shockley and Queisser (TFSQ) gives the results of more accurate calculations in the limit when the ambient and cell temperature (assumed to be equal at $T_{\rm s}$) is approximated by 0 K. As in the Carnot theory, this gives the highest efficiency of the whole range of efficiencies generated by all possible cell or ambient temperatures ($T_{\rm s}$) lying below the pump or sun temperature ($T_{\rm p}$).

(ii) The TFSQ result (here equation (3)) can yield several maxima for certain incident spectra $g(x)$. The highest of these is then the true (global) maximum efficiency furnished by this method.

(iii) The standard TFSQ result is valid for radiation in three dimensions. The present paper gives a generalization for an arbitrary number of dimensions.

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2. The TFSQ argument and photovoltaics

The usual TFSQ argument for the maximum efficiency of a photovoltaic device goes as follows. Let $x = h\nu/kT_{\rm p}$, where $T_{\rm p}$ is the pump temperature, e.g. the temperature of solar radiation received on earth. Let $g(x)\,{\rm d}x$ be the number of photon states between x and $x + {\rm d}x$, multiplied by a constant so that $g(x)$ represents a number flux. Let $x_{\rm g}$ be the energy gap $E_{\rm g}$ divided by $kT_{\rm p}$. Further, let

$$f(x) = 1/(\exp(x) - 1) \tag{1}$$

be the equilibrium photon number in one radiation mode. Then we assume that the pump surrounds the cell and that each absorbed photon contributes the energy gap to the photovoltaic energy output. The so-called 'ultimate' efficiency of the device is then

$$\eta_{\rm ult}(x_{\rm g}) = x_{\rm g} \int_{x_{\rm g}}^{\infty} g(x) f(x)\,{\rm d}x \Big/ D \tag{2}$$

where we have divided by

$$D = \int_0^{\infty} x g(x) f(x)\,{\rm d}x$$

i.e. the input energy flux $\Phi_{\rm p}$ divided by $kT_{\rm p}$:

$$D = \Phi_{\rm p}/kT_{\rm p}.$$

We would like to warn the reader that the name 'ultimate efficiency' is somewhat misleading, as it takes into account the first law of thermodynamics, but not the second law. We prefer to call it an *efficiency factor* instead of an *efficiency*. It only deserves the name *efficiency*, if the other efficiency factors, i.e. voltage factor and fill factor in present-day terminology (the latter being called impedance matching factor by Shockley and Queisser (SQ), the former, i.e. $qV_{\rm OC}/E_{\rm g}$, having not received a particular name from SQ) are equal to unity.

Since $\eta_{ult}(0) = 0$ and $\eta_{ult}(+\infty) = 0$, a maximum ultimate efficiency exists at $x_{\rm g} = x_{\rm g0}$, say, such that $0 < x_{\rm g0} < +\infty$. One finds that $x_{\rm g0}$ must divide the function $g(x)f(x)$ into two parts, so that the rectangle $x_{\rm g0}g(x_{\rm g0})f(x_{\rm g0})$ to the left of $x_{\rm g} = x_{\rm g0}$ has the same area as that found under the curve to the right of $x_{\rm g0}$, i.e.

$$x_{\rm g0} g(x_{\rm g0}) f(x_{\rm g0}) = \int_{x_{\rm g0}}^{\infty} g(x) f(x)\,{\rm d}x. \tag{3}$$

In fact (3) is an idealization of the general equation

$$x_{\rm g0} q(x_{\rm g0}) g(x_{\rm g0}) f(x_{\rm g0}) = \int_0^{\infty} q(x) g(x) f(x)\,{\rm d}x$$

where $q(x)$ is the quantum efficiency of the photovoltaic device, i.e. absorption efficiency times collection efficiency. Equation (3) is deduced from this general condition

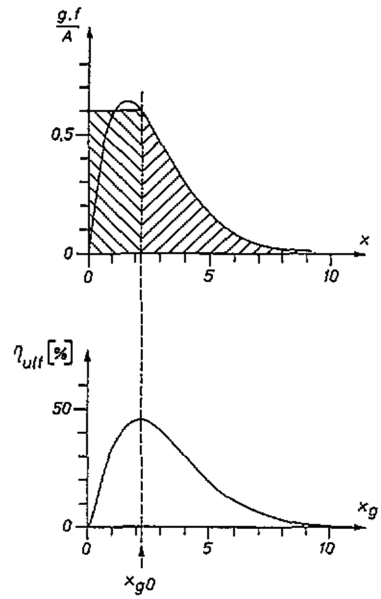

Figure 1. The classical function $x^2f(x)$, given by (1) and (4), and the corresponding function $\eta_{ult}(x_g)$, given by (2).

by putting $q(x)$ equal to zero beneath the bandgap and equal to unity above the bandgap.

Figure 1 shows the classical spectrum $g(x)f(x)$, where $g(x)$ is given by the traditional expression

$$g(x) = Ax^2 \tag{4}$$

where A is a constant. The corresponding curve $\eta_{ult}(x_g)$ is also displayed. It shows the well known maximum of 44% at x_g equal to $x_{g0} = 2.2$.

As pointed out in the introduction, equation (3) can yield several maxima x_{g0}. For example, we can replace (4) by

$$g(x) = A\left(\frac{x-\xi}{x+\xi}\right)^2 x^2$$

which has the same behaviour as (4) for both small and large x:

$$g(x) \approx Ax^2 \qquad \text{for } x \ll \xi$$

and

$$g(x) \approx Ax^2 \qquad \text{for } x \gg \xi.$$

The corresponding spectrum $g(x)f(x)$ can be interpreted as a black-body-like spectrum with an attenuation band around $x = \xi$. Now two maxima occur in the $\eta_{ult}(x_g)$ curve (provided ξ is chosen sufficiently large). What is more—for the particular value $\xi = 3.17$ both maxima are equal. This is illustrated in figure 2 for x_{g0} and x'_{g0}.

As pointed out by Dr R Förster (Humboldt Universität, Berlin), the function

$$g(x)f(x) = Ax^{-2}$$

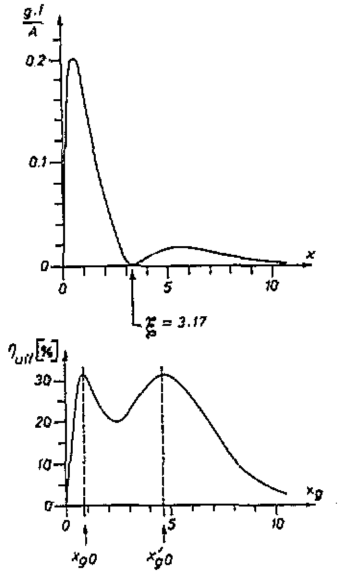

Figure 2. A possible function $g(x)f(x)$ and the corresponding function $\eta_{\rm ult}(x_{\rm g})$.

even satisfies the condition (3) at every point of the curve, suggesting an ultimate efficiency independent of bandgap. Since D diverges in this case, this example is, however, not physically meaningful.

Substituting (3) into (2), the maximum efficiency is

$$\eta_{\rm ult}(x_{\rm g0}) = x_{\rm g0}^2 g(x_{\rm g0}) f(x_{\rm g0})/D \tag{5}$$

where $x_{\rm g0}$ has to be substituted from the solution of (3).

In order to compare this approximate, but rather general, treatment with a more exact one, we shall consider the case of one-dimensional photovoltaics, where the exact calculation can be readily made analytically. One finds [4] for the exact value

$$\eta_{\max}\left(\frac{T_{\rm s}}{T_{\rm p}}\right) = 6\left[\frac{\log(2)}{\pi}\left(1 - \frac{T_{\rm s}}{T_{\rm p}}\right)\right]^2 \tag{6}$$

of relevance in the framework of noise in optic fibers and in electrical networks. On the other hand the fact that $g(x) = A$, means that (3) becomes

$$\frac{x_{\rm g0}}{\exp(x_{\rm g0}) - 1} = \log\left[\frac{1}{1 - \exp(-x_{\rm g0})}\right]$$

and hence

$$x_{\rm g0} = \log(2).$$

Substitution into (5) yields

$$\eta_{\rm ult}(x_{\rm g0}) = 6[\log(2)/\pi]^2. \tag{7}$$

One sees from (6) and (7) that

$$\eta_{\mathrm{max}}(0) = \eta_{\mathrm{ult}}(x_{\mathrm{g0}}). \tag{8}$$

Formula (8) can be interpreted as follows: in the limit for T_s going to 0 K, the *efficiency* η_{max} becomes equal to the *efficiency factor* η_{ult}. This is easily understood, by remarking that for $T_s = 0$, the two other efficiency factors, i.e. the voltage factor qV/E_g and the fill factor $(IV)_{\mathrm{max}}/I_{\mathrm{SC}}V_{\mathrm{OC}}$, are both unity. Here SC and OC refer to short-circuit and open-circuit conditions, respectively.

We now show that the result (8) has more general validity. For this we need to obtain an expression which has the general validity of (5) for the left-hand side of (8).

3. The general efficiency

In order to estimate the efficiency of the energy conversion in photovoltaics, we need an expression for the radiative energy flux Φ_p, which arrives from the pump. For simplicity we again assume that the pump surrounds the converter. If V denotes the voltage generated across the device, the current density $j(V)$ equals q times the number flux of electron–hole pairs which are generated by the incident radiation, reduced by the number flux of electron–hole pairs which recombine in order to produce the thermal emission from the cell. This is

$$I(V) = q \int_{x_g}^{\infty} \left[\frac{1}{\exp(x) - 1} - \frac{1}{\exp((T_p(x - v))/T_s) - 1} \right] g(x)\, \mathrm{d}x \tag{9}$$

where v equals qV/kT_p. The expression for the second term has been discussed in various references [5–8]. Thus the energy flux output is $VI(V)$, and therefore the efficiency is

$$\eta(v) = \frac{VI(V)}{q\Phi_p} = \frac{v}{D} \int_{x_g}^{\infty} \left[\frac{1}{\exp(x) - 1} - \frac{1}{\exp((T_p(x - v))/T_s) - 1} \right] g(x)\, \mathrm{d}x. \tag{10}$$

This is the required expression.

Maximizing first with respect to x_g, i.e.

$$\left[\frac{\partial \eta(v)}{\partial x_g} \right]_v = 0$$

leads to a remarkably simple optimum value of x_g, say x_{g1}, given by

$$x_{g1} = v/(1 - T_s/T_p).$$

The efficiency, optimized with respect to x_g, is

$$\eta = \frac{v}{D} \int_{v/(1-T_s/T_p)}^{\infty} \left[\frac{1}{\exp(x) - 1} - \frac{1}{\exp((T_p(x - v))/T_s) - 1} \right] g(x)\, \mathrm{d}x.$$

Optimization with respect to $v = (1 - T_s/T_p)x_{g1}$ is needed next. Thus

$$\mathrm{d}\eta/\mathrm{d}x_{g1} = 0$$

is needed, and gives

$$\frac{\mathrm{d}}{\mathrm{d}x_{g1}} x_{g1} \int_{x_{g1}}^{\infty} \left[\frac{1}{\exp(x) - 1} - \frac{1}{\exp((T_p(x - x_{g1}))/T_s) + x_{g1}) - 1} \right] g(x)\,\mathrm{d}x = 0. \tag{11}$$

This equation generalizes expression (3). The condition has the form

$$\frac{\mathrm{d}}{\mathrm{d}y} y \int_y^{\infty} [f(x) - h(x)] g(x)\,\mathrm{d}x = 0 \tag{12}$$

where the second term in the square brackets of (11) has been denoted by $h(x)$. Since $x > x_{g1}$, $h(x)$ vanishes in the limit $T_s \to 0$. In this limit the condition for maximum efficiency is precisely that which would be derived for the maximum of the ultimate efficiency (2) with respect to x_g. The optimum value of y is therefore the value which has been denoted by x_{g0}, and for $T_s \to 0$

$$\eta_{\max} = \frac{x_{g0}}{D} \int_{x_{g0}}^{\infty} g(x) f(x)\,\mathrm{d}x$$

where x_{g0} is given by (3). This means that (8) has been generalized to

$$\eta_{\max} = \eta_{\mathrm{ult}}(x_{g0}). \tag{13}$$

If one takes account of the limited solid angle subtended by the sun at the earth the argument is not significantly altered. It can be taken care of by an additional constant factor in equations (2), (5), (6) and (7) and in the first terms only of equations (9)–(12). The radiation from the rest of the surroundings should then also be taken into account (see, for instance [9–11]), but it is often negligible.

4. The dependence of the TFSQ optimum gap on the number of dimensions

The previous discussion leads to the following academic question concerning photovoltaics in n dimensions. In this case $f(x)$ is still given by (3), but

$$g(x) = A_n x^{n-1}$$

a generalization of the traditional

$$g(x) = A_3 x^2.$$

Here A_n is a constant arising from the number of modes of radiation in n dimensions. Although the explicit value of A_n can be calculated [12], we do not need it here, as it cancels out of the relevant equations (2) and (10).

We consider equation (2) maximized with respect to x_g. If the symbol a is used for x_{g0}, then

$$\eta_{ult}(a) = \frac{a}{\Gamma(n+1)\zeta(n+1)} \int_a^\infty \frac{x^{n-1}\,dx}{\exp(x)-1}. \tag{14}$$

This is the maximized ultimate efficiency for the case of negligible non-radiative recombination, incident black-body radiation, $T_s = 0$ and n dimensions, when a is a solution of

$$\frac{a^n}{\exp(a)-1} = \int_a^\infty \frac{x^{n-1}\,dx}{\exp(x)-1}. \tag{15}$$

For the same conditions the exact efficiency (10) gives

$$\eta(V) = \frac{qV}{kT_p\Gamma(n+1)\zeta(n+1)} \int_{x_g}^\infty \frac{x^{n-1}\,dx}{\exp(x)-1} \tag{16}$$

which is the same as (14) provided qV is taken as the energy gap E_g and x_g is replaced by x_{g0}. But this is irrelevant; the point of section 3 was to show that the *maximum* of (16) agrees with the result of (14) and (15) (as expressed in (13)). For $n = 1$ the whole matter is clear and has been summarized in section 2. We now ask for the value of a, as given by (15), in the limit of large n.

Substitution of $z = x/a$ converts (15) to

$$\int_1^\infty \frac{z^{n-1}\,dz}{\exp(az)-1} = \frac{1}{\exp(a)-1}.$$

Writing

$$r(z) = (n-1)\log(z) - az$$

and

$$s(z) = 1/(1-\exp(-az))$$

condition (15) is

$$\int_1^\infty \exp[r(z)]s(z)\,dz = \frac{1}{\exp(a)-1}. \tag{17}$$

The Laplace approximation of the integral is

$$\left[\frac{-2\pi}{r''(b)}\right]^{1/2} \exp[r(b)]s(b) \tag{18}$$

where b denotes the value of z for which $r(z)$ is maximum, which must lie in the range of integration. In the present case

$$b = (n-1)/a$$

such that

$$r(b) = (n-1)[\log(n-1) - \log(a) - 1] \qquad r''(b) = -a^2/(n-1)$$

and

$$s(b) = \frac{1}{1-\exp[-(n-1)]}. \tag{19}$$

Substituting (19) in (18) yields the following value of the integral:

$$\frac{(2\pi)^{1/2}}{a} \frac{\exp[(n-\frac{1}{2})\log(n-1) - (n-1)(\log(a)+1)]}{1-\exp[-(n-1)]}.$$

Substitution into condition (17) and subsequent inversion of both sides gives the following equation for a:

$$\exp(a) = \frac{a}{(2\pi)^{1/2}} \frac{1-\exp[-(n-1)]}{\exp[(n-\frac{1}{2})\log(n-1) - (n-1)(\log(a)+1)]} + 1.$$

Taking logarithms and using expansions of the type $\log(1+\epsilon) = \epsilon - \frac{1}{2}\epsilon^2 + \frac{1}{3}\epsilon^3$ when ϵ is small, the equation for a turns out to be

$$a/n - \log\left(\frac{a}{n}\right) = 1 + (1/2n)\log(n) + C \tag{20}$$

where

$$C \equiv \frac{1}{n^3} - \frac{1}{2n}\log(2\pi) - \frac{1}{n}\log[1-\exp(-a)] - \frac{1}{n}\log[1-\exp(-(n+1))]$$

can be neglected. The solution of (20) is

$$a \approx n - \sqrt{n\log(n)}. \tag{21}$$

To see the last step, observe from (20) that $a/n \approx 1$ for large n, so that one can put

$$a/n = 1 + \epsilon(n)$$

with $\epsilon(n) \ll 1$. Equation (20) is then

$$\epsilon - \log(1+\epsilon) \approx (1/2n)\log(n)$$

or

$$\epsilon^2(n) \approx (1/n)\log(n).$$

and one finds (21).

Numerical calculations (table 1) confirm the approximation for large n. Thus the method of TFSQ yields an optimum bandgap E_g which increases from $\log(2)\ kT_p$ for

Table 1. Check of result (21).

n	a/n from (21)	a/n numerically from (15)
1	1.000	0.693
2	0.411	0.718
3	0.395	0.723
4	0.411	0.725
10	0.520	0.729
100	0.785	0.840
1000	0.917	0.930
10^6	0.996	0.997

$n = 1$ through the well known value of 2.17 kT_p for $n = 3$ to the asymptotic value $n\ kT_\mathrm{p}$ for large n.

Applying this Laplace approximation to (14) also finally yields

$$\eta_\mathrm{ult}(a) \approx 1 - \sqrt{\frac{\log(n)}{n}}. \tag{22}$$

Again numerical calculations (table 2) confirm the asymptotic behaviour for large n. We see how η_ult increases from $6[\log(2)/\pi]^2$ for $n = 1$ through the well known TFSQ value of 44.0% for $n = 3$ to the asymptotic value 1 for large n.

Table 2. Check of result (22).

n	$\eta_\mathrm{ult}(a)$ from (22)	$\eta_\mathrm{ult}(a)$ numerically from (14)–(15)
1	1.000	0.292
2	0.411	0.385
3	0.395	0.440
4	0.411	0.477
10	0.520	0.580
100	0.785	0.799
1000	0.917	0.919
10^6	0.996	0.996

Figure 3 shows some ultimate efficiencie curves $\eta_\mathrm{ult}(x_\mathrm{g})$. We see how $a \equiv x_\mathrm{g0}$ as well as $\eta_\mathrm{ult}(a)$ increase with increasing n.

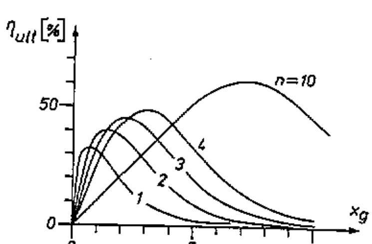

Figure 3. Some functions $\eta_\mathrm{ult}(x_\mathrm{g})$, for different number of dimensions.

5. Conclusion

The efficiency of a solar cell has here been discussed from two points of view:

(*i*) *the so-called ultimate efficiency of* SQ; *and*
(ii) a fundamental formulation of the efficiency.

The latter efficiency (ii) is always decreased by the back-radiation from the cell towards the surrounding space. If this term is reduced to zero, by assuming that the cell temperature is zero, then the maxima of (i) and (ii) with respect to the energy gap of the semiconductor are the same. This result holds for the general density of radiation modes.

The possibility of several maxima with respect to E_g in case (i) is exhibited by example. The increase of efficiency under (i) with dimensionality is also traced in detail.

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