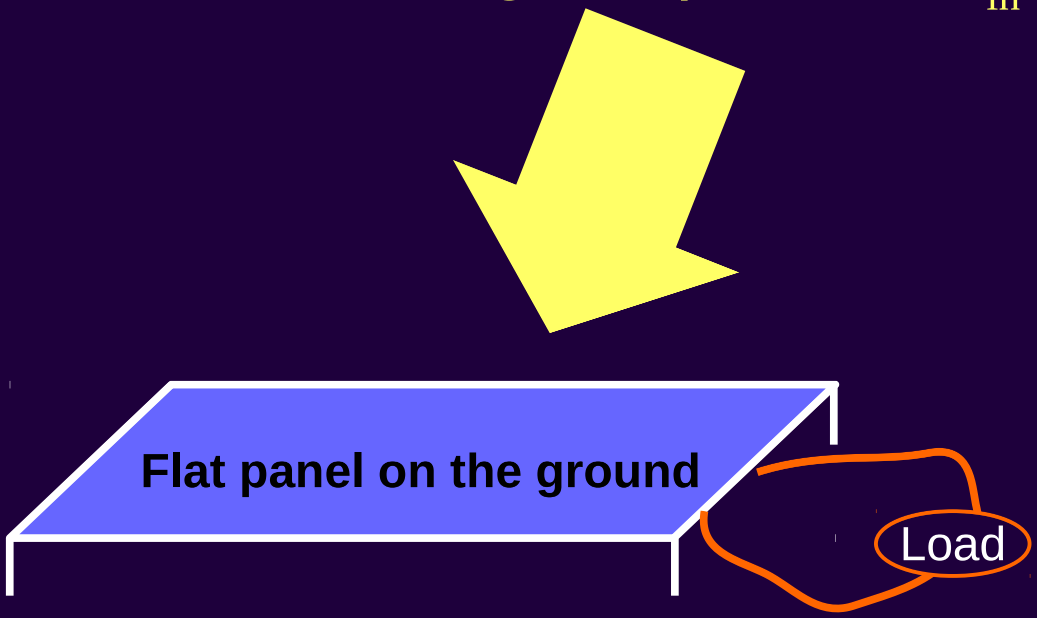
The Shockley-Queisser Limit and its Discontents

Steven Byrnes
Postdoc, Applied Physics, Harvard University
Feb. 19, 2015

steven.byrnes@gmail.com

Code to create all plots at:
http://sjbyrnes.com/sq.html

Definition of “solar cell efficiency”



Total sunlight power hitting the panel = P_{in}

Flat panel on the ground

Load

DC electric power = P_{out}

$= I \times V$

$$\boxed{\text{Efficiency} \equiv \frac{P_{\text{out}}}{P_{\text{in}}}}$$

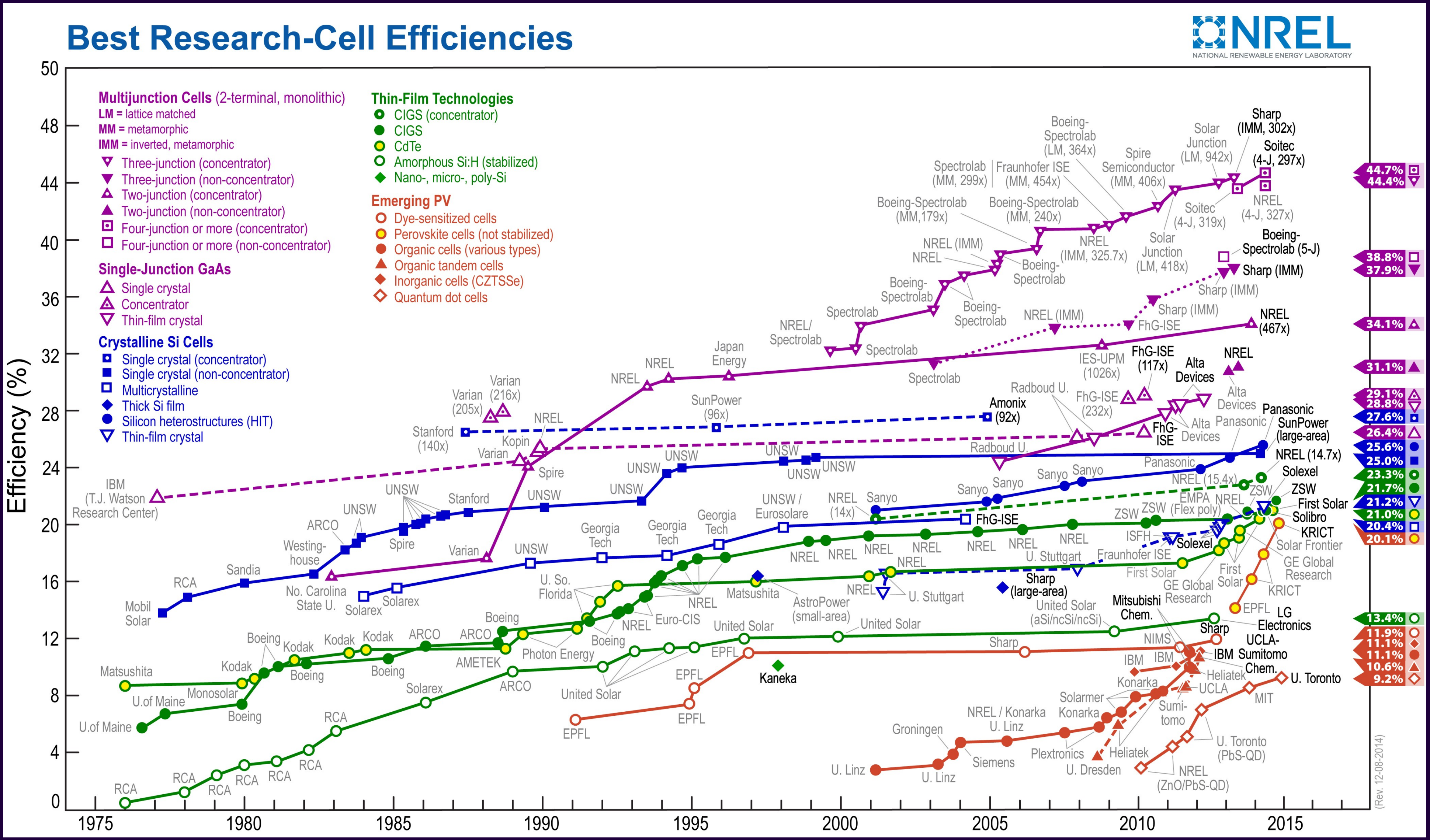
Solar cell efficiency – why it matters

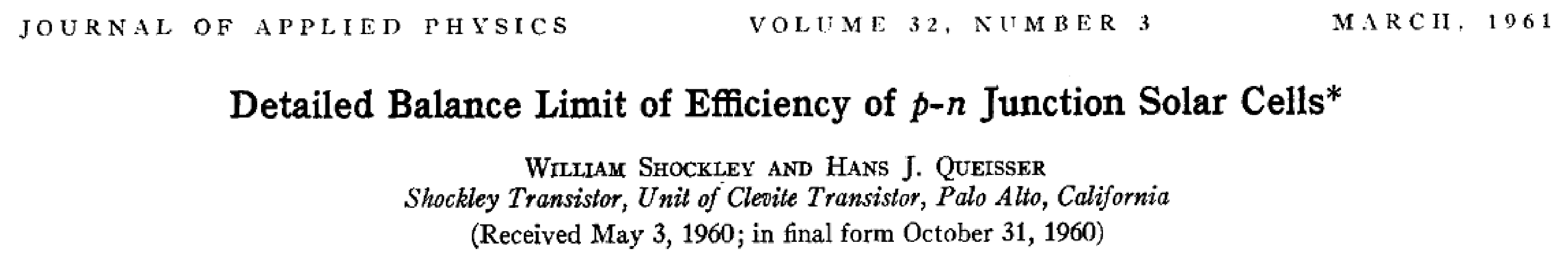
- If you replace a 15% efficient PV with a 20% efficient PV, other things equal...
  - Solar cell cost (per watt) goes down 25%
  - …

Solar cell efficiency – why it matters

- If you replace a 15% efficient PV with a 20% efficient PV, other things equal...
    - Solar cell cost (per watt) goes down 25%
    - Land acquisition cost (per watt) goes down 25%
    - Installation cost (per watt) goes down 25%
    - Cleaning cost (per watt) goes down 25%
    - Permitting cost (per watt) goes down 25%
    - …

Solar cell efficiency – why it matters



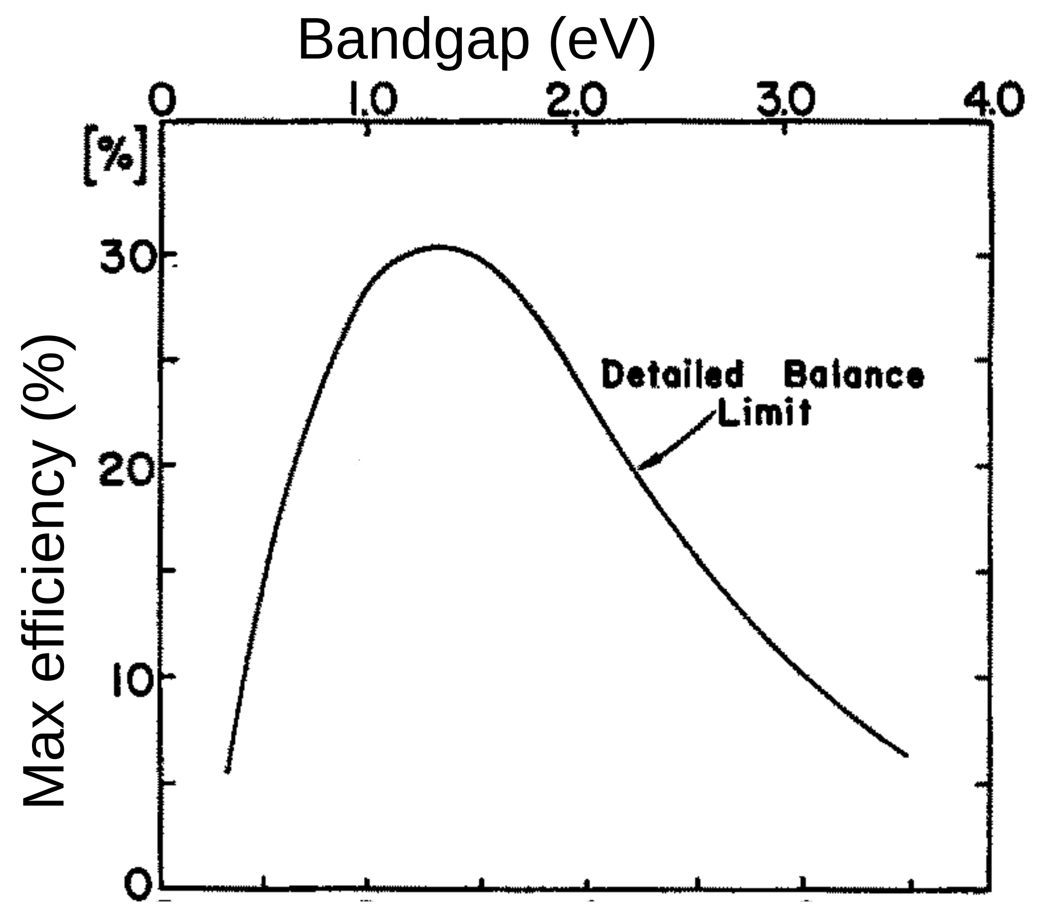


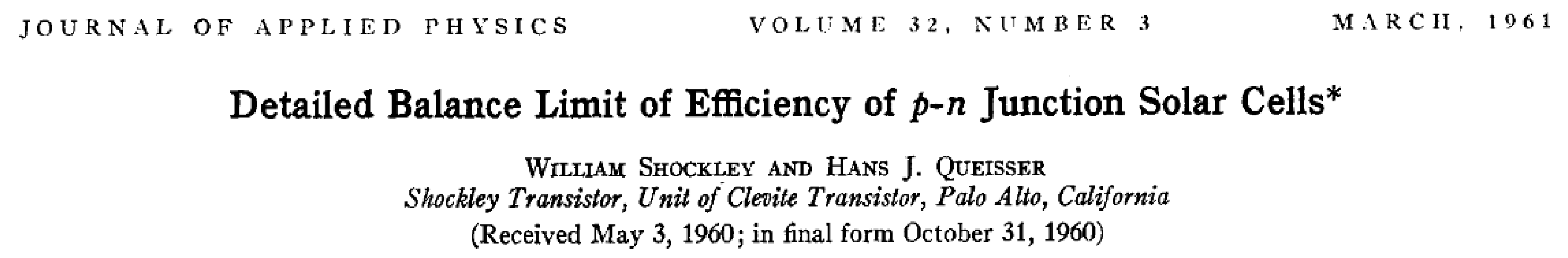
JOURNAL OF APPLIED PHYSICS VOLUME 32, NUMBER 3 MARCH, 1961

Detailed Balance Limit of Efficiency of *p-n* Junction Solar Cells*

WILLIAM SHOCKLEY AND HANS J. QUEISSER
Shockley Transistor, Unit of Clevite Transistor, Palo Alto, California

(Received May 3, 1960; in final form October 31, 1960)

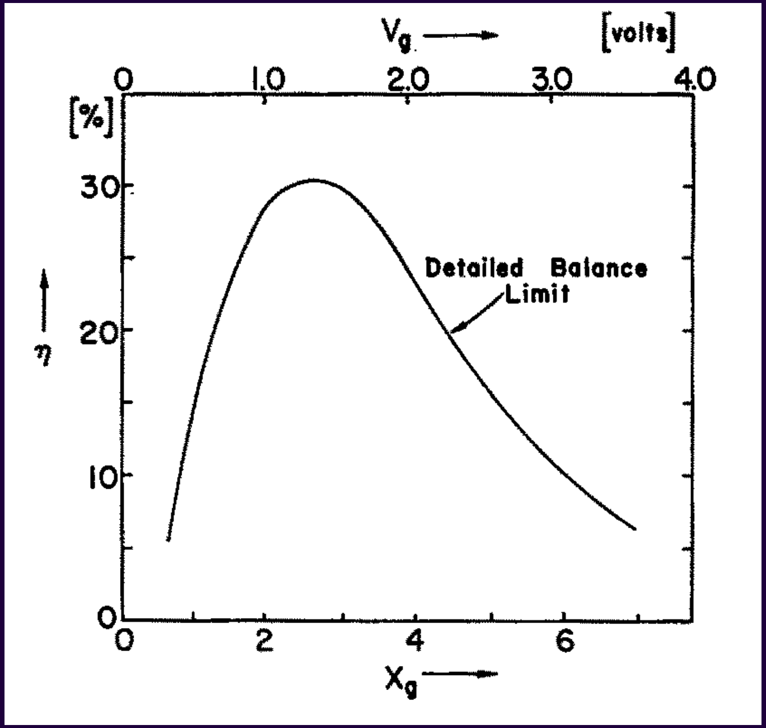




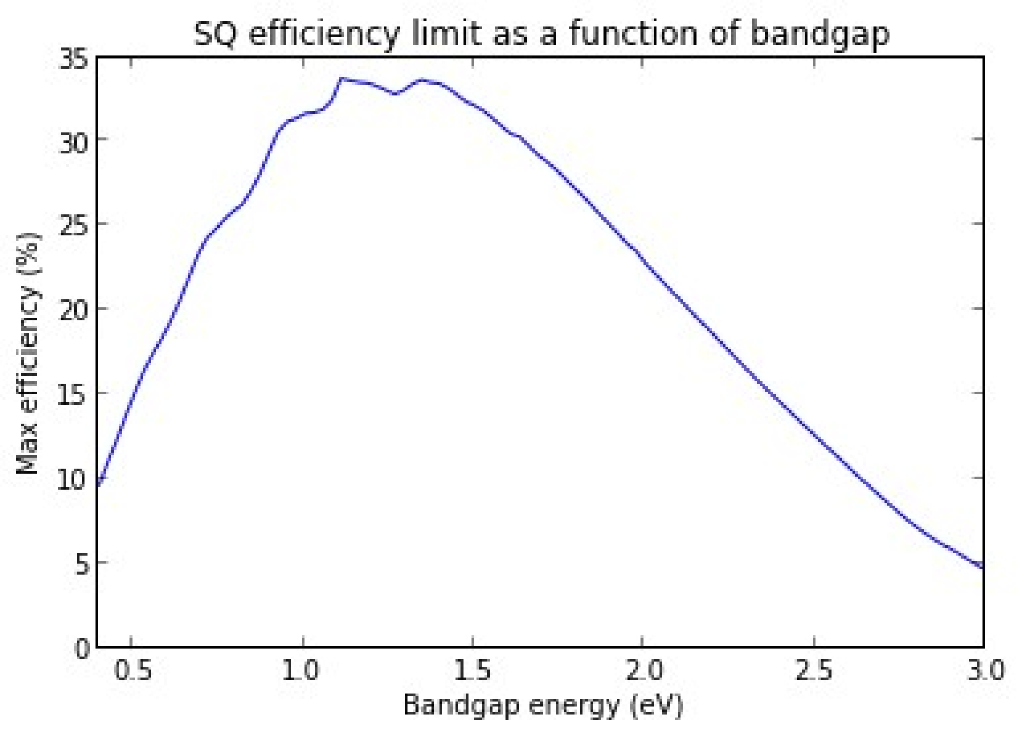
JOURNAL OF APPLIED PHYSICS VOLUME 32, NUMBER 3 MARCH, 1961

Detailed Balance Limit of Efficiency of *p-n* Junction Solar Cells*

WILLIAM SHOCKLEY AND HANS J. QUEISSER
Shockley Transistor, Unit of Clevite Transistor, Palo Alto, California
(Received May 3, 1960; in final form October 31, 1960)



In the original paper, they assumed the sun is a 6000K blackbody...


SQ efficiency limit as a function of bandgap

My reproduction, but using a realistic solar spectrum

Plan for today

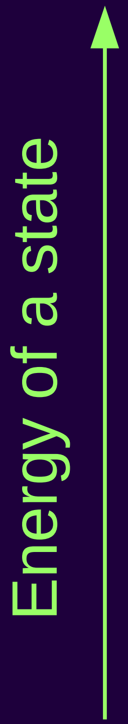
- Part 1: Go through the derivation of the Shockley-Queisser limit
  - ...assuming no prior knowledge of semiconductor device physics...
- Part 2: Tour of the various ways to exceed the limit

Electron states in solids

Every solid has a very large number of “electron states”

At any given time, each electron state is either empty or occupied by 1 electron.

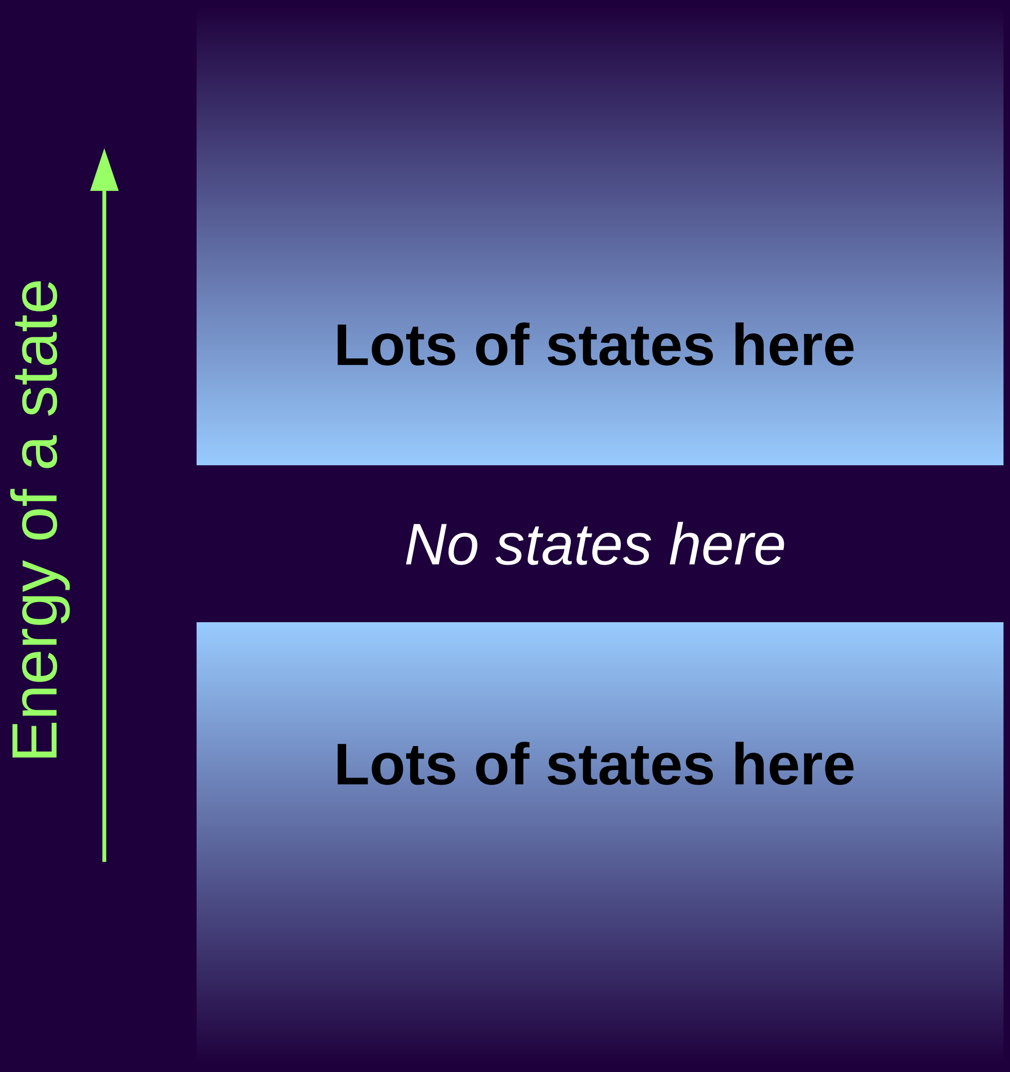
(Like a walk-up apartment building.)



Some states takes a lot of energy to occupy. Usually they are empty, especially at low temperature.

Other states take very little energy to occupy. Usually they are full.

Electron states in an inorganic semiconductor



Energy of a state

Lots of states here

“Conduction band”

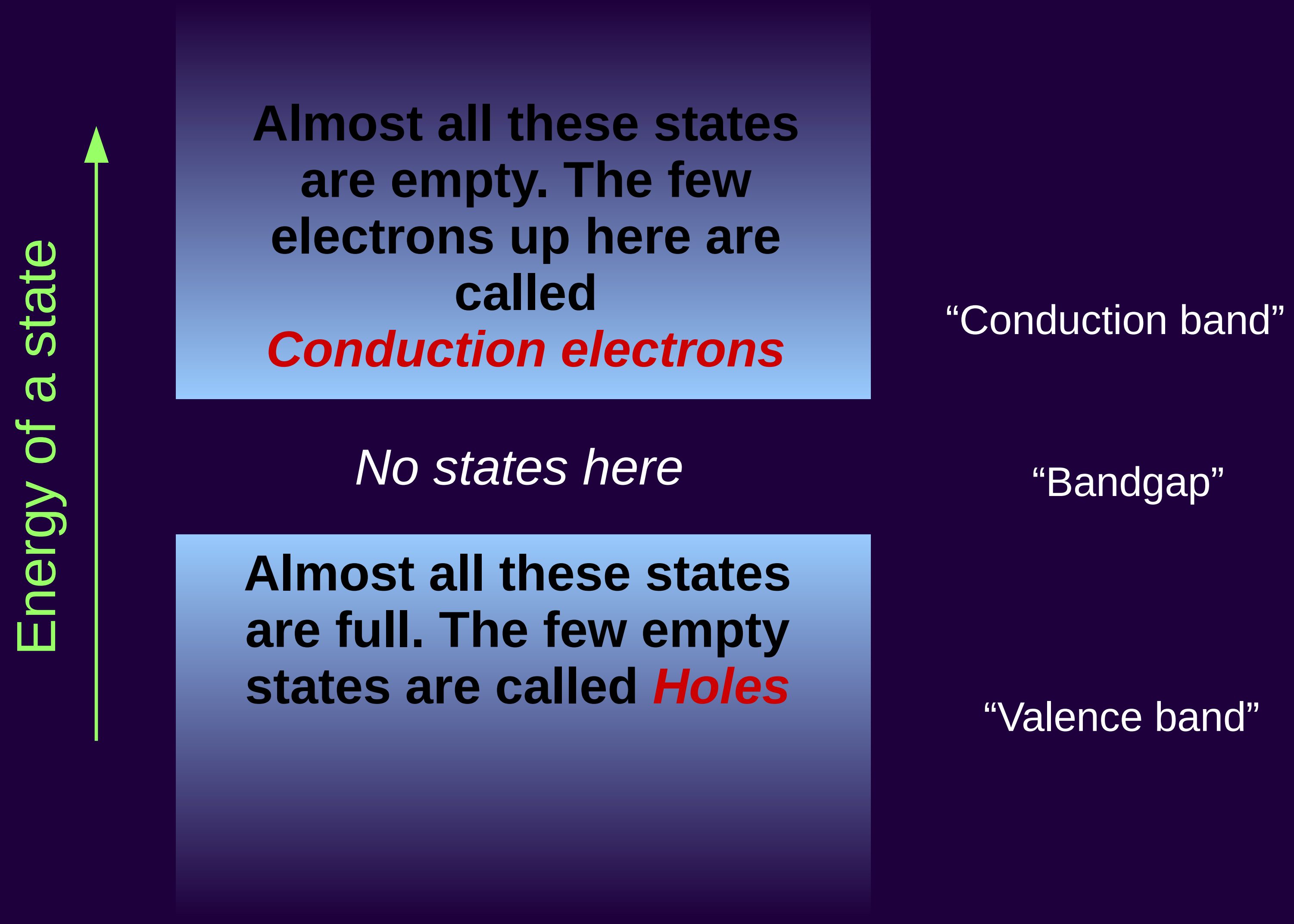
No states here

“Bandgap”

Lots of states here

“Valence band”

Electron states in an inorganic semiconductor



Almost all these states are empty. The few electrons up here are called ***Conduction electrons***

"Conduction band"

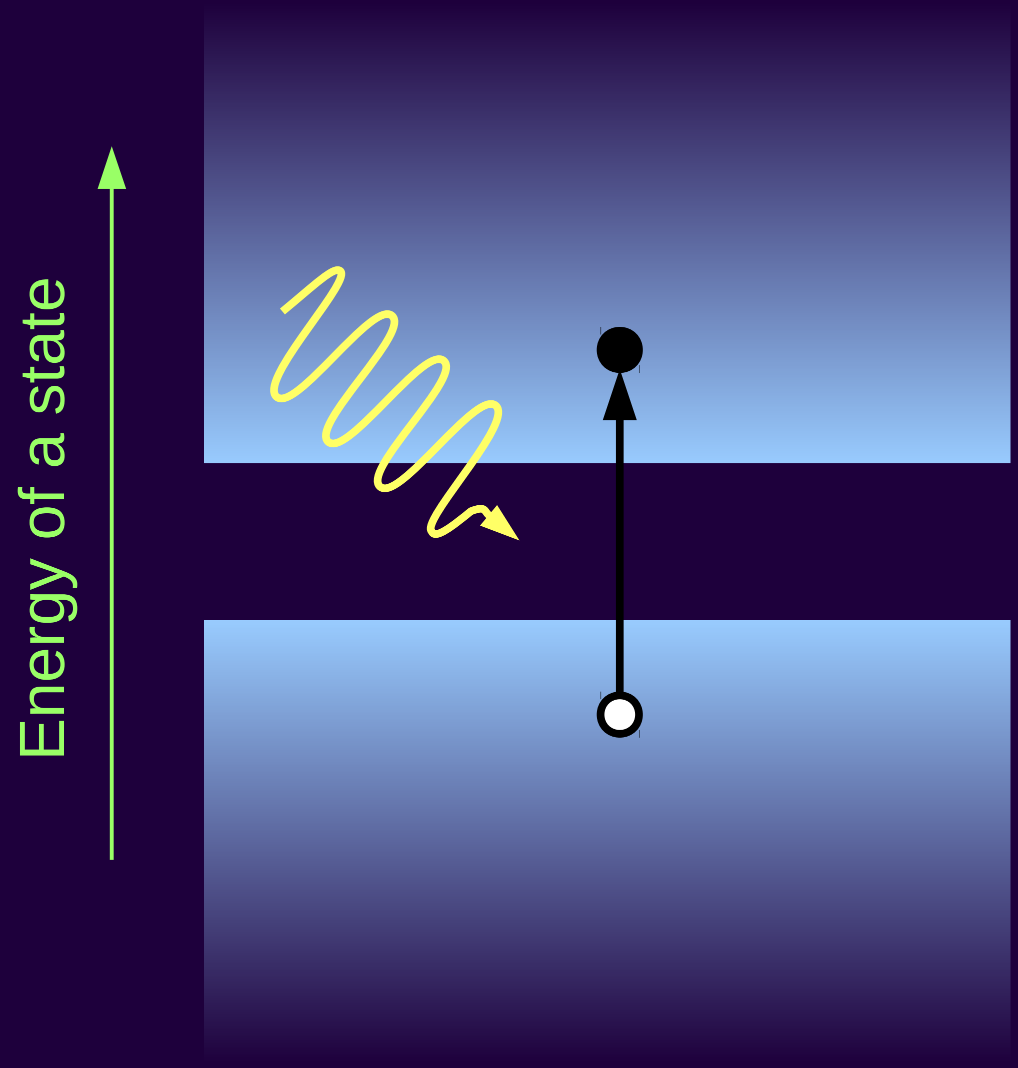
No states here

"Bandgap"

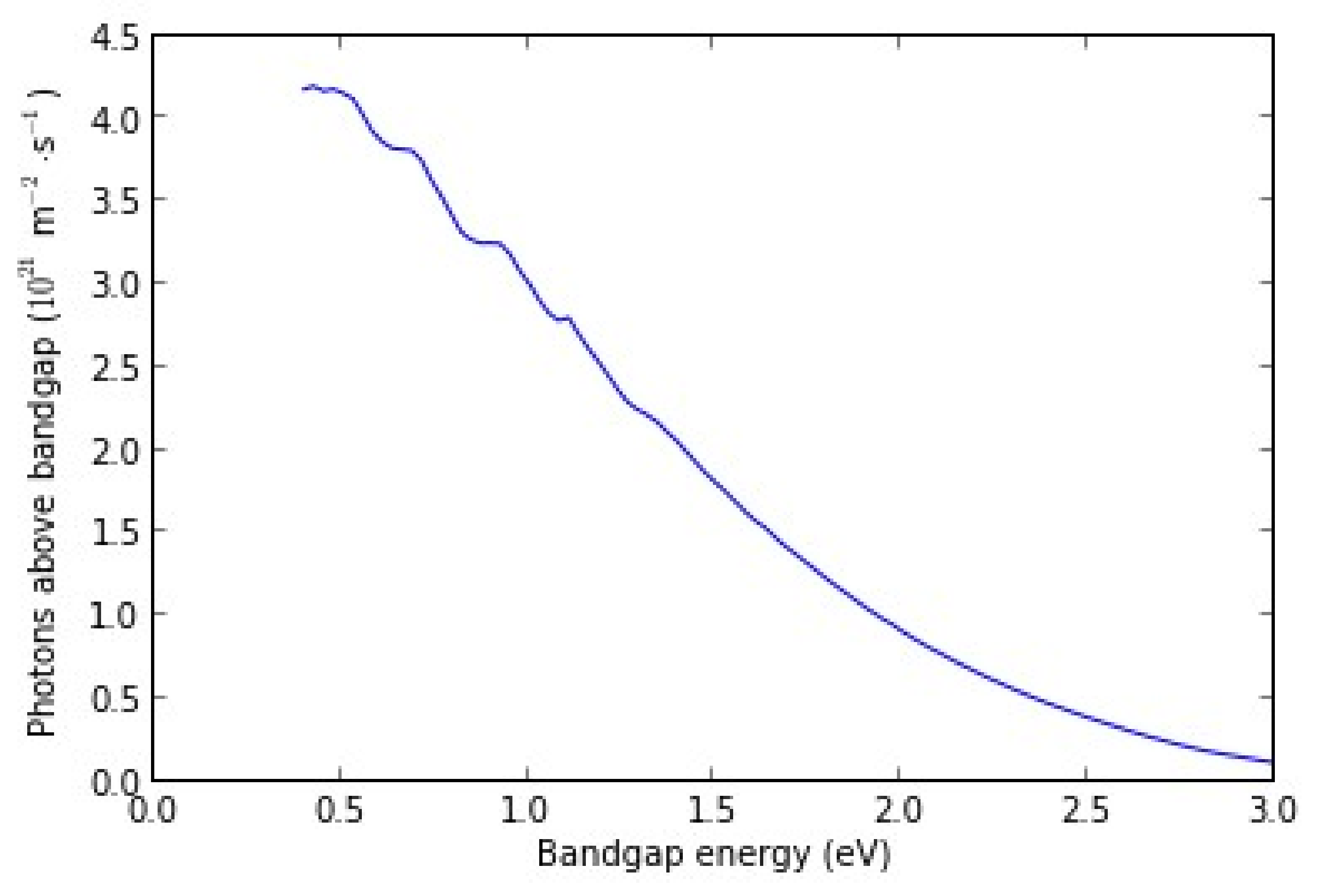
Almost all these states are full. The few empty states are called ***Holes***

"Valence band"

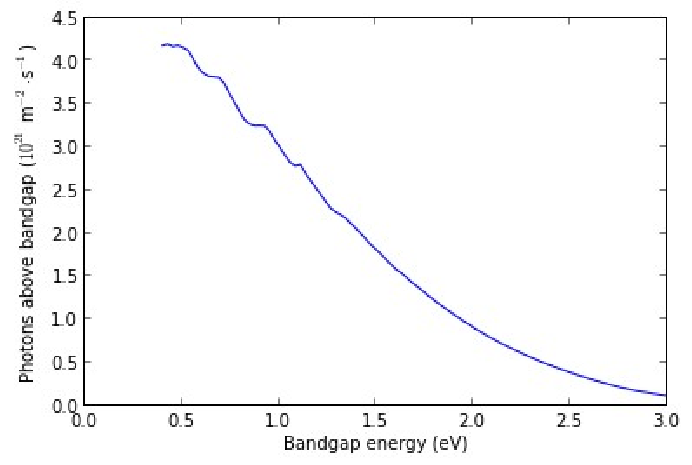
Photogeneration: Incident light creates electrons and holes



How much photogeneration?

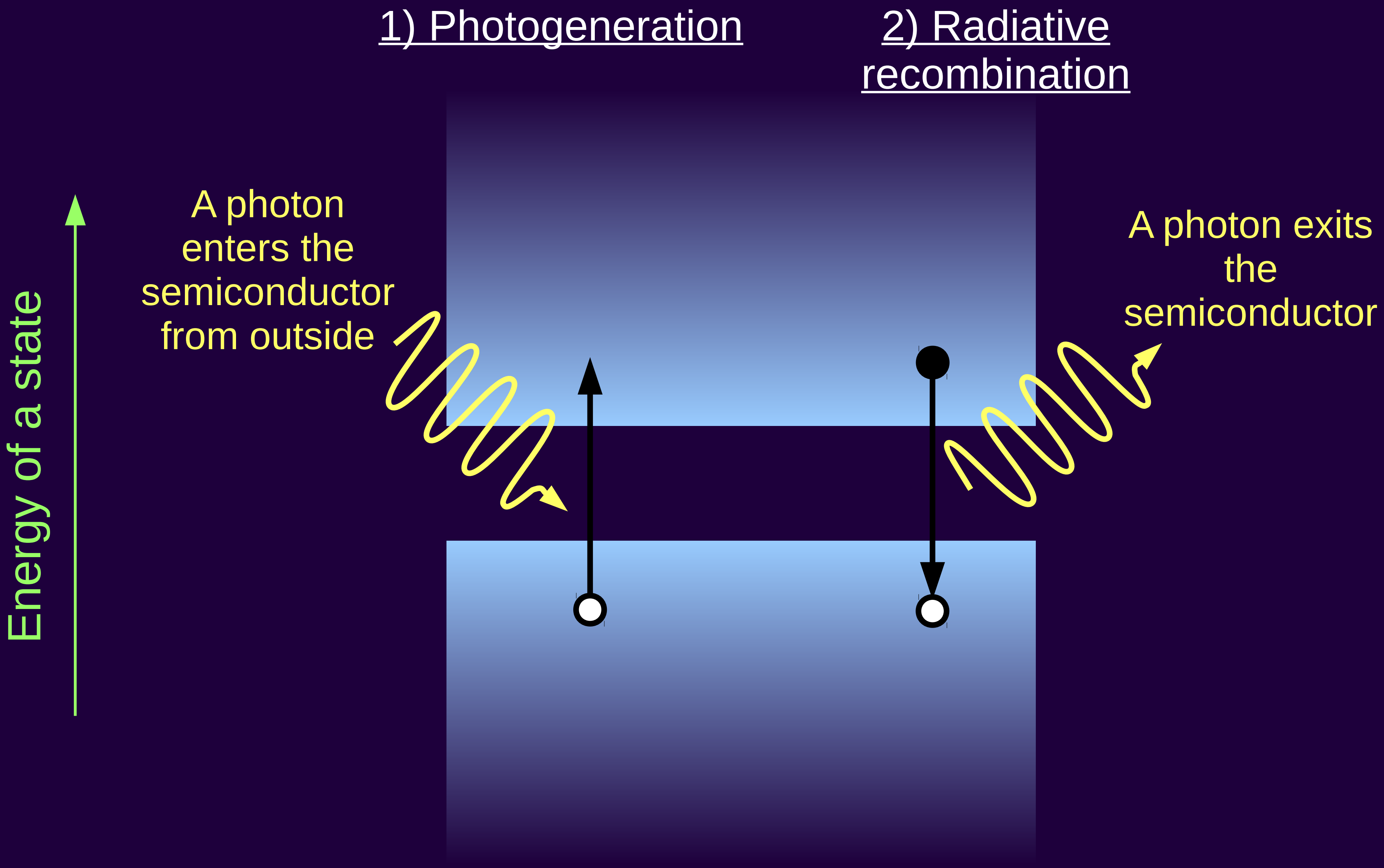


How much photogeneration?



- Assuming 100% of photons above the bandgap are absorbed, and 0% below.
  - (best case scenario)
- Assuming “typical” time-of-day, weather, latitude, etc.

Electrons and holes



1) Photogeneration

2) Radiative recombination

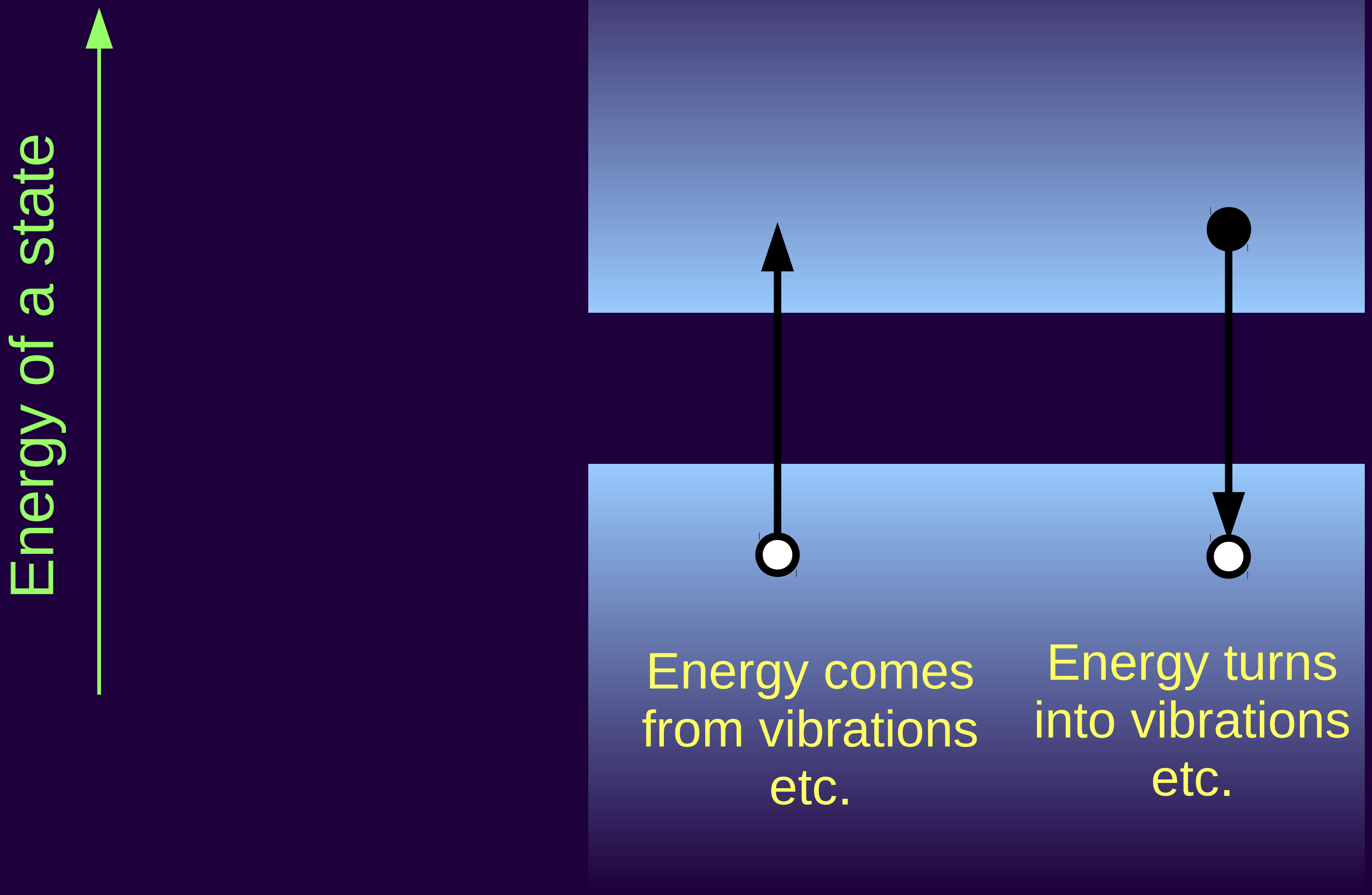
A photon enters the semiconductor from outside

A photon exits the semiconductor

Electrons and holes

<u>3) Nonradiative generation</u>

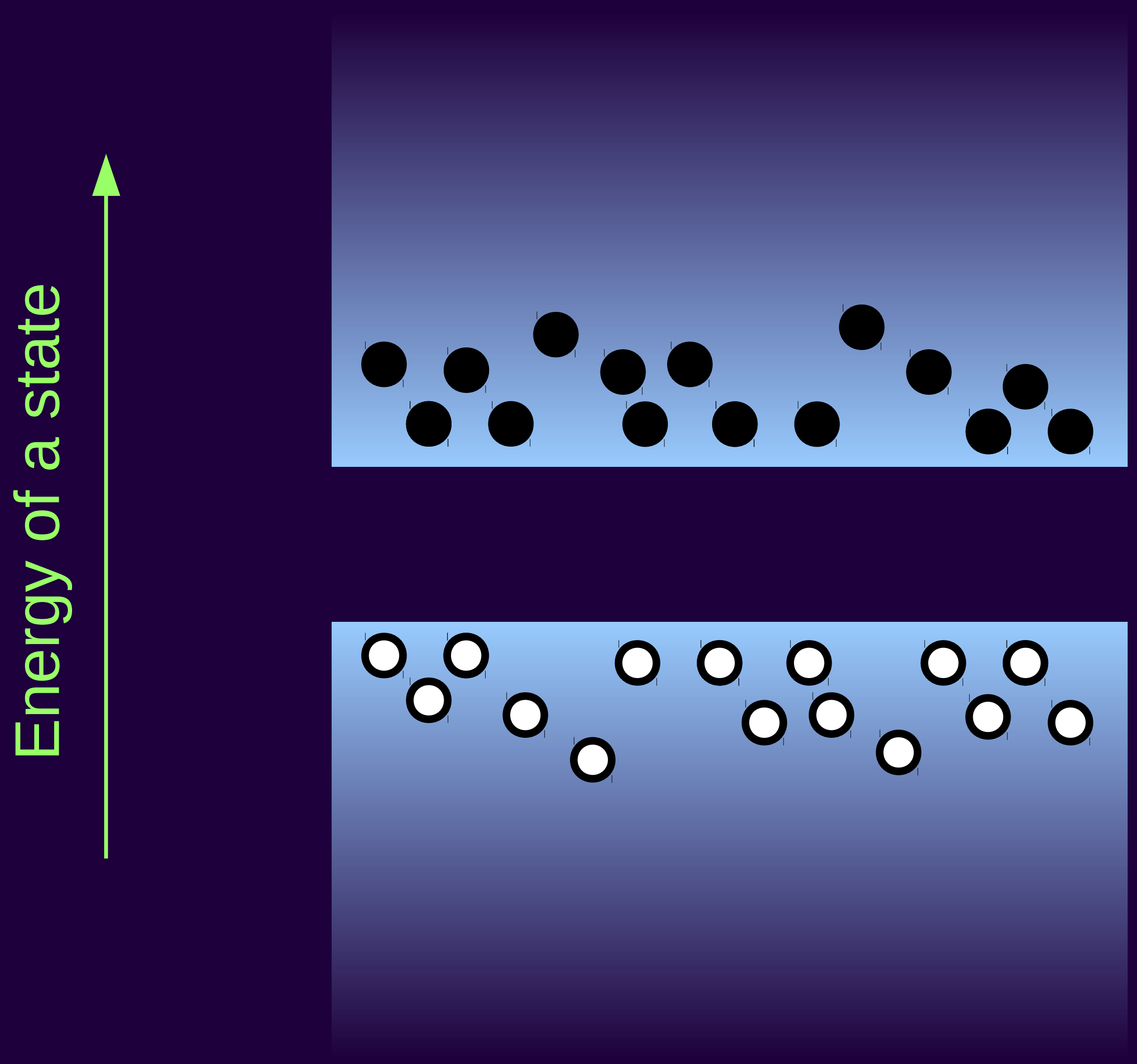
<u>4) Nonradiative recombination</u>



Energy comes from vibrations etc.

Energy turns into vibrations etc.

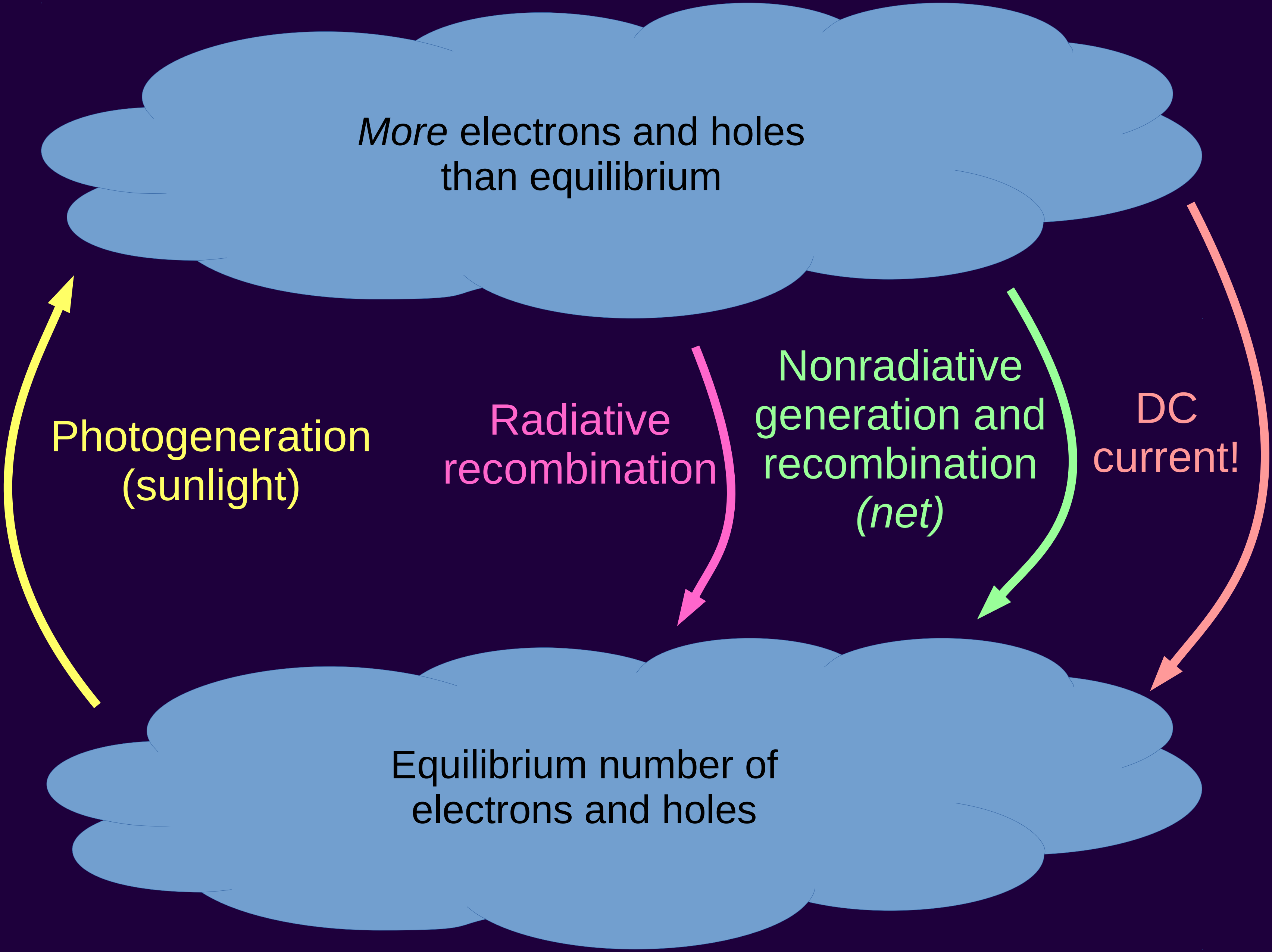
Electrons and holes



When a solar cell is running, it has *more* electrons and holes than it would in equilibrium.

Imagine a room full of oxygen and hydrogen gas – it “wants” to react into water.

Electrons and holes



More electrons and holes than equilibrium

Photogeneration (sunlight)

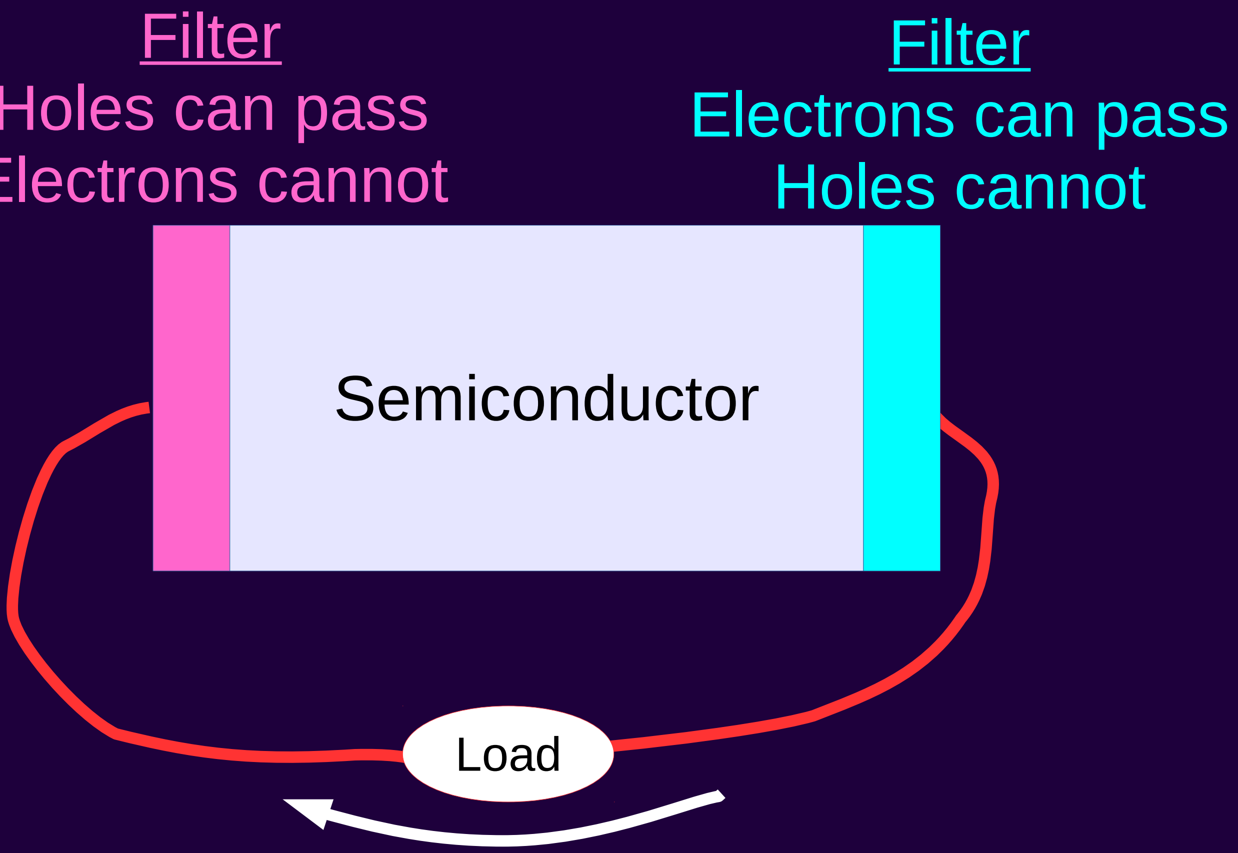
Radiative recombination

Nonradiative generation and recombination *(net)*

DC current!

Equilibrium number of electrons and holes

Electrons and holes

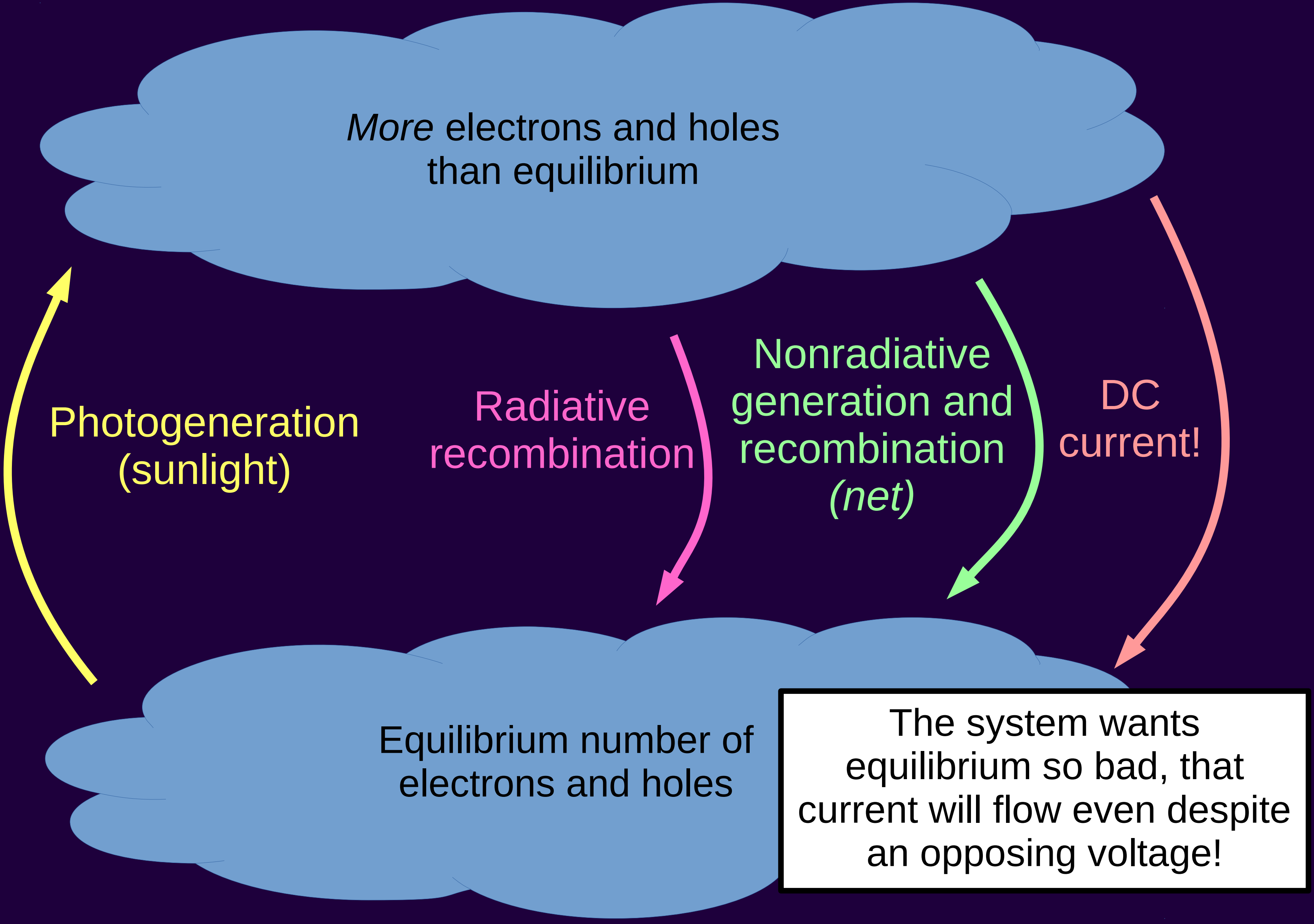


<u>Filter</u>
Holes can pass
Electrons cannot

<u>Filter</u>
Electrons can pass
Holes cannot

Each electron traveling this
way corresponds to the
removal of an electron & hole

Electrons and holes



More electrons and holes than equilibrium

Photogeneration (sunlight)

Radiative recombination

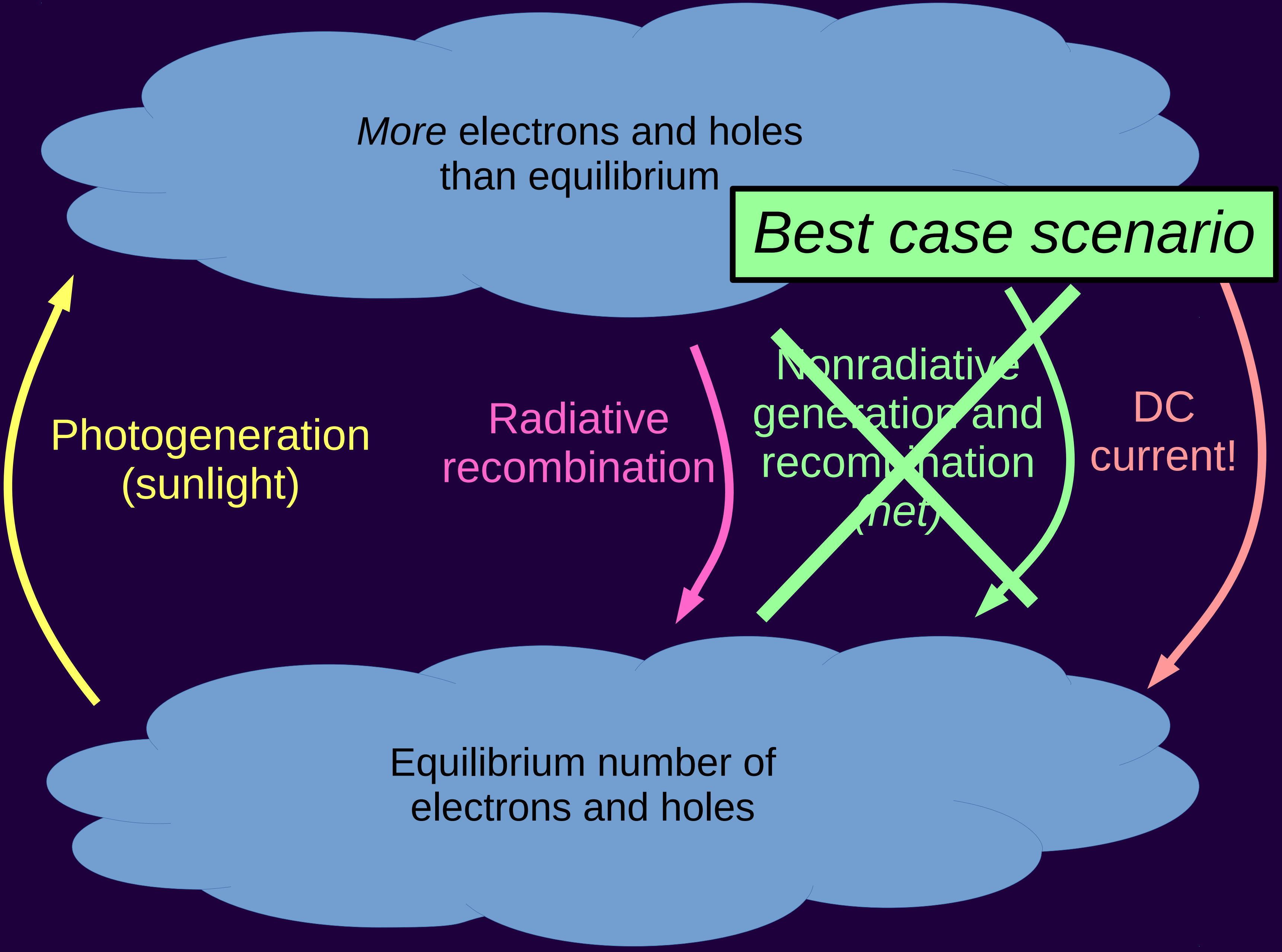
Nonradiative generation and recombination *(net)*

DC current!

Equilibrium number of electrons and holes

The system wants equilibrium so bad, that current will flow even despite an opposing voltage!

Electrons and holes



More electrons and holes than equilibrium

Best case scenario

Photogeneration (sunlight)

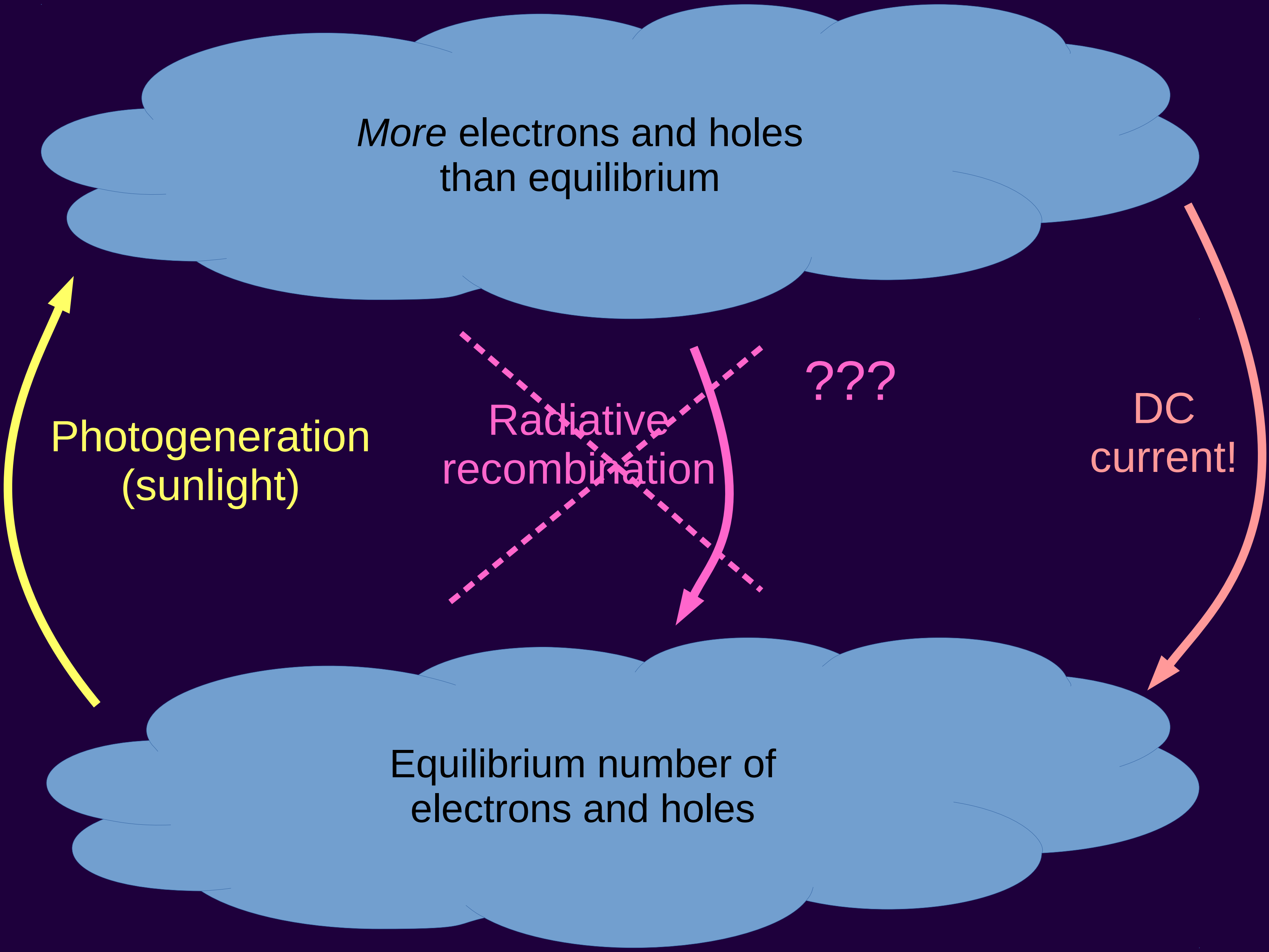
Radiative recombination

~~Nonradiative generation and recombination *(net)*~~

DC current!

Equilibrium number of electrons and holes

Electrons and holes



More electrons and holes
than equilibrium

Photogeneration
(sunlight)

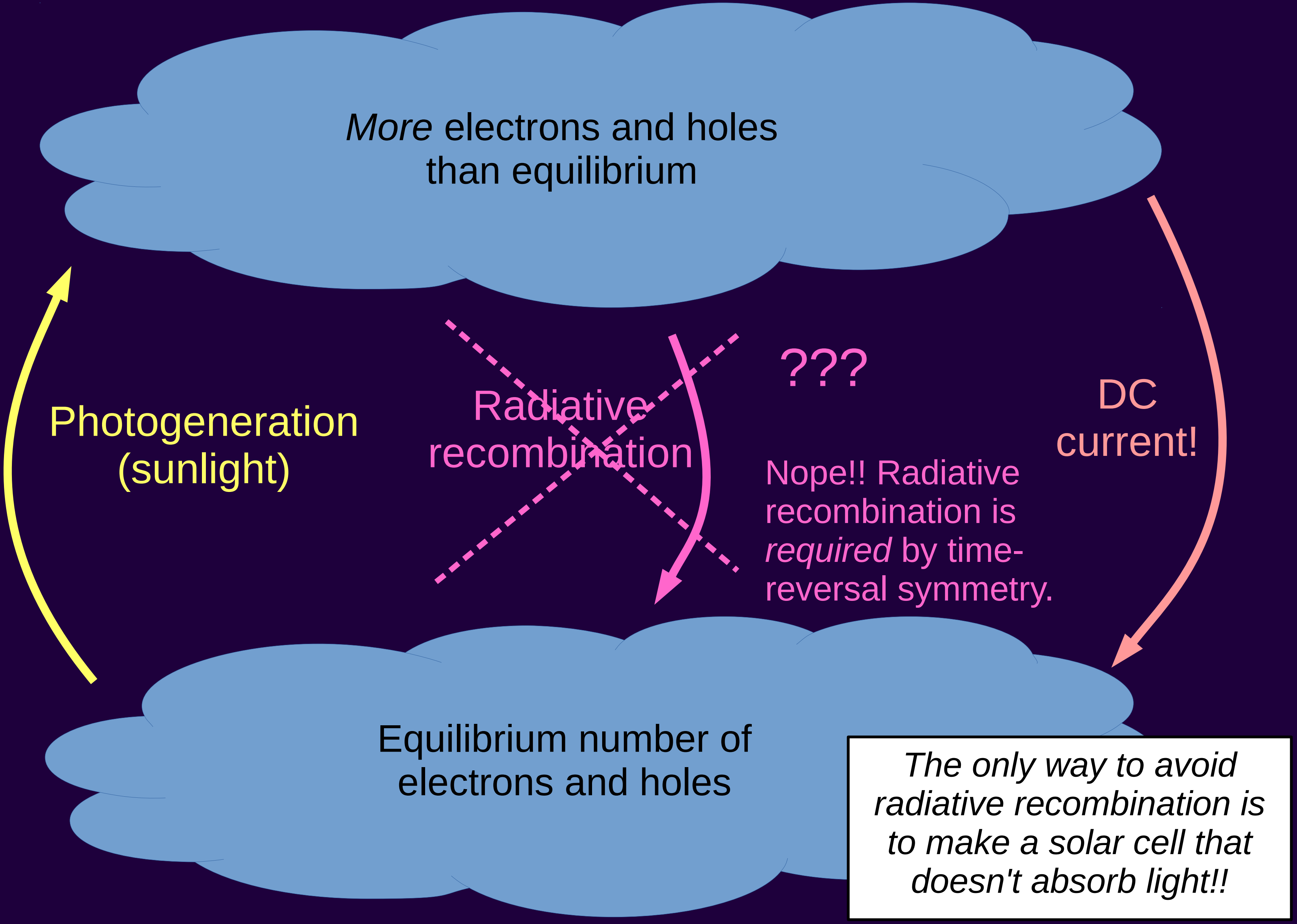
~~Radiative
recombination~~

???

DC
current!

Equilibrium number of
electrons and holes

Electrons and holes



More electrons and holes than equilibrium

Photogeneration (sunlight)

~~Radiative recombination~~

???

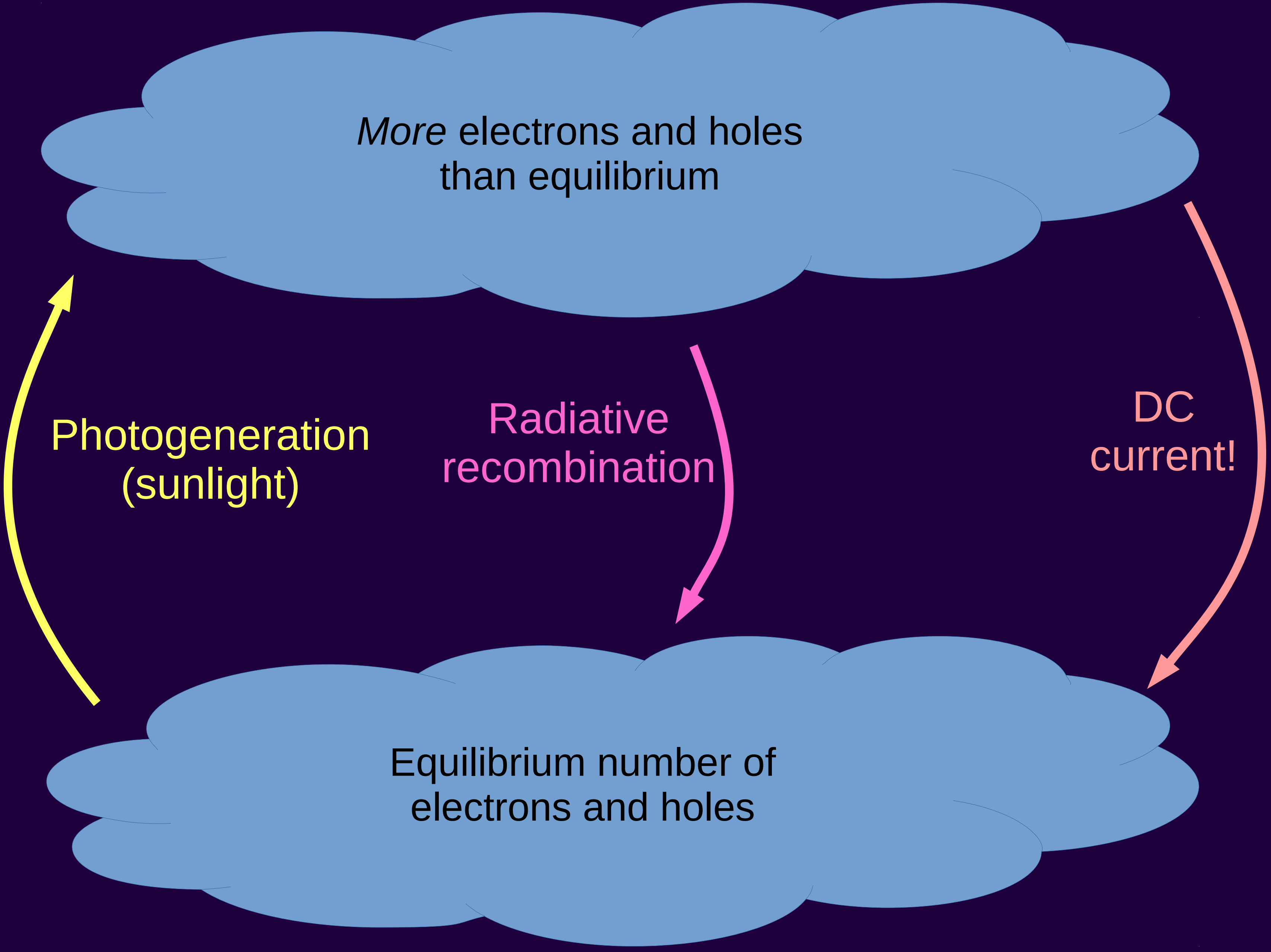
Nope!! Radiative recombination is *required* by time-reversal symmetry.

DC current!

Equilibrium number of electrons and holes

The only way to avoid radiative recombination is to make a solar cell that doesn't absorb light!!

Electrons and holes



More electrons and holes than equilibrium

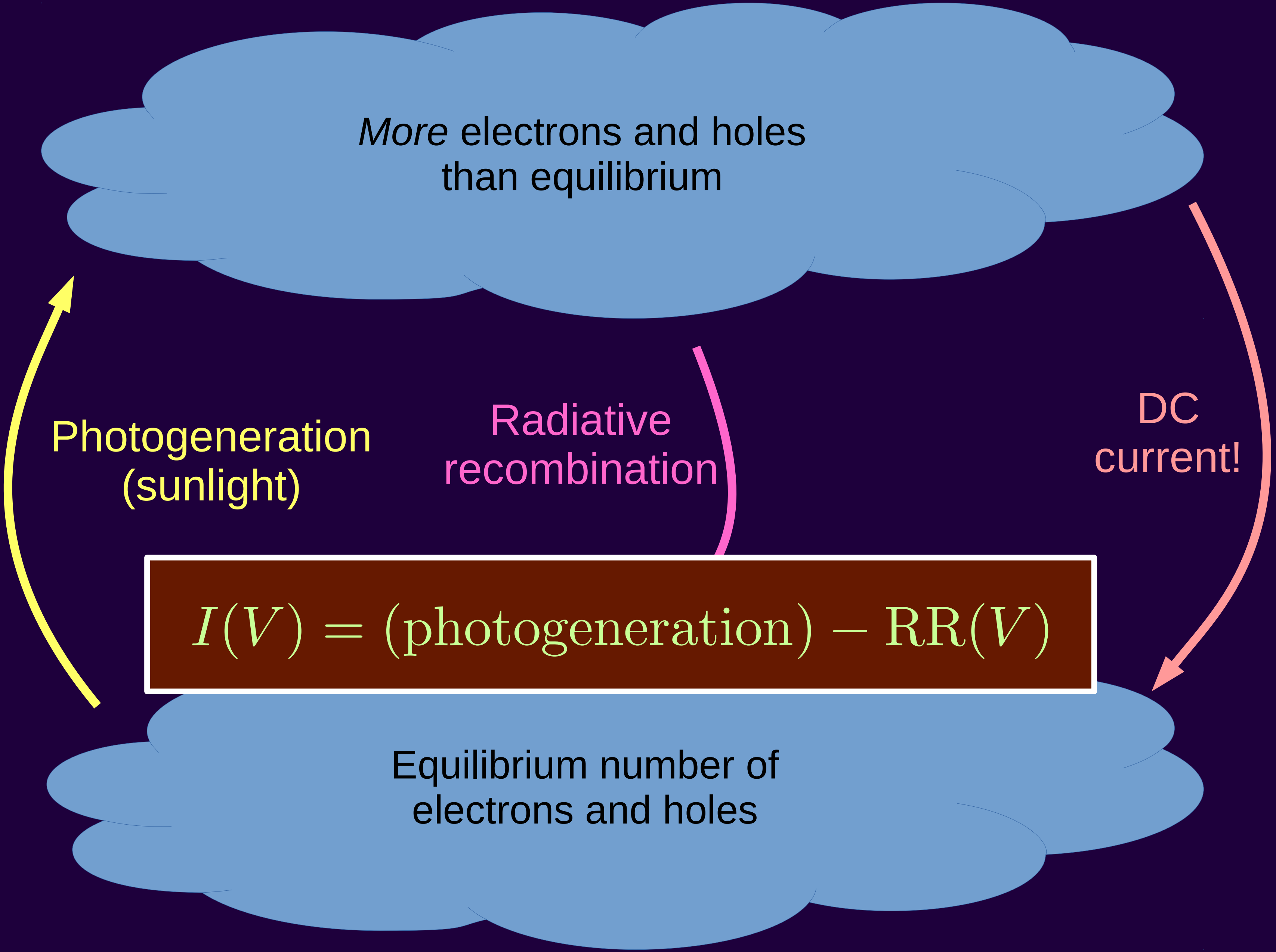
Photogeneration (sunlight)

Radiative recombination

DC current!

Equilibrium number of electrons and holes

Electrons and holes



More electrons and holes
than equilibrium

Photogeneration
(sunlight)

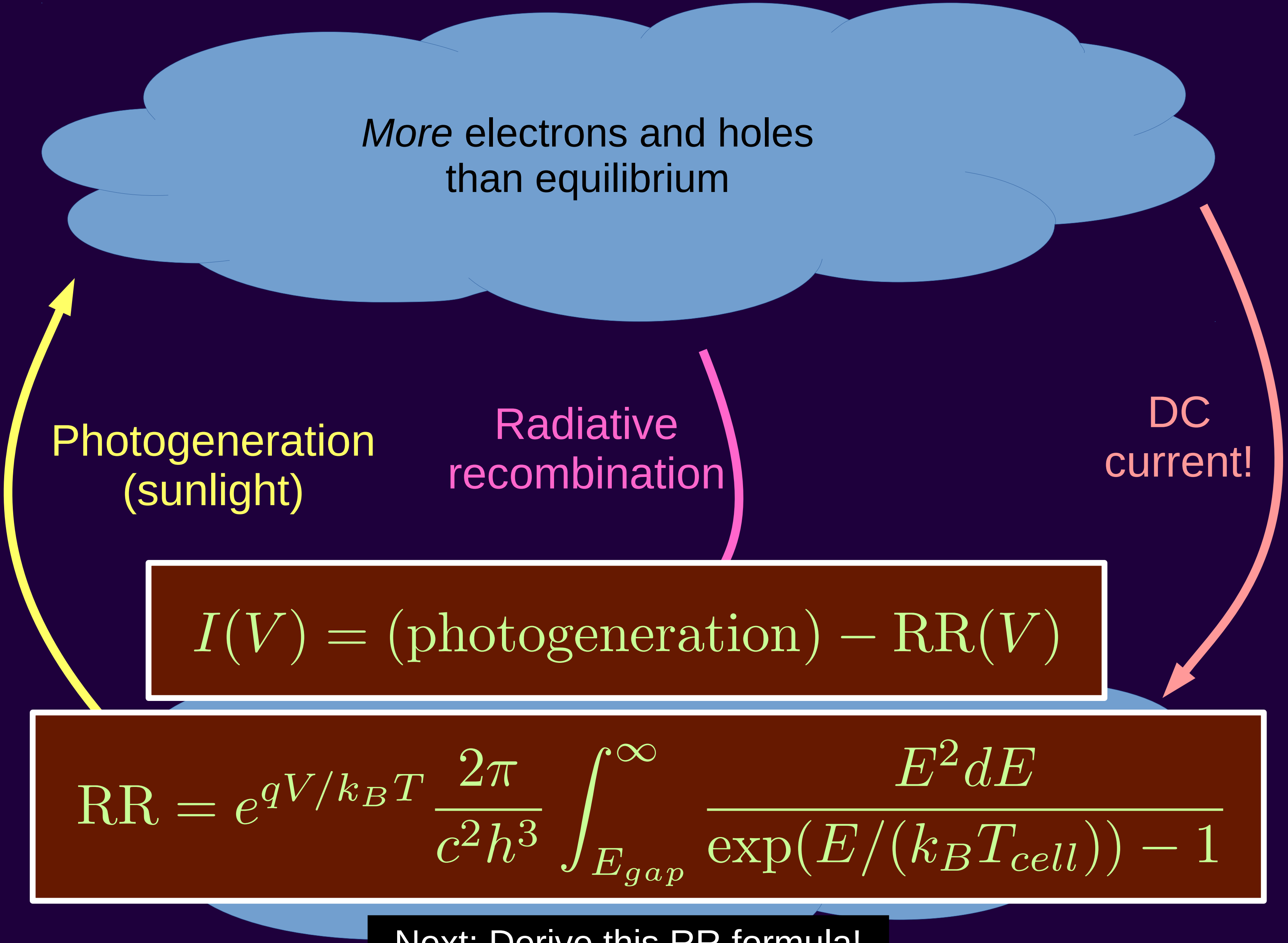
Radiative
recombination

DC
current!

$$I(V) = (\text{photogeneration}) - \text{RR}(V)$$

Equilibrium number of
electrons and holes

Electrons and holes



More electrons and holes than equilibrium

Photogeneration (sunlight)

Radiative recombination

DC current!

$$I(V) = (\text{photogeneration}) - \text{RR}(V)$$

$$\text{RR} = e^{qV/k_BT}\frac{2\pi}{c^2h^3}\int_{E_{gap}}^{\infty}\frac{E^2dE}{\exp(E/(k_BT_{cell}))-1}$$

Next: Derive this RR formula!

Radiative recombination (best case)

$$\mathrm{RR} = \underbrace{e^{qV/k_BT}}_{} \underbrace{\frac{2\pi}{c^2h^3}\int_{E_{gap}}^{\infty} \frac{E^2\,dE}{\exp(E/(k_BT_{cell}))-1}}_{}$$

<u>Planck's law ...</u>
Blackbody above the bandgap
Whitebody below the bandgap

More radiative recombination
at higher voltage...

(Familiar fact if you've used an LED!)

Radiative recombination (best case)

$$\mathrm{RR} = \underbrace{e^{qV/k_BT}}\,\underbrace{\frac{2\pi}{c^2h^3}\int_{E_{gap}}^{\infty}\frac{E^2dE}{\exp(E/(k_BT_{cell}))-1}}$$

Planck's law ...
Blackbody above the bandgap
Whitebody below the bandgap

More radiative recombination
at higher voltage...

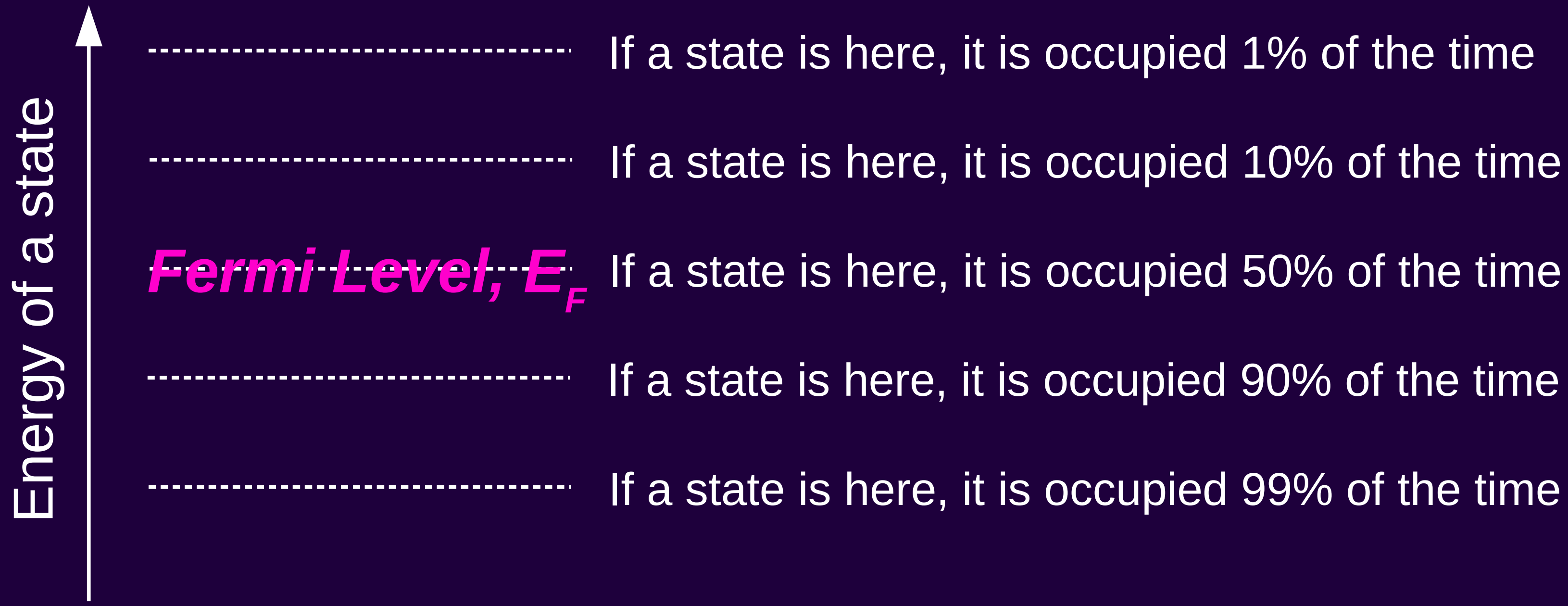
Why?
...Let's talk about quasi-fermi levels!

In thermodynamic equilibrium…

(no light, no voltage, no current, no temperature gradients…)

…the *Fermi-Dirac distribution* occurs

$$\boxed{P(E) = \frac{1}{1 + \exp((E - E_F)/(k_B T))}}$$



If a state is here, it is occupied 1% of the time

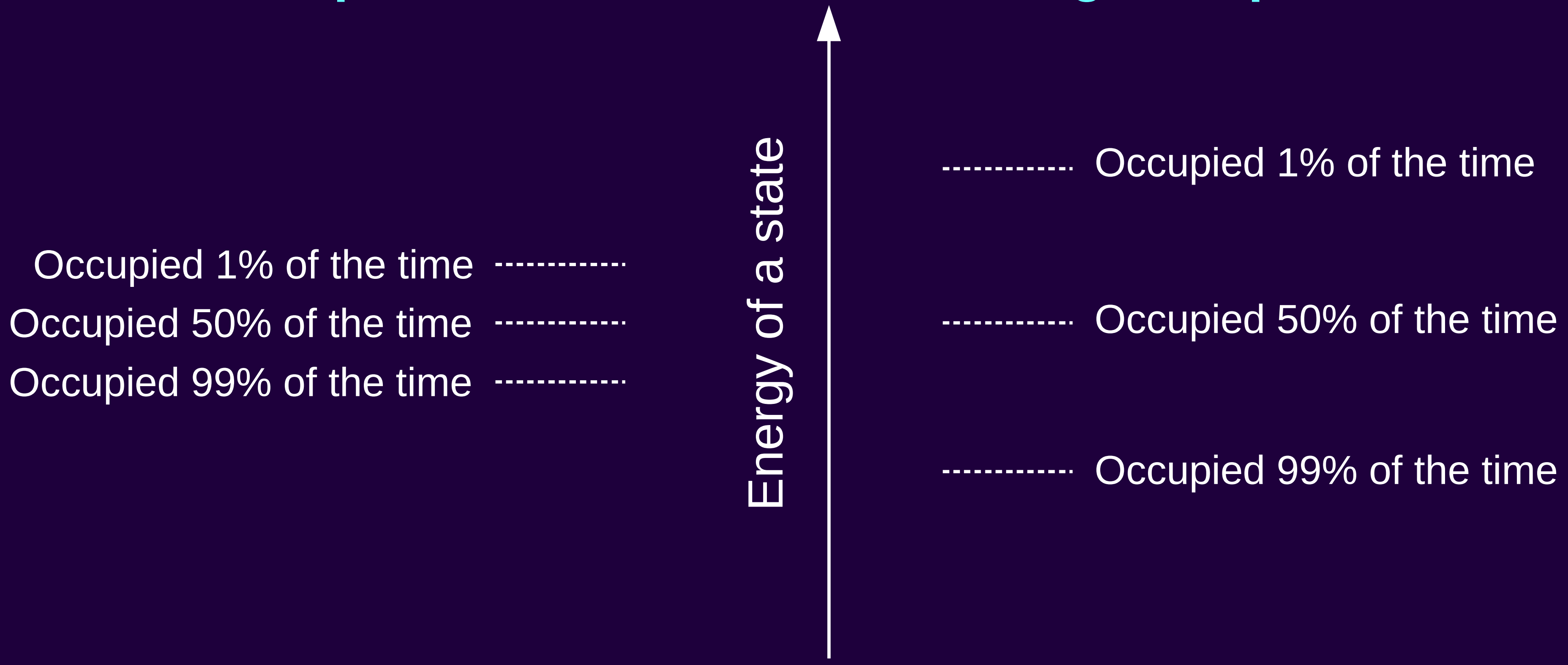
If a state is here, it is occupied 10% of the time

Fermi Level, E_F If a state is here, it is occupied 50% of the time

If a state is here, it is occupied 90% of the time

If a state is here, it is occupied 99% of the time

Fermi-Dirac distribution: Temperature



Low temperature

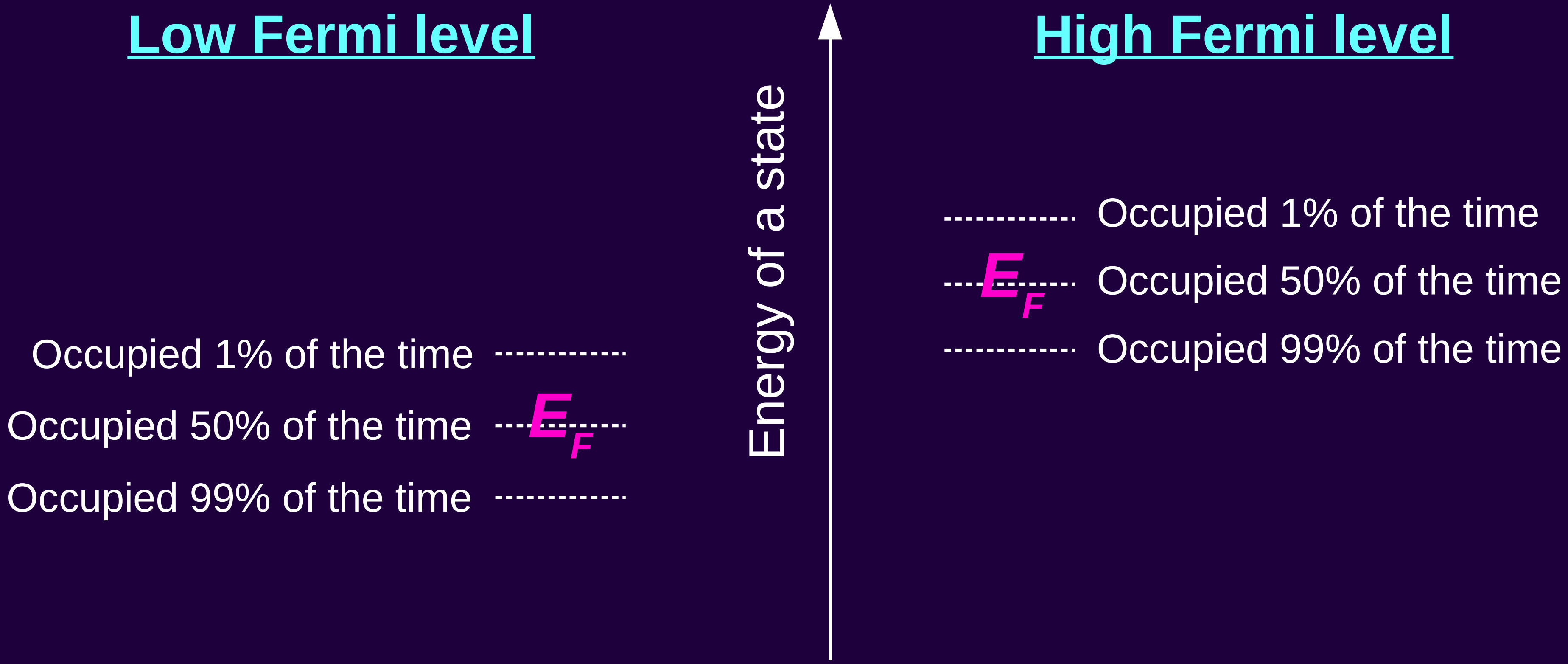
Occupied 1% of the time
Occupied 50% of the time
Occupied 99% of the time

Energy of a state

High temperature

Occupied 1% of the time
Occupied 50% of the time
Occupied 99% of the time

Fermi-Dirac distribution: Fermi level



Low Fermi level

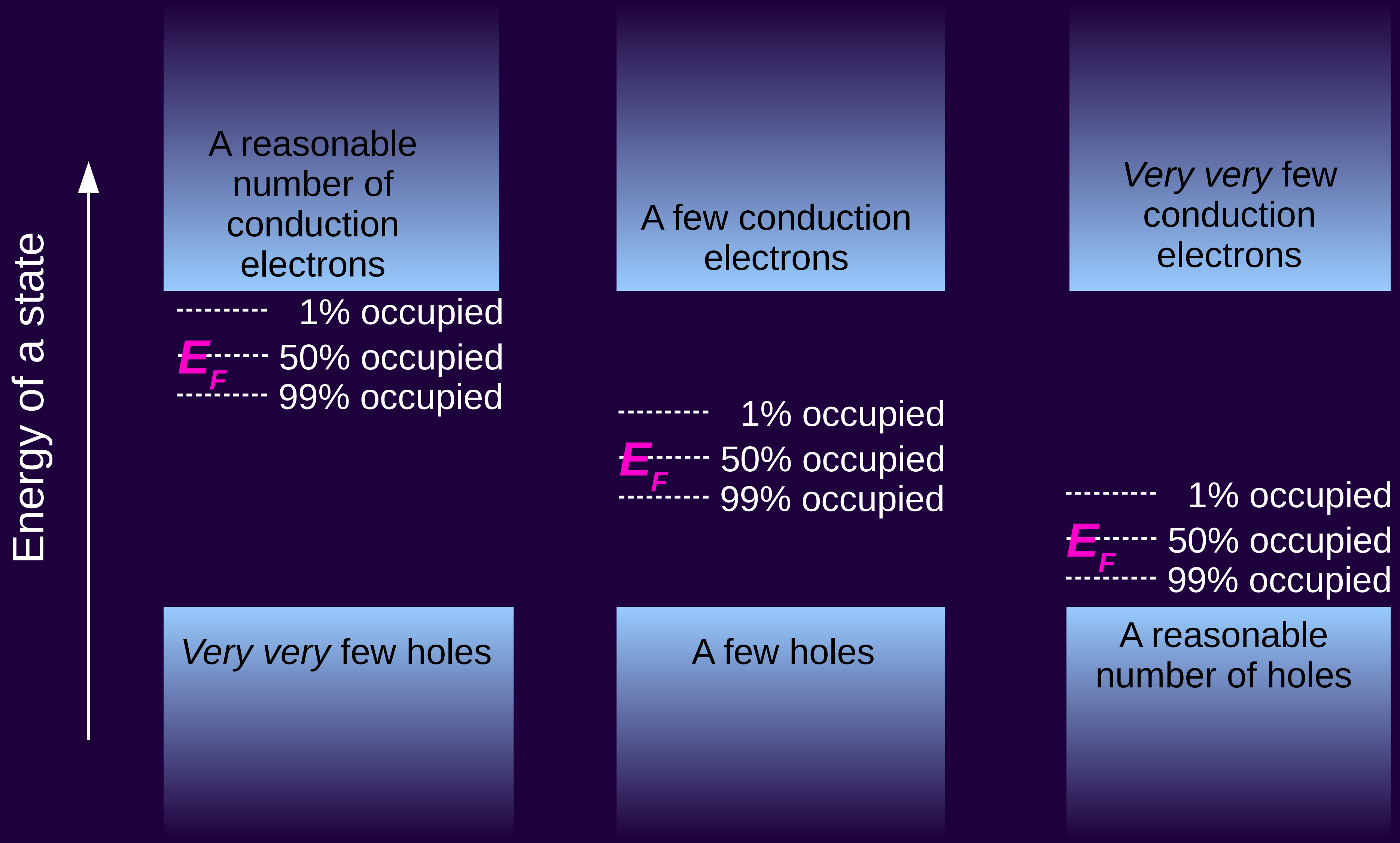
High Fermi level

Fewer electrons total

More electrons total

Equilibrium semiconductor

Various possibilities



Energy of a state

A reasonable number of conduction electrons

1% occupied

E_F 50% occupied

99% occupied

Very very few holes

A few conduction electrons

1% occupied

E_F 50% occupied

99% occupied

A few holes

Very very few conduction electrons

1% occupied

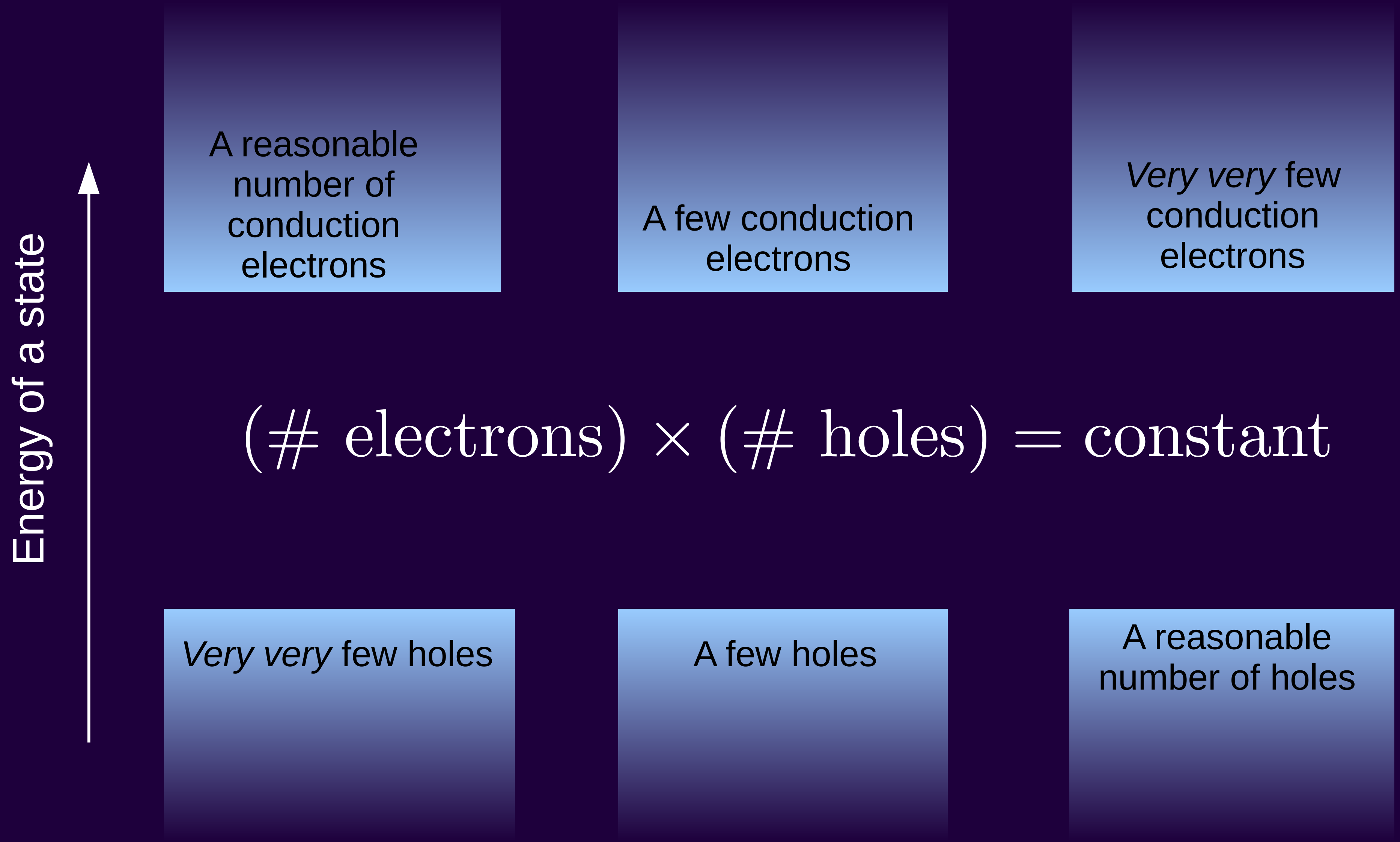
E_F 50% occupied

99% occupied

A reasonable number of holes

Equilibrium semiconductor

Various possibilities



A reasonable number of conduction electrons

A few conduction electrons

Very very few conduction electrons

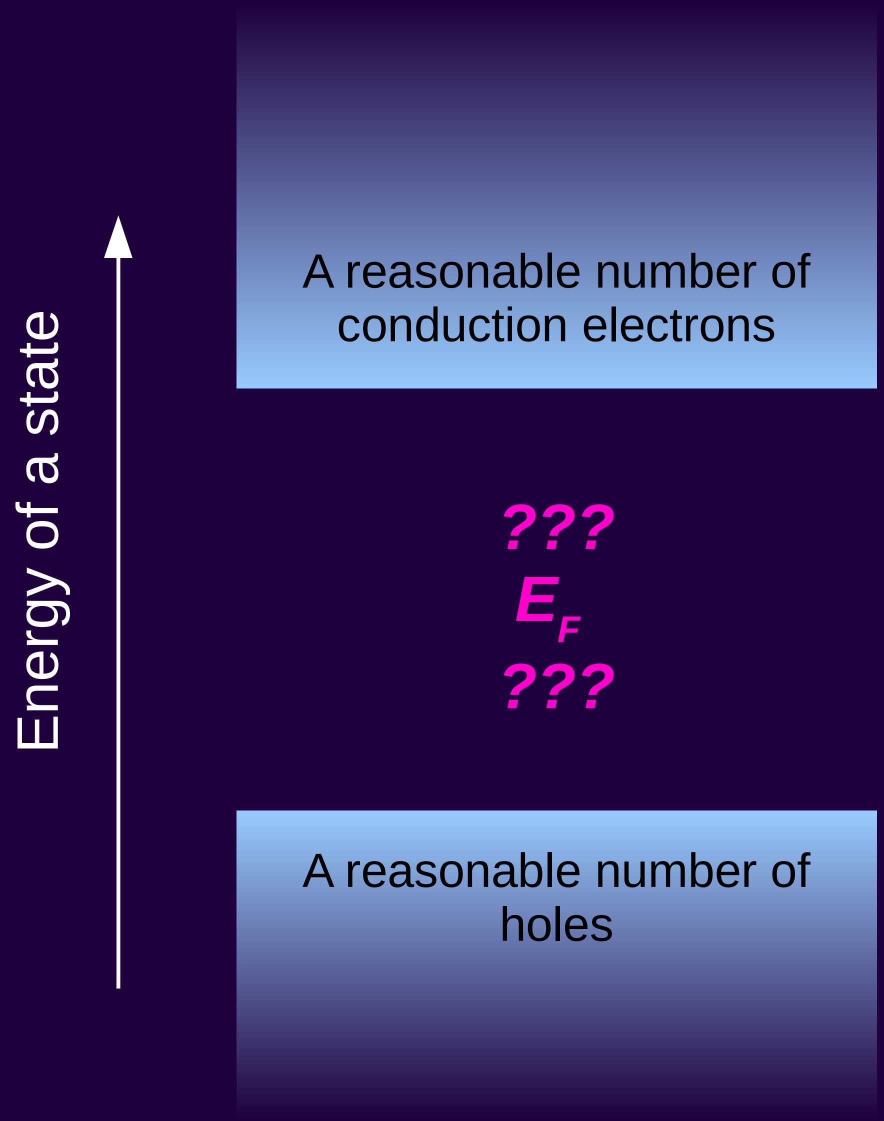
$$(\#\ \text{electrons}) \times (\#\ \text{holes}) = \text{constant}$$

Very very few holes

A few holes

A reasonable number of holes

Solar cell in operation...



Energy of a state

A reasonable number of conduction electrons

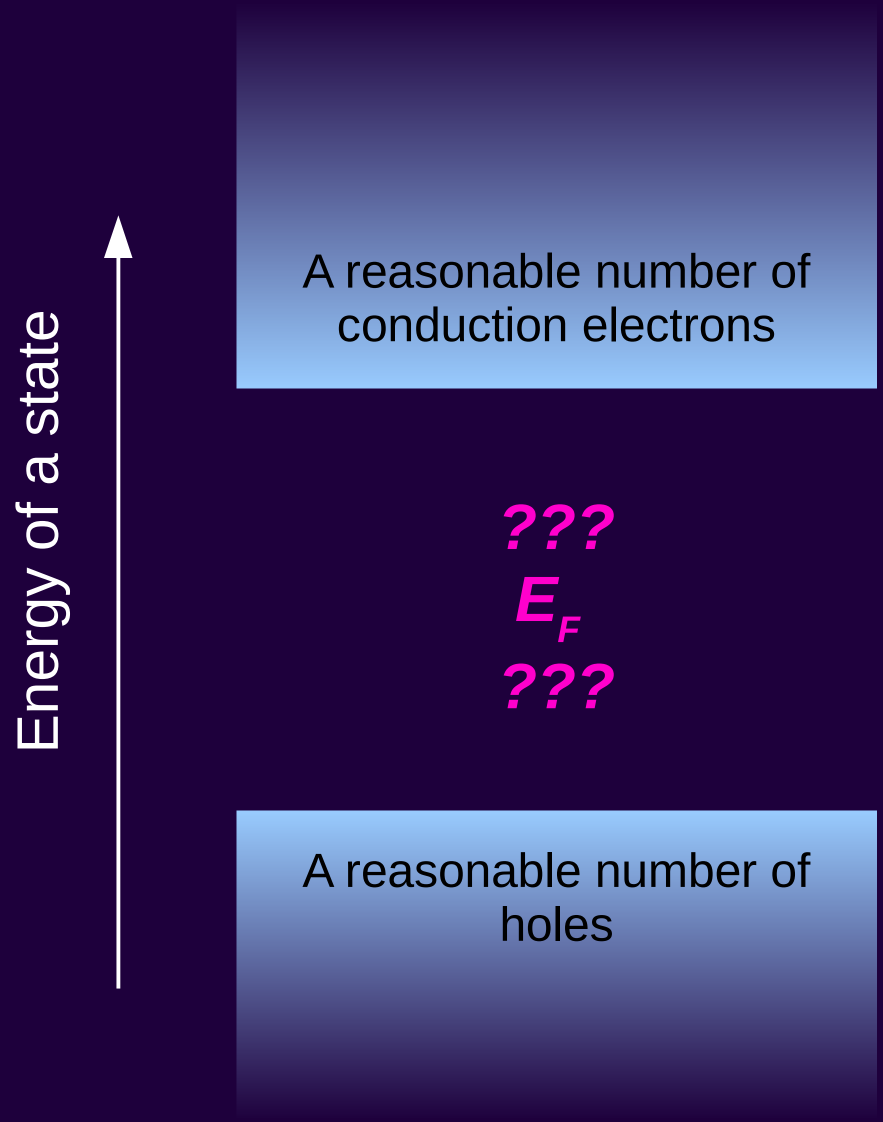
???

E_F

???

A reasonable number of holes

Solar cell in operation...



Energy of a state

A reasonable number of conduction electrons

???

E_F

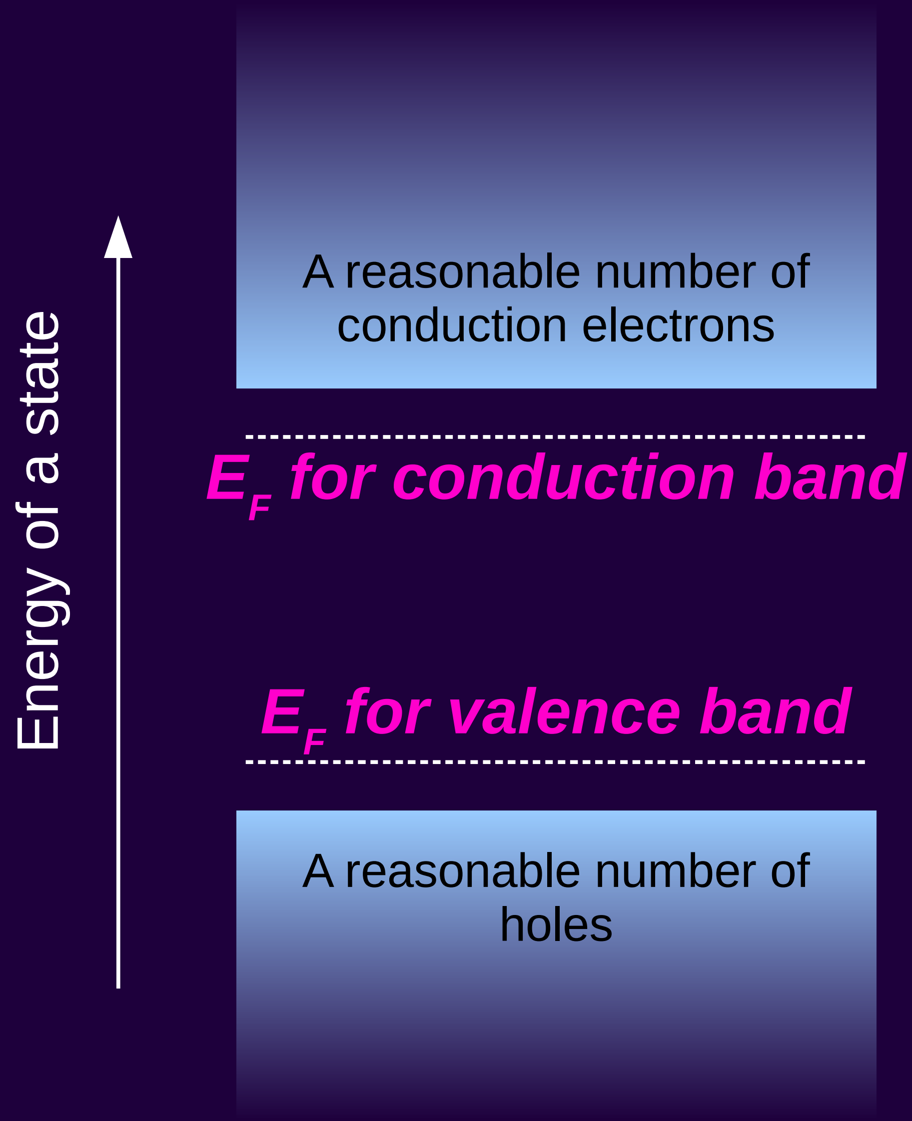
???

A reasonable number of holes

There is no Fermi level!

Fermi-Dirac distribution only happens in thermodynamic equilibrium.

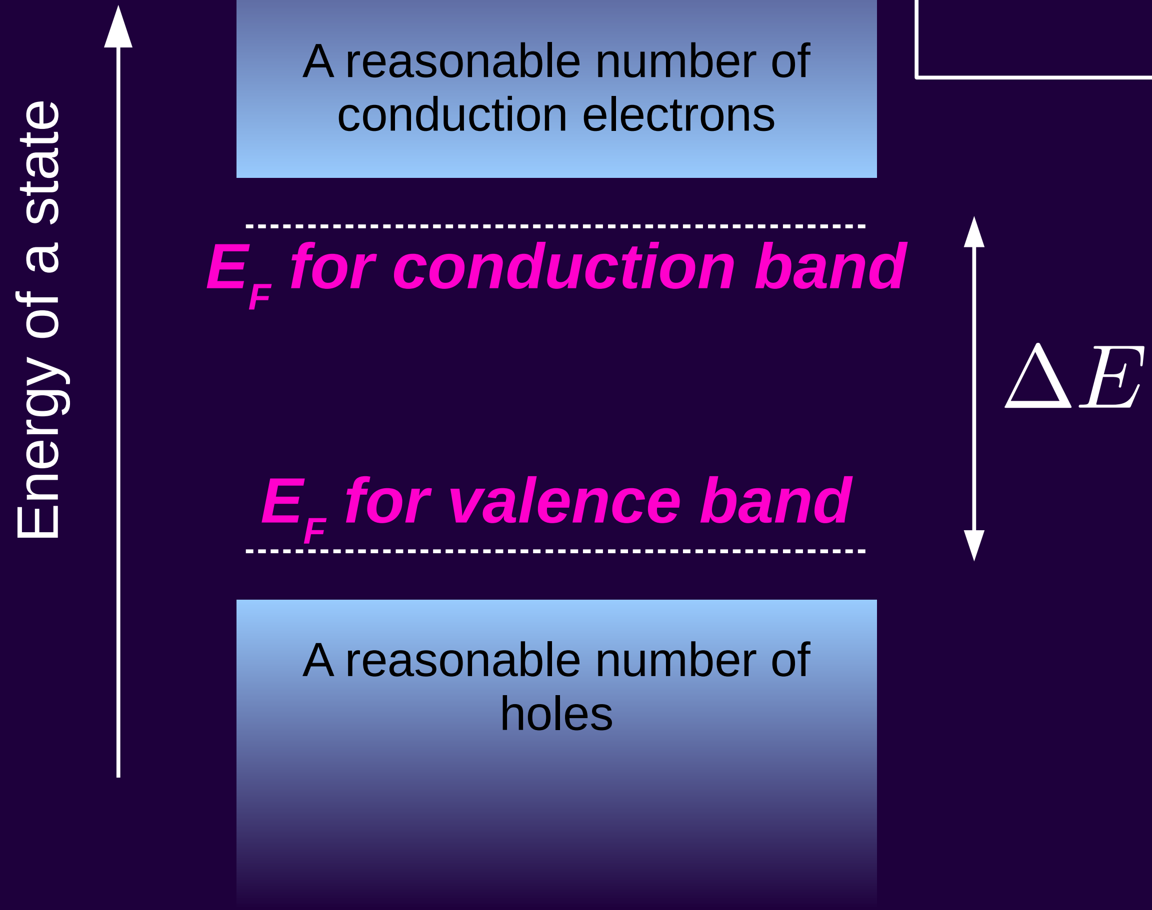
Quasi-Fermi level



…But it turns out that each band by itself does have a (Quasi) Fermi level

Quasi-Fermi level

$$(\#\ \text{electrons}) \times (\#\ \text{holes}) \propto \exp(\Delta E / k_B T)$$



Energy of a state

A reasonable number of conduction electrons

E_F for conduction band

ΔE

E_F for valence band

A reasonable number of holes

Kinetic theory

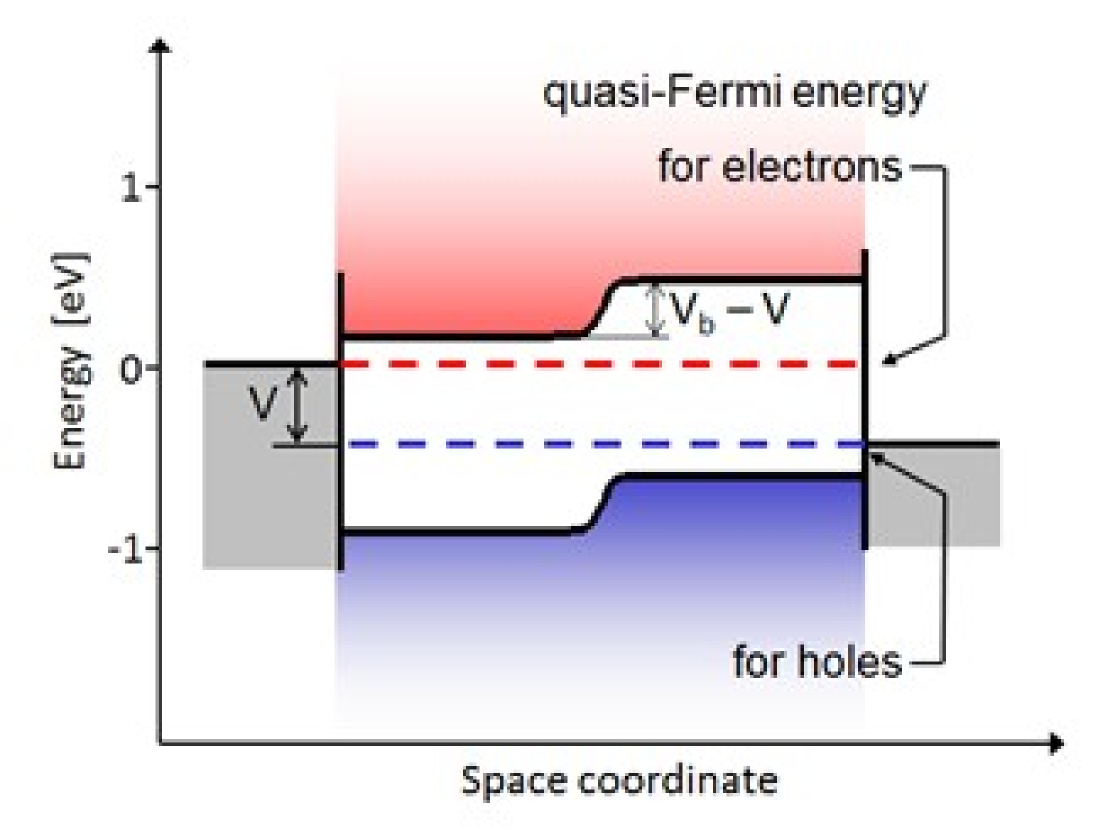
Radiative recombination rate is proportional to how often an electron bumps into a hole … therefore

$$\begin{aligned}&(\text{Radiative recombination})\\ &\qquad \propto (\#\ \text{electrons}) \times (\#\ \text{holes})\end{aligned}$$

Therefore:

$$\begin{aligned}&(\text{Radiative recombination})\\ &\qquad \propto \exp((\text{QFL split})/k_B T)\end{aligned}$$

External voltage



Best case scenario: External voltage = QFL splitting

With resistance etc: External voltage < QFL splitting

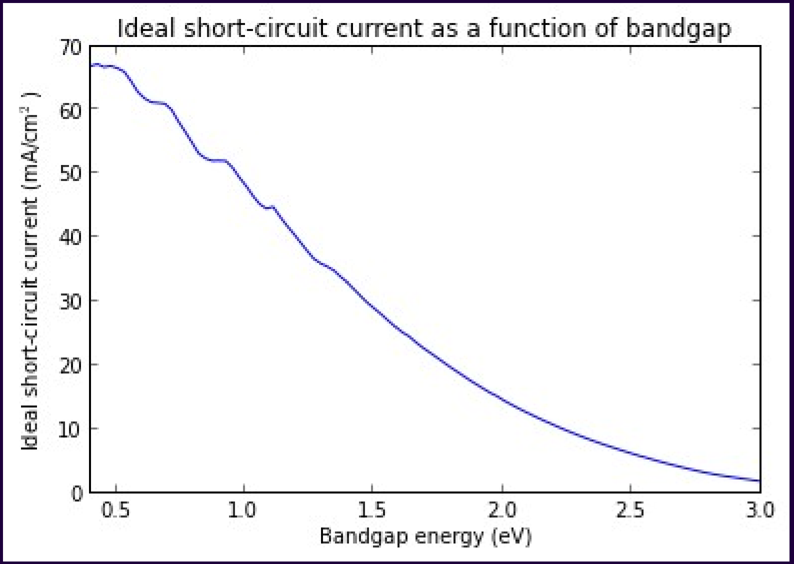
All done!

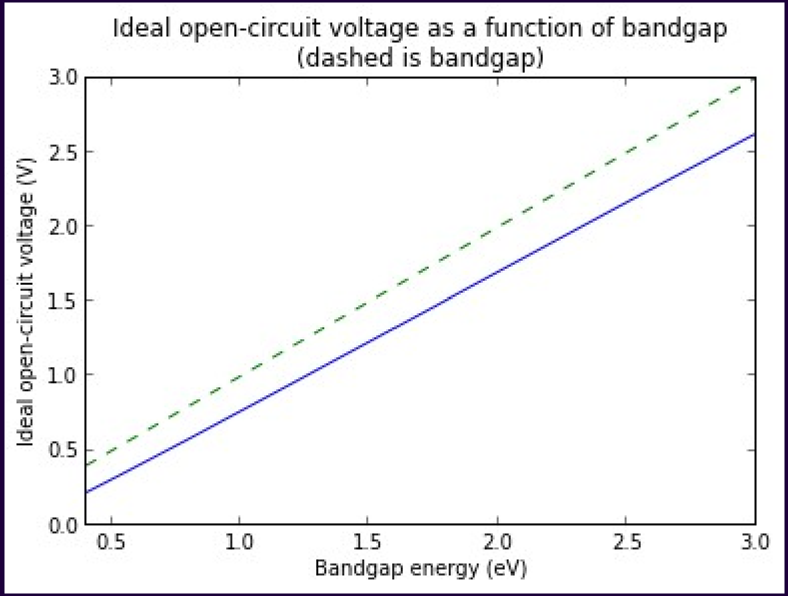
$$\boxed{\mathrm{RR} = e^{qV/k_B T} \frac{2\pi}{c^2 h^3} \int_{E_{gap}}^{\infty} \frac{E^2 dE}{\exp(E/(k_B T_{cell})) - 1}}$$

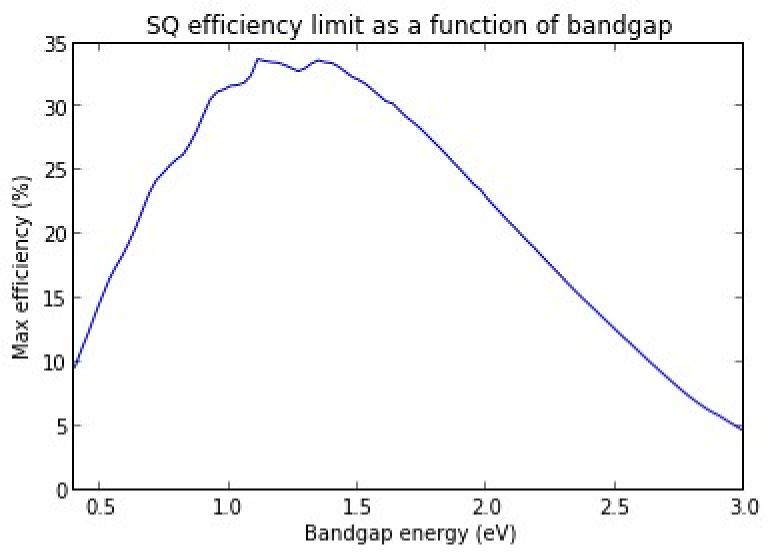
$$I(V) = I_{\mathrm{photogeneration}} - \mathrm{RR}$$

Photovoltaic performance

$$I(V) = I_{\text{photogeneration}} - \text{RR}$$



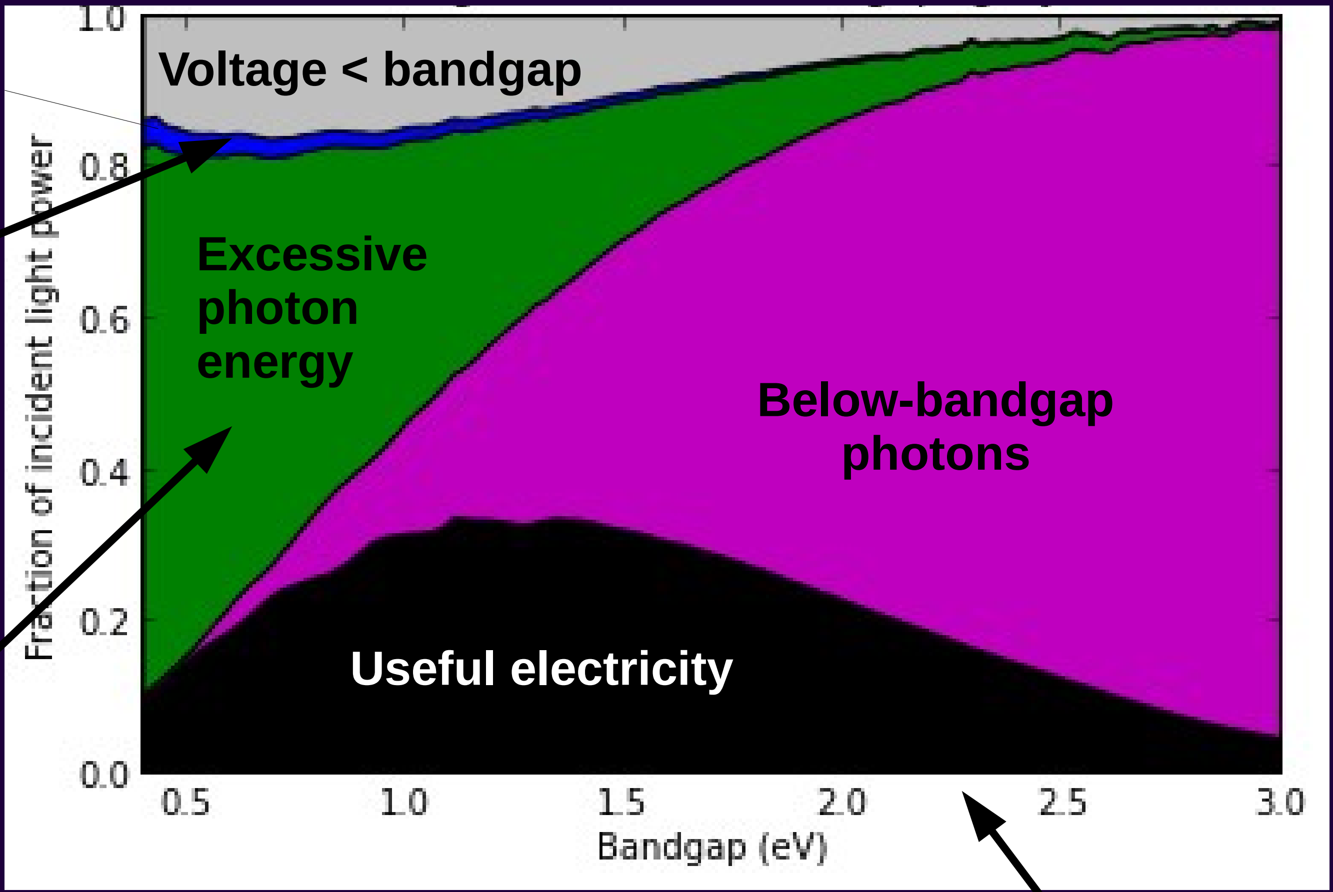




Power breakdown

Radiative recombination

Blue and gray is the inevitable tradeoff between low radiative recombination and high voltage.



A photon with the bandgap energy creates an e-h pair. A photon with ***way more*** than the bandgap energy still just creates an e-h pair. The extra energy is therefore a waste.

Recognize this? It's the S-Q limit curve from last slide, filled in.

Also subject to S-Q limit

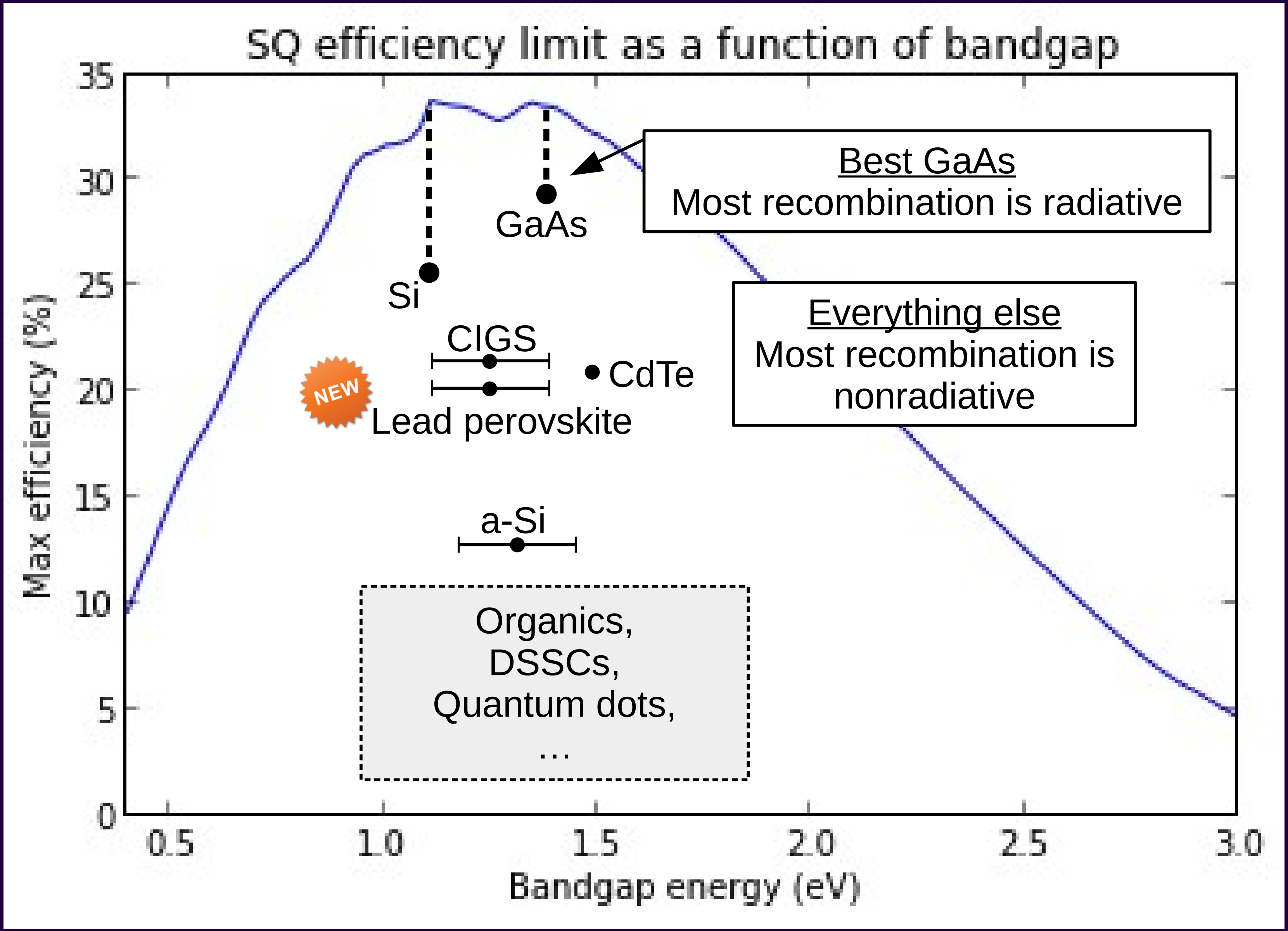
- Organic solar cells
- Dye-sensitized solar cells
- “Anomalous photovoltaic effect” (ferroelectrics etc.)
- Solar-to-fuel photochemical systems

Some produce kilovolts of voltage!! …But with tiny currents.

Efficiency numerator is the free energy of the chemical bonds created.

S-Q limit vs world record cells

… for which the limit applies

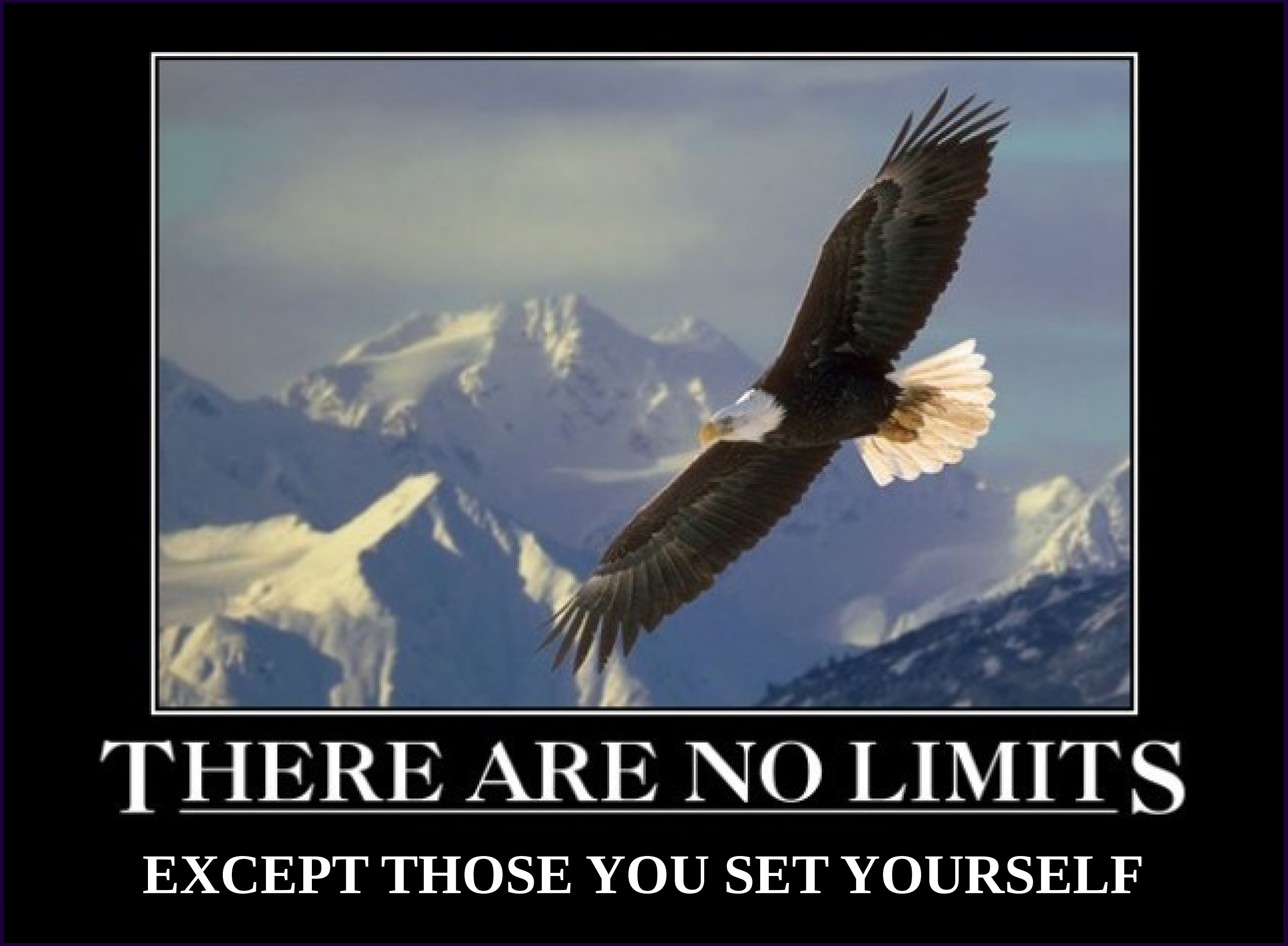


Best GaAs
Most recombination is radiative

Everything else
Most recombination is nonradiative

Organics,
DSSCs,
Quantum dots,
…

Part 2: Exceeding the SQ limit



Part 2: Exceeding the SQ limit

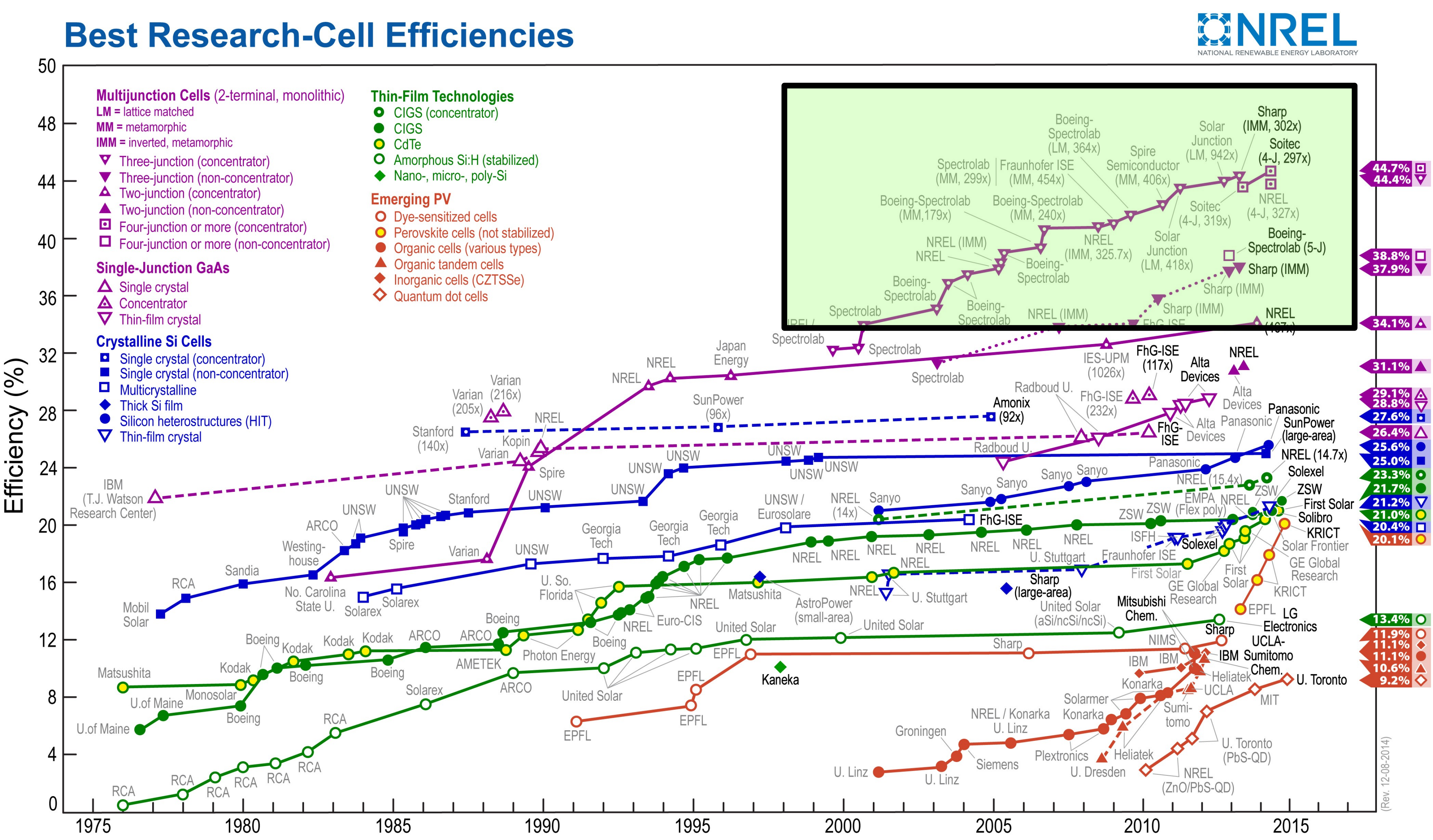
- Tandems
- Concentration
- Anisotropic re-radiation
- Magneto-optics
- Multiple exciton generation
- Intermediate bands
- Hot carriers

Not a comprehensive list!!
Just a sampling of especially
important / interesting
weird / fun …

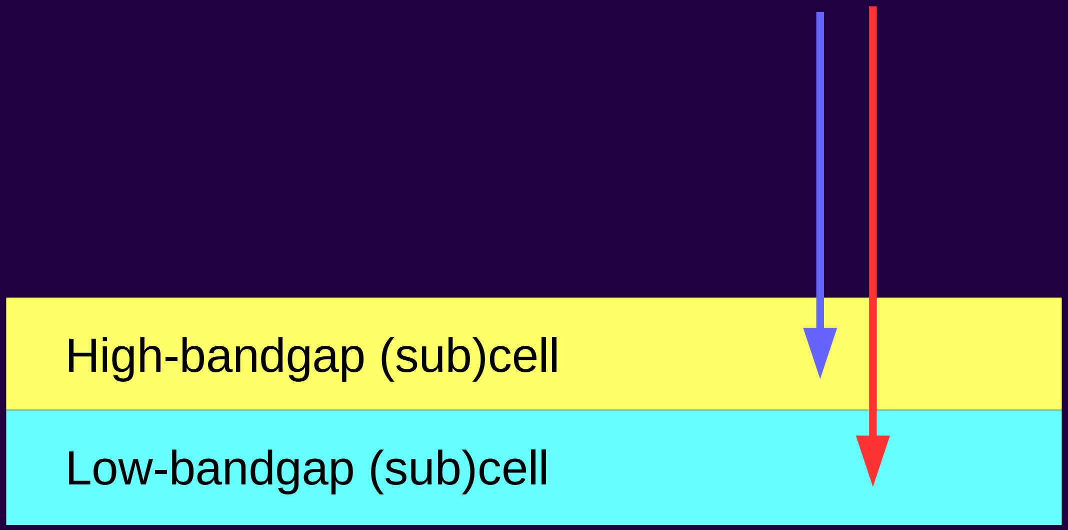
Part 2: Exceeding the SQ limit

- **Tandems**
- Concentration
- Anisotropic re-radiation
- Magneto-optics
- Multiple exciton generation
- Intermediate bands
- Hot carriers

Tandems (Multijunctions)

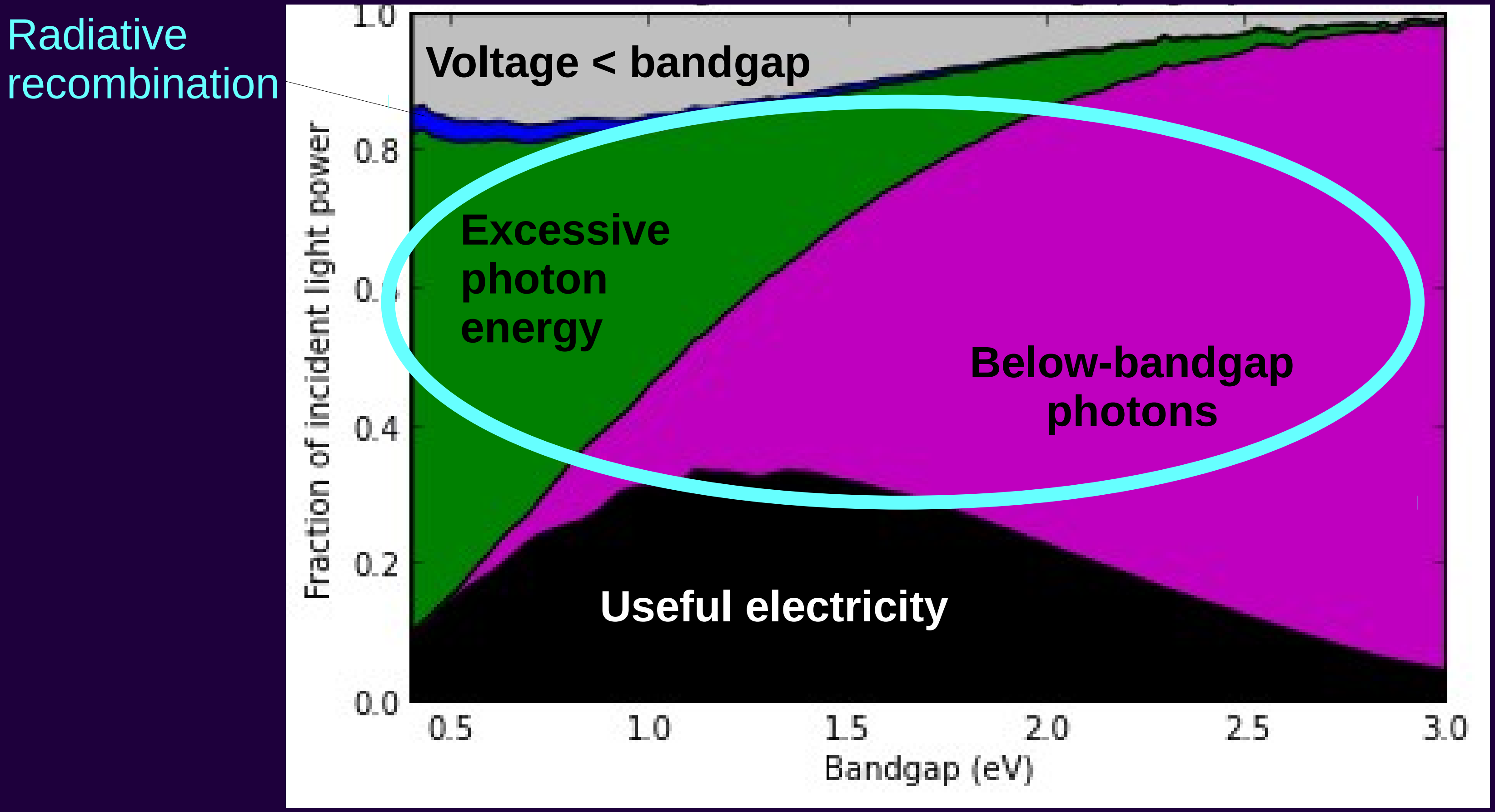


Tandem solar cells


High-bandgap (sub)cell

Low-bandgap (sub)cell

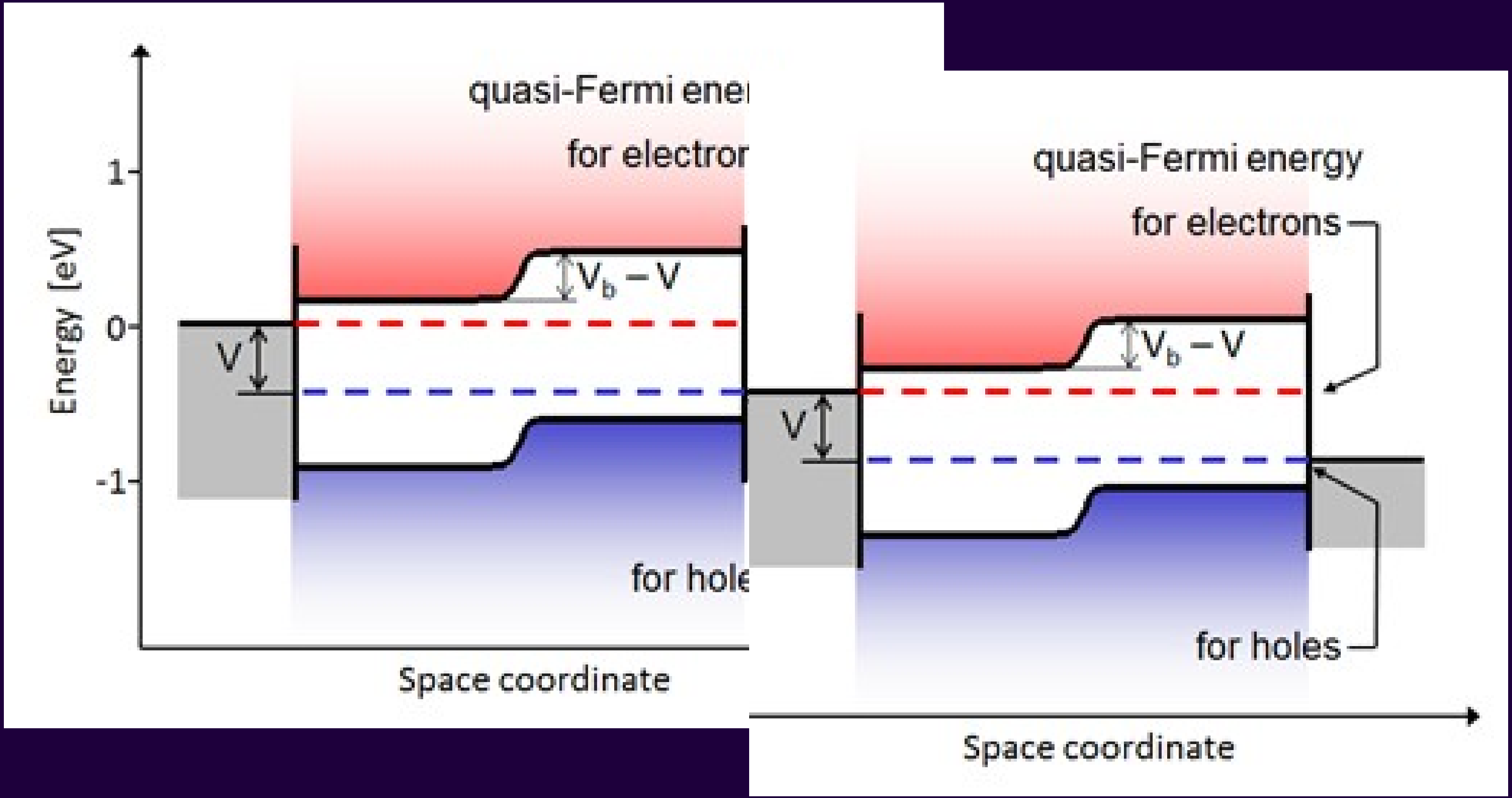
Tandem solar cells



Tandem solar cells

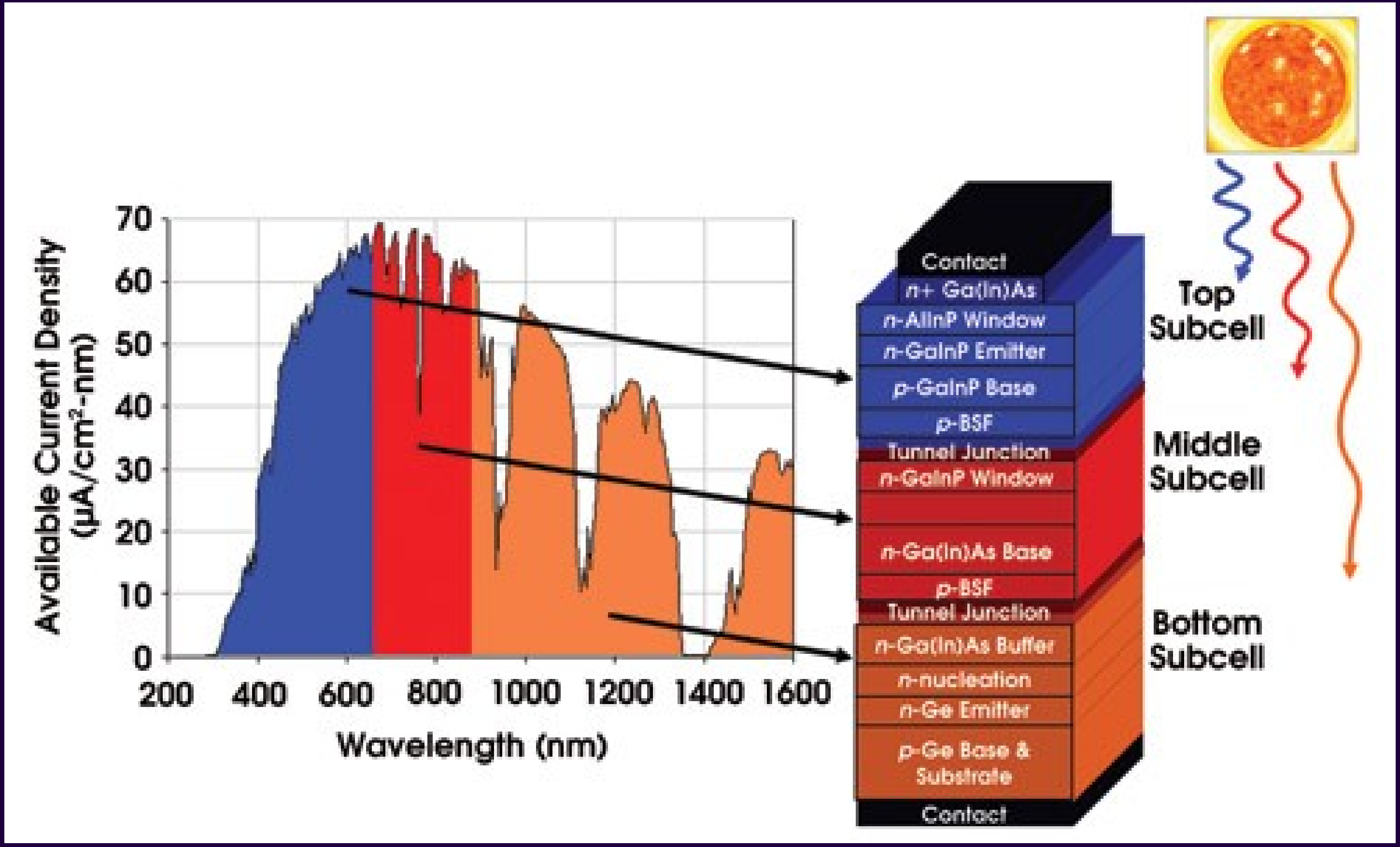
Where did S-Q go wrong?

When I said “(External voltage) ≤ (max QFL splitting)”



High-end tandems (III-V)

Unmatched efficiency … for \$100,000/m^2!



Low-end tandems

… For turning awful solar cells into mediocre ones!

- Multilayer amorphous silicon
  - Different bandgaps via process control or a-SiGe alloy.
- Multilayer organic, polymer, QD, DSSC, …

Tandem manufacturing constraints

- Generally all the different sub-cells are grown by the same type of process
  - CVD, sputtering, solution growth, etc.
- But there are various promising ideas for stacking cells that are grown separately …
  - For example, “silicon + III-V”

Would open up exponentially more possibilities…

Tandems – summary

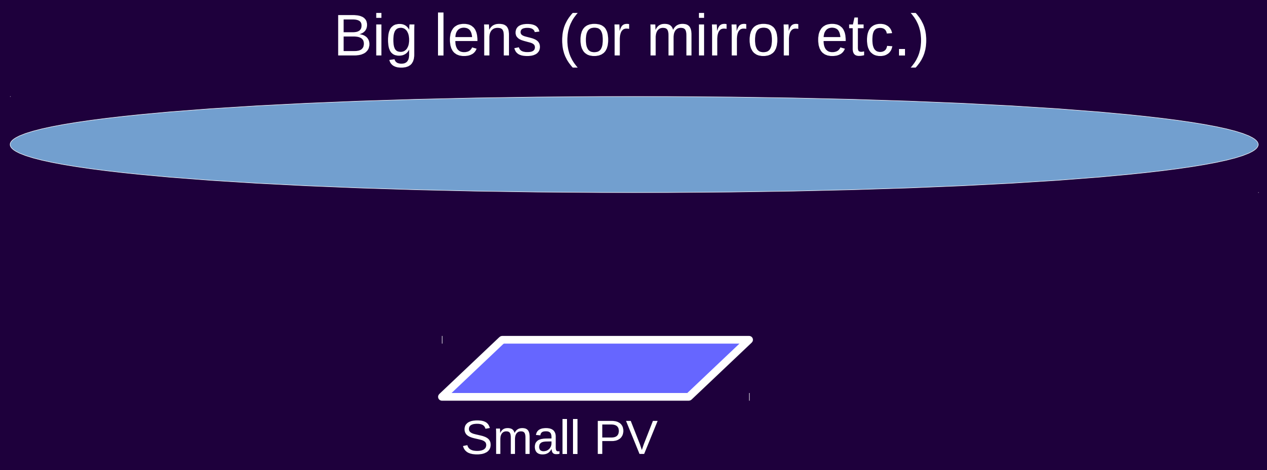
- A proven technique to increase solar cell efficiency beyond S-Q.
- A surprisingly small part of the (non-concentrated) market today.
  - The niche of **pretty-high-efficiency tandems** *(cheaper than \$100,000/m^2, but much more efficient than a-Si etc.)* is weirdly empty!
  - …Where are the tandems involving crystalline-silicon, CdTe, CIGS, etc.?

Watch this niche – I bet exciting and important
things will happen here sooner or later…

Part 2: Exceeding the SQ limit

- Tandems
- **Concentration**
- Anisotropic re-radiation
- Magneto-optics
- Multiple exciton generation
- Intermediate bands
- Hot carriers

Concentration

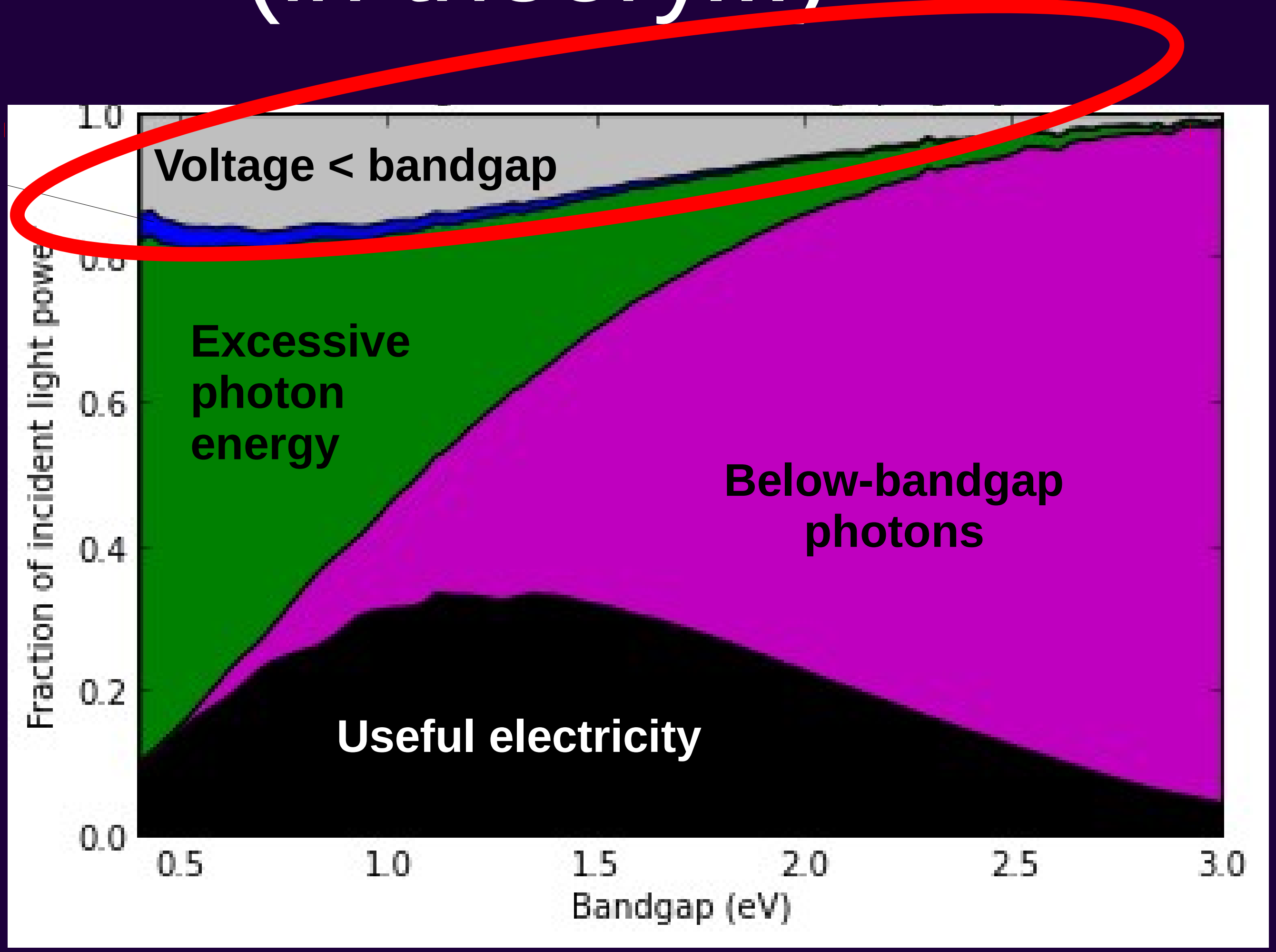


In theory, 100× more light gives *more* than 100× more electricity!

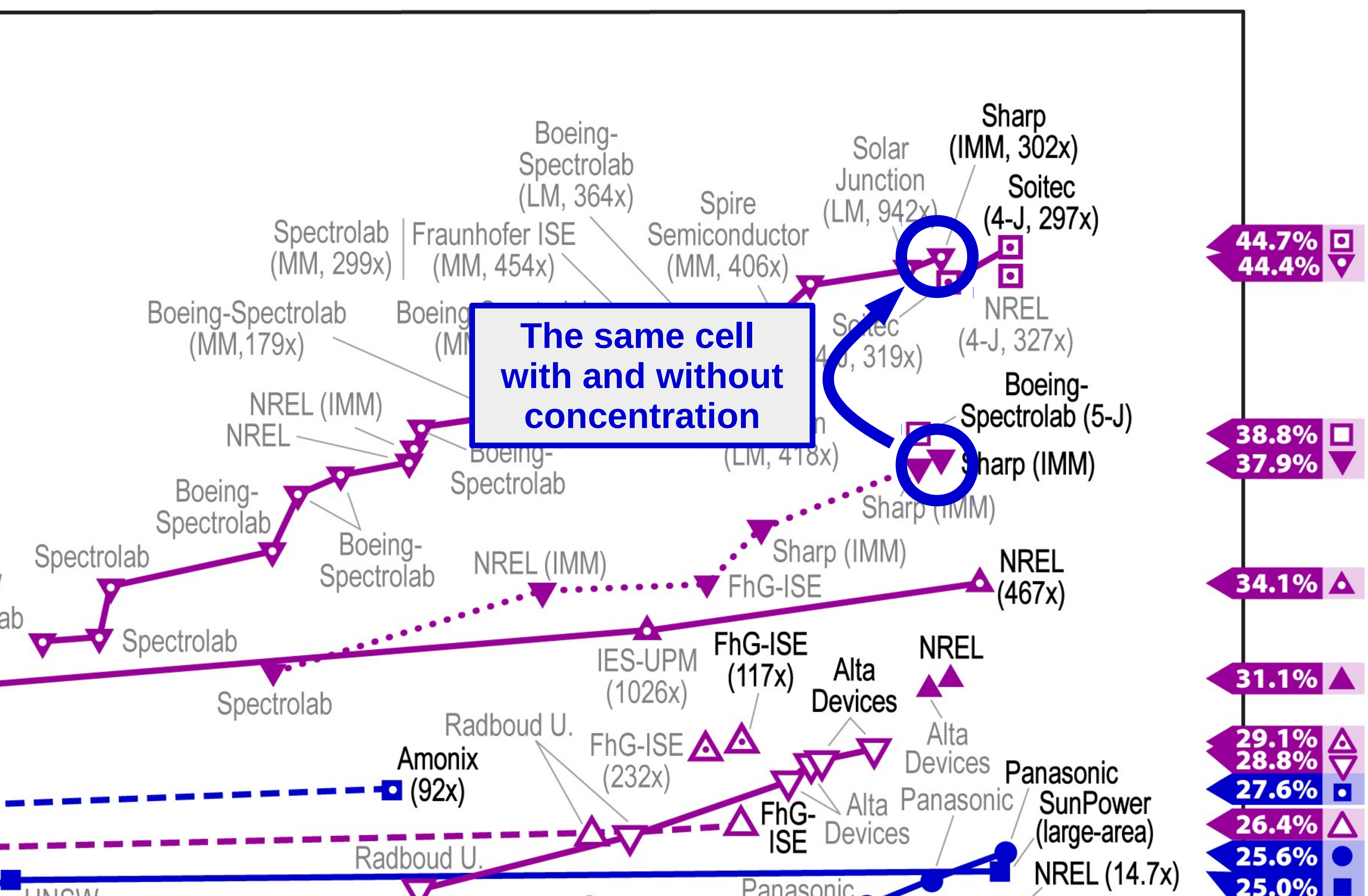
For example, I can operate with...
* 100× more photogeneration
* 100× more radiative recombination
* 100× more current
* Higher voltage!! (by 120mV)
* *More* than 100× more power

Concentration increases efficiency (in theory...)

Radiative recombination

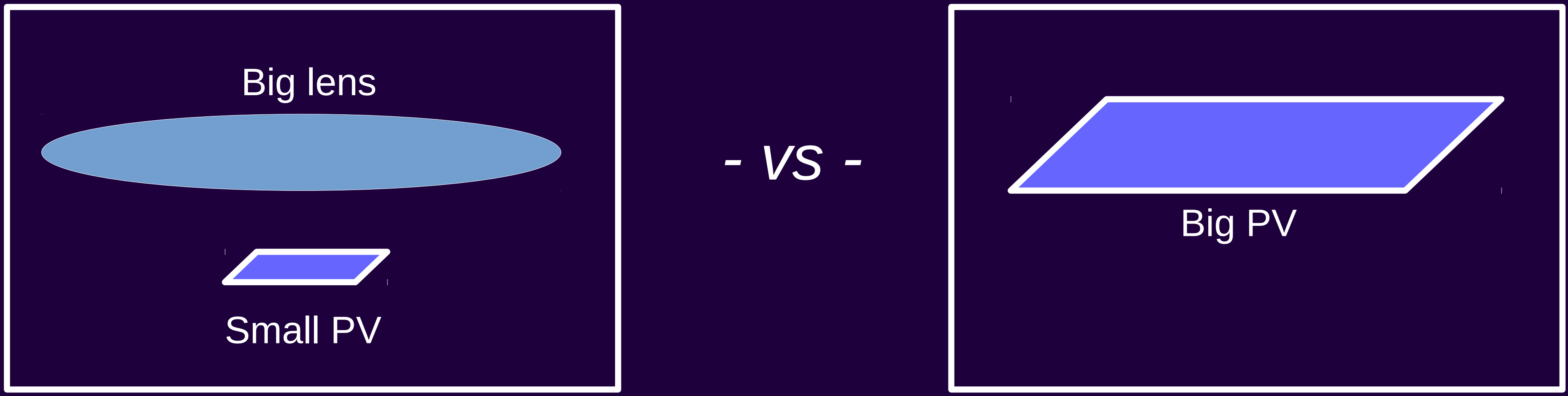


Concentration increases efficiency (in theory...)



The same cell with and without concentration

Concentration



Big lens

Small PV

- vs -

Big PV

- Actually, the efficiency boost of concentrated PV is an *illusion*!
  - You lose the diffuse light!
    - 15% at best, ~100% on a cloudy day.
  - Optical components are imperfect.
  - Solar cell can heat up, which lowers efficiency.
- The NREL chart efficiency measurements (previous slide) ignore all of these.

Concentration

- Concentration is ***NOT*** a *method of increasing the efficiency of a given solar cell*…
- Concentration is a *method for using $100,000/m^2 solar cells* without paying that much.

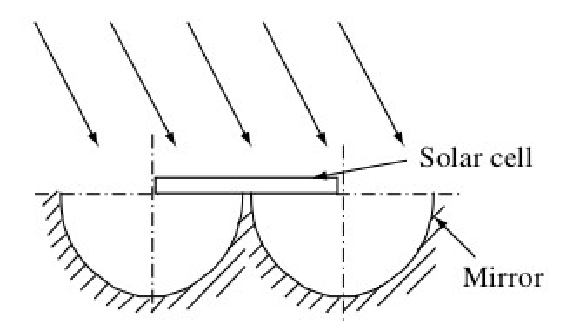
Concentration requires tracking the sun

- Utility-scale solar farms: No big deal
- Roofs etc.: Tracking is impractical

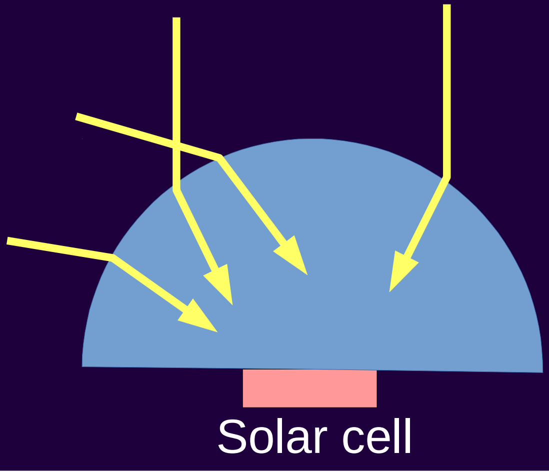
Concentration without tracking?

- "Non-tracking concentrators"
  - 2X from 2 faces
  - 2X from dielectric immersion
    - *adds bulk*
  - 2.5X from north-south restriction
    - *lose diffuse light*
  - Up to ~10X total in principle
- …It's not used in practice!
  - Adds complexity and expense for slight benefit.

2 faces



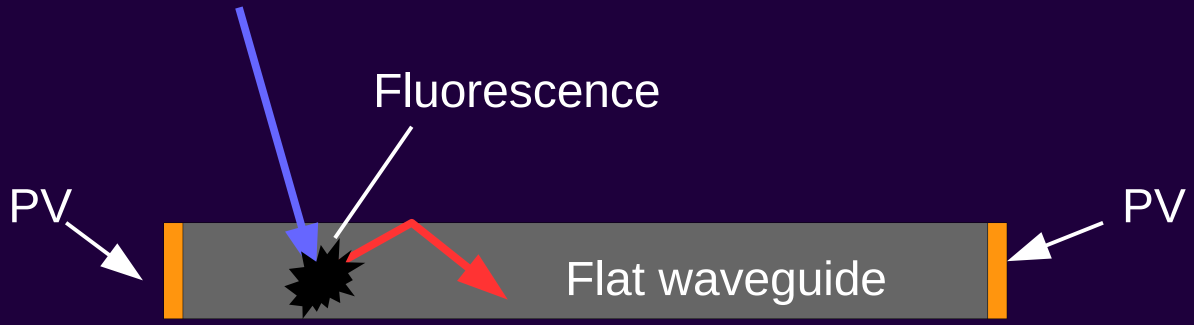
Dielectric immersion



Handbook of photovoltaic science and engineering, 2003, Ch. 11

Concentration without tracking?

- “Luminescent solar concentrators”
  - You don't lose the diffuse light!
  - ...but it alters the spectrum so that they are incompatible with the high-end tandems.

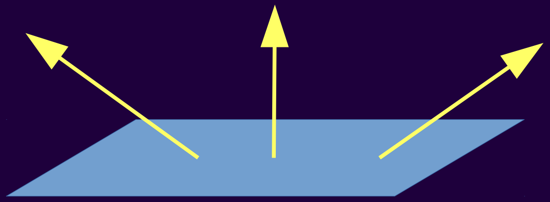


Part 2: Exceeding the SQ limit

- Tandems
- Concentration
- **Anisotropic re-radiation**
- Magneto-optics
- Multiple exciton generation
- Intermediate bands
- Hot carriers

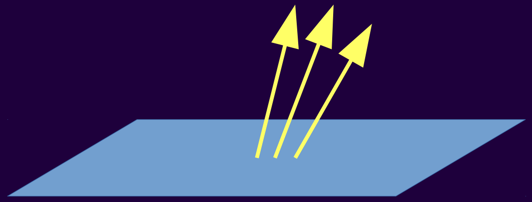
Anisotropic re-radiation

Earlier I assumed...



Radiative
recombination into
a hemisphere

Also possible...



Radiative
recombination into
only a small angle

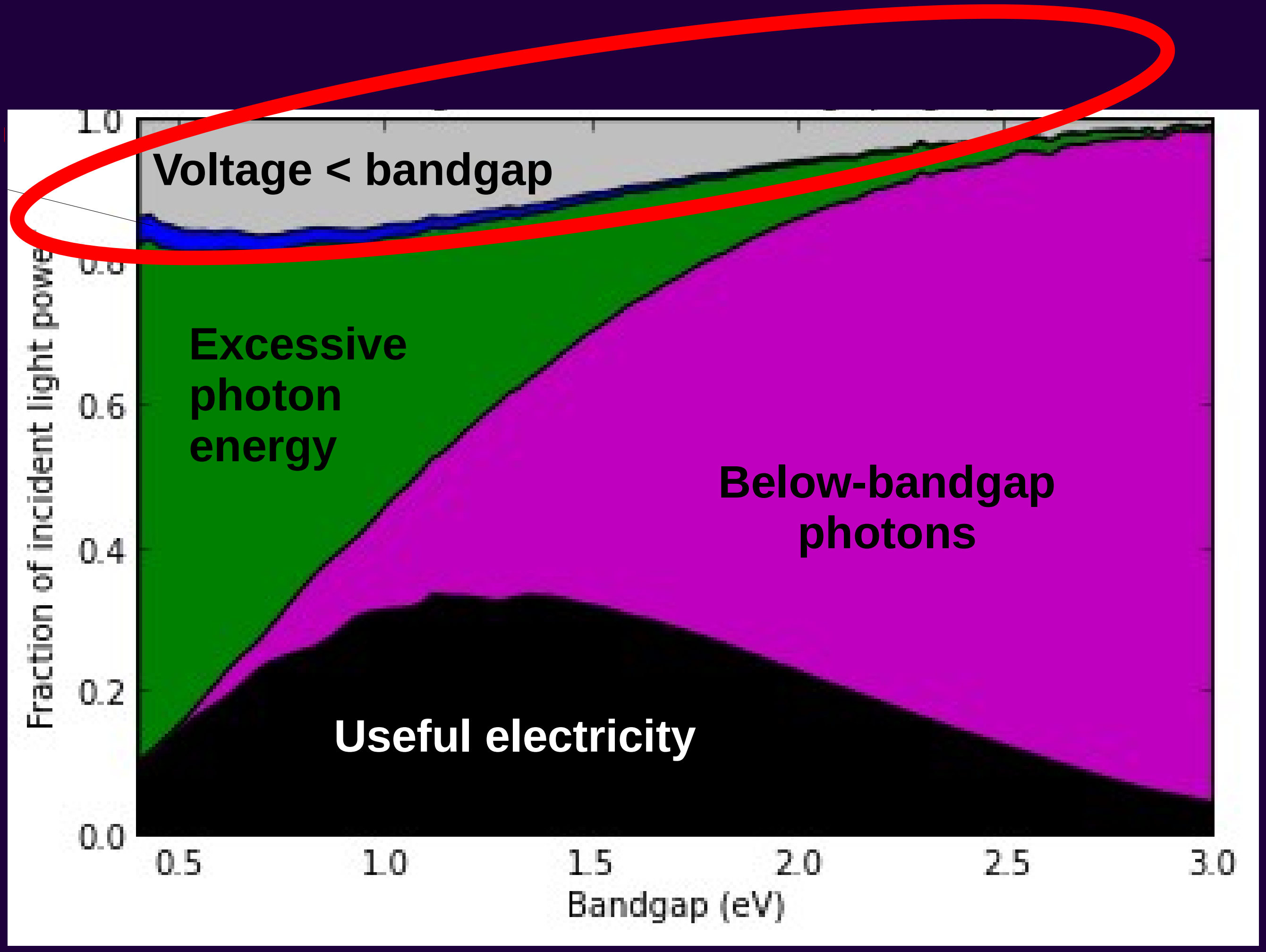
Less total radiative recombination
→ Higher efficiency limit than S-Q

Anisotropic re-radiation

- By reciprocity, the sun must be in the acceptance angle.
  - Tracking is required
  - You lose the diffuse light
- More importantly: Reduces radiative recombination but not nonradiative recombination.

→ *Not a serious way to increase efficiency.*

Anisotropic re-radiation (in theory)



Radiative recombination

Part 2: Exceeding the SQ limit

- Tandems
- Concentration
- Anisotropic re-radiation
- **Magneto-optics**
- Multiple exciton generation
- Intermediate bands
- Hot carriers

Time-reversal-symmetry breaking

- Earlier I related photogeneration to radiative recombination via **time-reversal symmetry**.
- Magneto-optics violate time-reversal symmetry!
  - Faraday rotators etc.
- So, can we exceed S-Q limit via magneto-optics?

Time-reversal-symmetry breaking

Long story short…

- Photogeneration and radiative recombination are still related, but in a more complicated way.

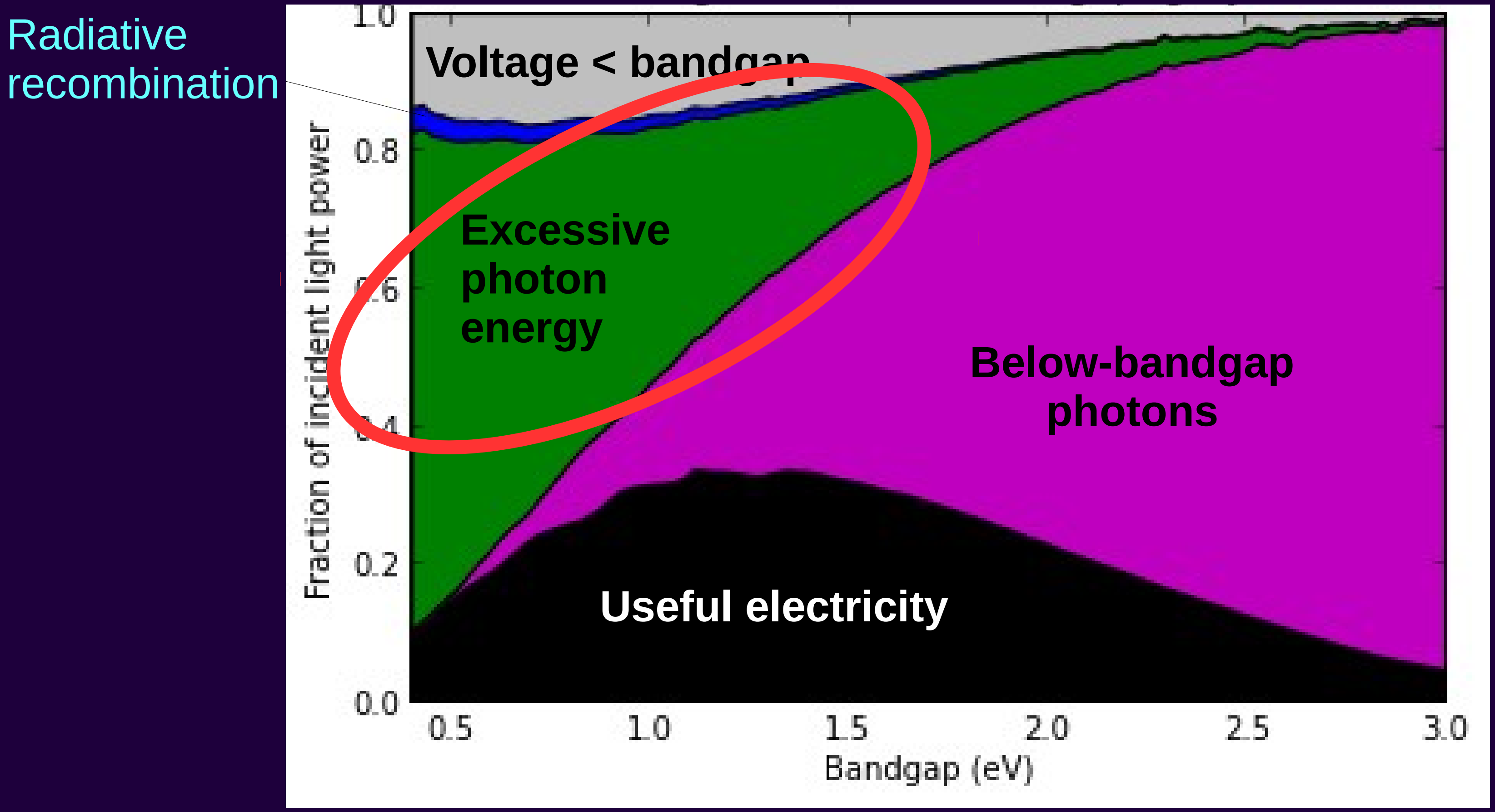
- Magneto-optics raises the theoretical limit slightly; probably no benefit in practice.

MA Green, Nano Lett. 2012, 12, 5985

Part 2: Exceeding the SQ limit

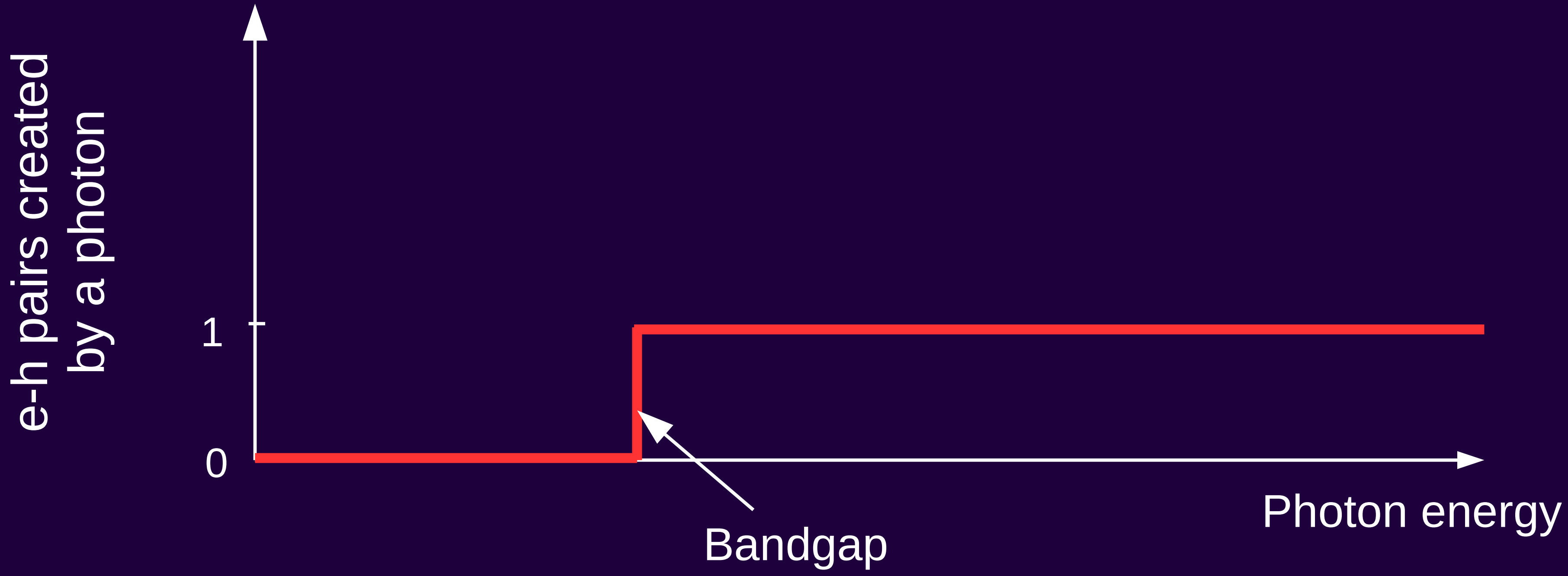
- Tandems
- Concentration
- Anisotropic re-radiation
- Magneto-optics
- **Multiple exciton generation**
- Intermediate bands
- Hot carriers

Multiple exciton generation



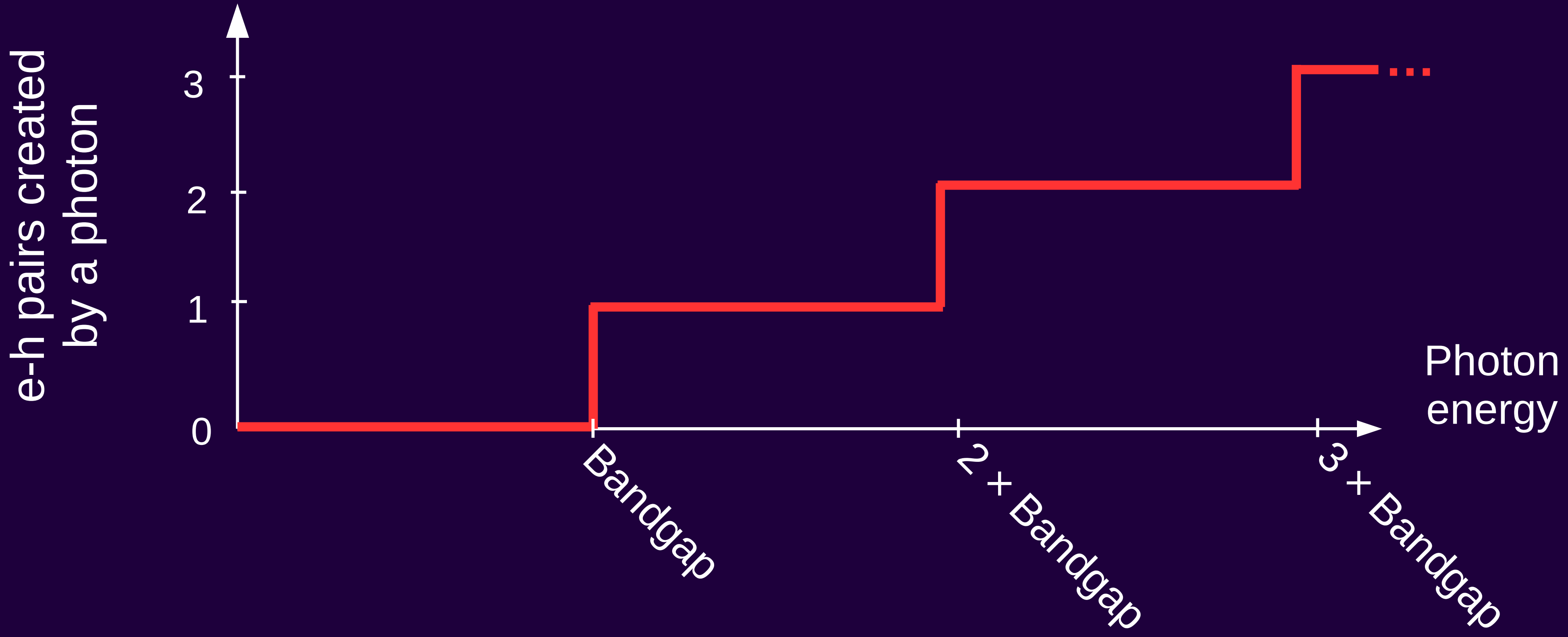
Multiple exciton generation

Shockley-Queisser assumption

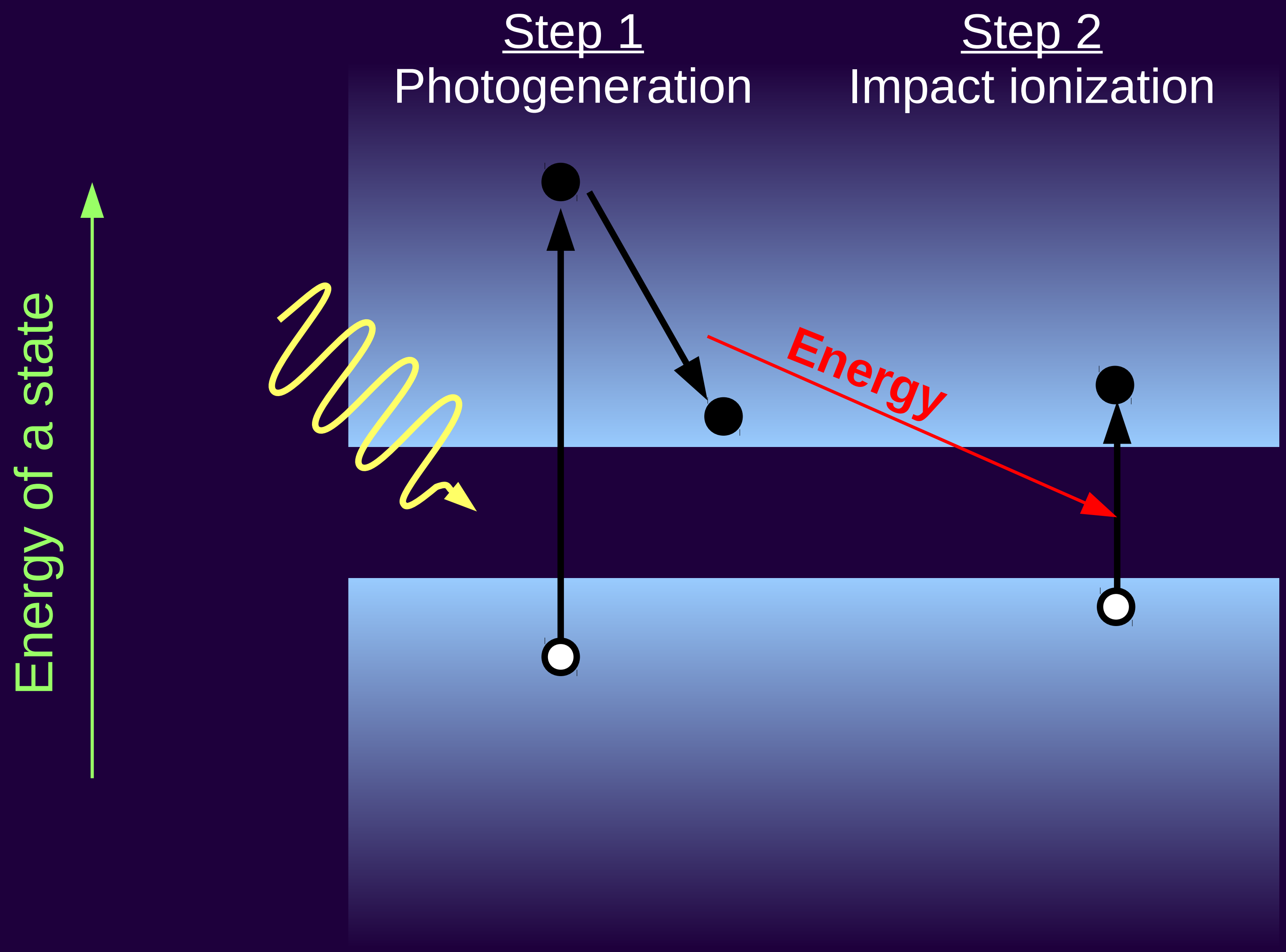


Multiple exciton generation

More optimistic



Multiple exciton generation



Problem with MEG

- Most materials do not have MEG!
  - Even the best ones do it only sometimes, well above 2 × bandgap

Problem with MEG

- Not an independent design parameter!
  - We cannot “add” MEG into a generic PV material that we already like. (At least, not while maintaining the good PV-related material properties.)
  - (Except in certain special cases – e.g. singlet-fission MEG in polymer PVs.)

- …Remember, only 5 material families get anywhere close to SQ limit. None happens to have MEG.

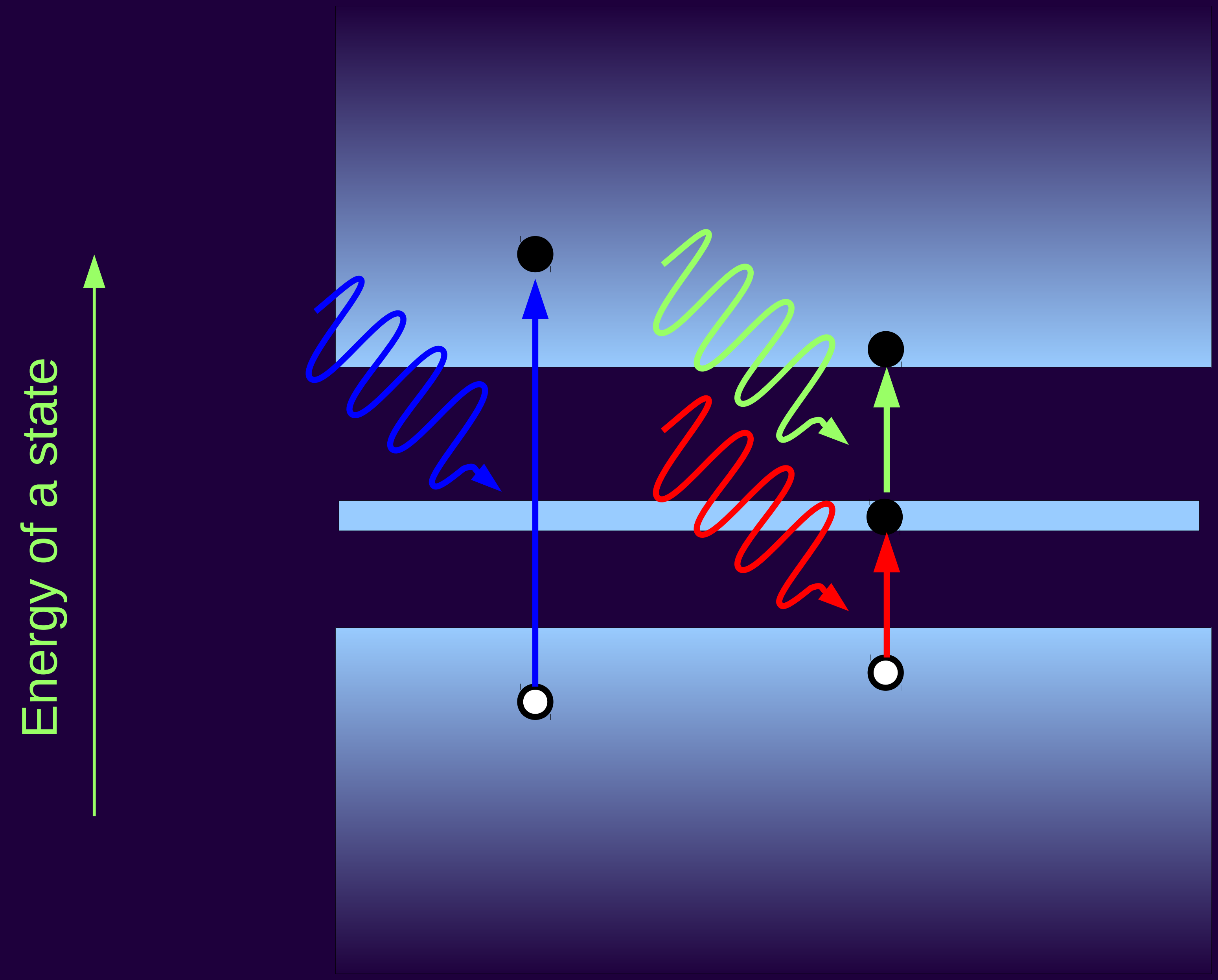
Problem with MEG

- So, MEG would be a nice thing to have when looking for solar cell materials
    - … Just like high absorption, low nonradiative recombination, cost, bandgap, stability, manufacturability, …

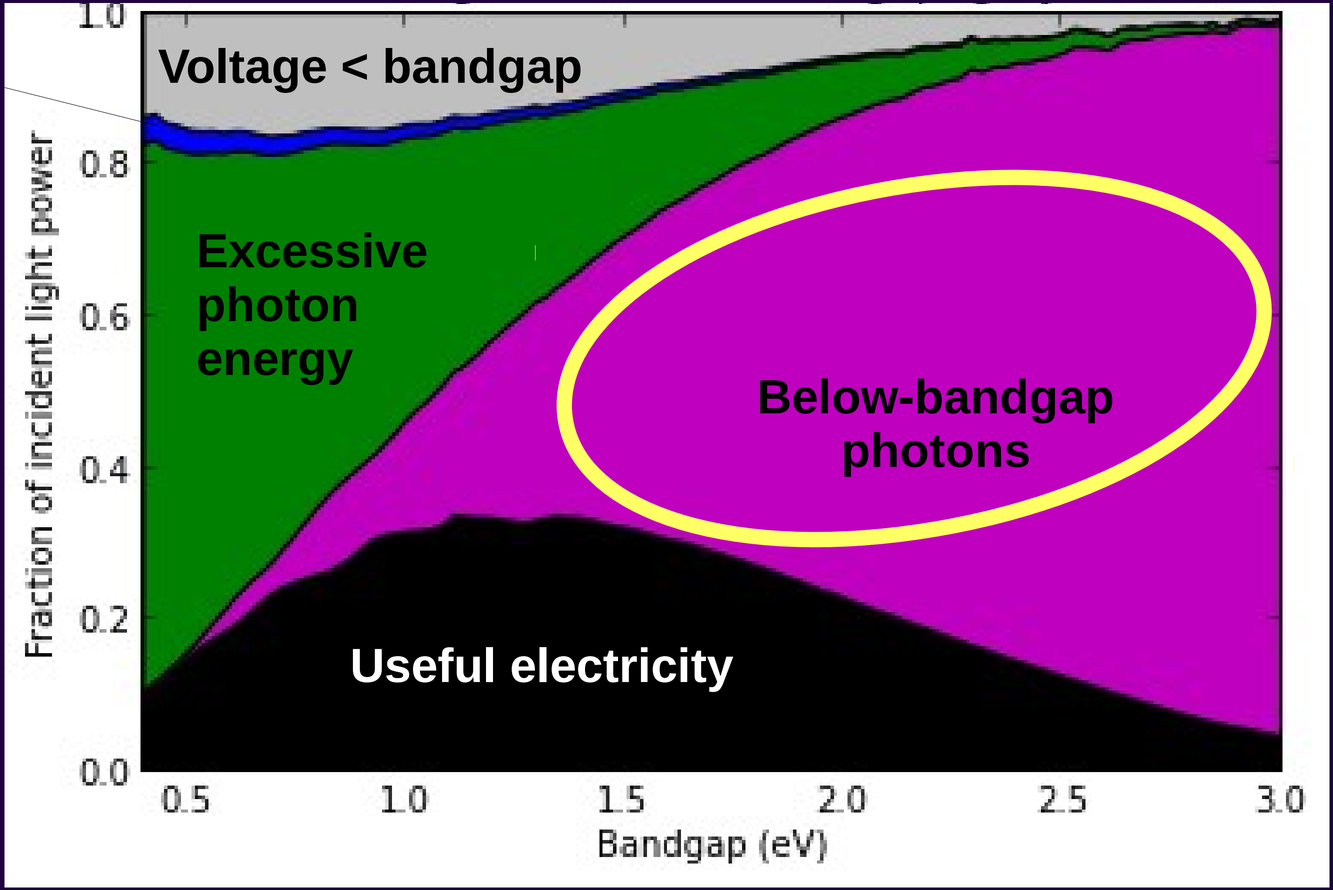
Part 2: Exceeding the SQ limit

- Tandems
- Concentration
- Anisotropic re-radiation
- Magneto-optics
- Multiple exciton generation
- **Intermediate bands**
- Hot carriers

Intermediate bands



Intermediate bands



Radiative recombination

Intermediate bands

- We know how to do this for many materials…
  - (Add appropriate defects, or mix in quantum dots)

- ...but normally it works out terribly!
  - Catalyzes nonradiative recombination.

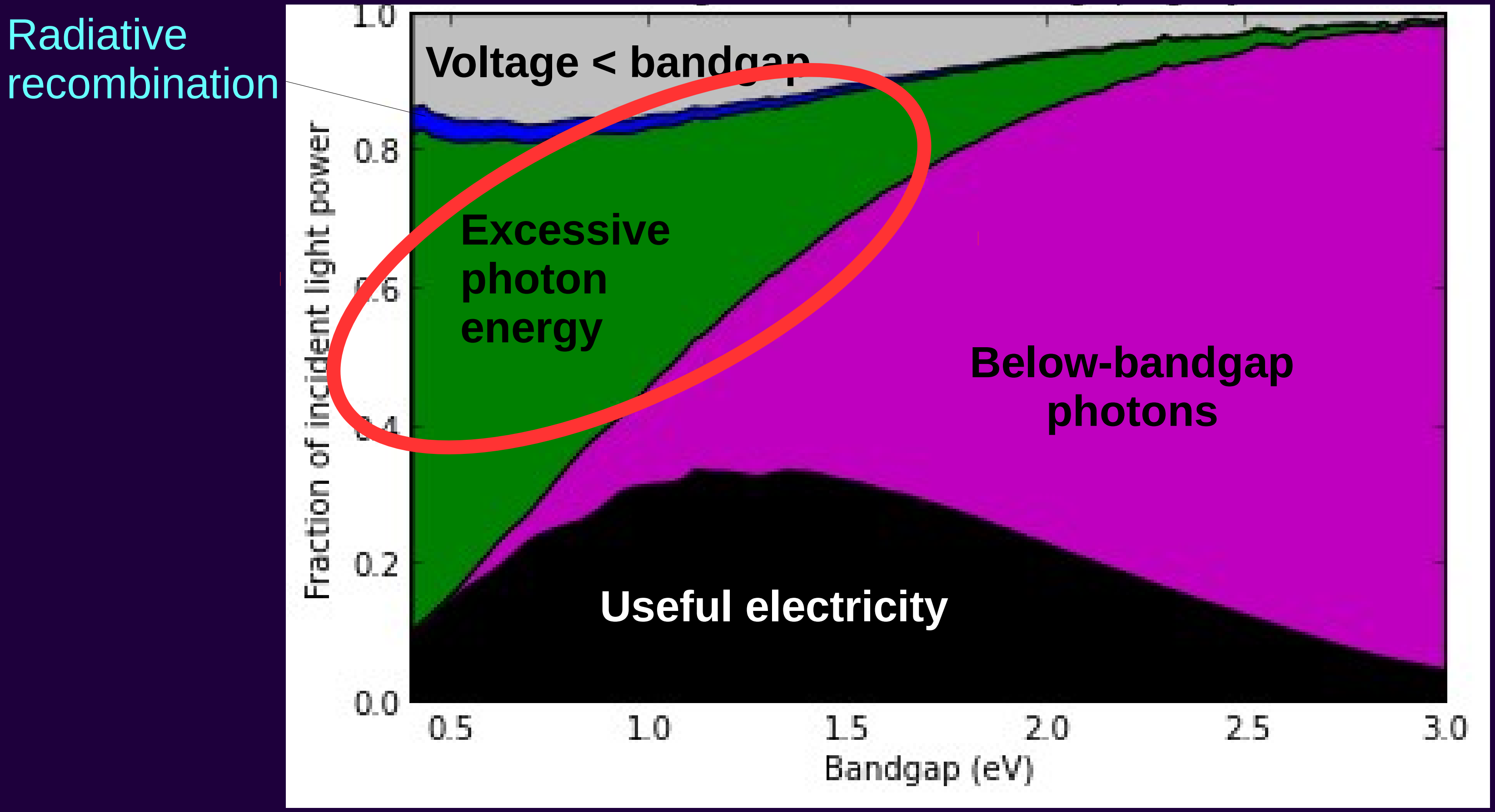
- Theory → It might work
- In practice → Nothing yet

Work in progress

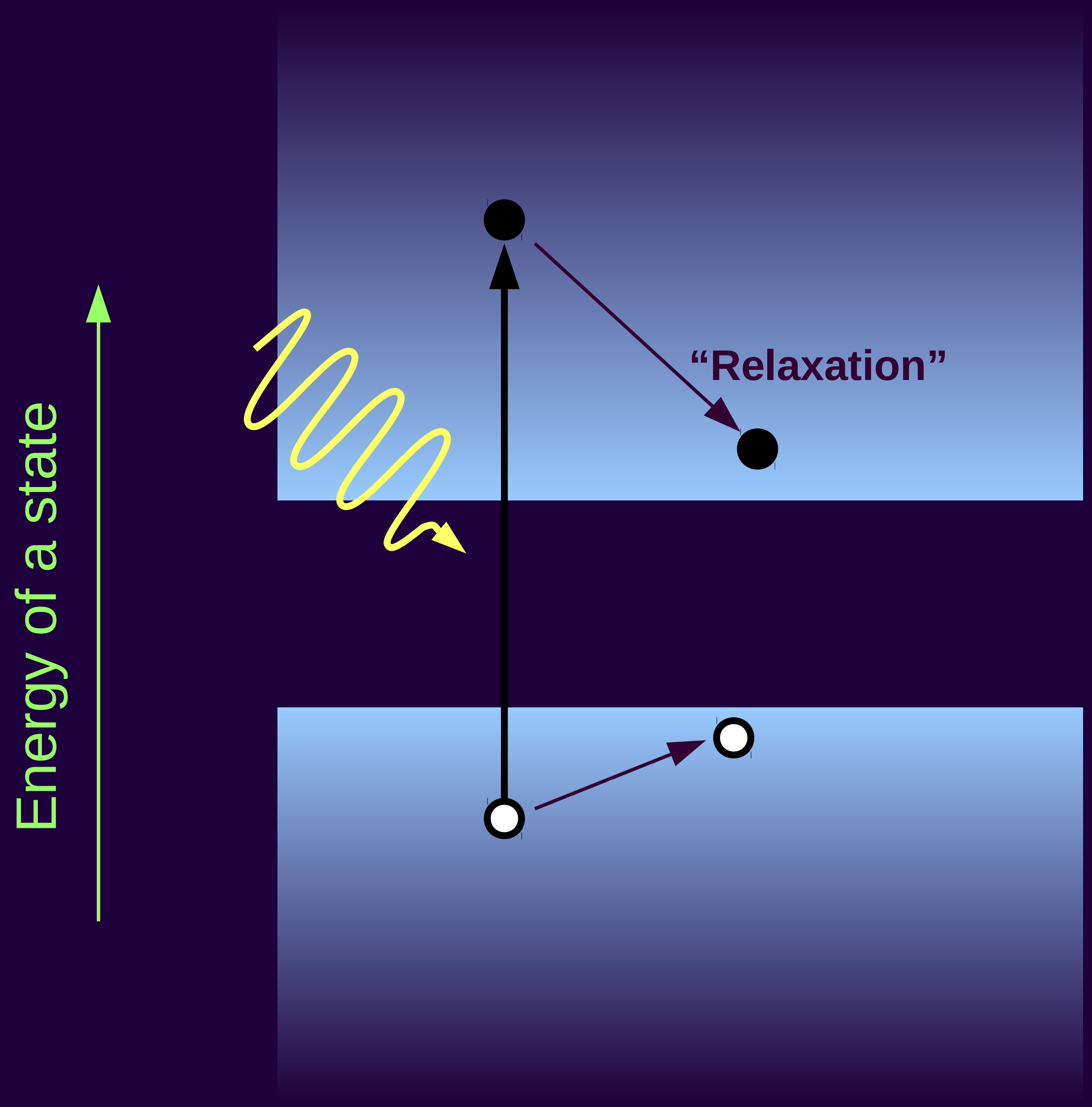
Part 2: Exceeding the SQ limit

- Tandems
- Concentration
- Anisotropic re-radiation
- Magneto-optics
- Multiple exciton generation
- Intermediate bands
- **Hot carriers**

Hot carrier solar cells



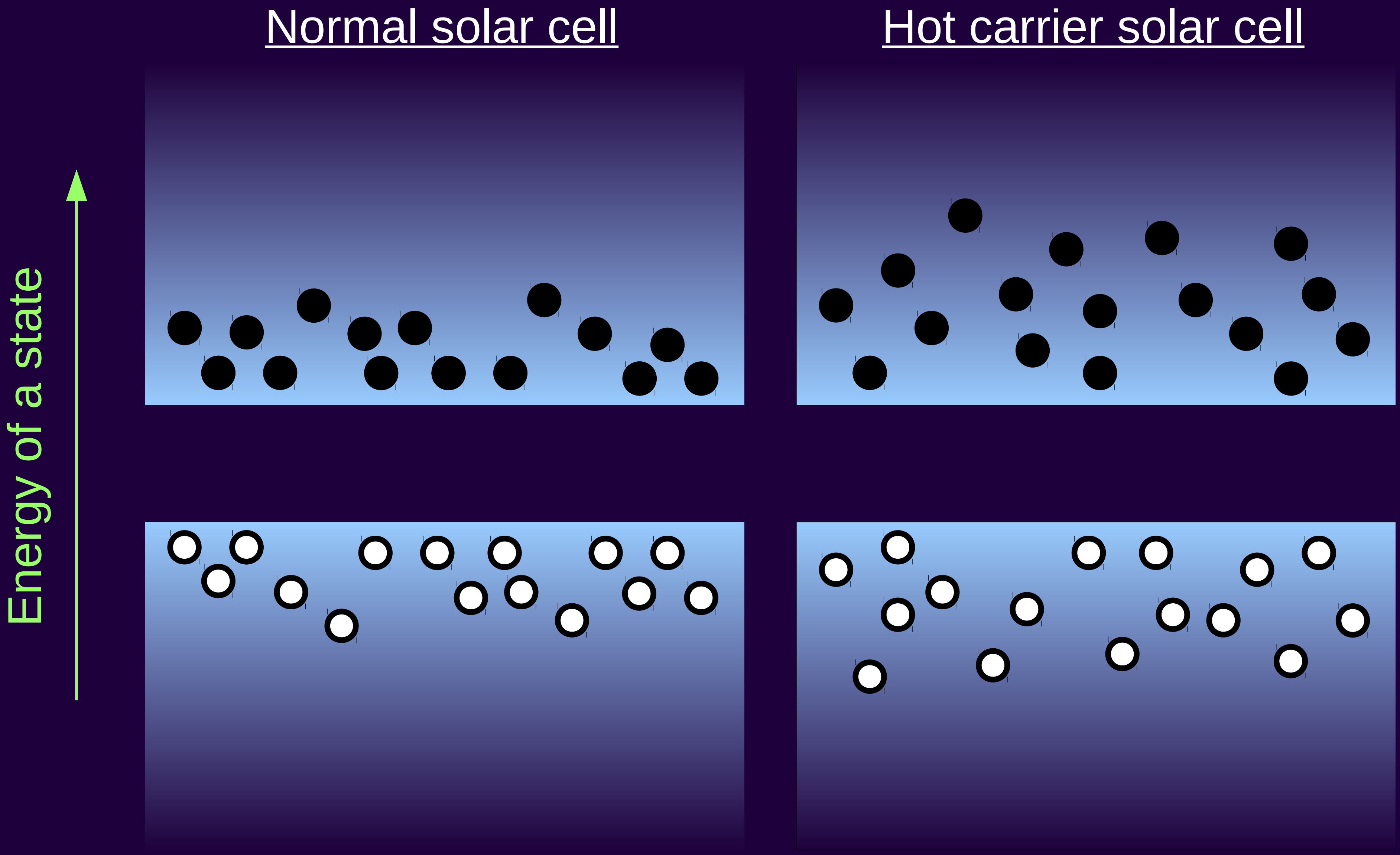
Hot carrier solar cells



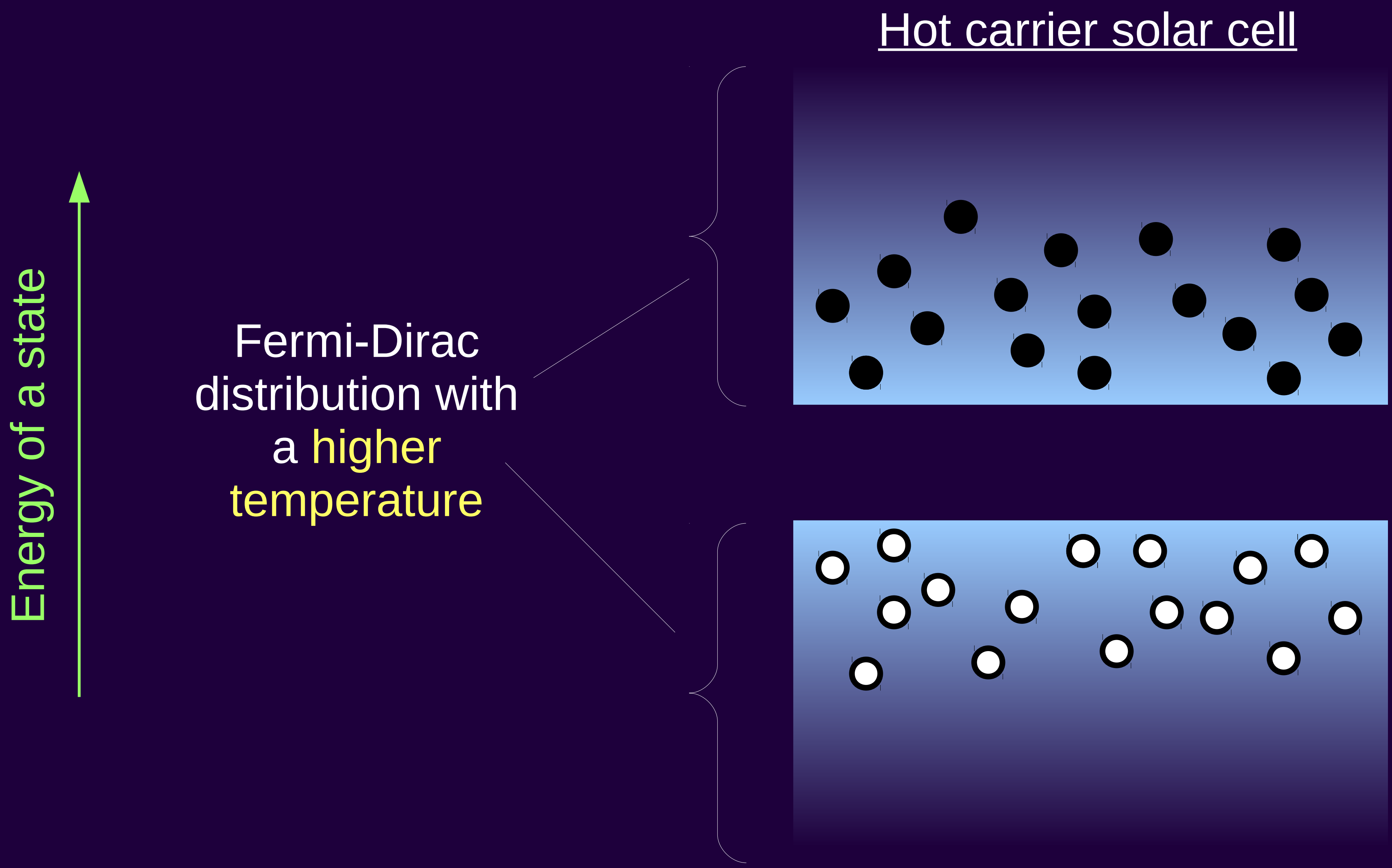
Energy goes to phonons

What if this can be prevented?

Hot carrier solar cells



Hot carrier solar cells



Hot carrier solar cell

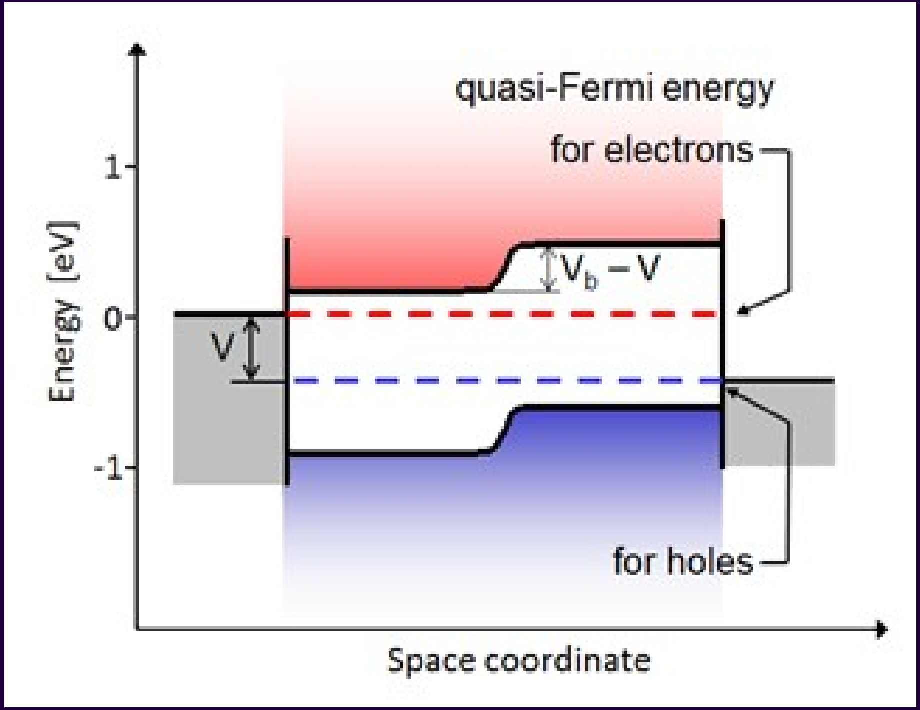
Energy of a state

Fermi-Dirac
distribution with
a higher
temperature

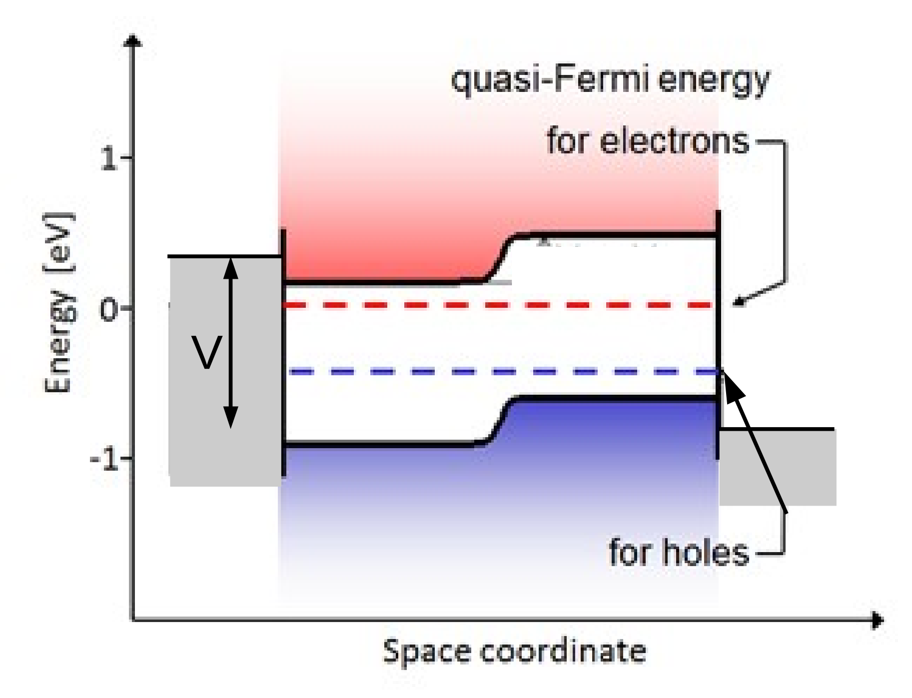
Hot carrier solar cells

Where did S-Q go wrong?

When I said "(External voltage) ≤ (max QFL splitting)"



Ideal normal solar cell
(from earlier)



Ideal hot-carrier solar cell

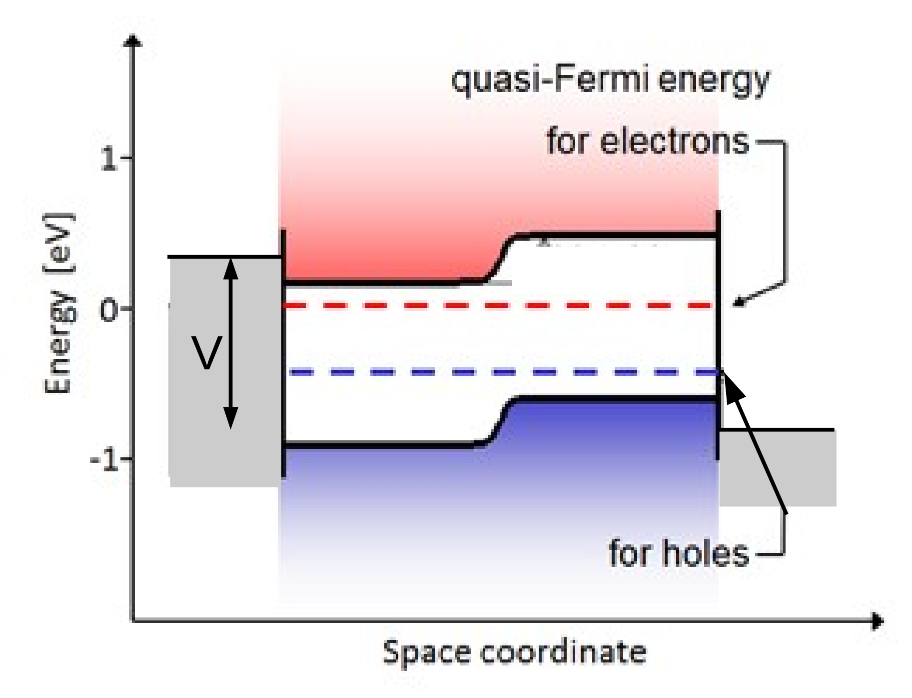
Hot carrier solar cells

Where did S-Q go wrong?

When I said “(External voltage) ≤ (max QFL splitting)”

Normally this doesn't work – the electrons and holes would *enter* the semiconductor instead of *exiting*!

(“Drift-diffusion equation”)

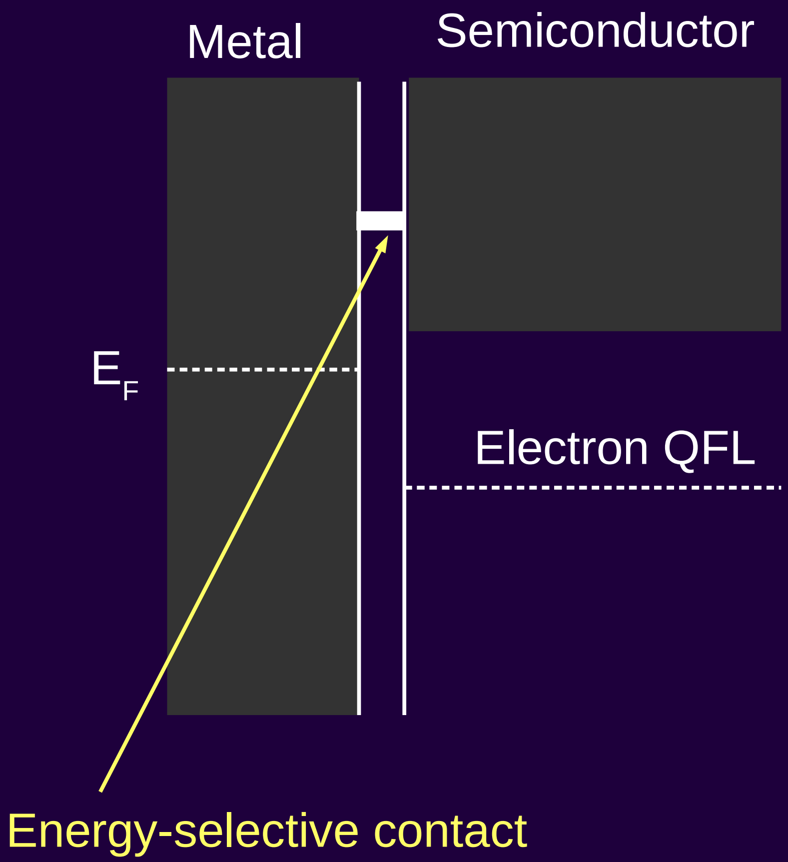


Ideal hot-carrier solar cell

Hot carrier solar cells

Where did S-Q go wrong?

When I said “(External voltage) ≤ (max QFL splitting)”



HOWEVER if...

- semiconductor electrons are hot,
- metal electrons are room temp.,
- “energy-selective contact”…

…Then the electrons can “flow uphill”.

Hot carrier solar cells – challenges

- How do you prevent the electrons from transferring energy to phonons within nanoseconds?
- How do you make an energy-selective contact?

Not totally impossible – and I'm happy people are working on it – but a *real* long shot

Any questions?

Thanks for your attention!!!

S-Q calculation implemented in Python
http://sjbyrnes.com/sq.html

Talk to me!
steven.byrnes@gmail.com