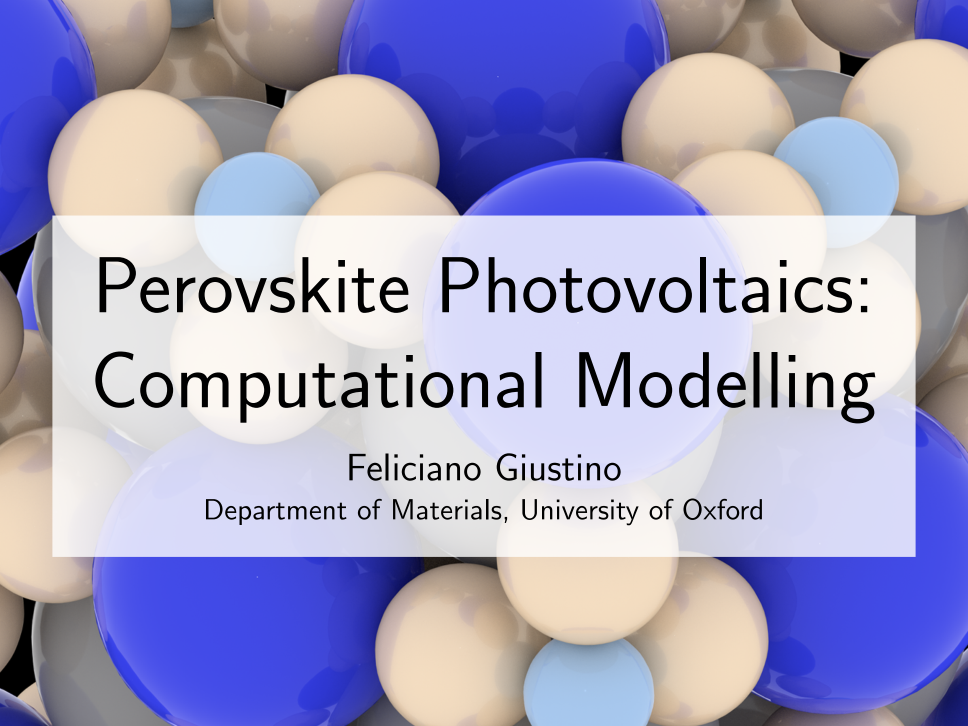
ICTP Caribbean School on Materials for Clean Energy

30 May - 5 June 2019, Cartagena, Colombia



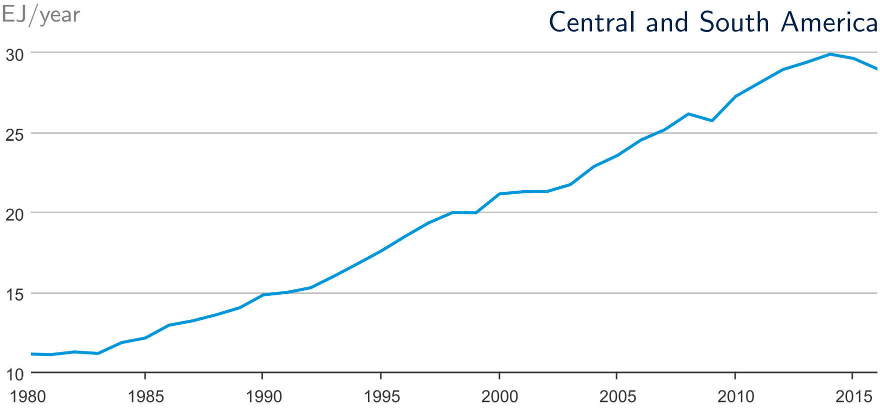
Perovskite Photovoltaics: Computational Modelling

Feliciano Giustino
Department of Materials, University of Oxford

Summary of lectures

- Energy & Photovoltaics
- Halide Perovskites
- Density functional theory
- Two examples on perovskite photovoltaics
  1. Modelling: Electron transport
  2. Design: Lead replacement

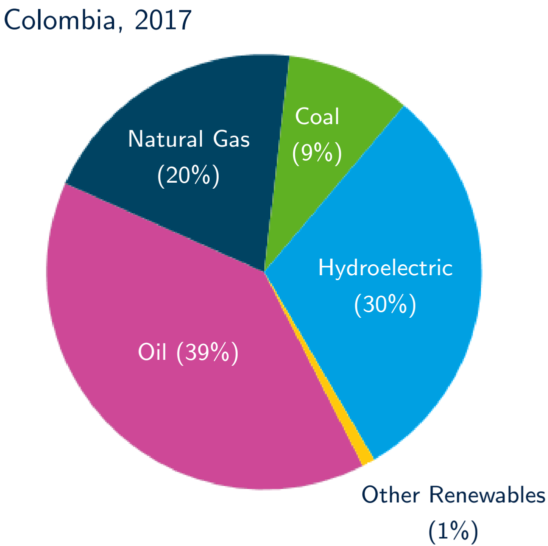
Primary energy consumption



2016: **32,000 kcal**/day/person

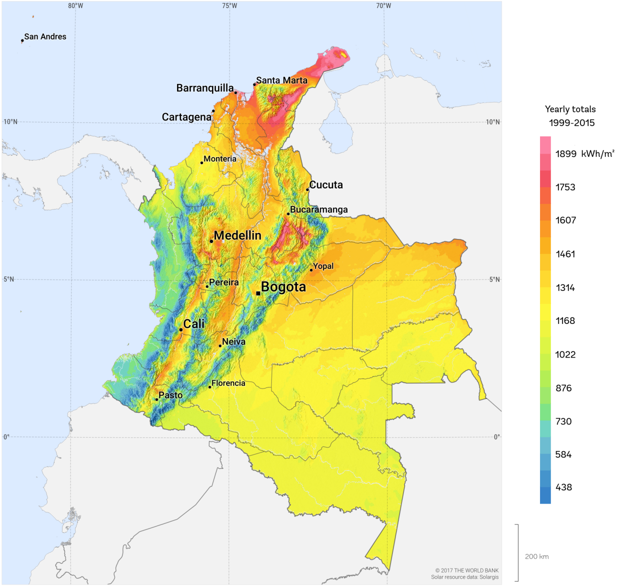
(85,000 kcal/day/person in EU)

Source: U.S. Energy Information Administration



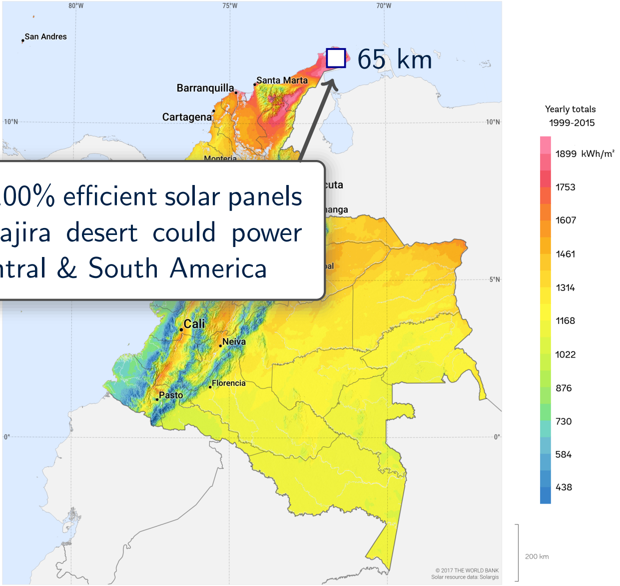
BP Statistical Review of World Energy (2018)

Solar irradiation in Colombia



2017 The World Bank, Solar resource data: Solargis

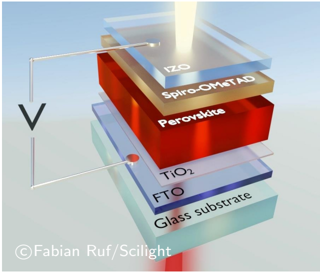
Solar irradiation in Colombia

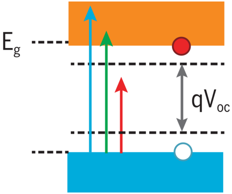


With 100% efficient solar panels La Guajira desert could power all Central & South America

2017 The World Bank, Solar resource data: Solargis

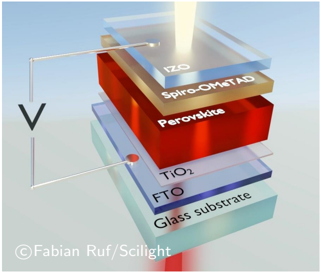
Shockley-Queisser limit

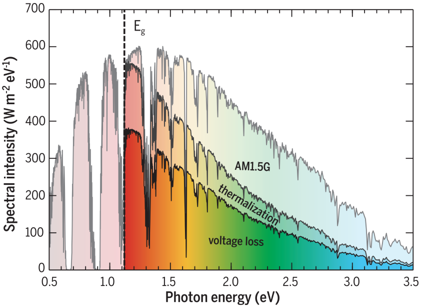


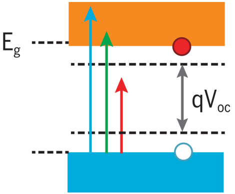


From: Polman et al., Science 352, aad4424 (2016)

Shockley-Queisser limit

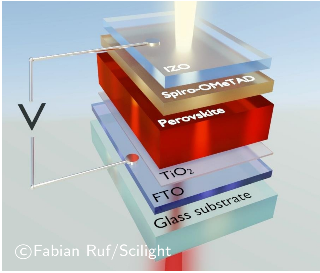


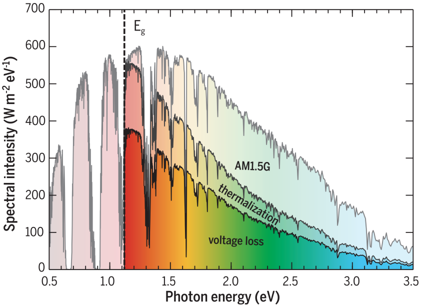


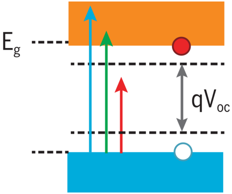


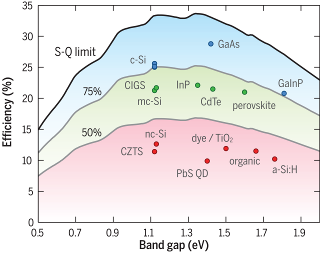
From: Polman et al., Science 352, aad4424 (2016)

Shockley-Queisser limit



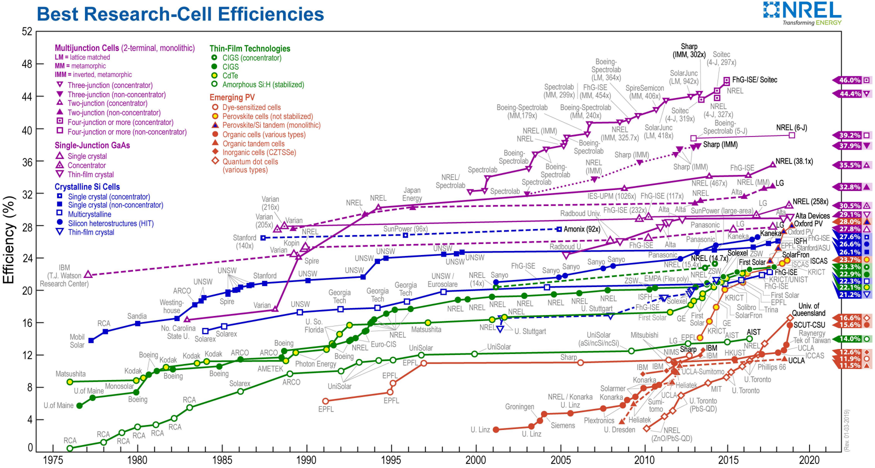






From: Polman et al., Science 352, aad4424 (2016)

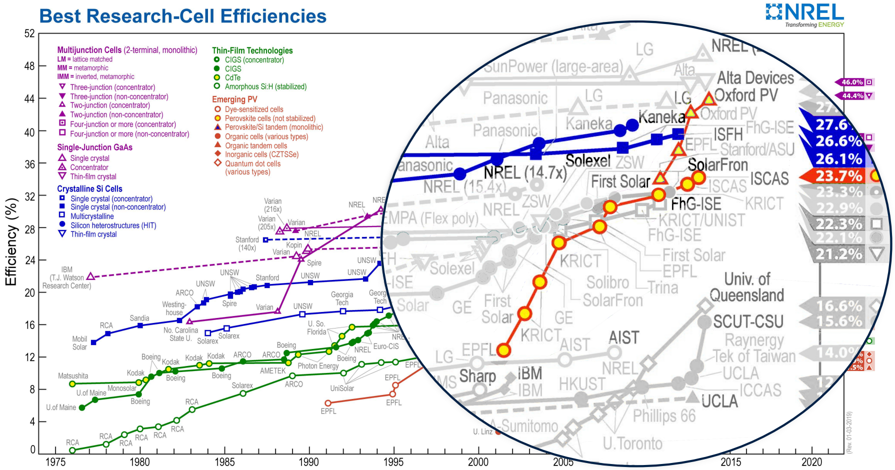
NREL Efficiency Tables



https://www.nrel.gov/pv/assets/pdfs/pv-efficiency-chart.20190103.pdf

NREL Efficiency Tables

23.7% ISCAS   28% OxfordPV (Si/Per)



https://www.nrel.gov/pv/assets/pdfs/pv-efficiency-chart.20190103.pdf

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REPORT

Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites

Michael M. Lee[1], Joël Teuscher[1], Tsutomu Miyasaka[2], Takurou N. Murakami[2,3], Henry J. Snaith[1,*]
+ See all authors and affiliations

Science 02 Nov 2012:
Vol. 338, Issue 6107, pp. 643-647
DOI: 10.1126/science.1228604

SCIENTIFIC REPORTS

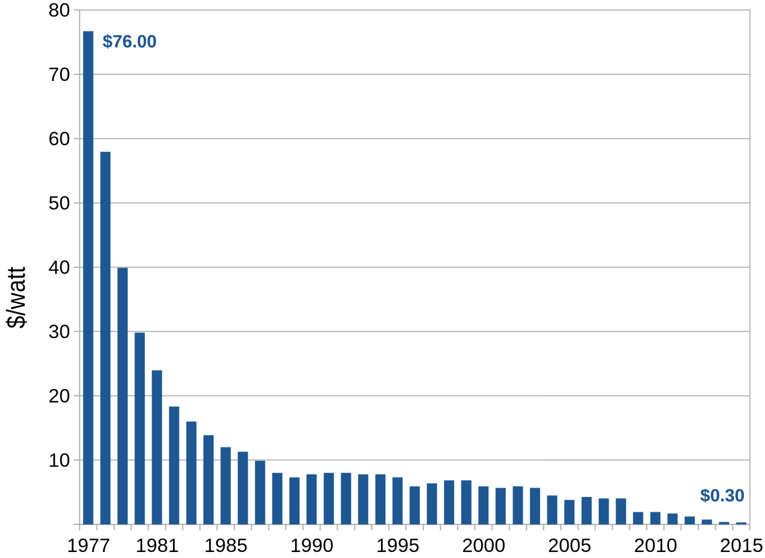
Article | OPEN | Published: 21 August 2012

Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%

Hui-Seon Kim, Chang-Ryul Lee, Jeong-Hyeok Im, Ki-Beom Lee, Thomas Moehl, Arianna Marchioro, Soo-Jin Moon, Robin Humphry-Baker, Jun-Ho Yum, Jacques E. Moser, Michael Grätzel & Nam-Gyu Park

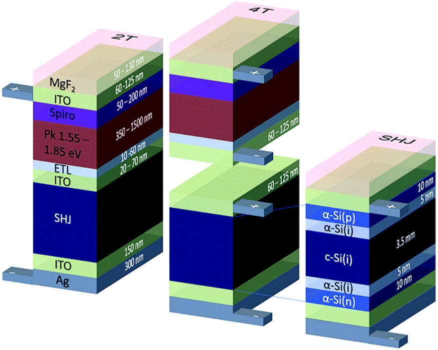
Scientific Reports **2**, Article number: 591 (2012) | Download Citation

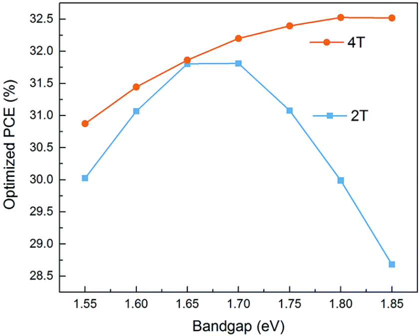
Cost of silicon solar cells



Bloomberg New Energy Finance & pv.energytrend.com

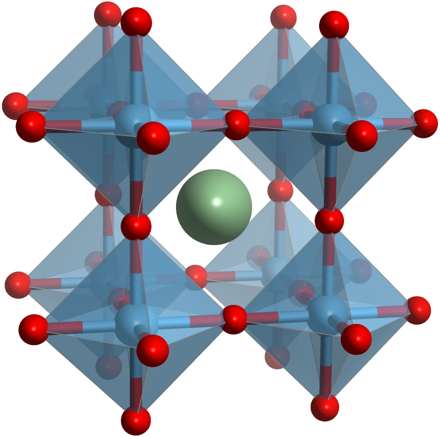
Silicon is unbeatable in price but we need more efficient cells:
silicon/perovskite **tandem** cells may be the future





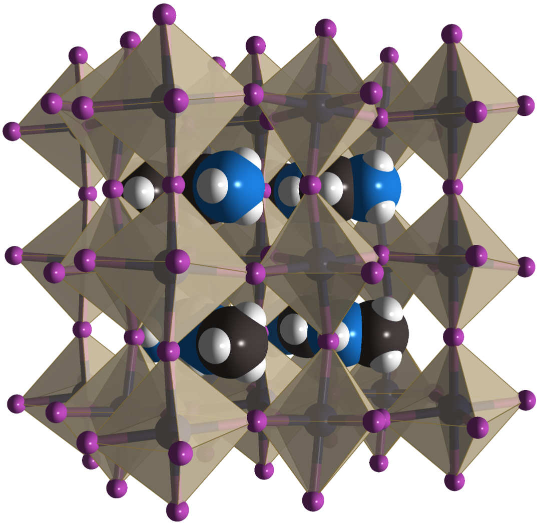
Hörantner and Snaith, Energy Environ. Sci. 10, 1983 (2017)

ABX_3



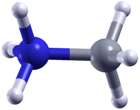
$Ca^{2+}Ti^{4+}O_3^{2-}$

$MAPbI_3$ (MA = methylammonium)

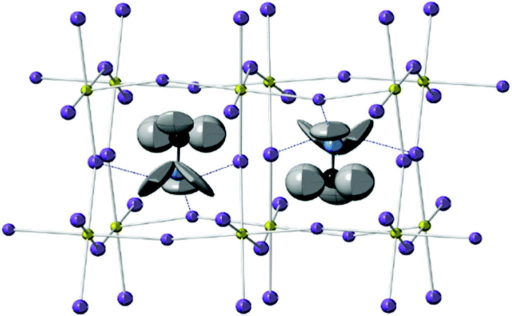


The organic cation

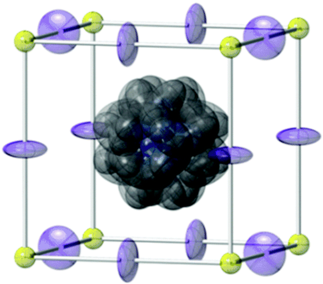
MA $= CH_3NH_3^+$



Orthorhombic, $T < 167$ K

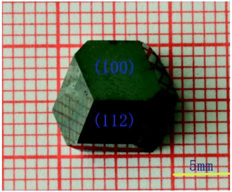


Cubic, $T > 327$ K

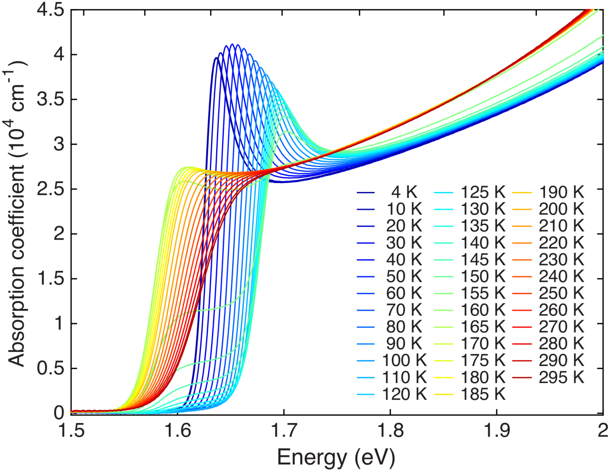


Weller et al., Chem. Commun. 51, 4180 (2015)

Optical properties of $MAPbI_3$



Dang et al., CrystEngComm 17, 665 (2015)



Davies et al., Nat. Commun. 9, 293 (2018)

1 Understanding electron transport

2 Finding non-toxic alternatives to Pb

Schrödinger's equation for the H atom

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi - \frac{e^2}{4\pi\epsilon_0|\mathbf{r}|}\psi = E_{\rm tot}\,\psi$$

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Many-body Schrödinger's equation

$$-\frac{\hbar^2}{2m_e}\sum\nolimits_i\nabla_i^2\,\Psi-\frac{\hbar^2}{2M_I}\sum\nolimits_I\nabla_I^2\,\Psi-\sum\nolimits_{i,I}\frac{e^2Z_I}{4\pi\epsilon_0|\mathbf{r}_i-\mathbf{R}_j|}\Psi$$

$$+\sum\nolimits_{I>J}\frac{e^2Z_IZ_J}{4\pi\epsilon_0|\mathbf{R}_I-\mathbf{R}_J|}\Psi+\sum\nolimits_{i>j}\frac{e^2}{4\pi\epsilon_0|\mathbf{r}_i-\mathbf{r}_j|}\Psi=E_{\rm tot}\,\Psi$$

Schrödinger's equation for the H atom

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi - \frac{e^2}{4\pi\epsilon_0|\mathbf{r}|}\psi = E_{\rm tot}\,\psi$$

Many-body Schrödinger's equation

$$-\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2\,\Psi - \frac{\hbar^2}{2M_I}\sum_I \nabla_I^2\,\Psi - \sum_{i,I}\frac{e^2 Z_I}{4\pi\epsilon_0|\mathbf{r}_i - \mathbf{R}_j|}\Psi$$

$$+\sum_{I>J}\frac{e^2 Z_I Z_J}{4\pi\epsilon_0|\mathbf{R}_I - \mathbf{R}_J|}\Psi + \sum_{i>j}\frac{e^2}{4\pi\epsilon_0|\mathbf{r}_i - \mathbf{r}_j|}\Psi = E_{\rm tot}\,\Psi$$

Density-functional theory (DFT) and Kohn-Sham equations

$$-\frac{\hbar^2}{2m_{\mathrm{e}}}\nabla^2 \psi_n + V_{\mathrm{SCF}}\,\psi_n = E_n\,\psi_n$$

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$$-\frac{\hbar^2}{2m_{\rm e}}\nabla^2\,\psi_n + V_{\rm SCF}\,\psi_n = E_n\,\psi_n$$

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Density-functional theory (DFT) and Kohn-Sham equations

$$-\frac{\hbar^2}{2m_\mathrm{e}}\nabla^2\,\psi_n + V_\mathrm{SCF}\,\psi_n = E_n\,\psi_n$$

$$n(\mathbf{r}) = \sum_{n\in\mathrm{occ}} |\psi_n(\mathbf{r})|^2$$

$$V_\mathrm{SCF}(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0}\left[\sum\nolimits_I \frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|} - \int \frac{n(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\right] + V_{xc}[n(\mathbf{r})]$$

Density-functional theory (DFT) and Kohn-Sham equations

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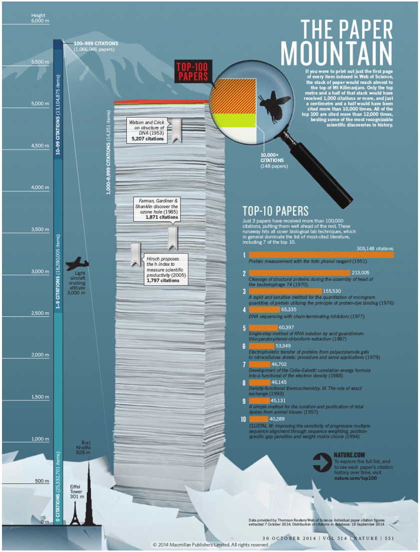
$$V_\mathrm{SCF}(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0}\left[\sum\nolimits_I \frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|} - \int \frac{n(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\right] + V_{xc}[n(\mathbf{r})]$$

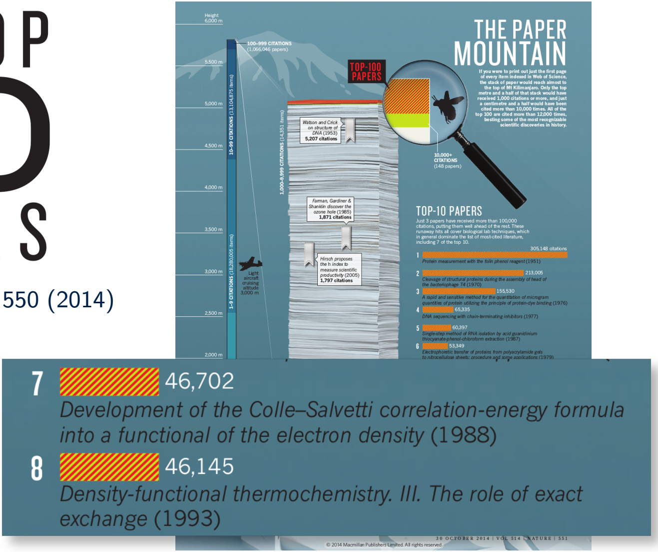
THE TOP 100 PAPERS

Van Norden, Nature 514, 550 (2014)

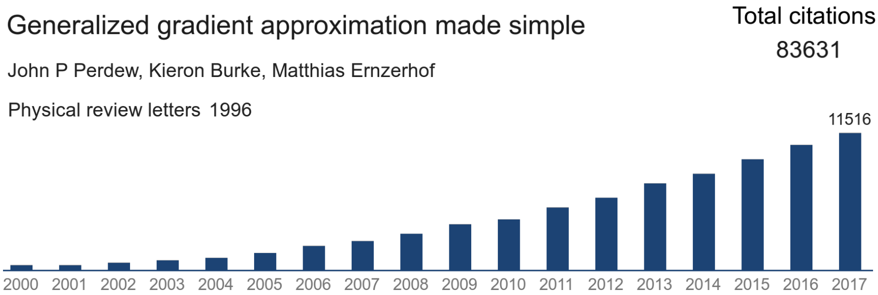


THE TOP 100 PAPERS

Van Norden, Nature 514, 550 (2014)

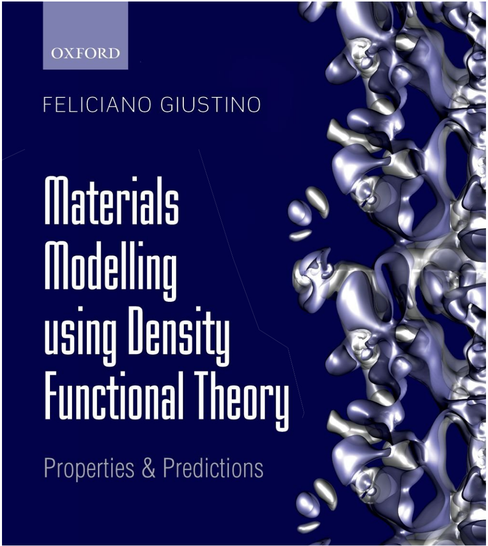


Popularity of DFT



The B3LYP papers that ranked 7th and 8th in 2014 are now at ~75k cites

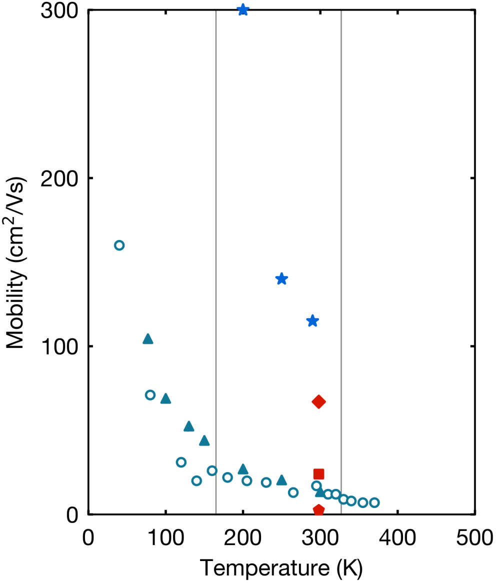
DFT is included in the undegraduate curriculum at Oxford since 2010



1 Understanding electron transport

2 Finding non-toxic alternatives to Pb

Measured carrier mobility of $MAPbI_3$



Thin Films

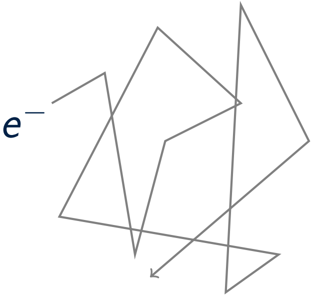
- Optical pump, THz probe
  Milot et, AFM. 25, 6218 (2015)
- Photoconductivity
  Karakus et, JPCL 6, 4991 (2015)

Single Crystals

- Space-sharge-limited current
  Shi et, Science 347, 519 (2015)
- Time-of-flight
  Dong et, Science 347, 967 (2015)
- Dark current-voltage
  Saidaminov et, NC 6, 7586 (2015)
- Time-of-flight
  Shrestha et, JPPC 122, 5935 (2018)

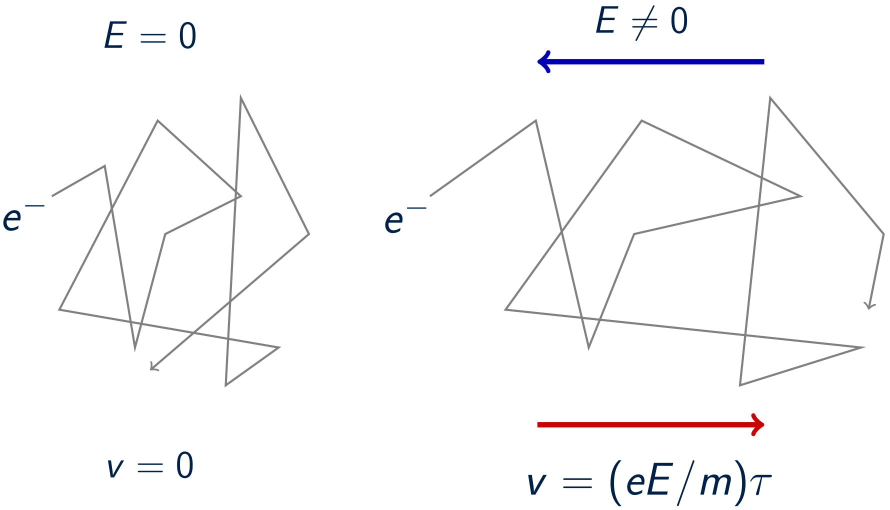
Electron mobility from first principles

$E = 0$



$v = 0$

Electron mobility from first principles



Electron mobility from first principles

μ mobility

$$v = \frac{e\,\tau}{m}\,E$$

Scattering processes (e.g. phonons)

Band structure

Carrier mobility from the electric current

$$\left.\begin{aligned} v &= \mu E \\ J &= -env \end{aligned}\right\} \quad \mu = -\frac{1}{en}\frac{\partial J}{\partial E}$$

Carrier mobility from the electric current

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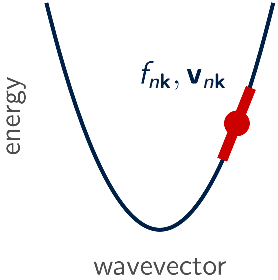
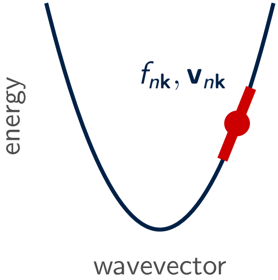


$$\mathbf{J} = -\frac{e}{\Omega}\frac{1}{N_{\mathbf{k}}}\sum_{n\mathbf{k}} f_{n\mathbf{k}}\,\mathbf{v}_{n\mathbf{k}}$$

Carrier mobility from the electric current

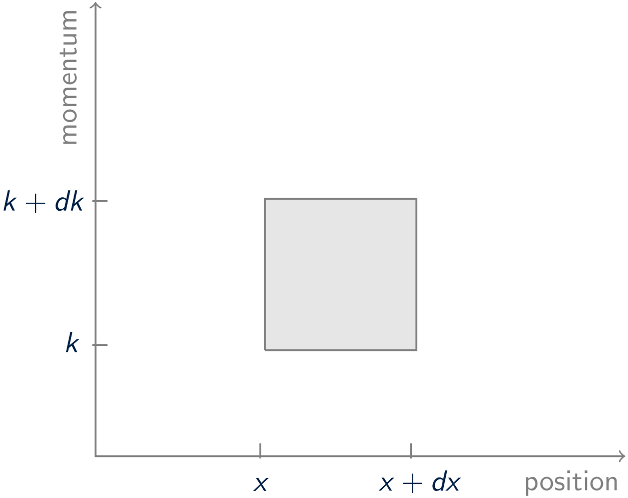
$$\left.\begin{aligned} v &= \mu E \\ J &= -env \end{aligned}\right\} \quad \mu = -\frac{1}{en}\frac{\partial J}{\partial E}$$



$$\mathbf{J} = -\frac{e}{\Omega}\frac{1}{N_\mathbf{k}}\sum_{n\mathbf{k}} f_{n\mathbf{k}}\mathbf{v}_{n\mathbf{k}}$$

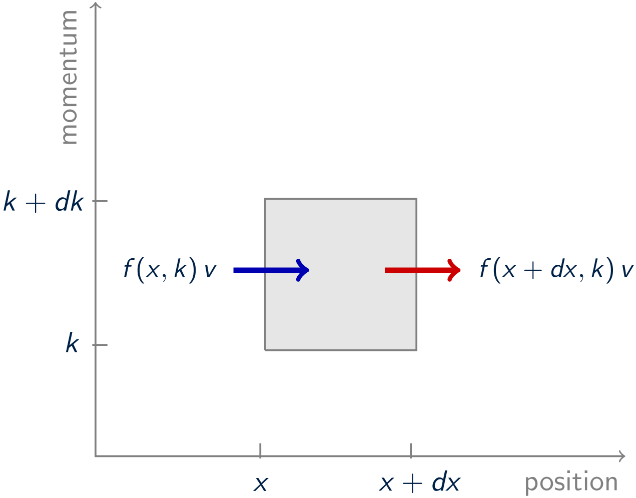
$$\mu_{\mathrm{e},\alpha\beta} = -\frac{1}{N_\mathrm{e}}\sum_{n\mathbf{k}} \mathbf{v}_{n\mathbf{k}} \left.\frac{\partial f_{n\mathbf{k}}}{\partial E_\beta}\right|_{\mathbf{E}=0}$$

Boltzmann transport equation



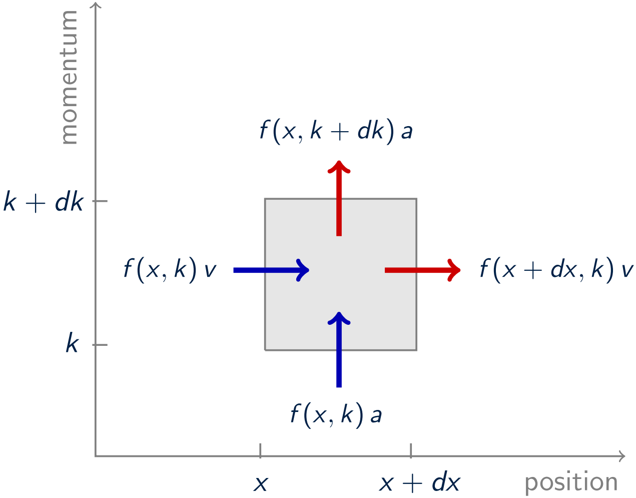
Lundstrom, Fundamentals of carrier transport, CUP 2000

Boltzmann transport equation



Lundstrom, Fundamentals of carrier transport, CUP 2000

Boltzmann transport equation



Lundstrom, Fundamentals of carrier transport, CUP 2000

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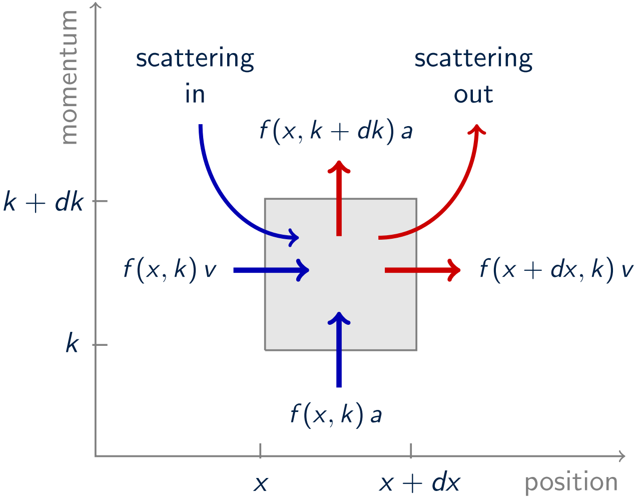


Lundstrom, Fundamentals of carrier transport, CUP 2000

Boltzmann transport equation

$$(-e)\mathbf{E}\cdot\frac{1}{\hbar}\frac{\partial f_{n\mathbf{k}}}{\partial \mathbf{k}} = \frac{2\pi}{\hbar}\sum_{m\nu}\int\frac{d\mathbf{q}}{\Omega_{\mathrm{BZ}}}|g_{mn\nu}(\mathbf{k},\mathbf{q})|^2$$

$$\times\Big\{ (1-f_{n\mathbf{k}})f_{m\mathbf{k}+\mathbf{q}}\delta(\varepsilon_{n\mathbf{k}}-\varepsilon_{m\mathbf{k}+\mathbf{q}}+\hbar\omega_{\mathbf{q}\nu})(1+n_{\mathbf{q}\nu})$$

$$+(1-f_{n\mathbf{k}})f_{m\mathbf{k}+\mathbf{q}}\delta(\varepsilon_{n\mathbf{k}}-\varepsilon_{m\mathbf{k}+\mathbf{q}}-\hbar\omega_{\mathbf{q}\nu})n_{\mathbf{q}\nu}$$

$$-f_{n\mathbf{k}}(1-f_{m\mathbf{k}+\mathbf{q}})\delta(\varepsilon_{n\mathbf{k}}-\varepsilon_{m\mathbf{k}+\mathbf{q}}-\hbar\omega_{\mathbf{q}\nu})(1+n_{\mathbf{q}\nu})$$

$$-f_{n\mathbf{k}}(1-f_{m\mathbf{k}+\mathbf{q}})\delta(\varepsilon_{n\mathbf{k}}-\varepsilon_{m\mathbf{k}+\mathbf{q}}+\hbar\omega_{\mathbf{q}\nu})n_{\mathbf{q}\nu}\Big\}\Big\}$$

Li, Phys. Rev. B 92, 075405 (2015)

Poncé, Margine & FG, Phys. Rev. B 97, 121201 (2018)

Sohier et al., Phys. Rev. Mater. 2, 114010 (2018)

Software implementation

EPW®

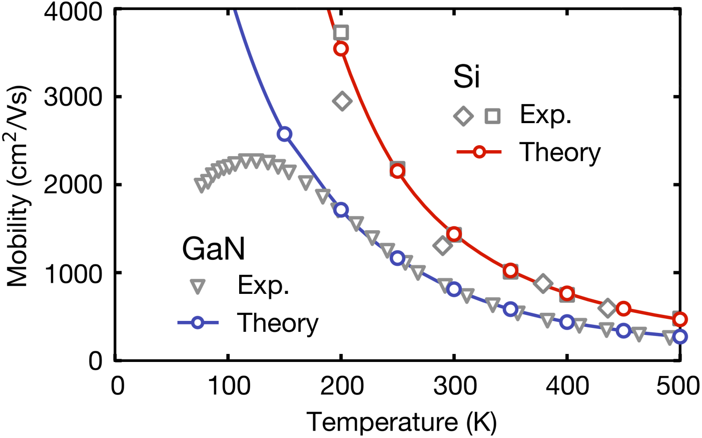
epw.org.uk

QUANTUMESPRESSO

www.quantum-espresso.org

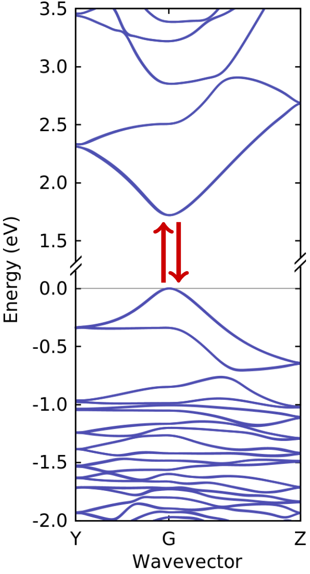
Experimental validation of the method

Electron mobilities of Si and GaN



Poncé, Schlipf & FG, ACS Energy Letters 4, 456 (2019)

Band structure of $MAPbI_3$



Orthorhombic *Pnma* structure, DFT+GW

Filip & FG, PRB 90, 245145 (2014)

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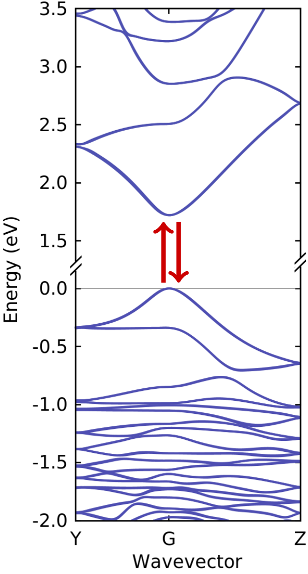
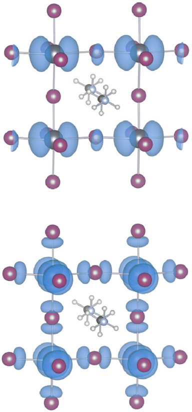


Orthorhombic *Pnma* structure, DFT+GW



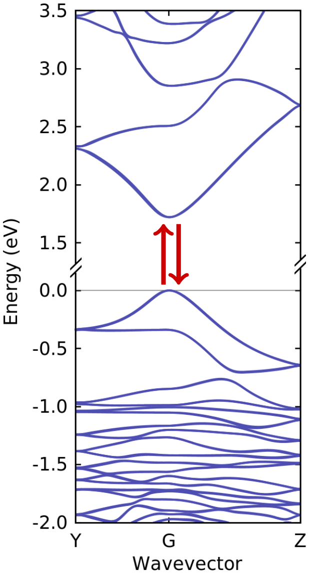
Pb-6p

Pb-6s + I-5p

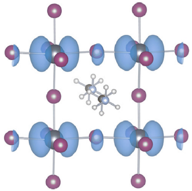
Brivio, Walker, Walsh,
APL Mater 1, 042111 (2013)

Filip & FG, PRB 90, 245145 (2014)

Band structure of $MAPbI_3$

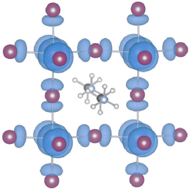


Orthorhombic *Pnma* structure, DFT+GW



Pb-6*p*

$m^* = 0.22\, m_e$



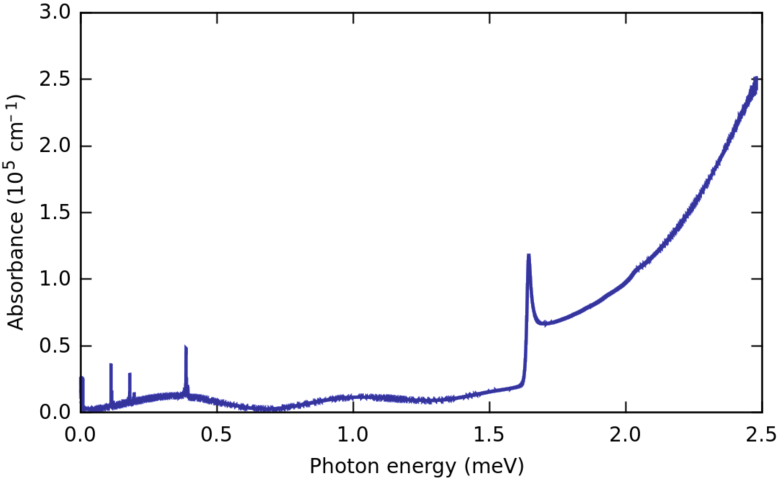
Pb-6*s* + I-5*p*

$m^* = 0.23\, m_e$

Brivio, Walker, Walsh,
APL Mater 1, 042111 (2013)

Filip & FG, PRB 90, 245145 (2014)

Fourier Transform Infrared Spectrum by M. Johnston, Oxford



Perez-Osorio et al., J. Phys. Chem. C 119, 25703 (2015)

Phonons and infrared spectrum of $MAPbI_3$

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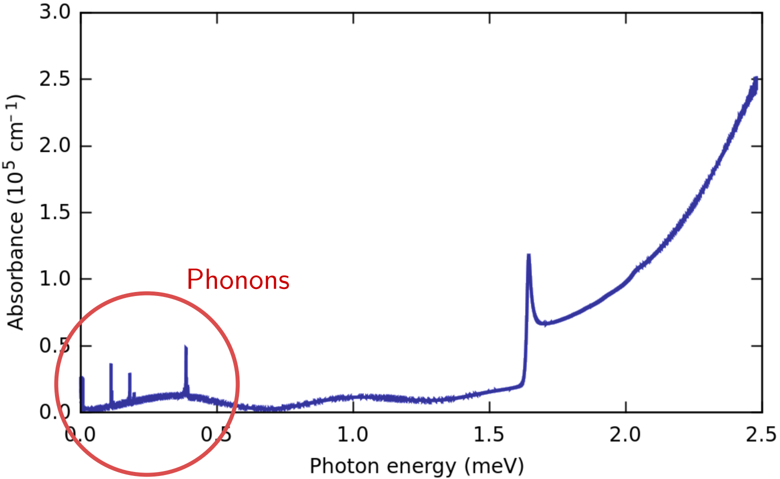

Perez-Osorio et al., J. Phys. Chem. C 119, 25703 (2015)

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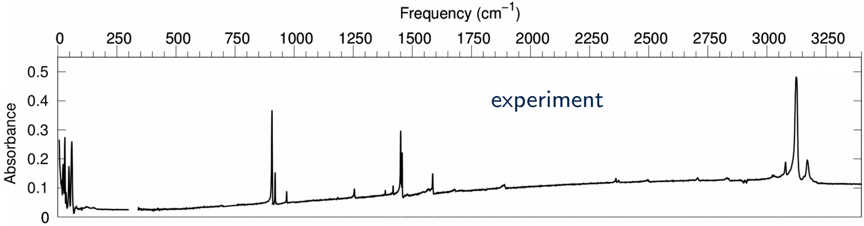

Perez-Osorio et al., J. Phys. Chem. C 119, 25703 (2015)

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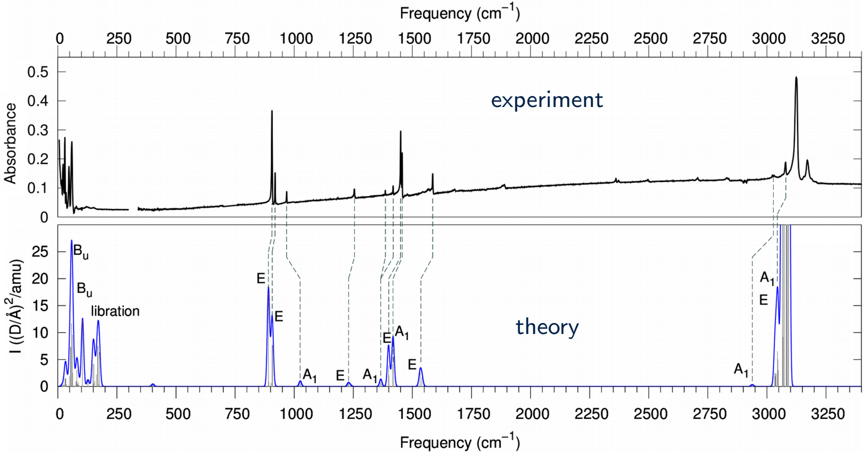

Perez-Osorio et al., J. Phys. Chem. C 119, 25703 (2015)

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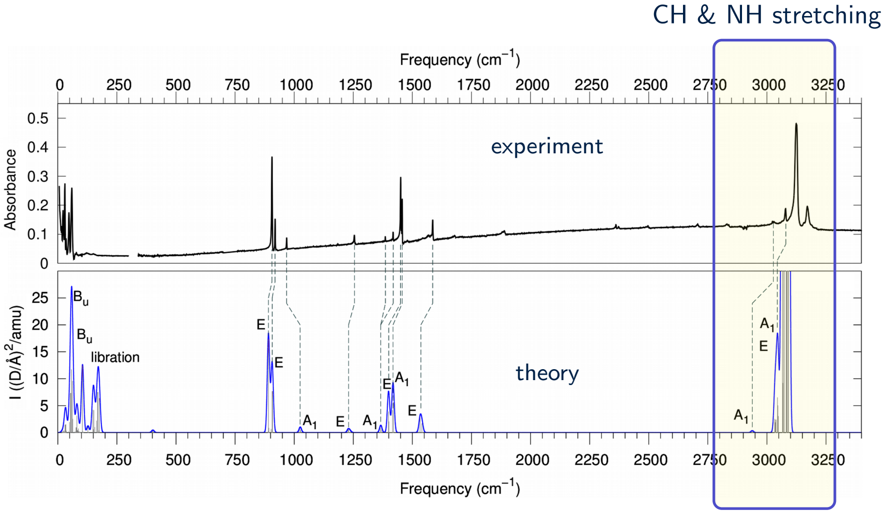

Perez-Osorio et al., J. Phys. Chem. C 119, 25703 (2015)

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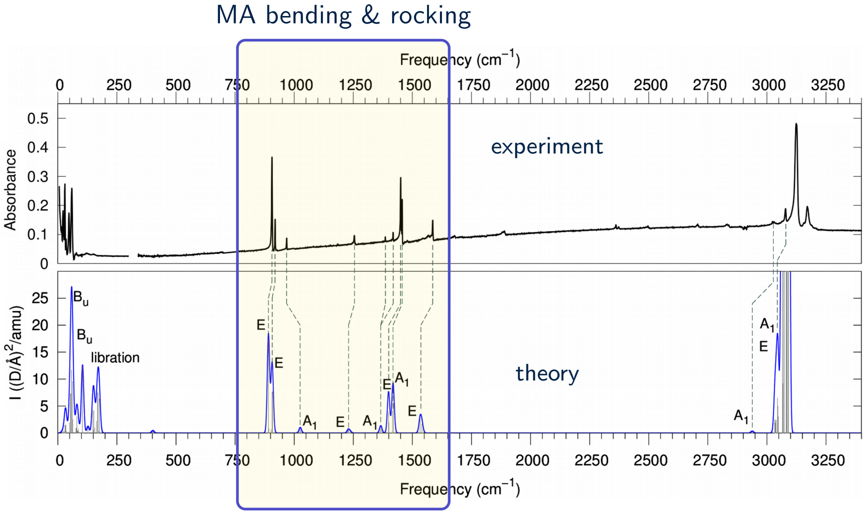
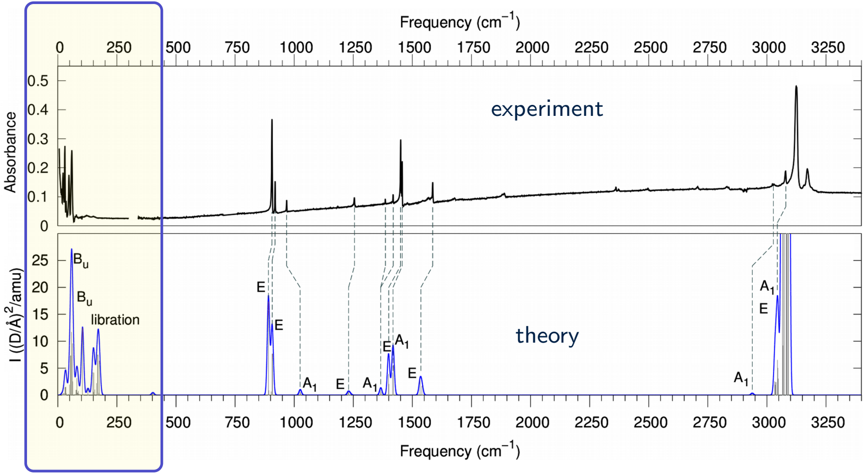


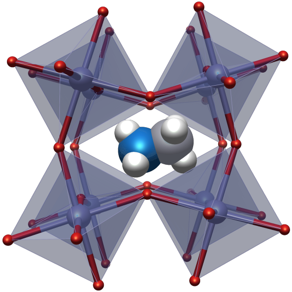
Perez-Osorio et al., J. Phys. Chem. C 119, 25703 (2015)

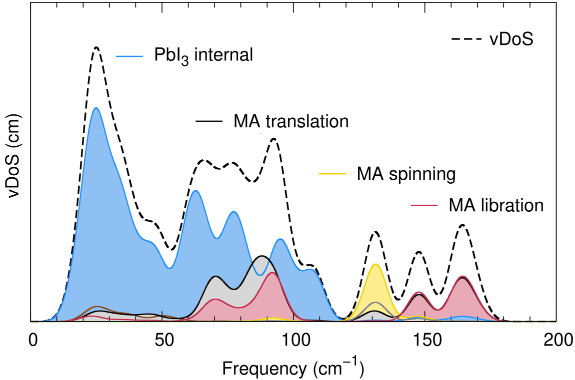
Pb-I stretching, bending, rocking & MA librations



Perez-Osorio et al., J. Phys. Chem. C 119, 25703 (2015)

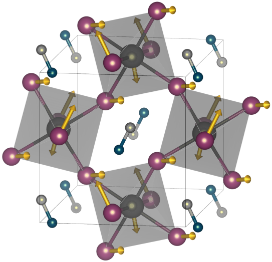
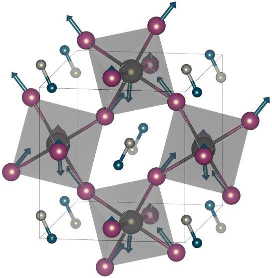
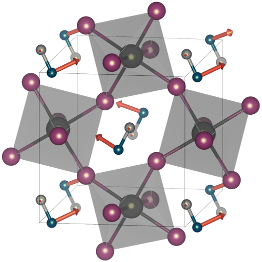
Vibrational density of states





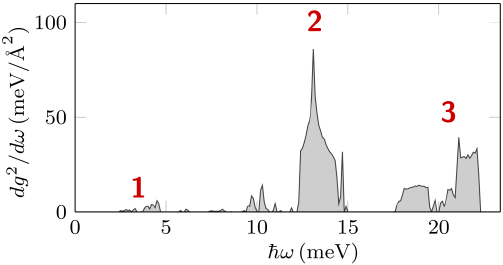
Pérez, Milot, Filip, Patel, Herz, Johnston & FG, J Phys Chem C 119, 25703 (2015)

Fröhlich electron-phonon coupling in $MAPbI_3$

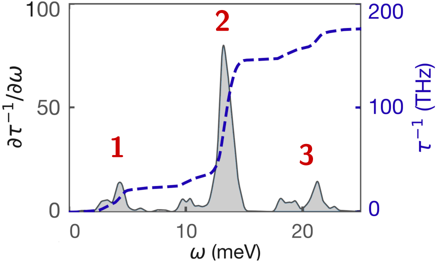
Pb-I-Pb bending	Pb-I stretching	MA librations & translations
		
3.9 meV	13 meV	20.4 meV
1	**2**	**3**

Schlipf, Poncé & FG, Phys Rev Lett 121, 086402 (2018)

Phonon contribution to carrier relaxation rates



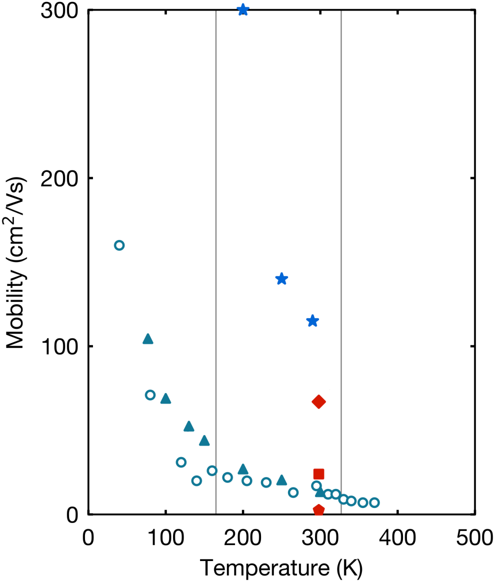
Strength of electron-phonon coupling



Electron relaxation time

Poncé, Schlipf & FG, ACS En Lett 4, 456 (2019)

Theoretical vs. measured mobility of $MAPbI_3$



Thin Films

- Optical pump, THz probe
  Milot et, AFM. 25, 6218 (2015)
- Photoconductivity
  Karakus et, JPCL 6, 4991 (2015)

Single Crystals

- Space-sharge-limited current
  Shi et, Science 347, 519 (2015)
- Time-of-flight
  Dong et, Science 347, 967 (2015)
- Dark current-voltage
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- Time-of-flight
  Shrestha et, JPPC 122, 5935 (2018)

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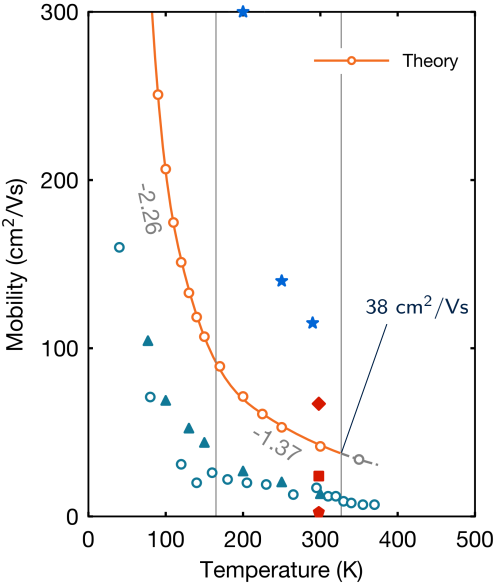

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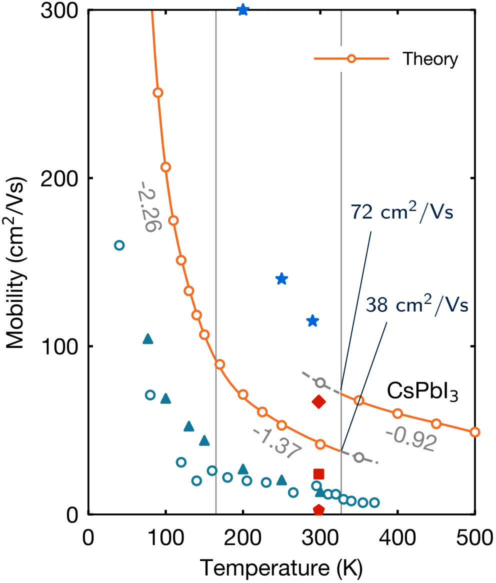

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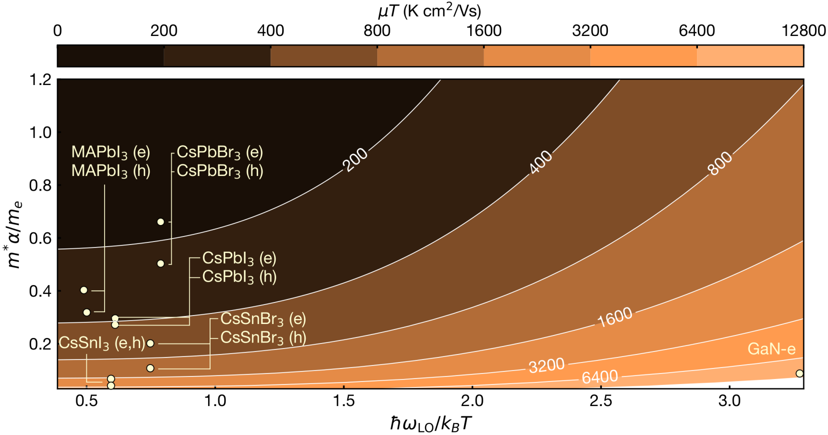
  Shrestha et, JPPC 122, 5935 (2018)

How to engineer high-mobility perovskites

$$\frac{\mu}{e\hbar/m_\mathrm{e}\, k_\mathrm{B}\, T} = \frac{0.052\,(\hbar\omega_\mathrm{LO}/k_\mathrm{B}\, T)^{3.3} + 0.34}{(\alpha\, m^*/m_\mathrm{e})}$$

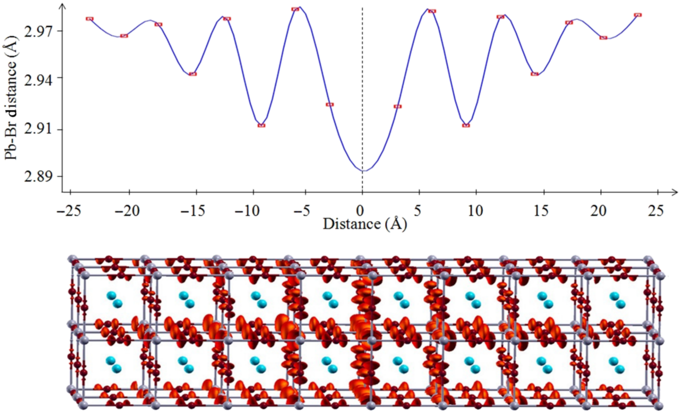
Poncé, Schlipf & FG, ACS En Lett 4, 456 (2019)

$$\frac{\mu}{e\hbar/m_e\, k_B T} = \frac{0.052\,(\hbar\omega_{LO}/k_B T)^{3.3} + 0.34}{(\alpha\, m^*/m_e)}$$



Poncé, Schlipf & FG, ACS En Lett 4, 456 (2019)

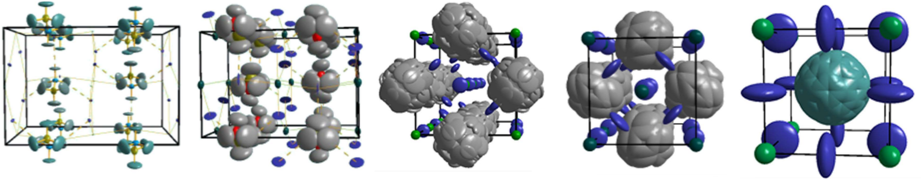
Polarons in lead-halide perovskites ($CsPbBr_3$)



Miyata et al., Sci. Adv. Sci. Adv. 3, e1701217 (2017)

Additional remarks

Neutron power diffraction of deuteradted $MAPbI_3$ (d_6-MA = CD_3ND_3)



10 K 130 K 190 K 300 K 350 K

Modelling the room-temperature phase requires configurational average

Whitfield et al., Sci. Rep. 6, 35685 (2016)

Take-home messages

- Halide perovskites are a promising new class of semiconducting materials
- Realistic potential for PV deployment and commercialization
- *Ab initio* calculations are important to clarify the microscopic mechanisms underpinning solar cell operation

Recommended reading

Metal halide perovskites for energy applications
Zhang, Eperon & Snaith
Nature Energy 1, 16048 (2016)
https://doi.org/10.1038/nenergy.2016.48

Opportunities and challenges for tandem solar cells using metal halide perovskite semiconductors
Leijtens, Bush, Prasanna & McGehee
Nature Energy 3, 828 (2018)
https://doi.org/10.1038/s41560-018-0190-4

Acknowledgments

Oxford Theory

Marina Filip
Miguel Angel Pérez
George Volonakis
Samuel Poncé
Martin Schlipf
Carla Verdi

Oxford Experiments

Rebecca Milot
Jay Patel
Laura Herz
Mike Johnston
Adam Wright
Giles Eperon
Henry Snaith

Louvain Theory

Aurélie Champagne
Gian Marco Rignanese

Cambridge Experiments

Richard Phillips