1.021, 3.021, 10.333, 22.00 : Introduction to Modeling and Simulation : Spring 2012

Part II – Quantum Mechanical Methods : Lecture 4

Application of QM Modeling to Solar Thermal Fuels

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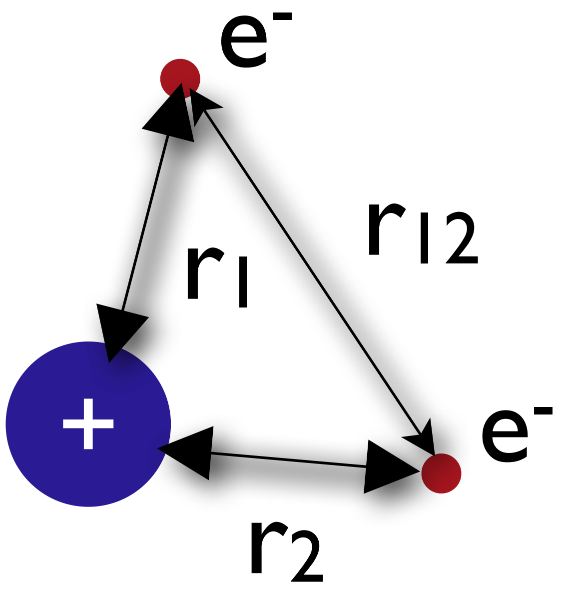
Part II Topics

1. It’s a Quantum World: The Theory of Quantum Mechanics
2. Quantum Mechanics: Practice Makes Perfect
3. From Many-Body to Single-Particle; Quantum Modeling of Molecules
4. Application of Quantum Modeling of Molecules: Solar Thermal Fuels
5. Application of Quantum Modeling of Molecules: Hydrogen Storage
6. From Atoms to Solids
7. Quantum Modeling of Solids: Basic Properties
8. Advanced Prop. of Materials: What else can we do?
9. Application of Quantum Modeling of Solids: Solar Cells Part I
10. Application of Quantum Modeling of Solids: Solar Cells Part II
11. Application of Quantum Modeling of Solids: Nanotechnology

Lesson outline

- Review
- Interactive calculations and discussion on the H2
- First application of QM modeling: Solar Thermal Fuels
- Interactive calculations and discussion on candidate fuels.

Review: Next? Helium



$$H\psi = E\psi$$

$$\left[H_1 + H_2 + W\right]\psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2)$$

$$\left[T_1 + V_1 + T_2 + V_2 + W\right]\psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2)$$

$$\left[-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}\right]\psi(r_1, r_2) = E\psi(r_1, r_2)$$

cannot be solved analytically

problem!

Review: The Multi-Electron Hamiltonian

$H\psi = E\psi$

Remember the good old days of the 1-electron H-atom??

They're over!

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}\right]\psi(\vec{r}) = E\psi(\vec{r})$$

$$H = -\sum_{i=1}^{N}\frac{\hbar^2}{2M_i}\nabla^2_{\mathbf{R}_i} + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\ i\neq j}}^{N}\frac{Z_iZ_je^2}{\left|\mathbf{R}_i-\mathbf{R}_j\right|} - \frac{\hbar^2}{2m}\sum_{i=1}^{n}\nabla^2_{\mathbf{r}_i} - \sum_{i=1}^{N}\sum_{j=1}^{n}\frac{Z_ie^2}{\left|\mathbf{R}_i-\mathbf{r}_j\right|} + \frac{1}{2}\sum_{i=1}^{n}\sum_{\substack{j=1\\ i\neq j}}^{n}\frac{e^2}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}$$

kinetic energy of ions

kinetic energy of electrons

electron-electron interaction

potential energy of ions

electron-ion interaction

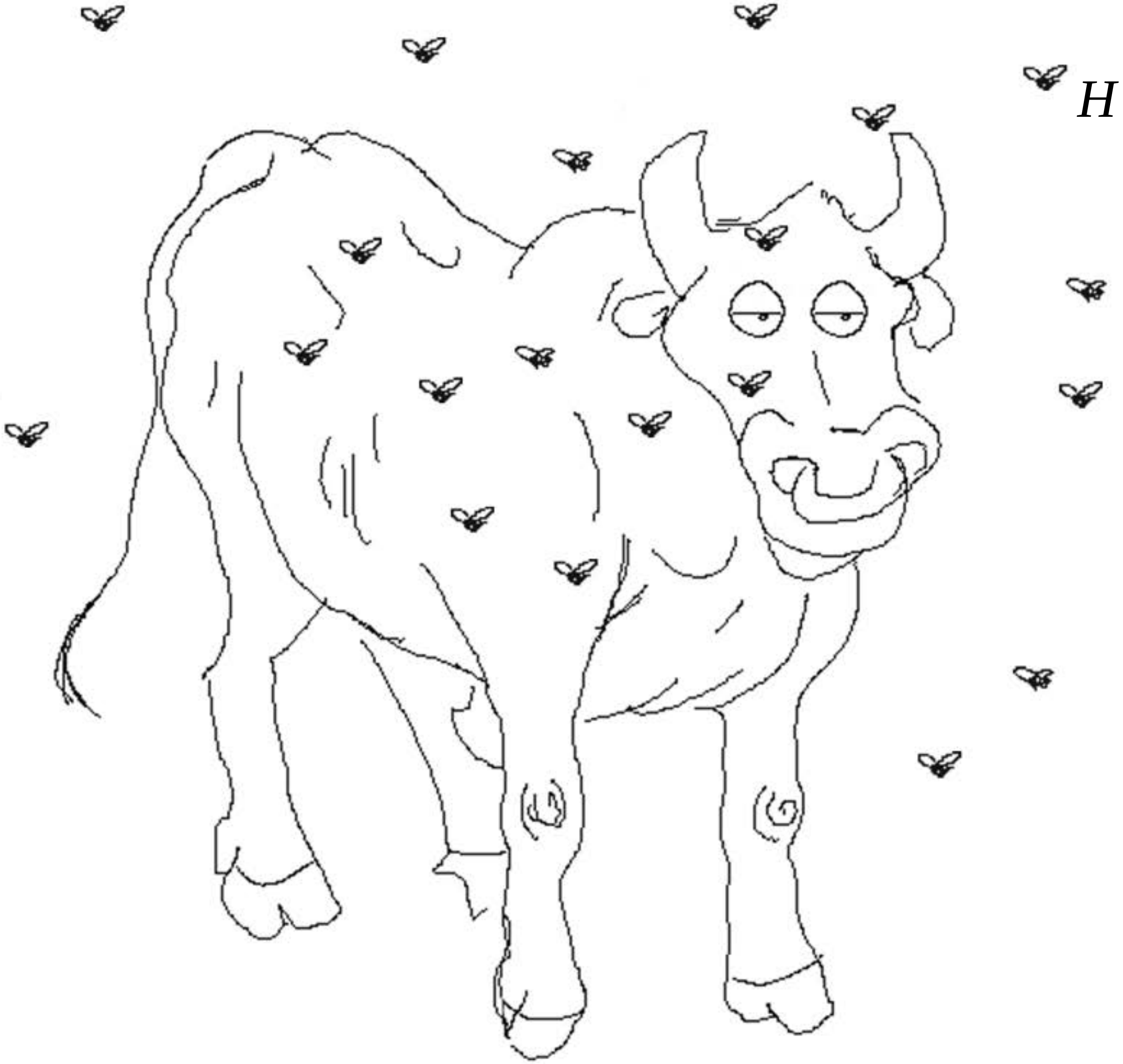
Multi-Atom-Multi-Electron Schrödinger Equation

$$H\left(\mathbf{R}_1,\ldots,\mathbf{R}_N;\mathbf{r}_1,\ldots,\mathbf{r}_n\right)\Psi\left(\mathbf{R}_1,\ldots,\mathbf{R}_N;\mathbf{r}_1,\ldots,\mathbf{r}_n\right) = E\,\Psi\left(\mathbf{R}_1,\ldots,\mathbf{R}_N;\mathbf{r}_1,\ldots,\mathbf{r}_n\right)$$

Born-Oppenheimer Approximation

Electrons and nuclei
as "separate" systems

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{n}\nabla^2_{\mathbf{r}_i} - \sum_{i=1}^{N}\sum_{j=1}^{n}\frac{Z_i e^2}{\left|\mathbf{R}_i - \mathbf{r}_j\right|} + \frac{1}{2}\sum_{i=1}^{n}\sum_{\substack{j=1\\ i\neq j}}^{n}\frac{e^2}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}$$



Born-Oppenheimer Approximation

Electrons and nuclei
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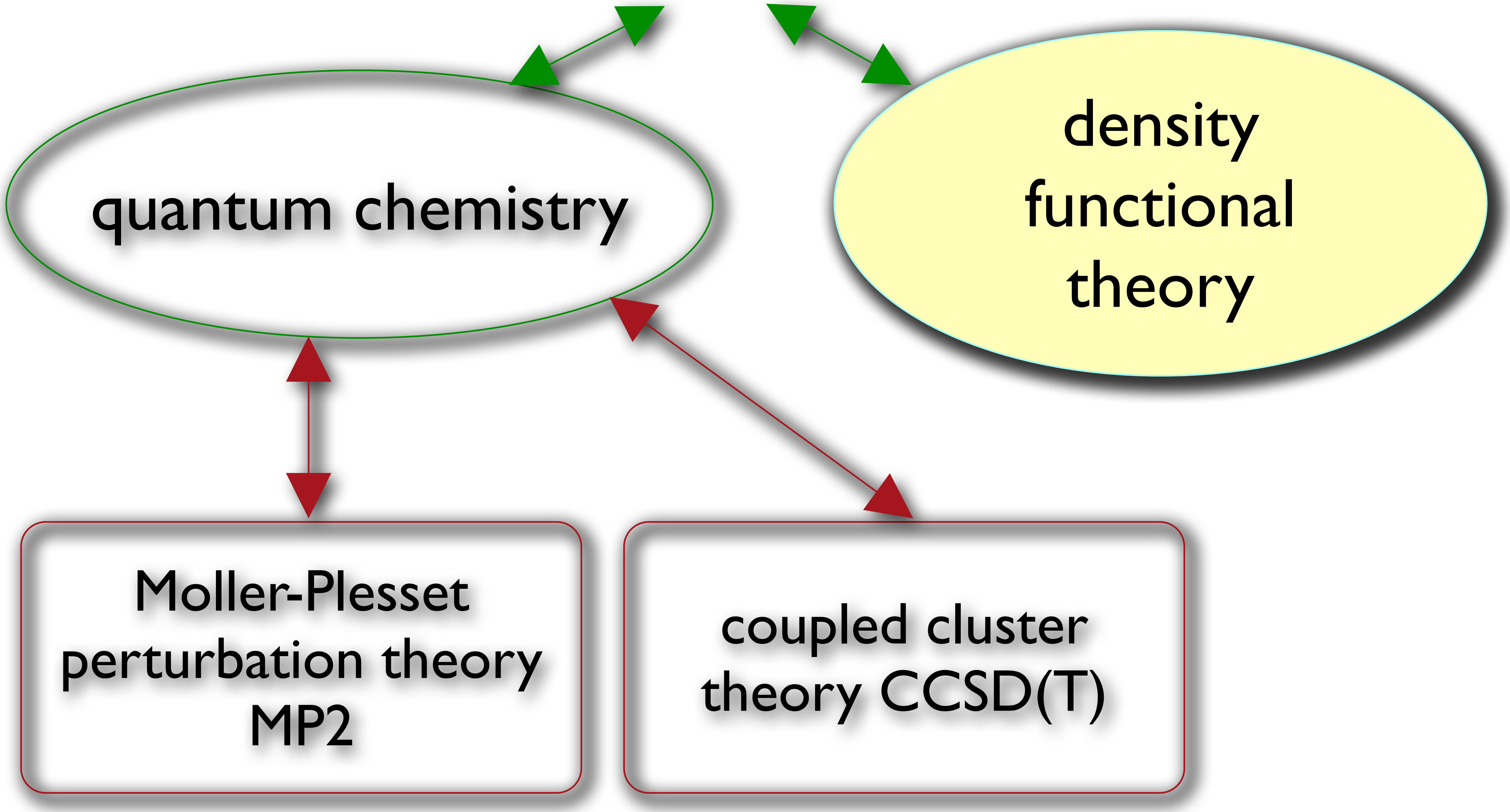
$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{n}\nabla^2_{\mathbf{r}_i} - \sum_{i=1}^{N}\sum_{j=1}^{n}\frac{Z_i e^2}{\left|\mathbf{R}_i - \mathbf{r}_j\right|} + \frac{1}{2}\sum_{i=1}^{n}\sum_{\substack{j=1\\ i\neq j}}^{n}\frac{e^2}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}$$

... but this is an approximation!

- electrical resistivity
- superconductivity
- ....

Review: Solutions



quantum chemistry

density functional theory

Moller-Plesset perturbation theory MP2

coupled cluster theory CCSD(T)

Review: Why DFT?

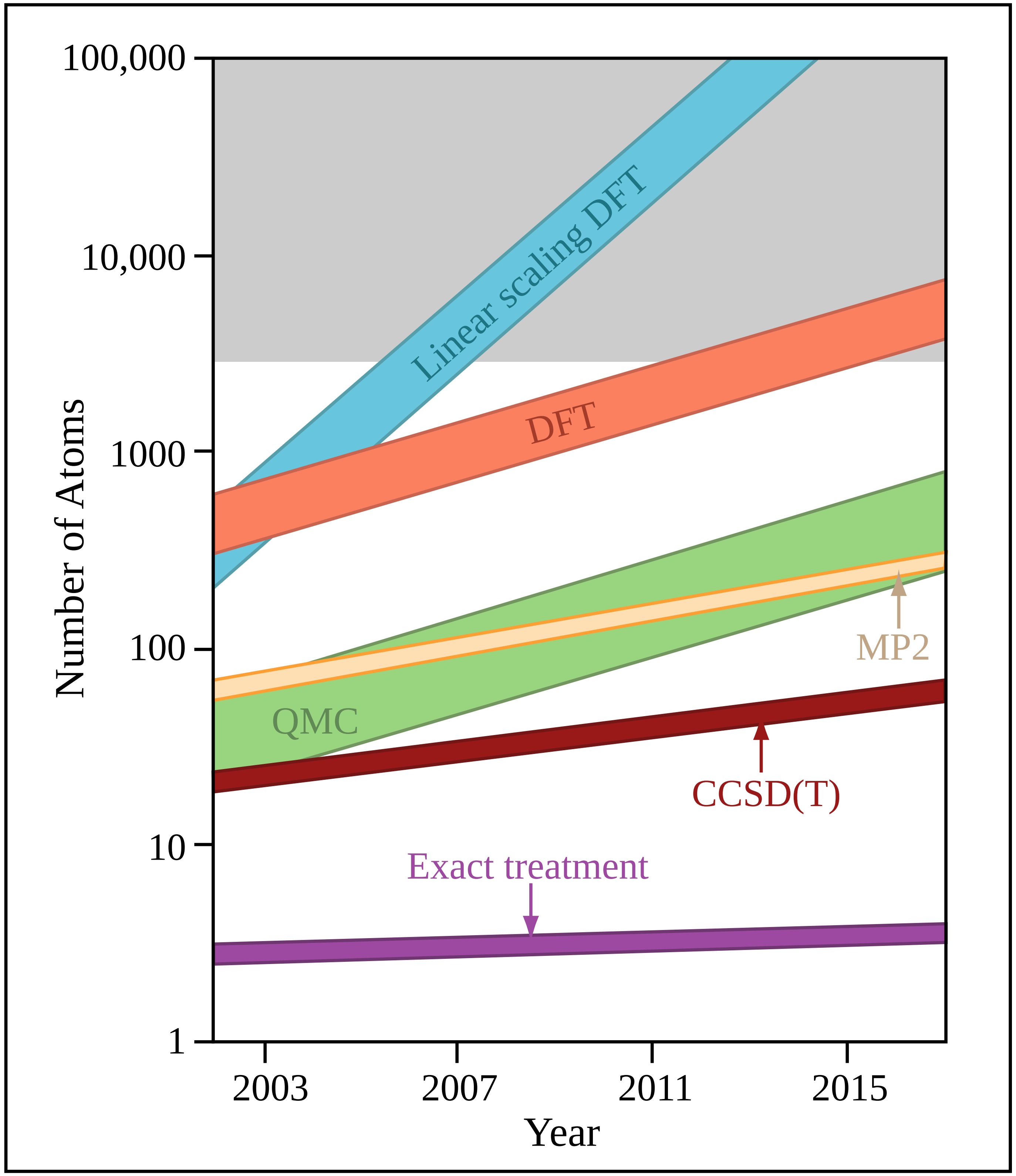


Image by MIT OpenCourseWare.

Review: DFT

$$\psi = \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$$

wave function: complicated!

$$n = n(\vec{r})$$

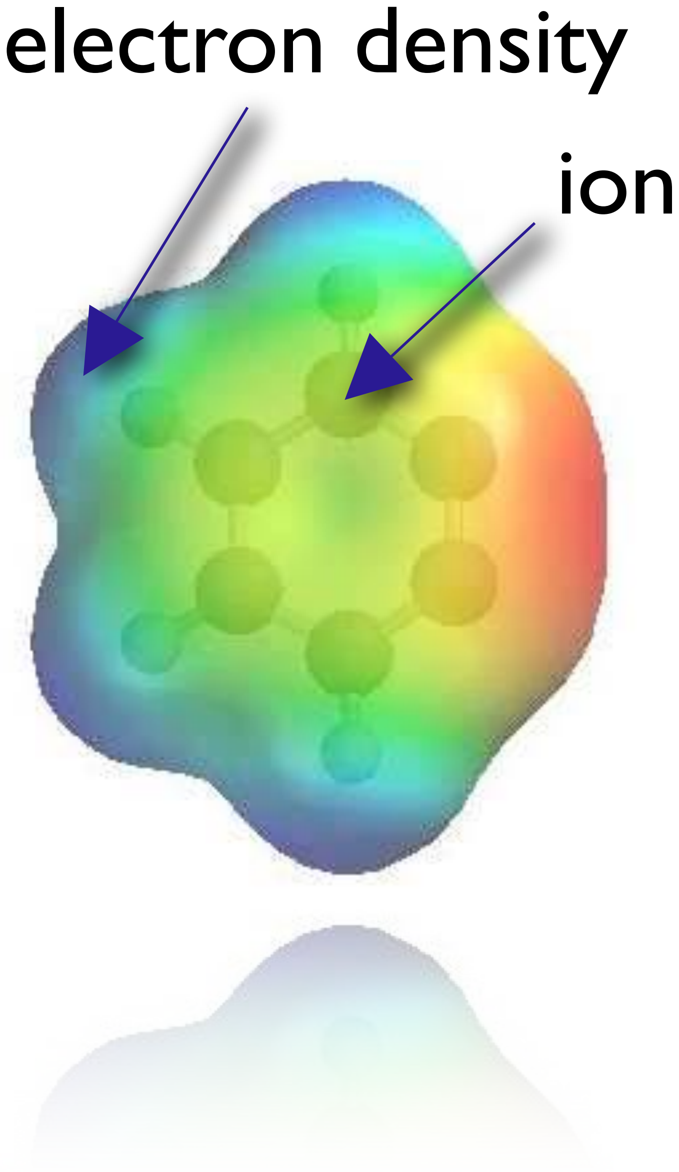
electron density: easy!

Walter Kohn

DFT 1964

All aspects of the electronic structure of a system of interacting electrons, in the ground state, in an "external" potential, are determined by *n*(***r***)

Review: DFT



The ground-state energy is a functional
of the electron density.

$$E[n] = T[n] + V_{ii} + V_{ie}[n] + V_{ee}[n]$$

kinetic
ion-ion
ion-electron
electron-electron

The functional is minimal at the exact ground-state electron density $n(\mathbf{r})$

The functional exists... but it is unknown!

Review: DFT

$$E[n] = T[n] + V_{ii} + V_{ie}[n] + V_{ee}[n]$$

kinetic ion-ion ion-electron electron-electron

electron density $n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$

$$E_{\text{ground state}} = \min_{\phi} E[n]$$

Find the wave functions that minimize the energy using a functional derivative.

Review: DFT

Finding the minimum leads to
Kohn-Sham equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_s(\vec{r})\right]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r}),$$

$$V_s = V + \int \frac{e^2 n_s(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\mathrm{d}^3r' + V_{\mathrm{XC}}[n_s(\vec{r})],$$

ion potential

Hartree potential

exchange-correlation potential

equations for non-interacting electrons

Review: DFT

$$V_s = V + \int \frac{e^2 n_s(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} \mathrm{d}^3 r' + V_{\mathrm{XC}}[n_s(\vec{r})],$$

Only one problem: v_{xc} not known!

approximations necessary

local density
approximation
LDA

general gradient
approximation
GGA

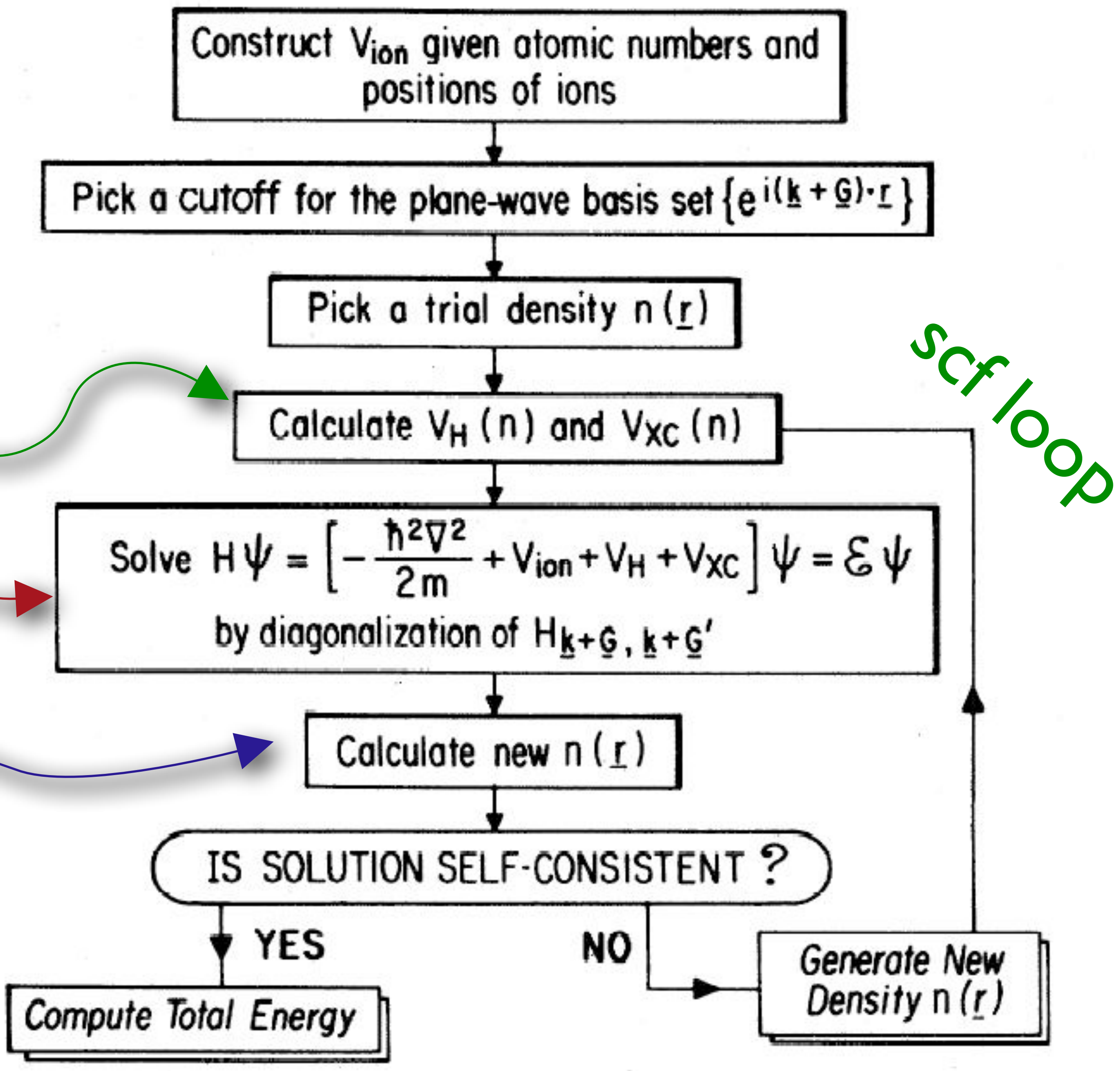
Review: Self-consistent cycle

Kohn-Sham equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_s(\vec{r})\right]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r}),$$

$$V_s = V + \int \frac{e^2 n_s(\vec{r}')}{|\vec{r} - \vec{r}'|}\mathrm{d}^3r' + V_{\mathrm{XC}}[n_s(\vec{r})],$$

$$n(\boldsymbol{\vec{r}}) = \sum_i |\phi_i(\boldsymbol{\vec{r}})|^2$$



Review: DFT calculations

scf loop

```
total energy =   -84.80957141 Ry
total energy =   -84.80938034 Ry
total energy =   -84.81157880 Ry
total energy =   -84.81278531 Ry
total energy =   -84.81312816 Ry
total energy =   -84.81322862 Ry
total energy =   -84.81323129 Ry
```

exiting loop;
result precise enough

At the end we get:

1) electronic charge density

2) total energy

Structure

Elastic constants

Vibrational properties

...

Review: Basis functions

Matrix eigenvalue equation:

$$\psi = \sum_i c_i \phi_i$$

expansion in orthonormalized basis functions

$$H\psi = E\psi$$

$$H \sum_i c_i \phi_i = E \sum_i c_i \phi_i$$

$$\int d\vec{r}\ \phi_j^* H \sum_i c_i \phi_i = E \int d\vec{r}\ \phi_j^* \sum_i c_i \phi_i$$

$$\sum_i H_{ji} c_i = E c_j$$

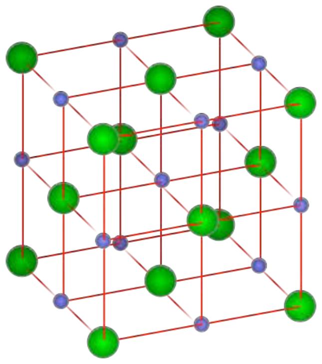
$$\mathcal{H}\vec{c} = E\vec{c}$$

Review: Plane waves as basis functions

plane wave expansion: $$\psi(\vec{r}) = \sum_j c_j \underbrace{\boxed{e^{i\vec{G}_j\cdot\vec{r}}}}_{\text{plane wave}}$$

Cutoff for a maximum G is necessary and results in a finite basis set.

Plane waves are periodic,
thus the wave function is periodic!



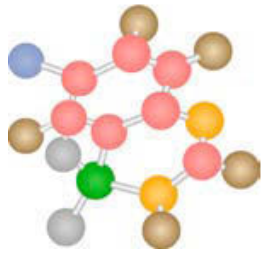


Image by MIT OpenCourseWare.

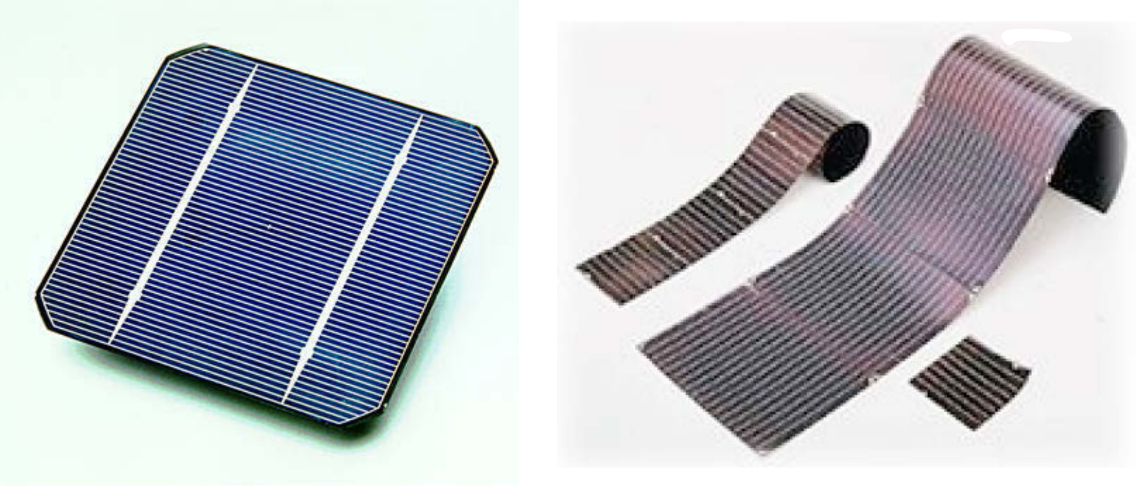
periodic crystals:
Perfect!!!

atoms, molecules:
OK but be careful!!!

First Application Example: Solar Chemical Fuels

Materials will determine the future of renewable energy

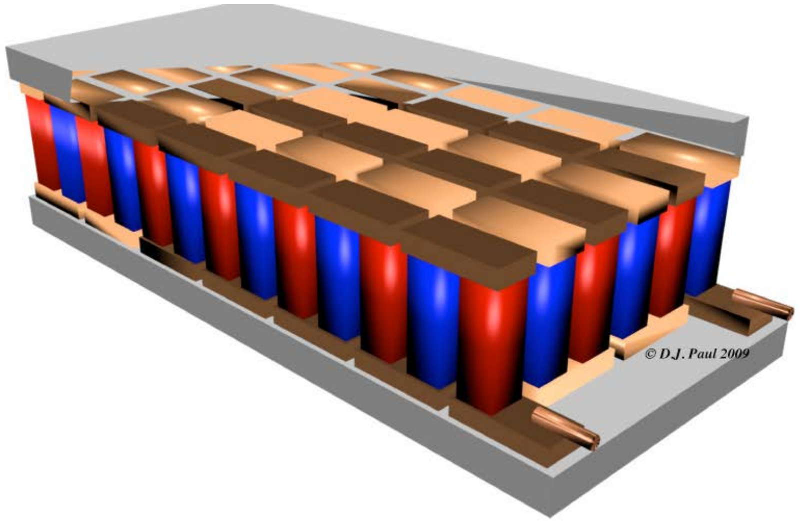
Solar PV

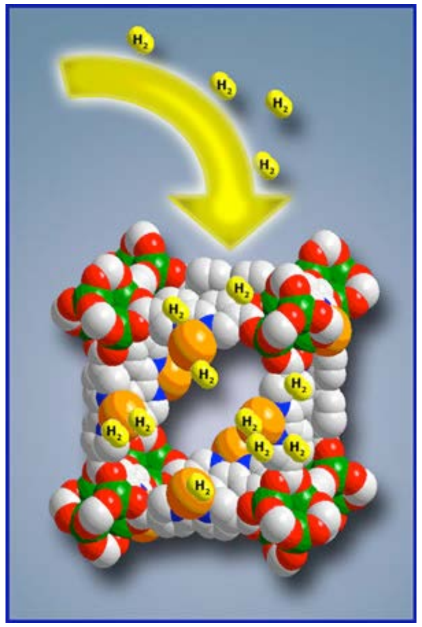


Biofuels

Batteries

Thermoelectrics





Hydrogen Storage

Solar Thermal

The Materials Design Age

- Stone Age

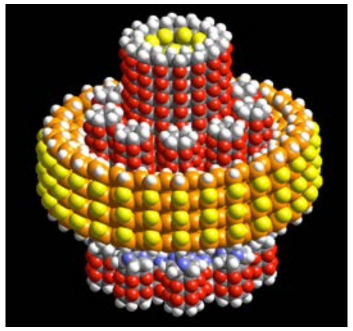
- Iron Age

- Bronze Age

- Industrial Age

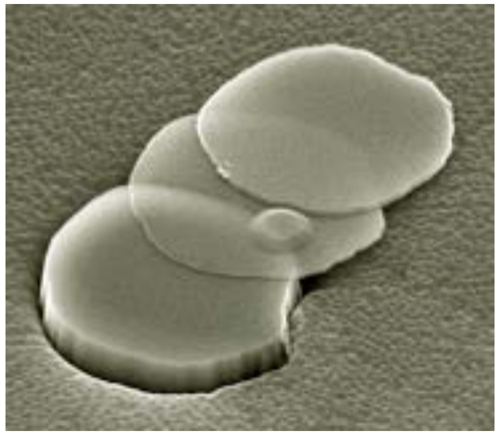
- Plastic Age

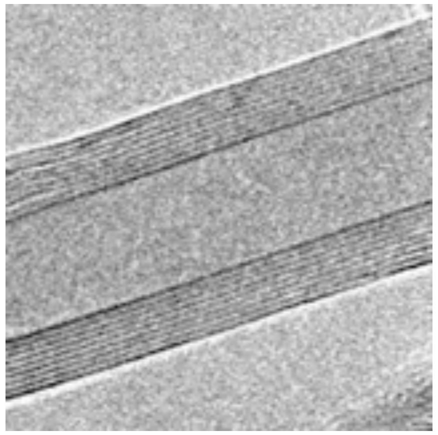
- Silicon Age

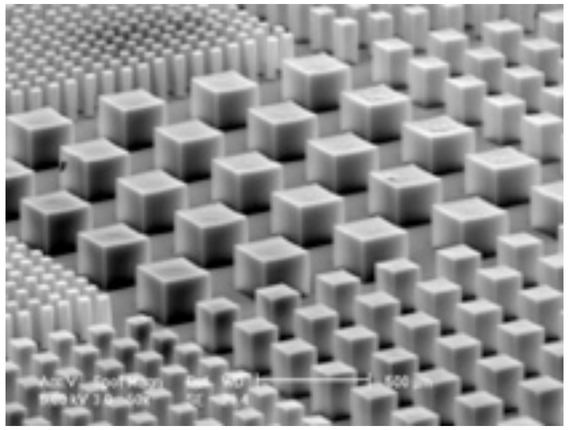


- Materials Design

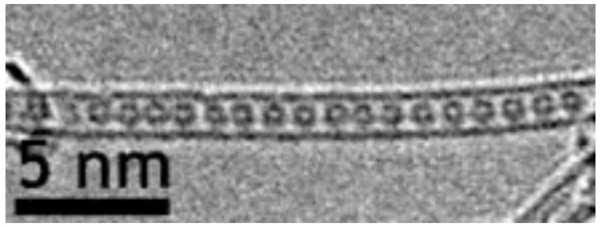
Let's look at a single element:

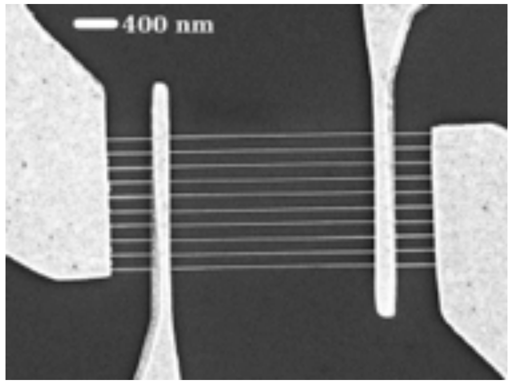






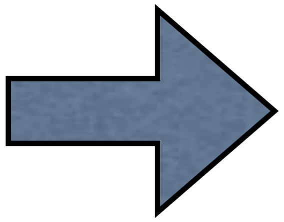
carbon





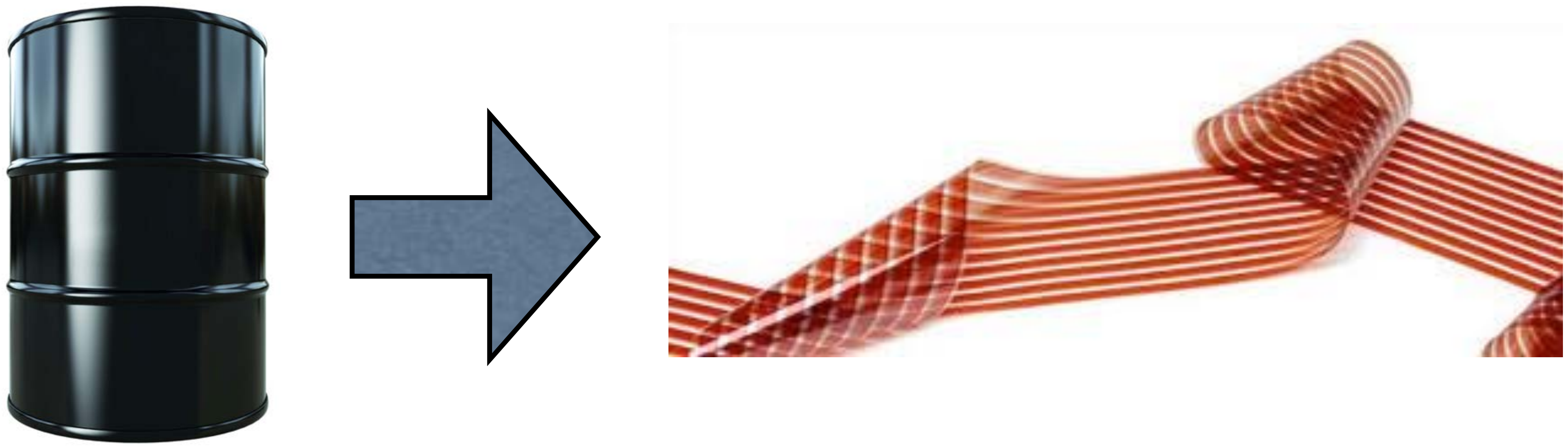
Carbon in Energy to Date

One Barrel of oil (159 liters) = 1.73 MWh of energy.



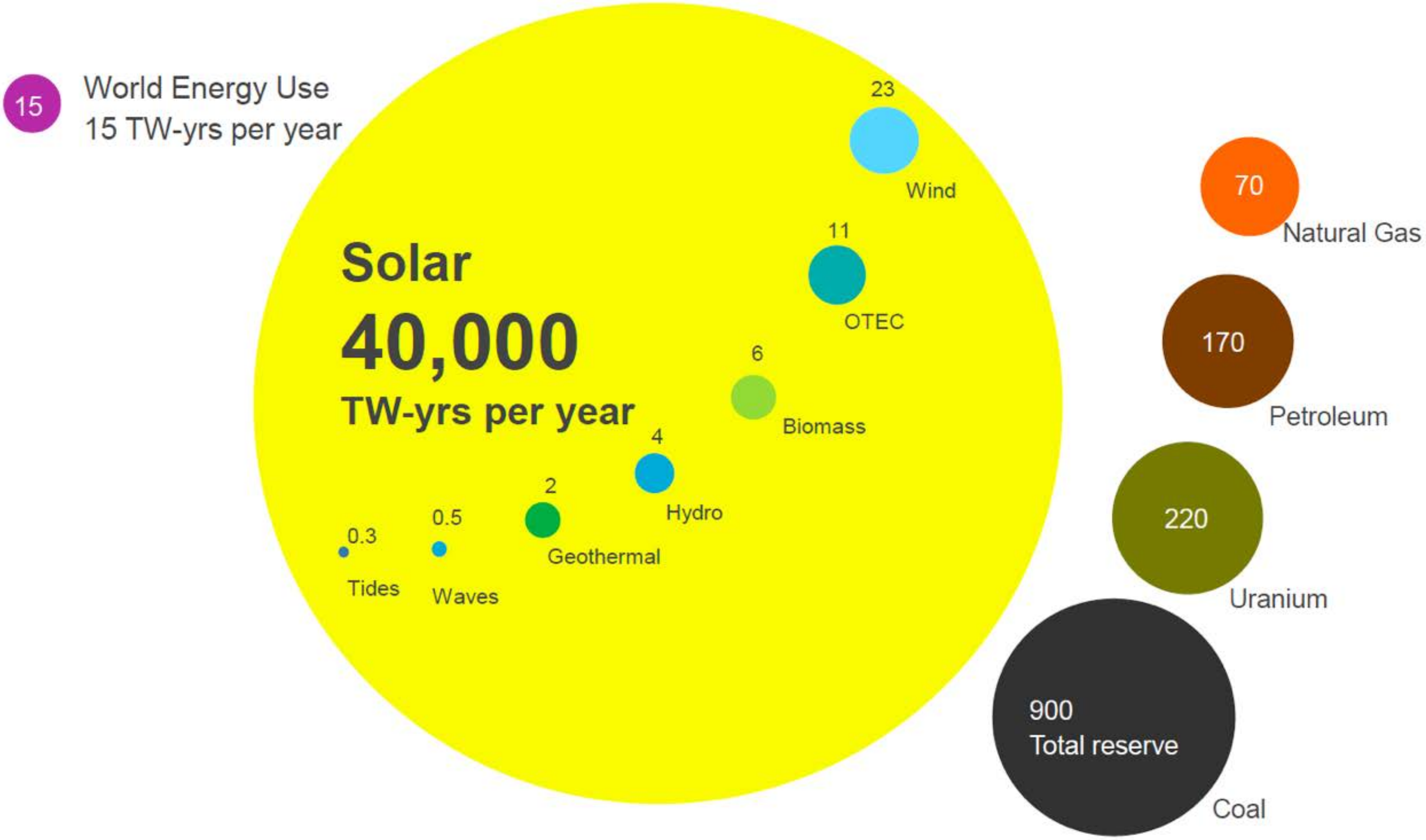
Same C: 10^5 X Improvement

That same 1 barrel could be used to make the plastic needed for thin-film solar cells.



The solar cells could generate ~16,000 MWh of energy over their lifetime, or 10,000 X as much

Solar Resource

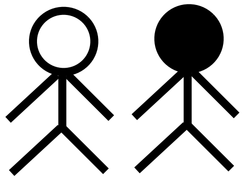


Perez et al.

Solar Energy Harvesting

Photovoltaics

40000 TW

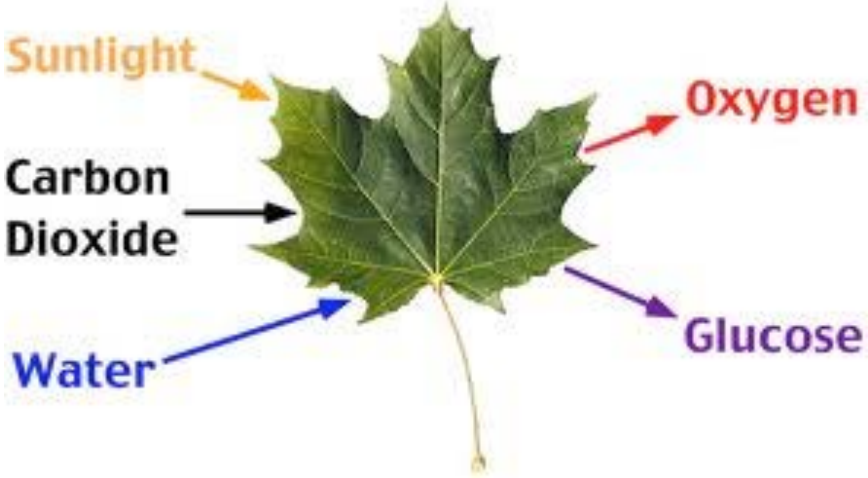


15 TW

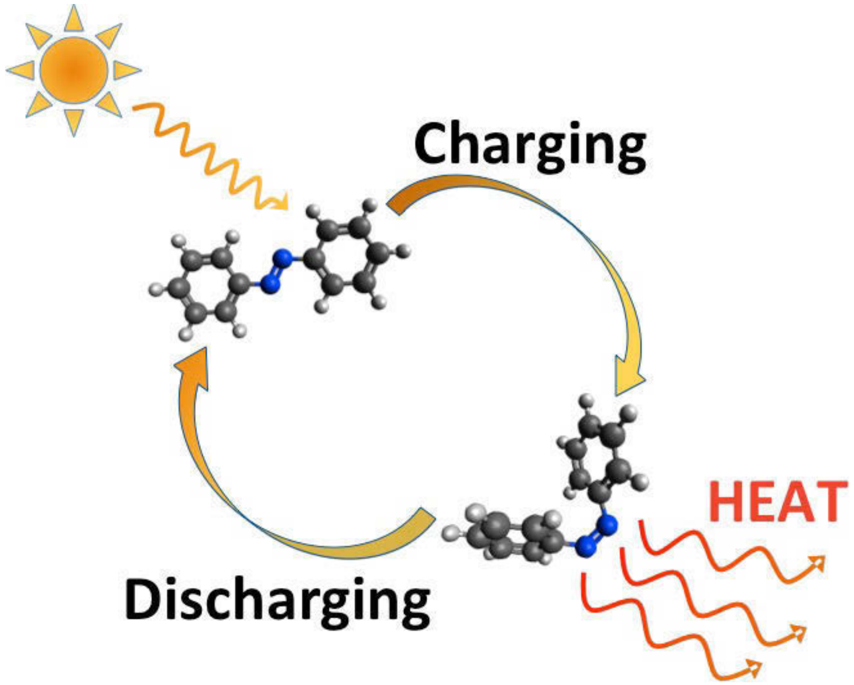
Solar Thermal

Crescent Dunes, NV

Photosynthesis



Solar Thermal Fuels

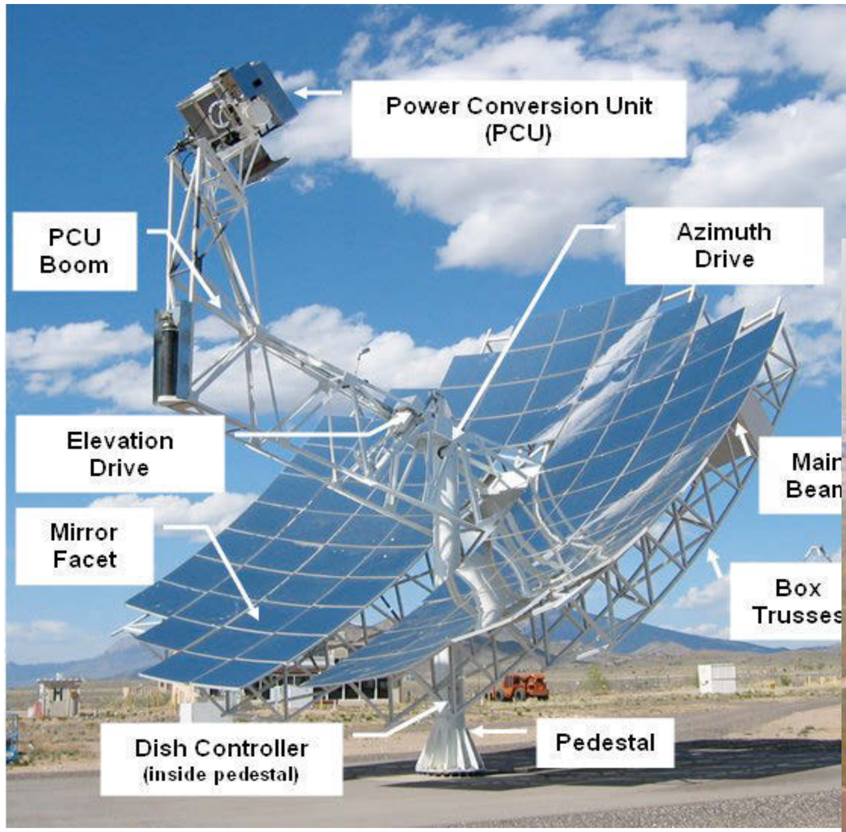


Solar to Heat

Hot Water

Parabolic Dish / Stirling Engines

Reflectors (Parabolic Troughs)



Solar Towers (a.k.a. "Power Towers")

Solar Thermal: Sunlight-->Heat: Concentrating

PS10, 11 MW Solar Tower
(Sanlucar la Mayor, Seville)

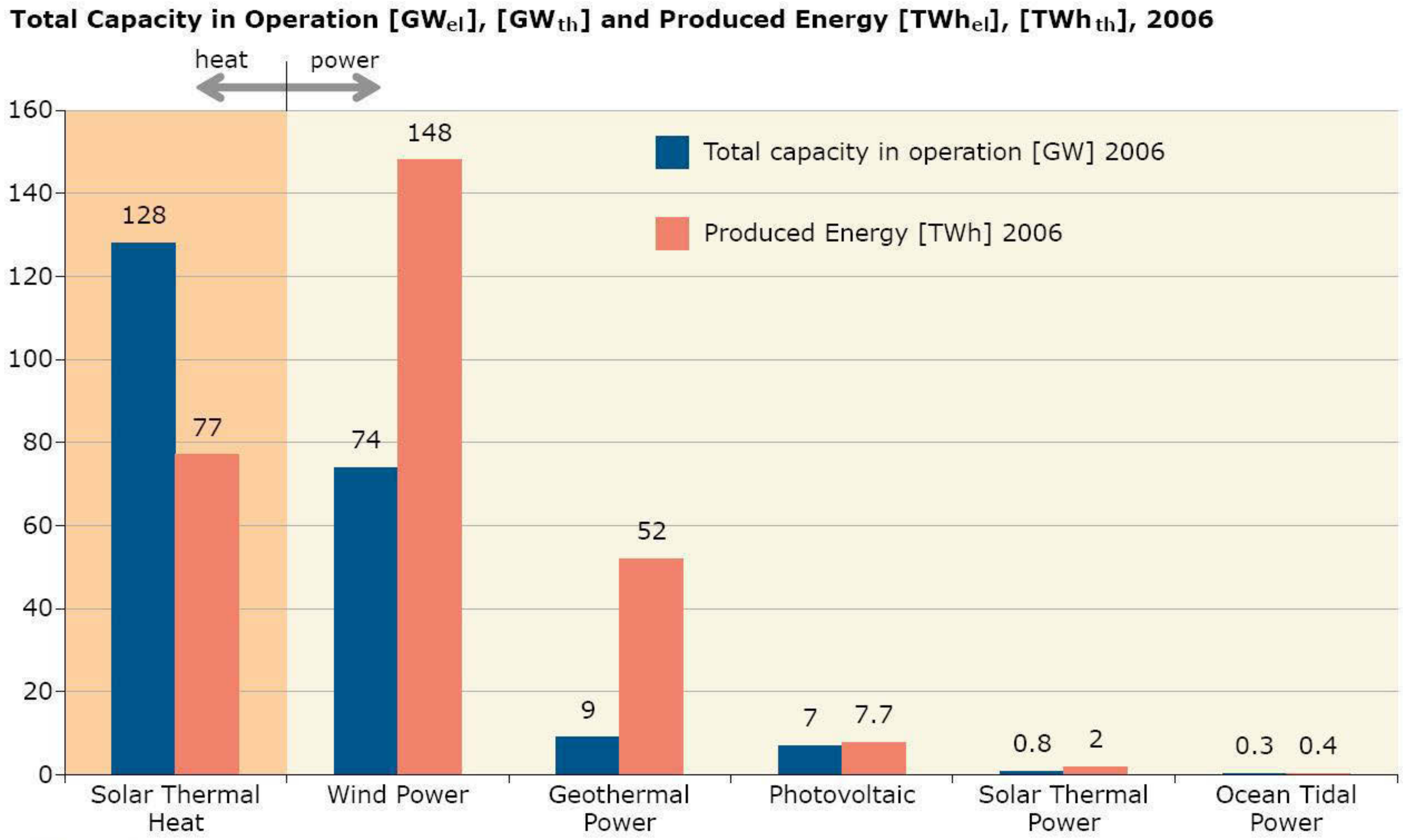


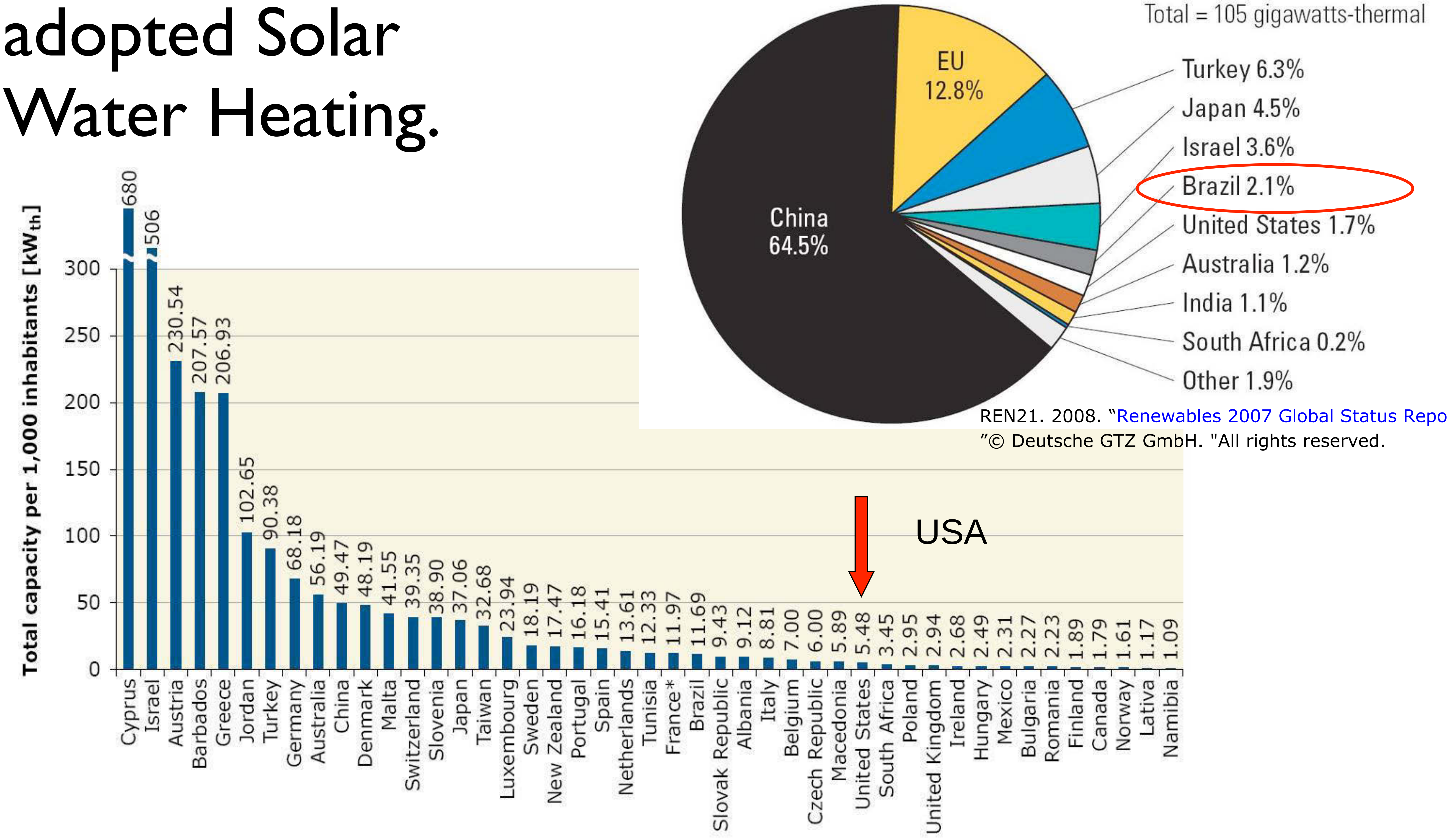
Figure 2: Total capacity in operation [GW_{el}], [GW_{th}] 2006 and annually energy generated [TWh_{el}], [TWh_{th}].
Sources: EPIA, GEWC, EWEA, EGEC, REN21 and IEA SHC 2008

Challenges with Solar Thermal Power:

- Losses in storage
- Auxiliary heating
- Highly reflective coatings + tracking
- Large footprint and cost
- Not transportable, no distribution “as heat”

USA has not widely adopted Solar Water Heating.

Figure 8. Solar Hot Water/Heating Capacity Existing, Selected Countries, 2006



REN21. 2008. "Renewables 2007 Global Status Report." © Deutsche GTZ GmbH. "All rights reserved.

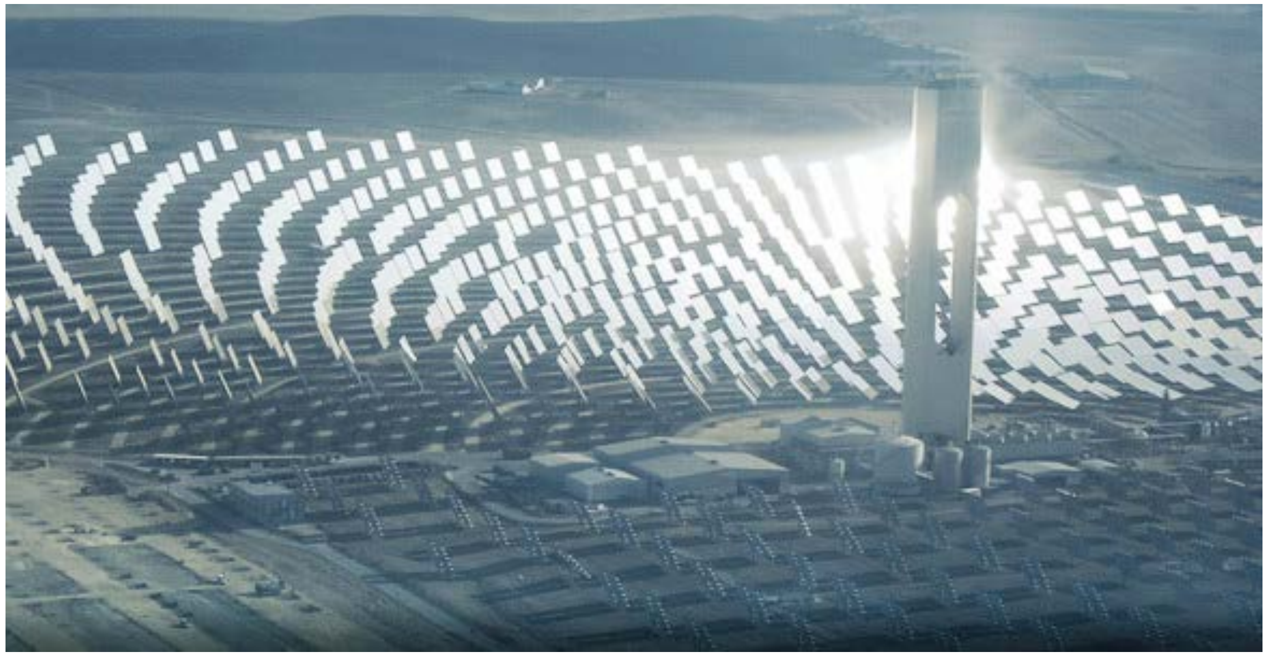
* France: includes Overseas Departments

Figure 6: Total capacity of glazed flat-plate and evacuated tube collectors in operation at the end of 2006 in kW$_{th}$ per 1,000 inhabitants

From Weiss, W. I. Bergmann, and G. Faninger. "Solar heat worldwide 2008: Markets and contributions to the energy supply 2006." © International Energy Agency.

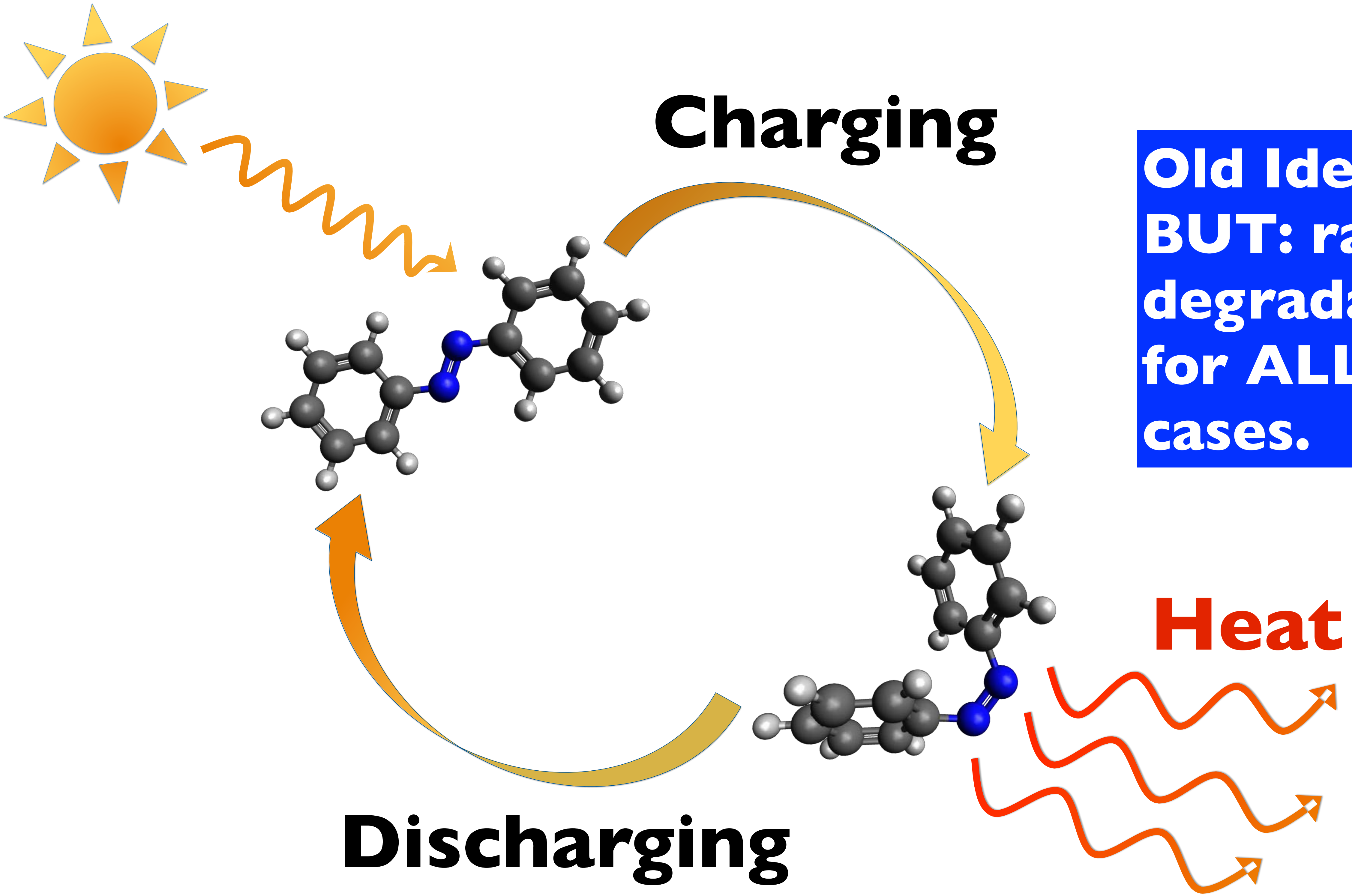
Some Challenges with Solar Thermal

- Losses in storage
- Auxiliary heating
- Highly reflective (and clean) coatings
- Tracking components
- Large storage facilities
- Not transportable, can't be distributed "as heat"



11 MW Solar Tower in Sanlucar la Mayor, Seville © source unknown. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/help/faq-fair-use/.

Solar-Chemical :
Heat stored in chemical bonds



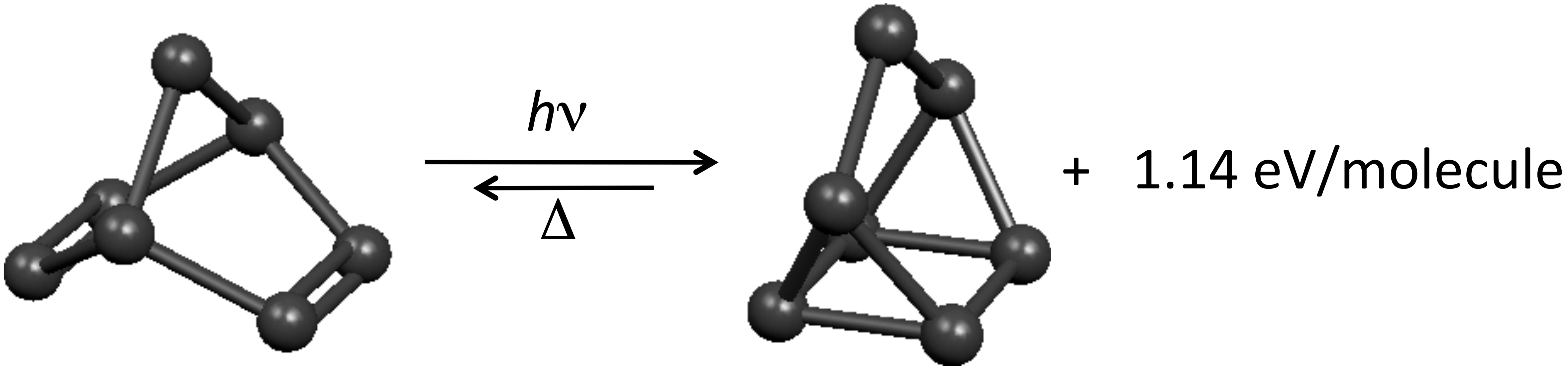
Charging

Old Idea, BUT: rapid degradation for ALL cases.

Heat

Discharging

Blast from the past (70's/80's)…



Norbornadiene

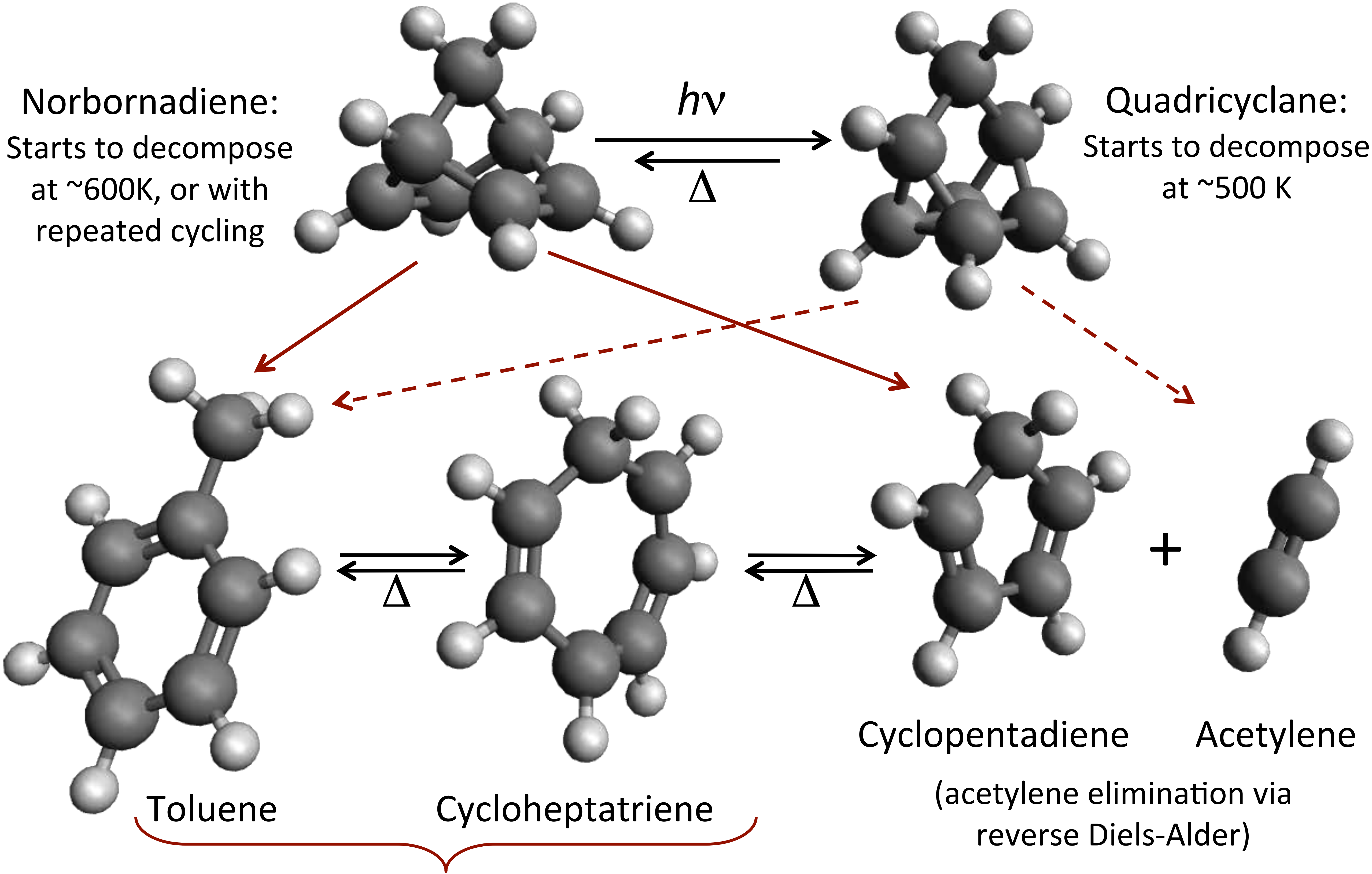
Quadricyclane

BUT: Poor cycling, rapid degradation for ALL cases.

> "… a photochemical solar energy storage plant, although technically feasible, is not economically justified."

Ind. Eng. Chem. Prod. Res. Dev., 1983, 22 (4), pp 627–633

Decomposition products



Norbornadiene:
Starts to decompose at ~600K, or with repeated cycling

Quadricyclane:
Starts to decompose at ~500 K

Toluene

Cycloheptatriene

Stable up to ~1000 K

Cyclopentadiene

Acetylene

(acetylene elimination via reverse Diels-Alder)

J. Phys. Chem. A 102, 9202-9212 (1998)

Efforts to prevent decomposition

“donor-acceptor” norbornadienes: ~10^3 cycles

2,3-disubstituted norbornadienes:
can be cycled “many times”

No magic bullet – always a trade-off between:

- quantum yield
- absorption efficiency
- stored energy
- thermal stability of the quadricyclane
- cyclability

Russian Chem. Rev. 71, 917-927 (2002)

Why revisit solar thermal fuels *now?*

Computational power for high-throughput materials design

+

Technology for atomic-scale engineering

Rapid computational screening of thousands of materials

Potential to synthesize systems designed with atomic-scale control

Example: Time to perform calculations for 100,000 known crystalline materials:

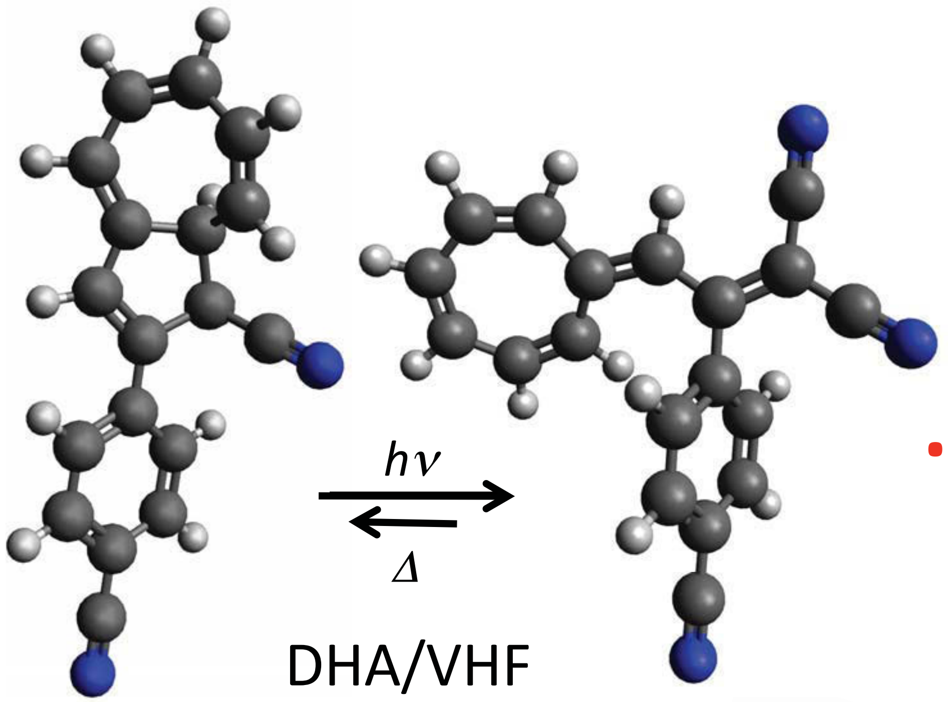
1980: 30 years
2012: few days

The time is ripe to tackle this generation-old concept with a new "arsenal" of science/technology capabilities.

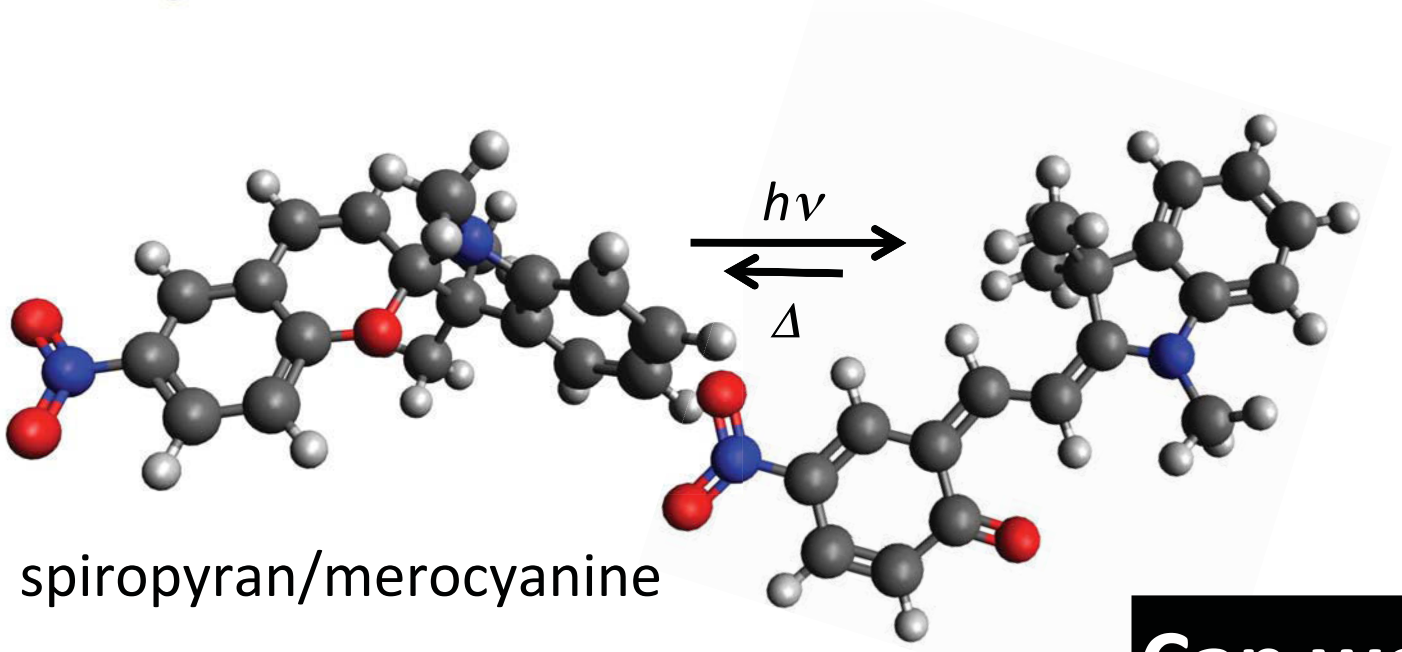
A novel approach to solar thermal fuels

There are many, many photoactive molecules...

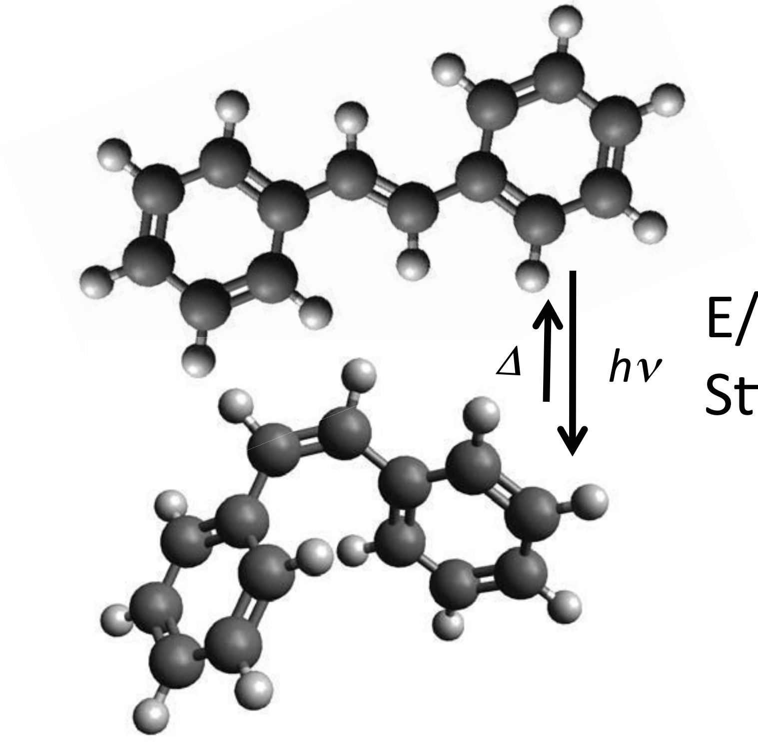
...that are terrible solar thermal fuels.



DHA/VHF



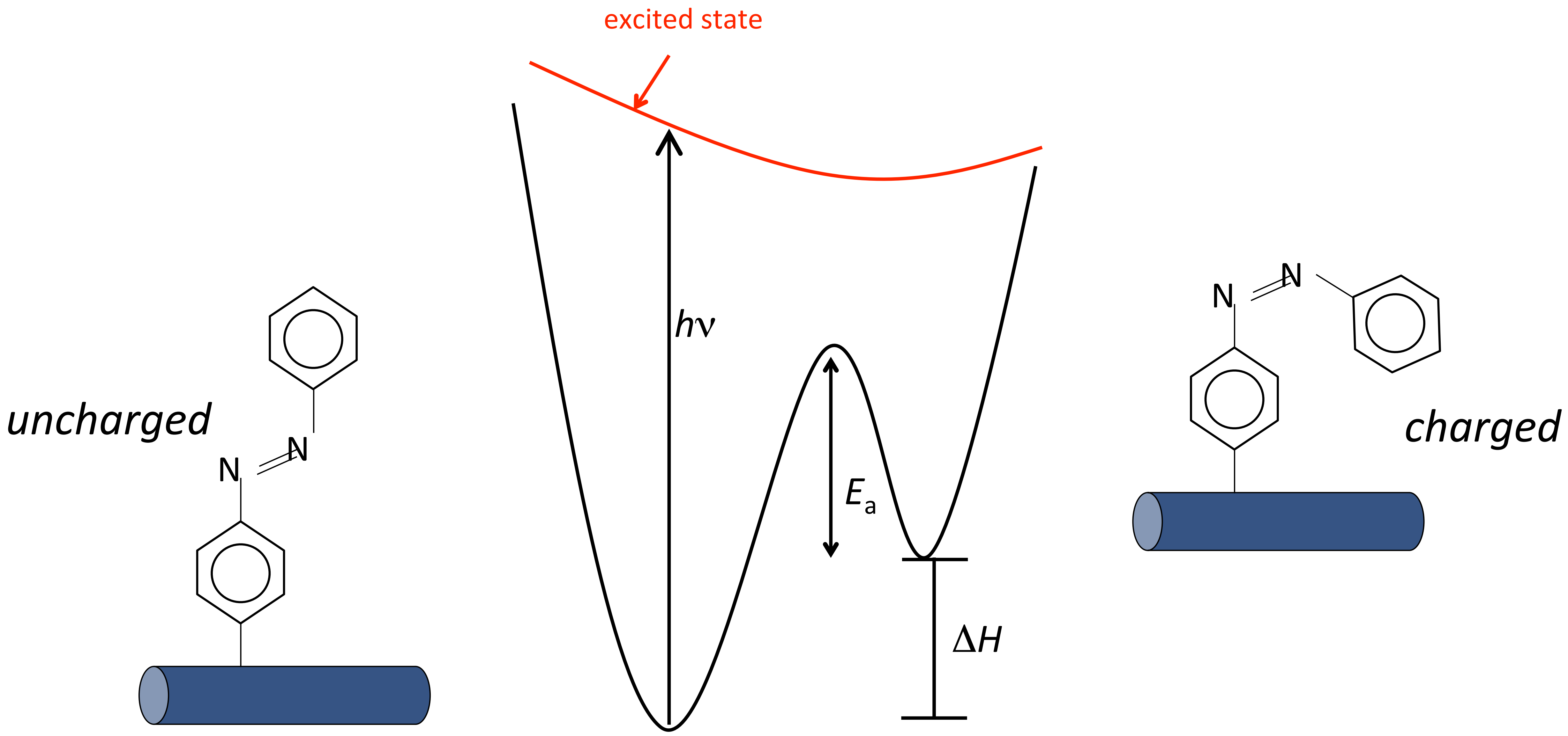
spiropyran/merocyanine



E/Z-Stilbene

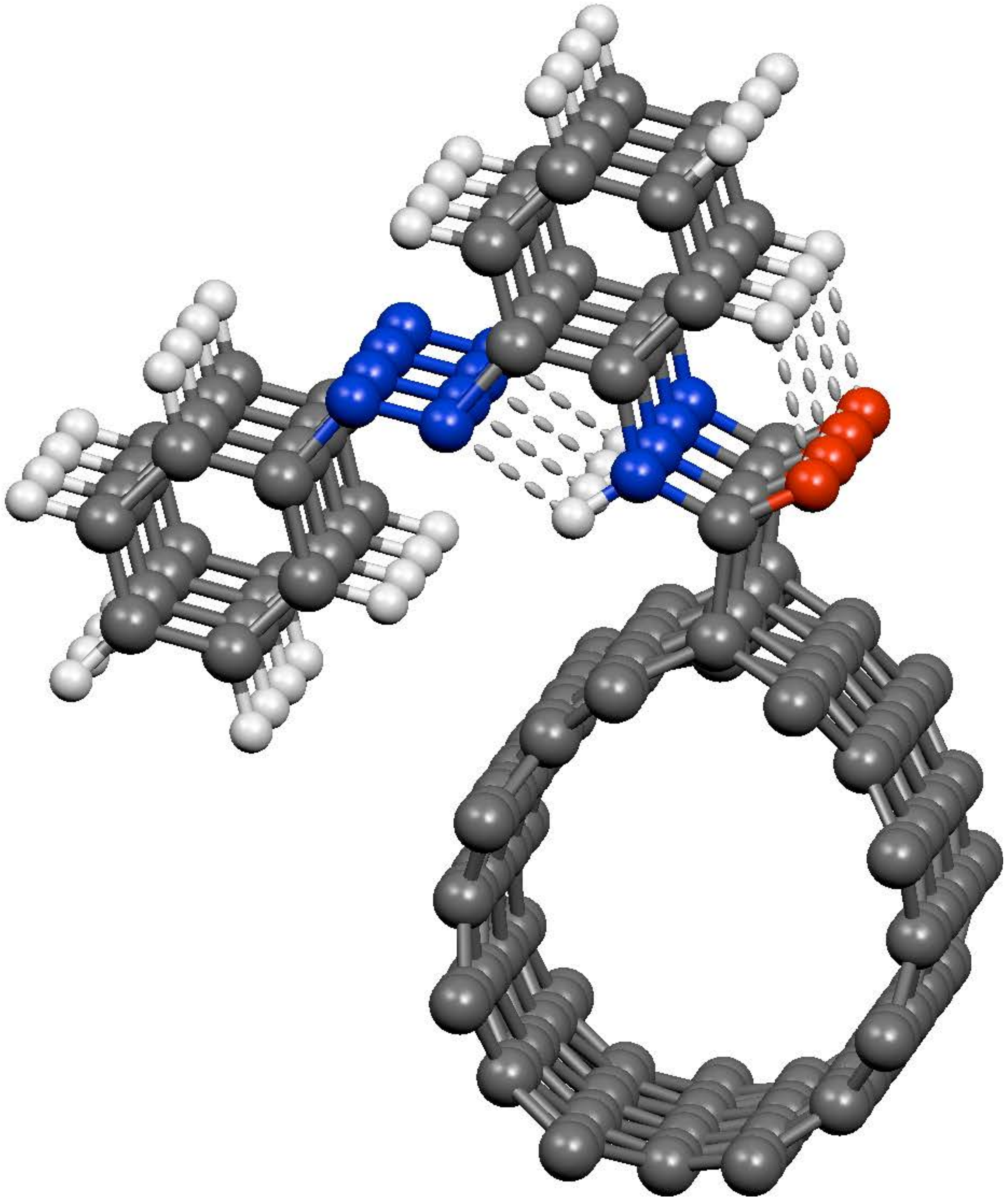
Can we turn them into good ones?

A new approach: combine photomolecule with template



The azobenzene/CNT system

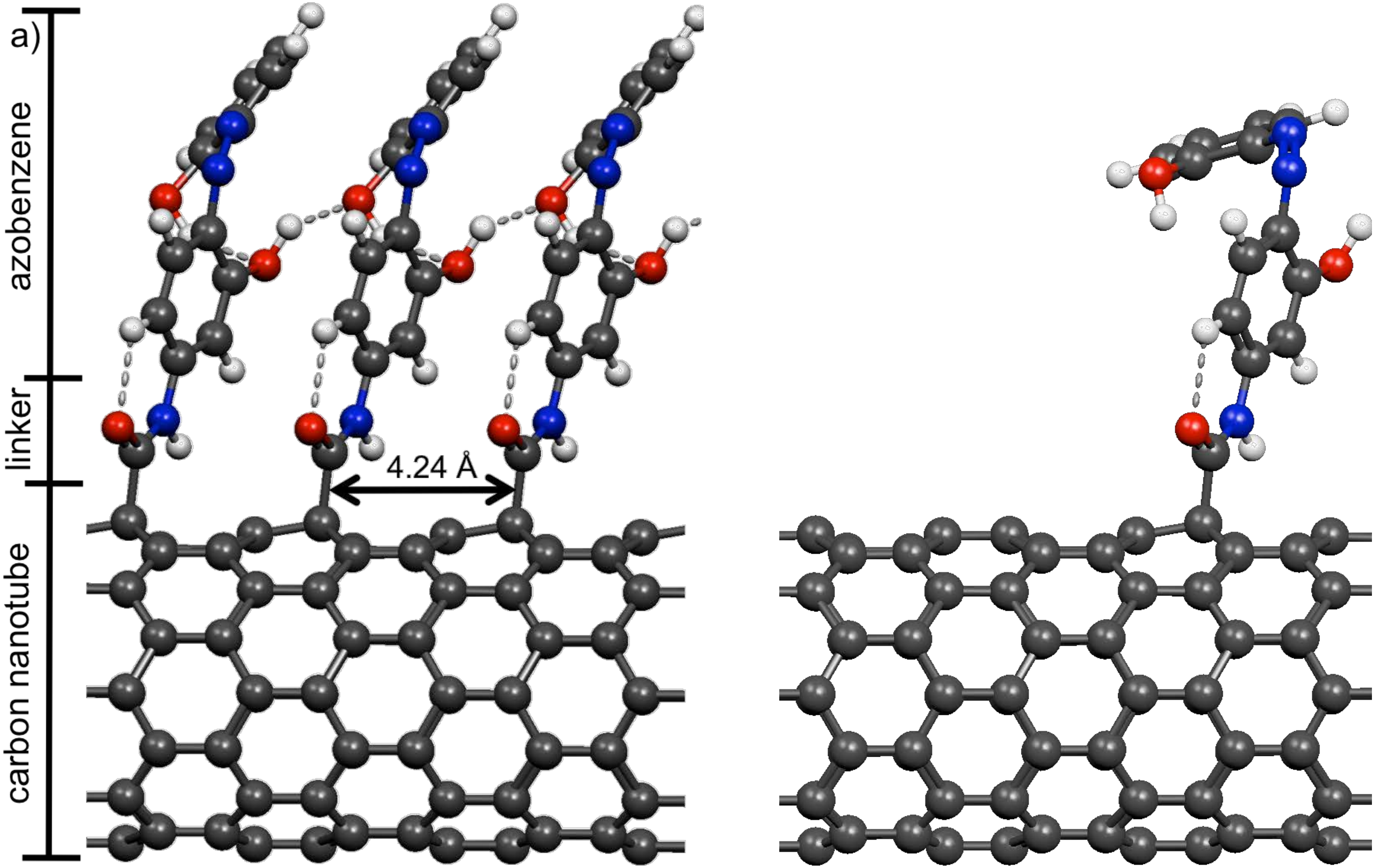
- Already synthesized*
- Photoactivity experimentally demonstrated*
- Not previously considered for energy storage



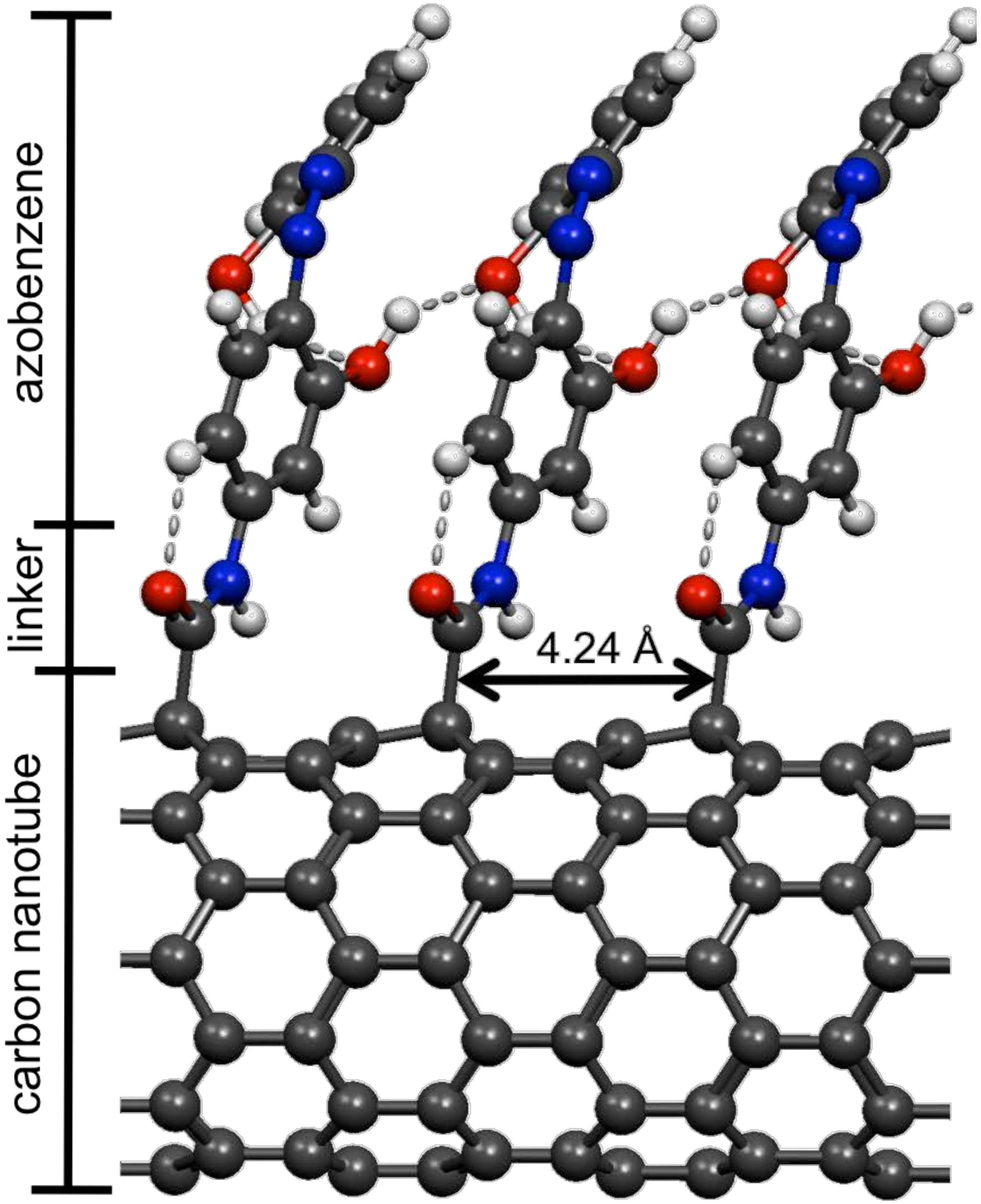
trans-azobenzene/CNT

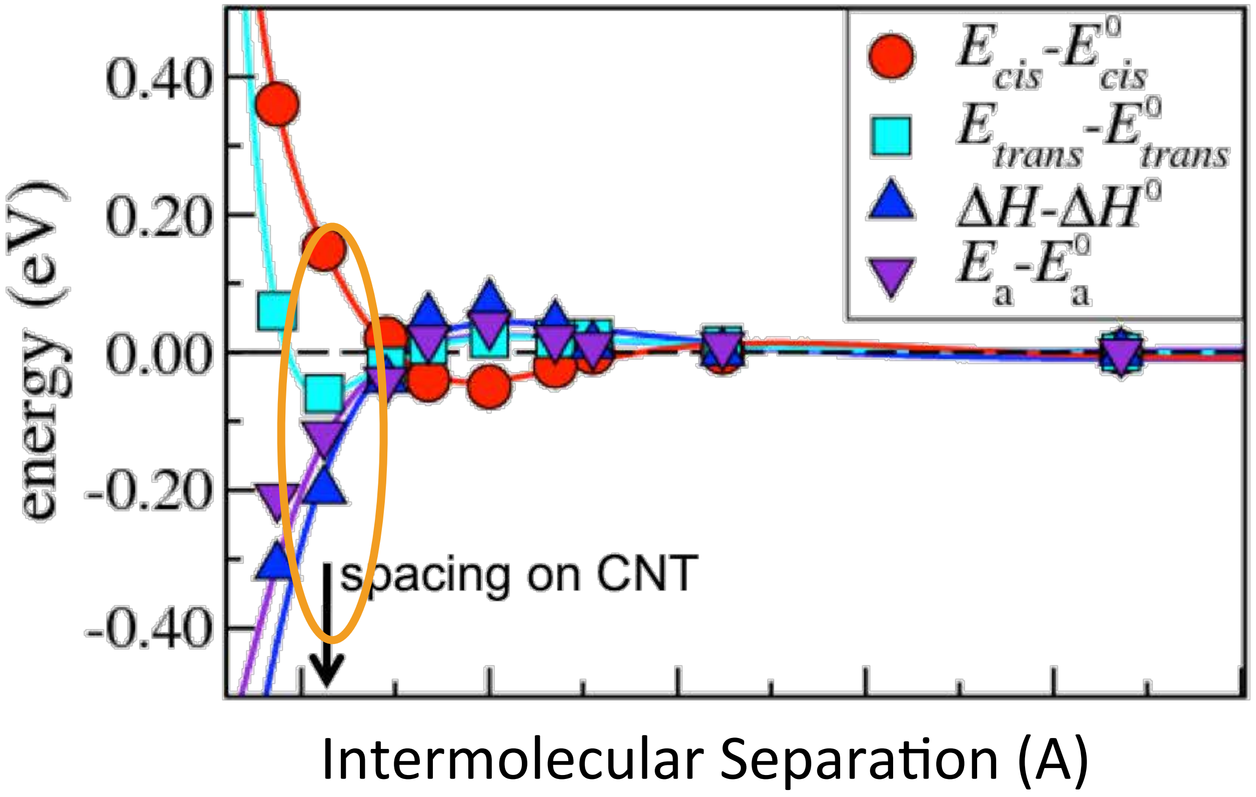
**e.g.*, see Feng, *et. al*, J. Appl. Phys. (2007); Simmons *et. al*, PRL (2007)

Role of the CNT template



Role of the CNT template

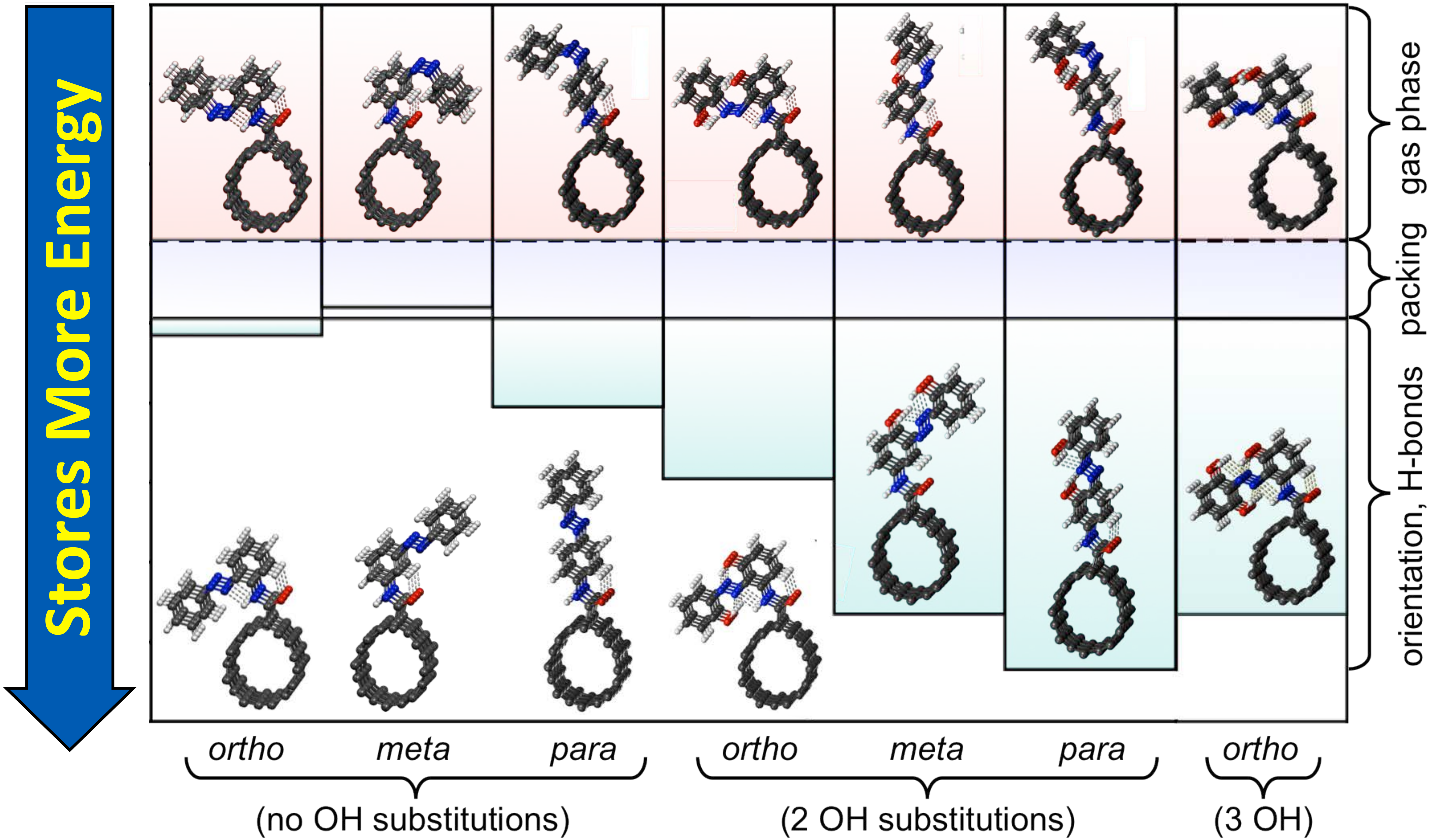




Rigid substrate – fixes inter-molecular distances over long range, enabling:

- steric inhibition
- π-stacking
- hydrophobic interactions

Enables design of specific intermolecular interactions – not available in free azobenzene



Stores More Energy

gas phase

packing

orientation, H-bonds

ortho *meta* *para*

(no OH substitutions)

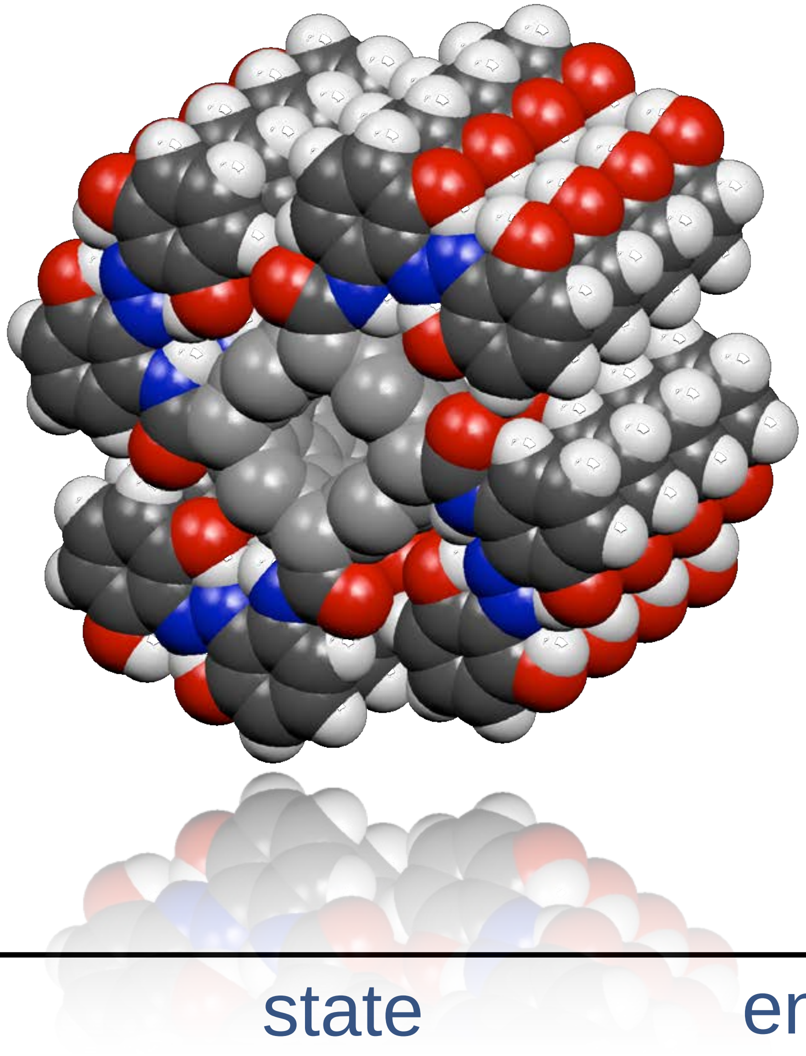
ortho *meta* *para*

(2 OH substitutions)

ortho

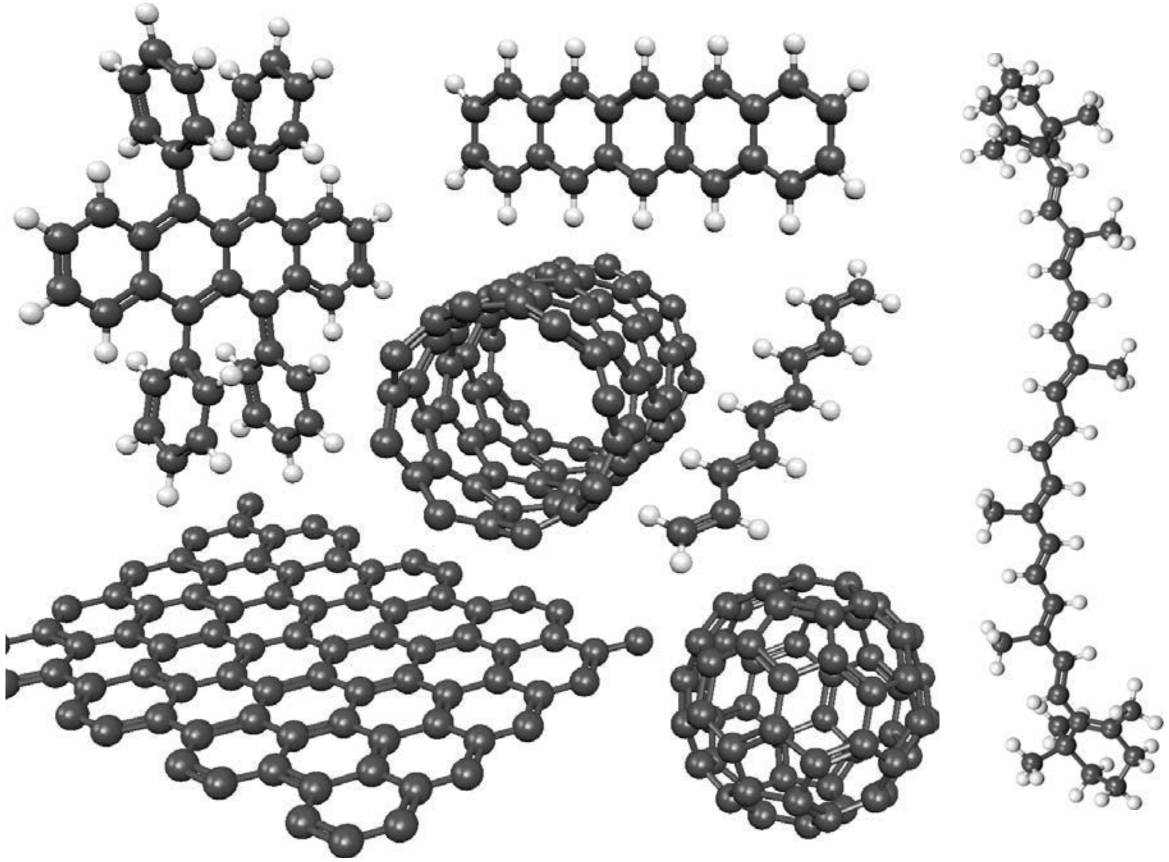
(3 OH)

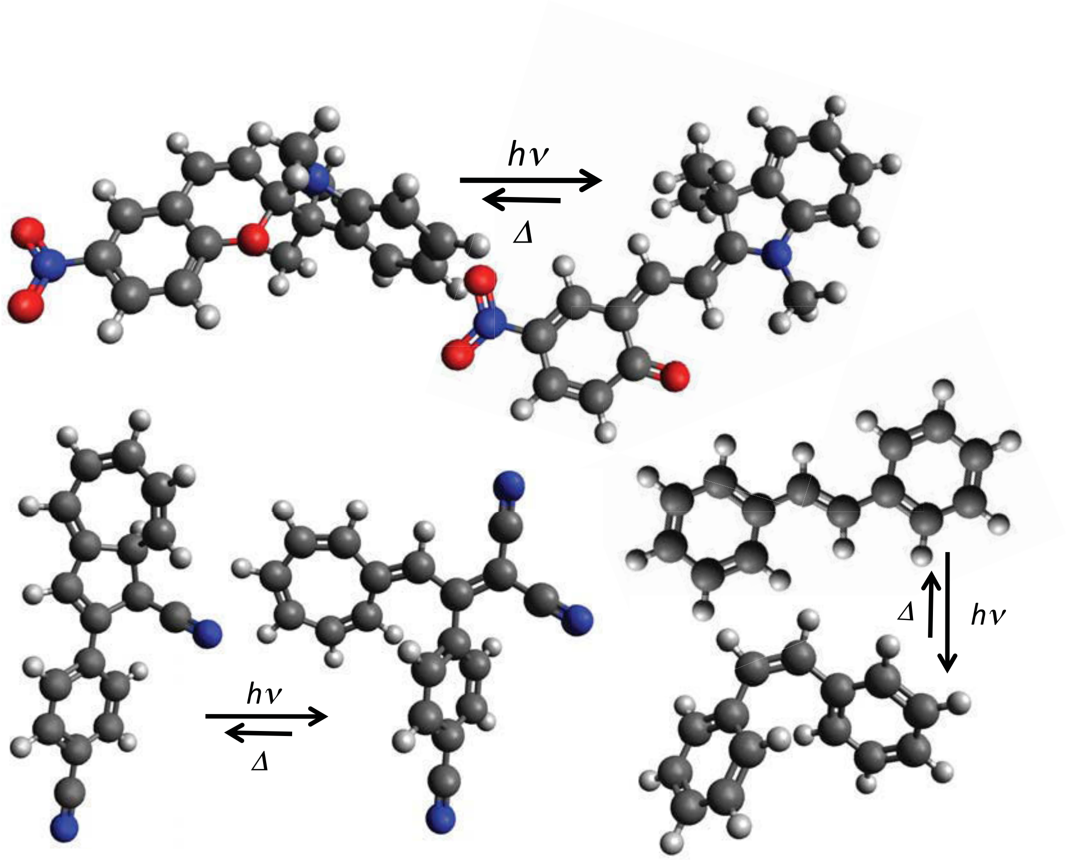
Energy density comparison



system	state	energy density (Wh/L)
Ru-fulvalene	solution (toluene)	0.02
azobenzene	solution (H_2O)	0.000002
azobenzene	powder	90
azobenzene/CNT	soln. or powder	up to 690
Li-ion battery		200-600

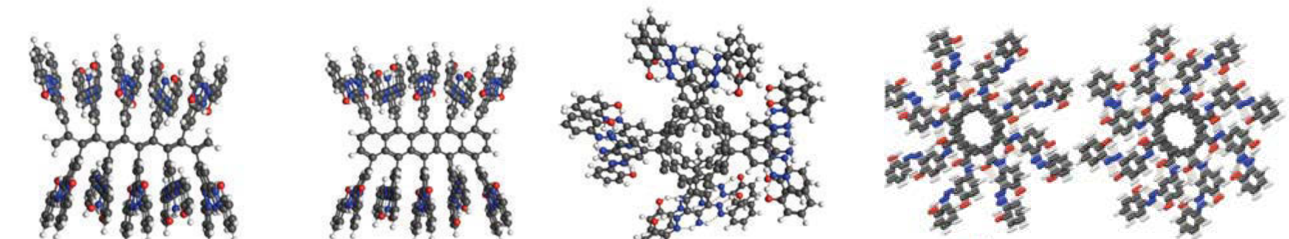
New Materials for Solar Thermal Fuels

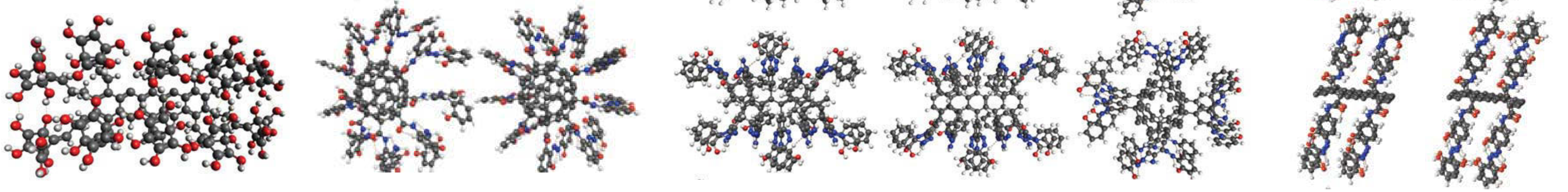




Template Materials + **Photoactive Molecules**

= **New Chemistry Platform for Solar Thermal Fuels**





Solar Thermal Fuel Applications

- Solar cooker: developing countries
- Solar cooker: hiking & outdoor / military
- Solar autoclave: developing countries
- Medical sanitation
- Milk pasteurization: rural
- Thin film window heating supplement
- On-site storage: power generation
- Gas/oil industry
- Military off-grid heat
- Building heating
- NASA/maritime
- CSP auxiliary heat supply
- De-icing (windows, planes, power lines)

The Case for Solar Cookers

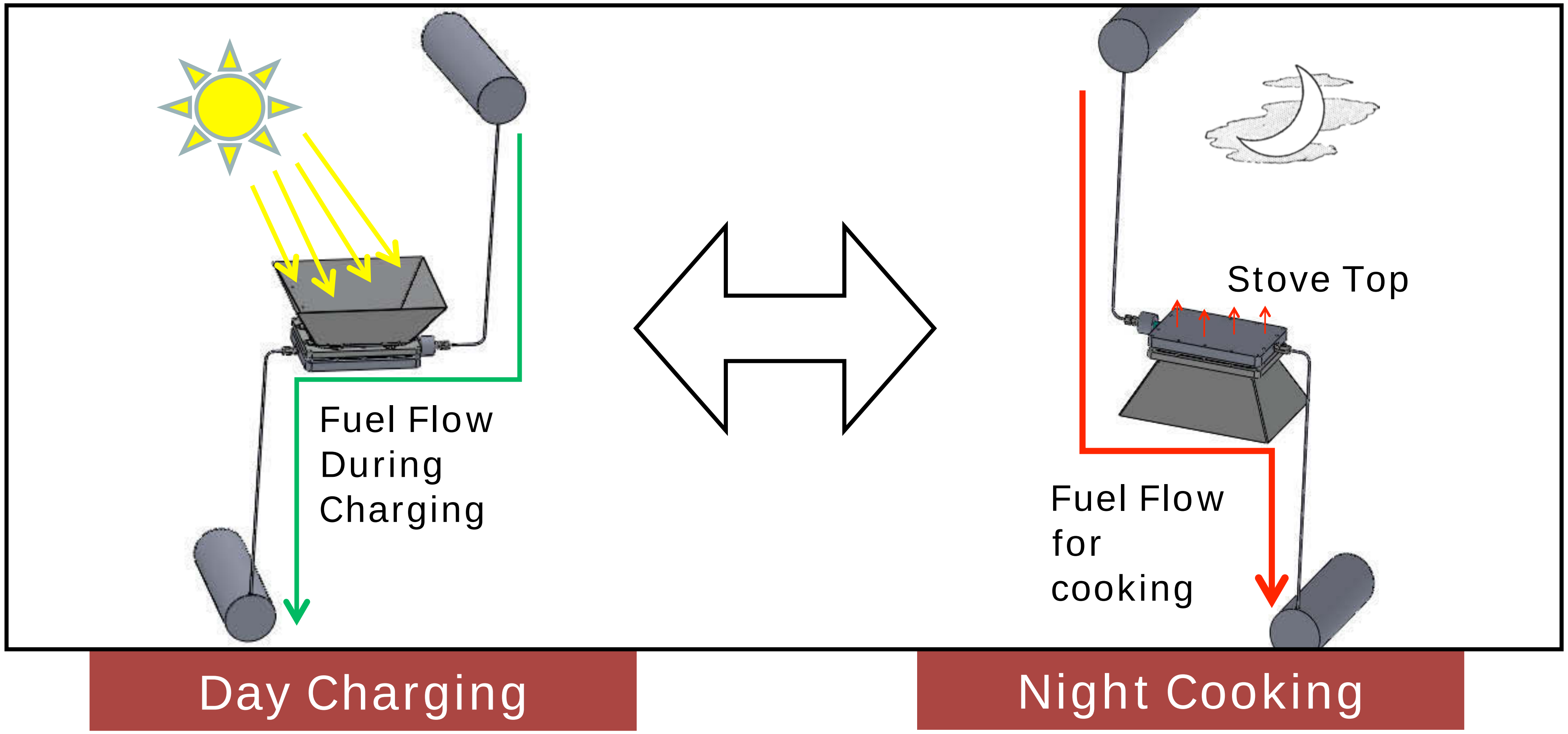
Problems with Cooking Off-Grid

- Cooking fuel (e.g., wood) is increasingly scarce, expensive, and time-intensive to find
- Smoke in not-well ventilated areas causes respiratory problems

Existing Solar Ovens

- Can only cook while the sun is out
- Are cumbersome and heavy to transport
- Cannot be turned ‘on’ and ‘off’

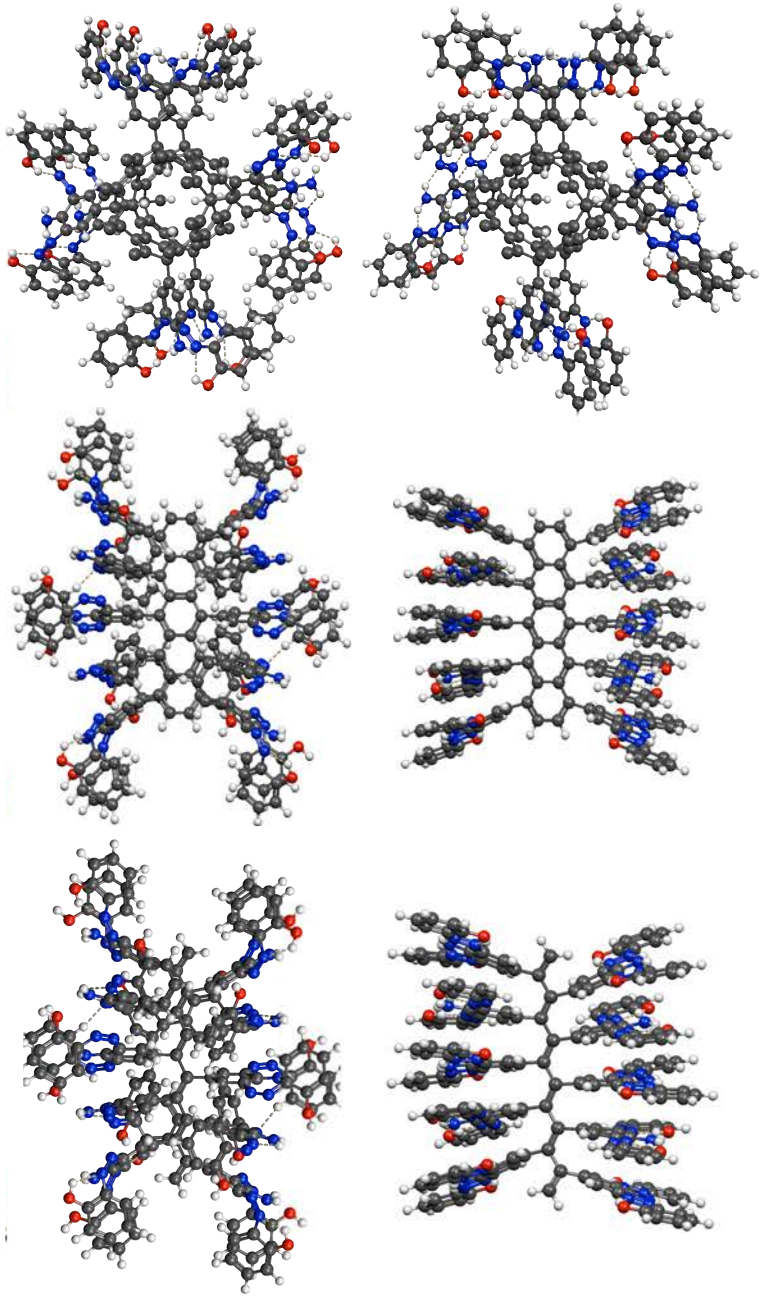
Solar Cooker: Using the Sun to Cook at Night



- Charging: slow flow through solar collector during the day.
- Cooking: device is turned upside down.
- Cost estimate <$200. Weight=<5 kg, floor space=1 sq. ft.
- 5 hours of charge time = boil liters of water or cook at 300C for ~1 hour.

Materials Design Full Cycle

Simulation



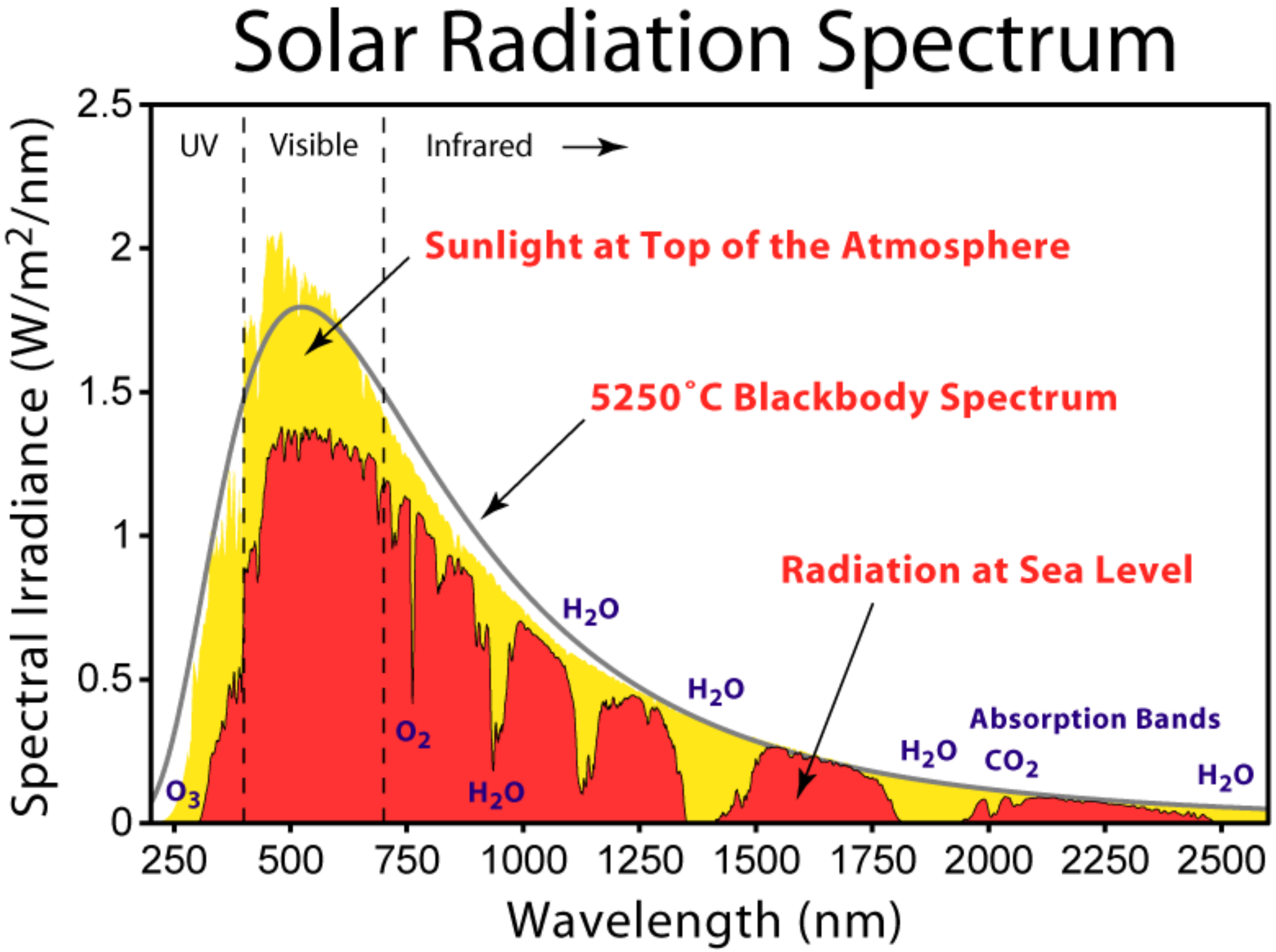
Synthesis

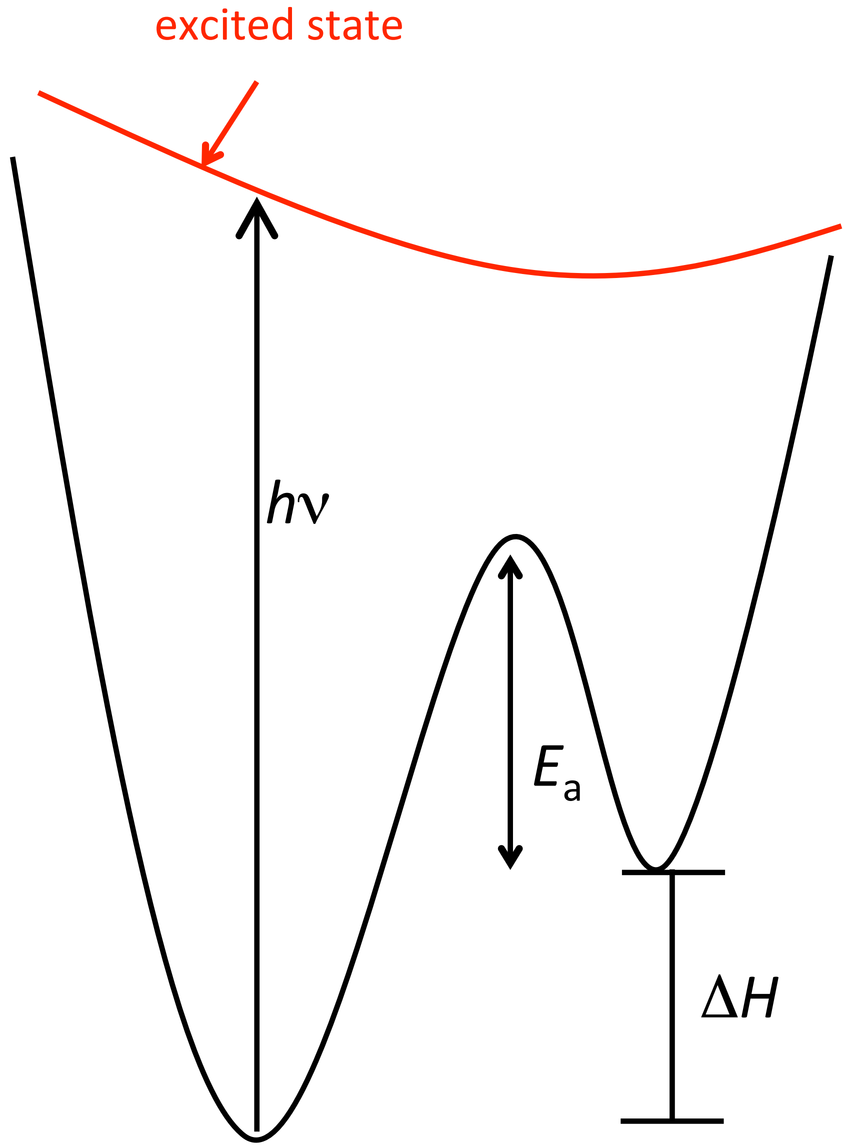
Testing

Prototype

Grossman Group, MIT.

So Why do We Need QM?





3.021J / 1.021J / 10.333J / 18.361J / 22.00J Introduction to Modelling and Simulation
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