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

Part II – Quantum Mechanical Methods : Lecture 5

More QM Modeling for Solar Thermal Fuels, Plus a Little H-Storage

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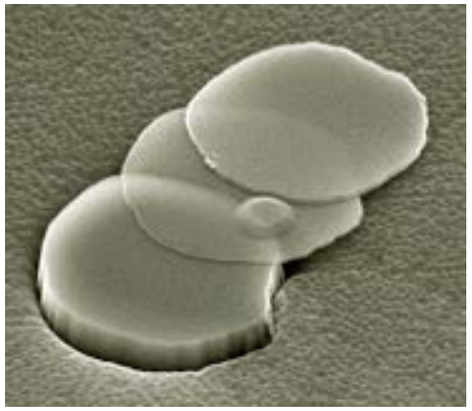
Part II Topics

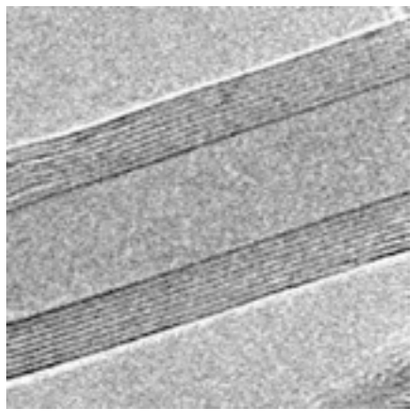
1. It's a Quantum World: The Theory of Quantum Mechanics
2. Quantum Mechanics: Practice Makes Perfect
3. From Many-Body to Single-Particle: Quantum Modeling of Molecules
4. Application of Quantum Modeling of Molecules: Solar Thermal Fuels
5. Application of Quantum Modeling of Molecules: Hydrogen Storage
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

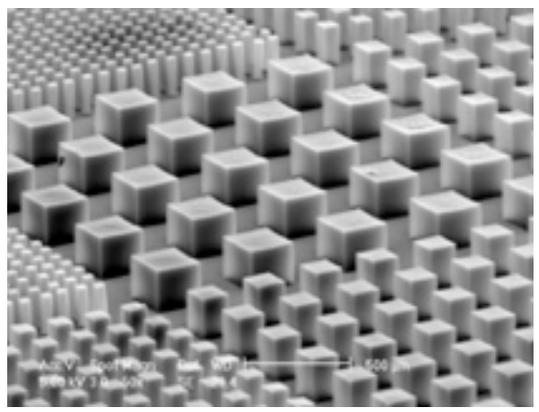
Lesson outline

- Feeling good about energy levels
- Continued discussion of solar thermal fuels
- Interactive calculations and discussion on candidate fuels
- Hydrogen storage

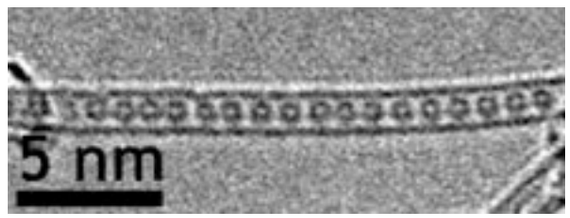
Let’s look at a single element:

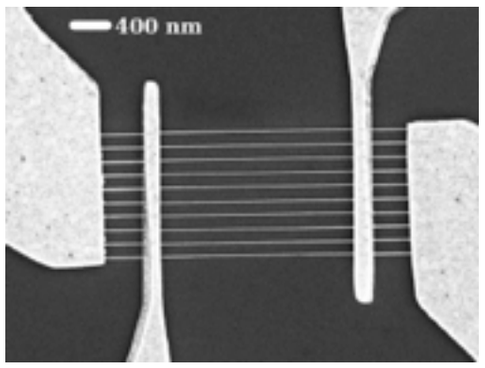






carbon



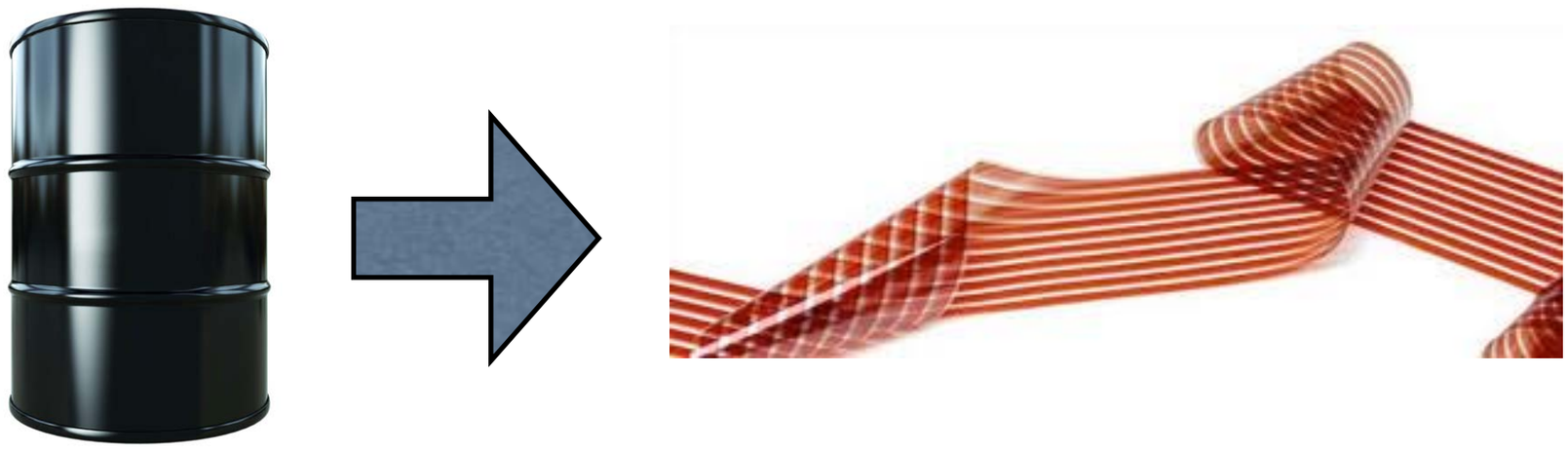


Carbon in Energy to Date

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.

Energy Levels and Basis Sets

Let's pause and feel our oneness with these things.

Energy Levels

$$H\psi(\vec{r}) = E\psi(\vec{r})$$

The S. Eq. leads to wavefunctions

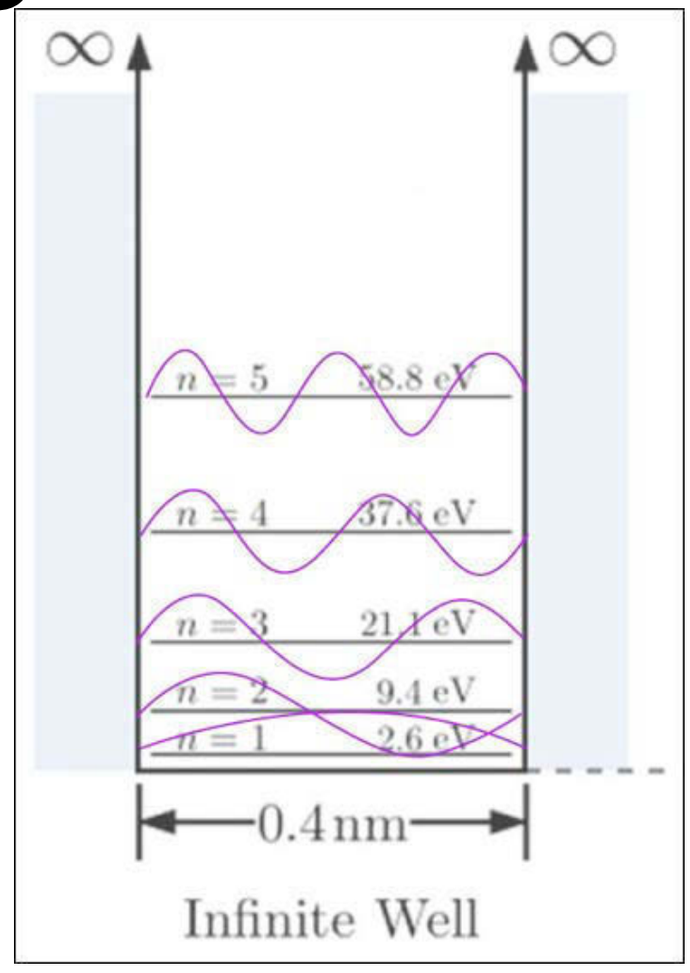
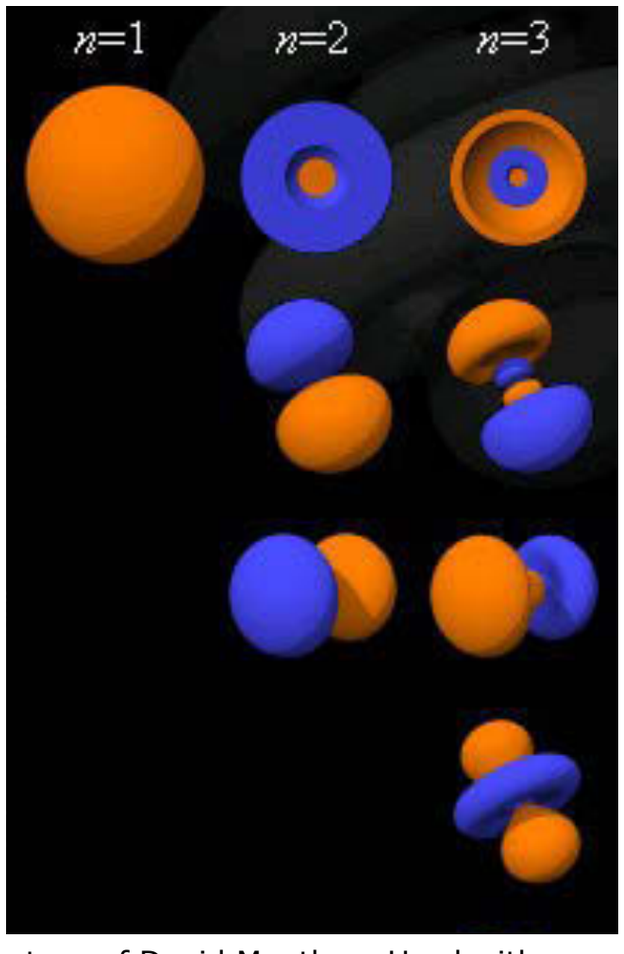


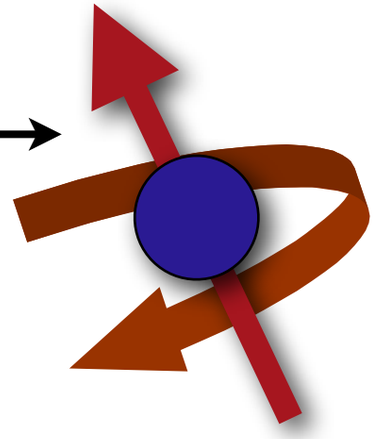
Image adapted from Wikimedia Commons, http://commons.wikimedia.org.



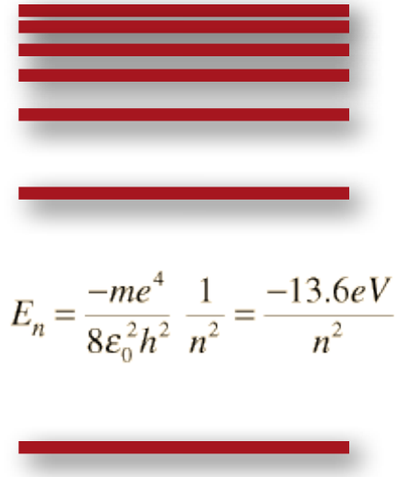
Courtesy of David Manthey. Used with permission.
Source: http://www.orbitals.com/orb/orbtable.htm.

Which squared lead to probability distributions

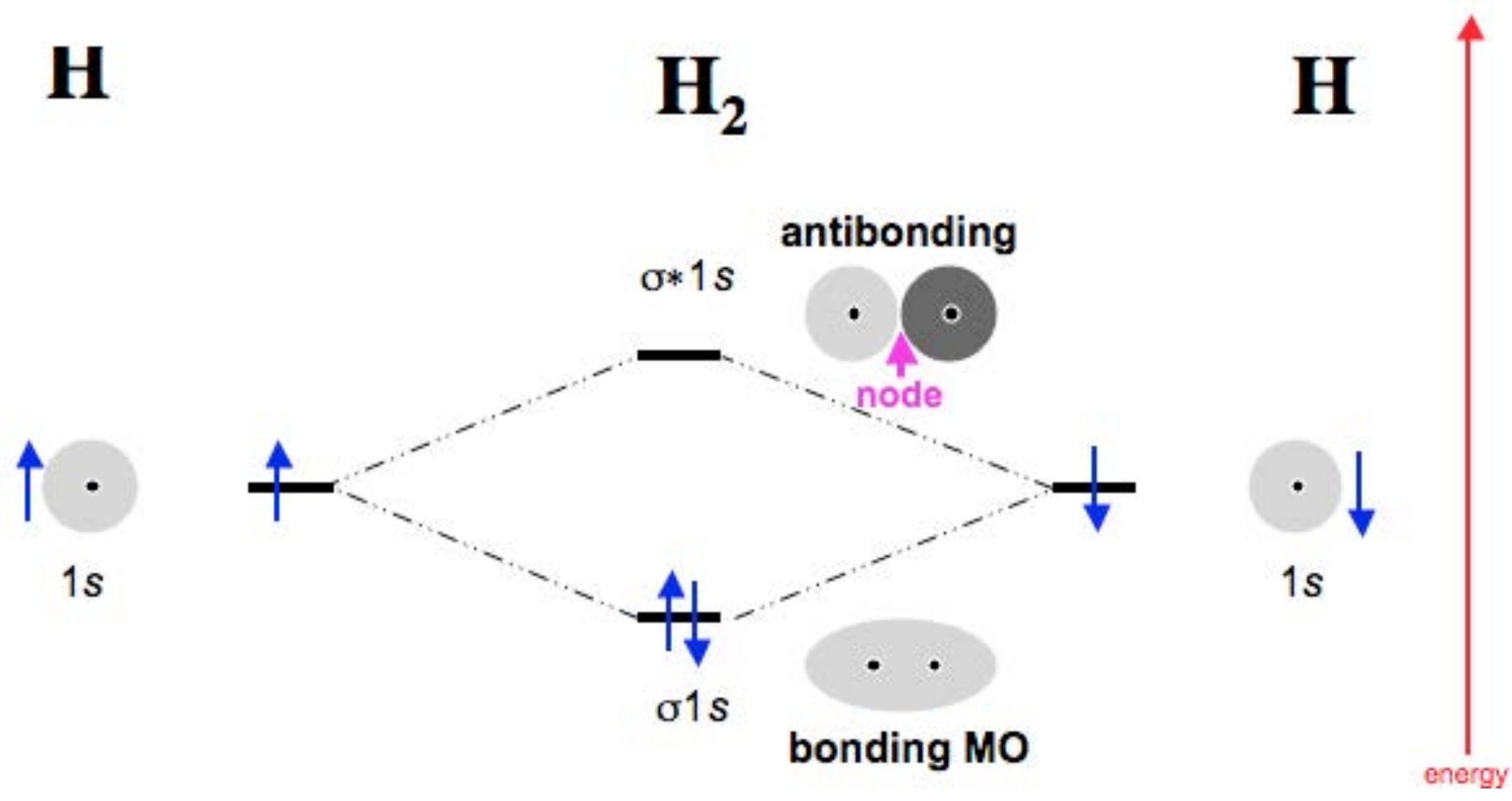
Which once spin is taken into account



Tells us about energy levels!



Energy Levels



Courtesy of Mark R. Leach on meta-synthesis.com.

http://www.meta-synthesis.com/webbook/39_diatomics/diatomics.html

Review: Basis functions

Matrix eigenvalue equation:

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

expansion in orthonormalized basis functions

$$H\psi = E\psi$$

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

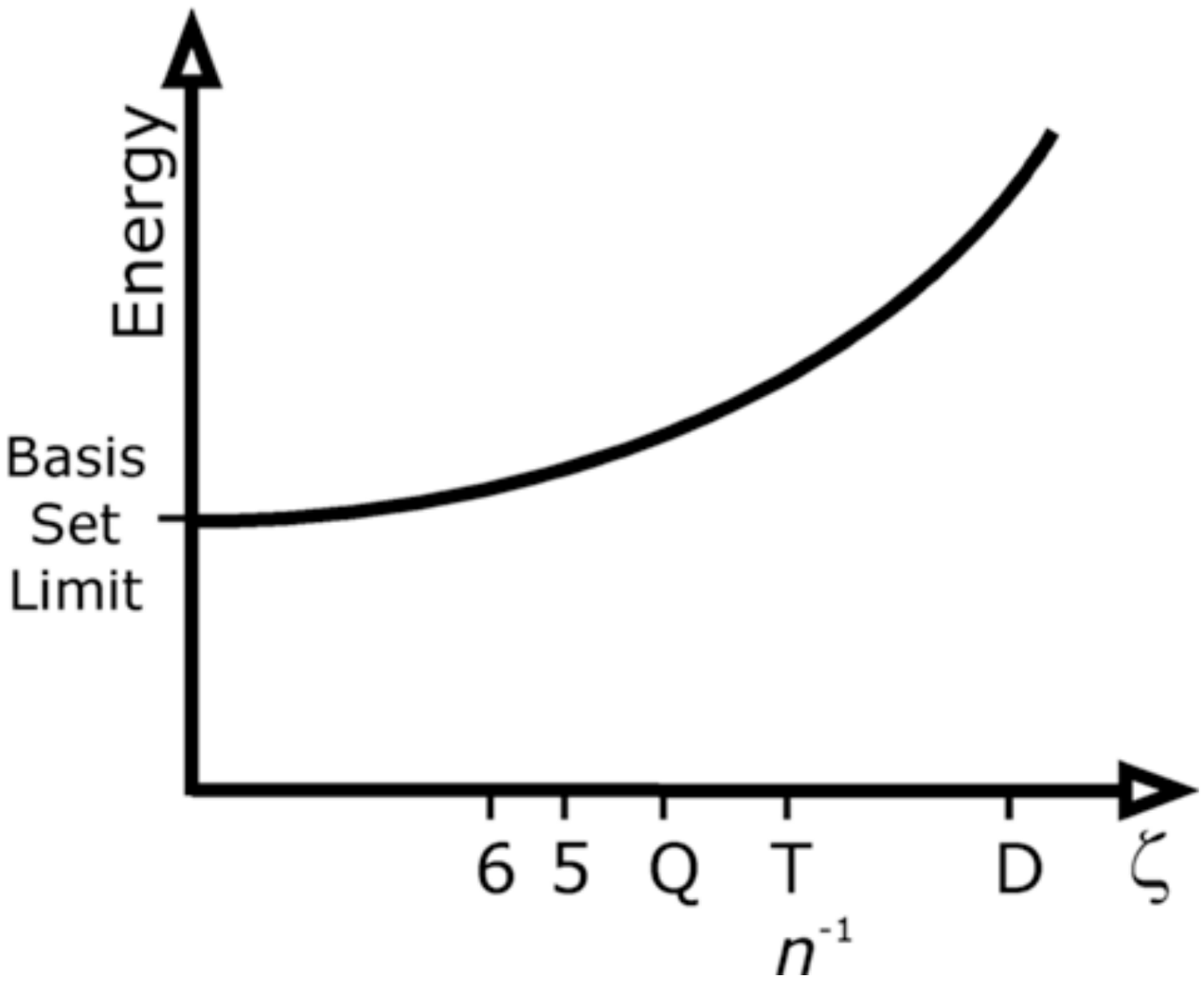
$$\int d\vec{r}\, \phi_j^* H \sum_i c_i \phi_i = E \int d\vec{r}\, \phi_j^* \sum_i c_i \phi_i$$

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

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

Basis Set Convergence

When is a basis set converged?



- Many basis sets have been made for different elements.*
- You can make your own one too.
- This can lead to big tables (but chemists love big tables!).

* see, e.g., bse.pnl.gov

Basis Set Convergence

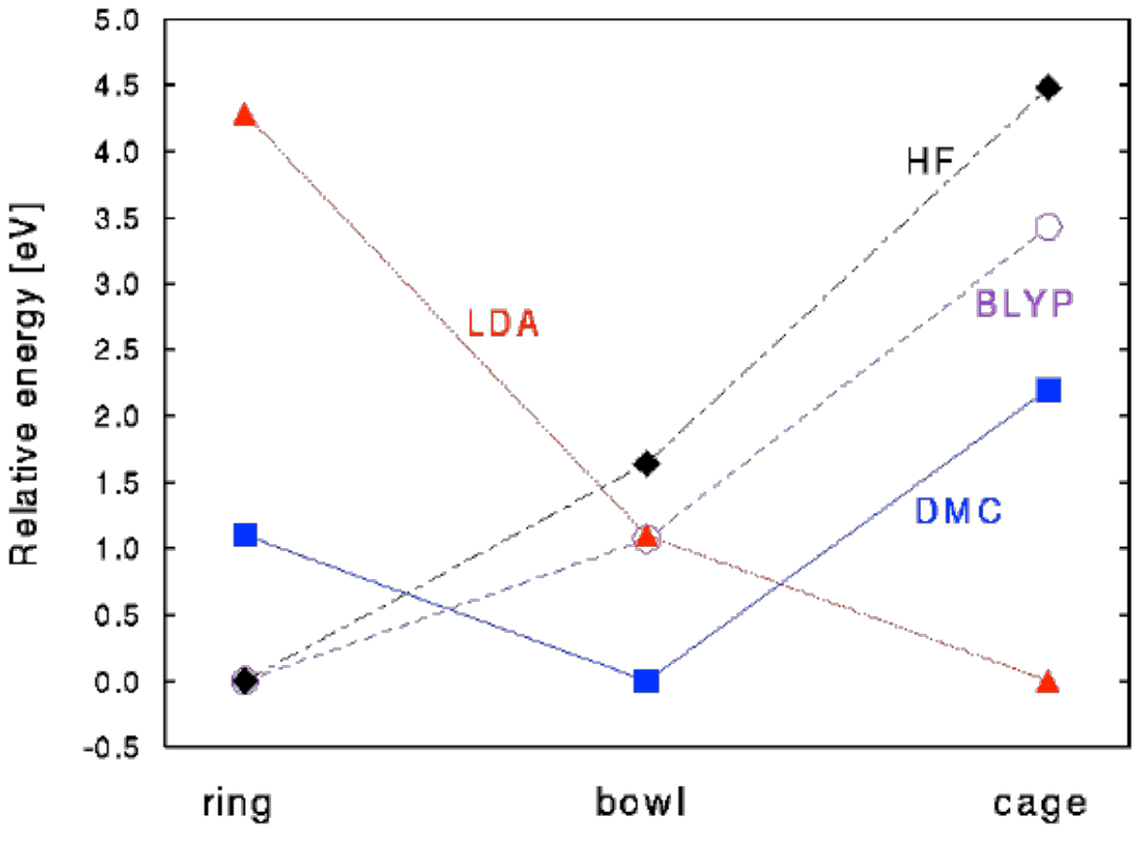
Table 2:

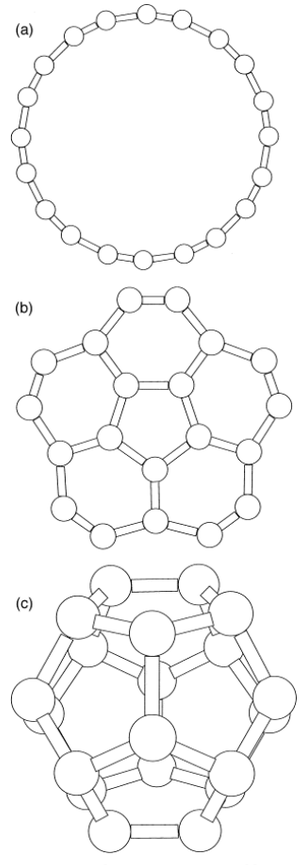
	STO-3G	3-21G	6-31G	6-31 G*	6-31 G**	6-31++ G**	6-311++ G(2d,2p)	6-311++ G(3df,3pd)	cc-pVDZ	cc-pVTZ	cc-pVQZ	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	Ave. Error
# basis fncs	14	26	26	38	50	62	94	150	48	116	230	82	184	344	
HF															
E (binding)	-5.92	-10.97	-7.84	-5.62	-5.54	-5.03	-4.07	-4.00	-5.76	-4.45	-4.01	-3.91	-3.74	-3.73	5.52
E (CP)	6.58	4.95	0.84	0.93	0.98	0.62	0.31	0.30	1.90	0.74	0.30	0.20	0.04	0.01	
E (+ CP)	0.66	-6.02	-7.00	-4.69	-4.56	-4.41	-3.76	-3.70	-3.86	-3.71	-3.71	-3.71	3.70	-3.71	3.59
MP2															
E (binding)	-6.55	-12.63	-8.38	-7.32	-7.05	-6.41	-5.36	-5.30	-7.47	-6.08	-5.49	-5.26	-5.18	-5.09	5.31
E (CP)	8.91	7.94	1.67	2.23	2.40	1.64	0.91	0.74	3.82	1.72	0.82	0.83	0.47	0.24	
E (+ CP)	2.36	-4.69	-6.71	-5.09	-4.65	-4.77	-4.45	-4.56	-3.65	-4.36	-4.67	-4.43	-4.71	-4.86	2.66
MP4(SDTQ)															
E (binding)	-5.42	-12.14	-8.11	-7.02	-6.76	-6.24	-5.35	-5.30	-7.22	-5.98	-5.44	-5.30	-5.21	-5.08	4.77
E (CP)	7.82	7.49	2.11	2.03	2.06	1.67	0.98	0.77	3.60	1.73	0.83	0.93	0.48	0.20	
E (+ CP)	2.40	-4.65	-6.00	-4.99	-4.70	-4.57	-4.37	-4.55	-3.62	-4.25	-4.61	-4.37	-4.73	-4.88	2.41
CCD															
E (binding)	-5.04	-11.79	-7.92	-6.73	-6.48	-5.98	-5.02	-5.01	-6.80	-5.53	-5.06	-4.95	-4.90	-4.80	4.88
E (CP)	7.53	7.31	1.52	1.93	2.03	1.45	0.80	0.67	3.25	1.38	0.61	0.76	0.43	0.18	
E (+ CP)	2.49	-4.48	-6.40	-4.80	-4.45	-4.53	-4.22	-4.34	-3.55	-4.15	-4.45	-4.19	-4.48	-4.62	2.36
CISD															
E (binding)	-2.97	-6.66	-2.08	3.80	4.69	5.95	9.37	9.37	4.69	10.23	12.04	8.67	11.64	12.74	22.65
E (CP)	7.72	7.33	1.59	1.89	1.93	1.44	0.79	0.67	3.19	1.32	0.58	0.77	0.41	0.18	
E (+ CP)	4.75	0.67	-0.49	5.69	6.62	7.39	10.16	10.04	7.88	11.55	12.62	9.44	12.05	12.91	18.29
QCISD															
E (binding)	-5.12	-11.98	-8.04	-6.83	-6.59	-6.07	-5.10	-5.06	-6.95	-5.63	-5.13	-5.01	-4.95	-4.84	4.91
E (CP)	0.30	7.70	1.73	2.09	2.16	1.53	0.84	0.69	3.46	1.48	0.67	0.77	0.43	0.18	
E (+ CP)	-4.82	-4.28	-6.31	-4.74	-4.43	-4.54	-4.26	-4.37	-3.49	-4.15	-4.46	-4.24	-4.52	-4.66	2.43
SVWN															
E (binding)	-20.04	-22.10	-15.53	-12.99	-12.70	-10.77	-9.47	-9.28	-14.77	-10.58	-9.57	-9.22	-9.03	-8.98	10.64
E (CP)	13.05	15.09	2.30	3.96	4.31	1.15	0.56	0.42	7.18	1.08	1.01	0.30	0.11	0.06	

What else?

After the basis set is converged, is the calculation "right"?

example: what is the most stable structure of 20 carbon atoms?

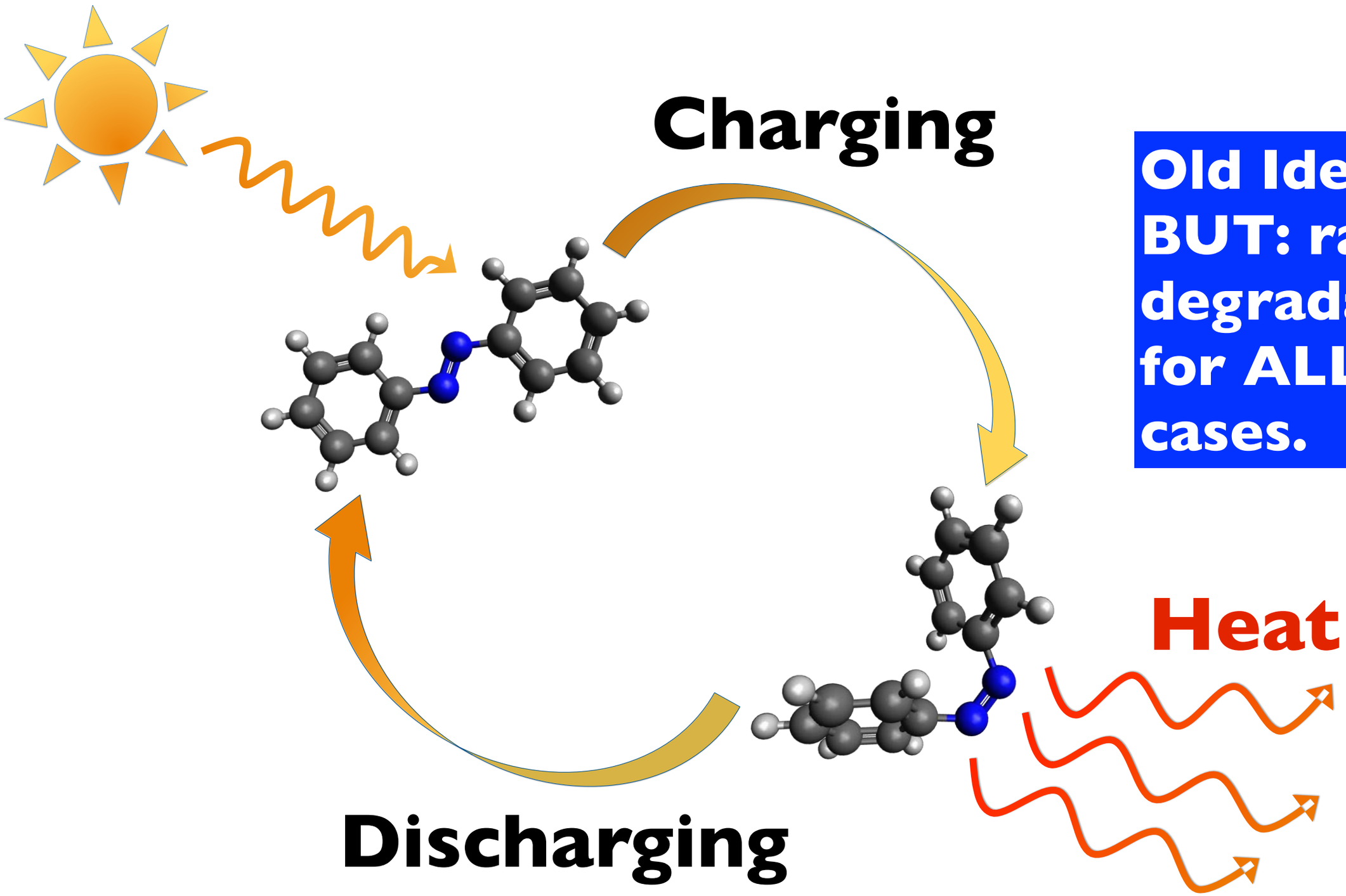




Hmmmm....

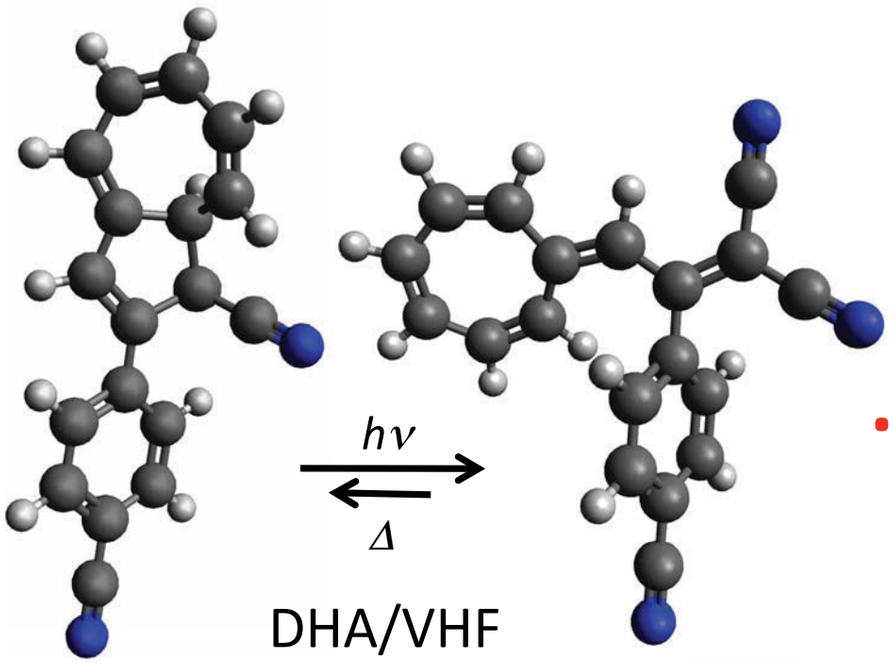
Back to our first application example: Solar Chemical Fuels

Solar-Chemical :
Heat stored in chemical bonds



Old Idea, BUT: rapid degradation for ALL cases.

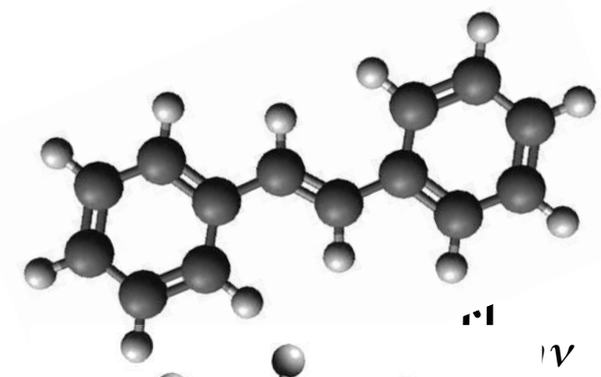
A novel approach to solar thermal fuels



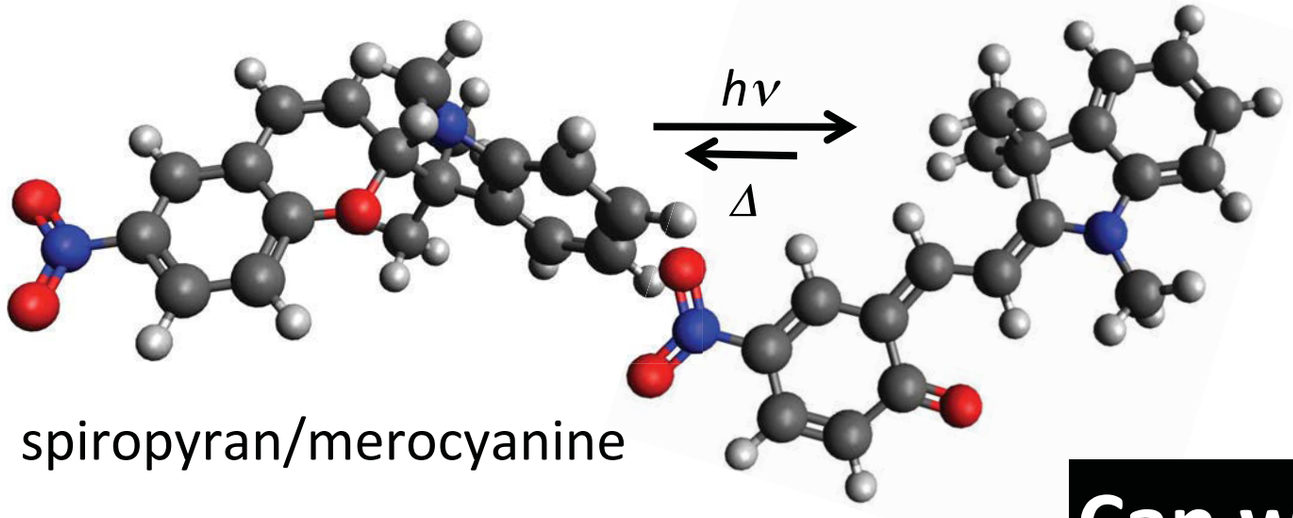
DHA/VHF

There are many, many photoactive molecules...

...that are terrible solar thermal fuels.



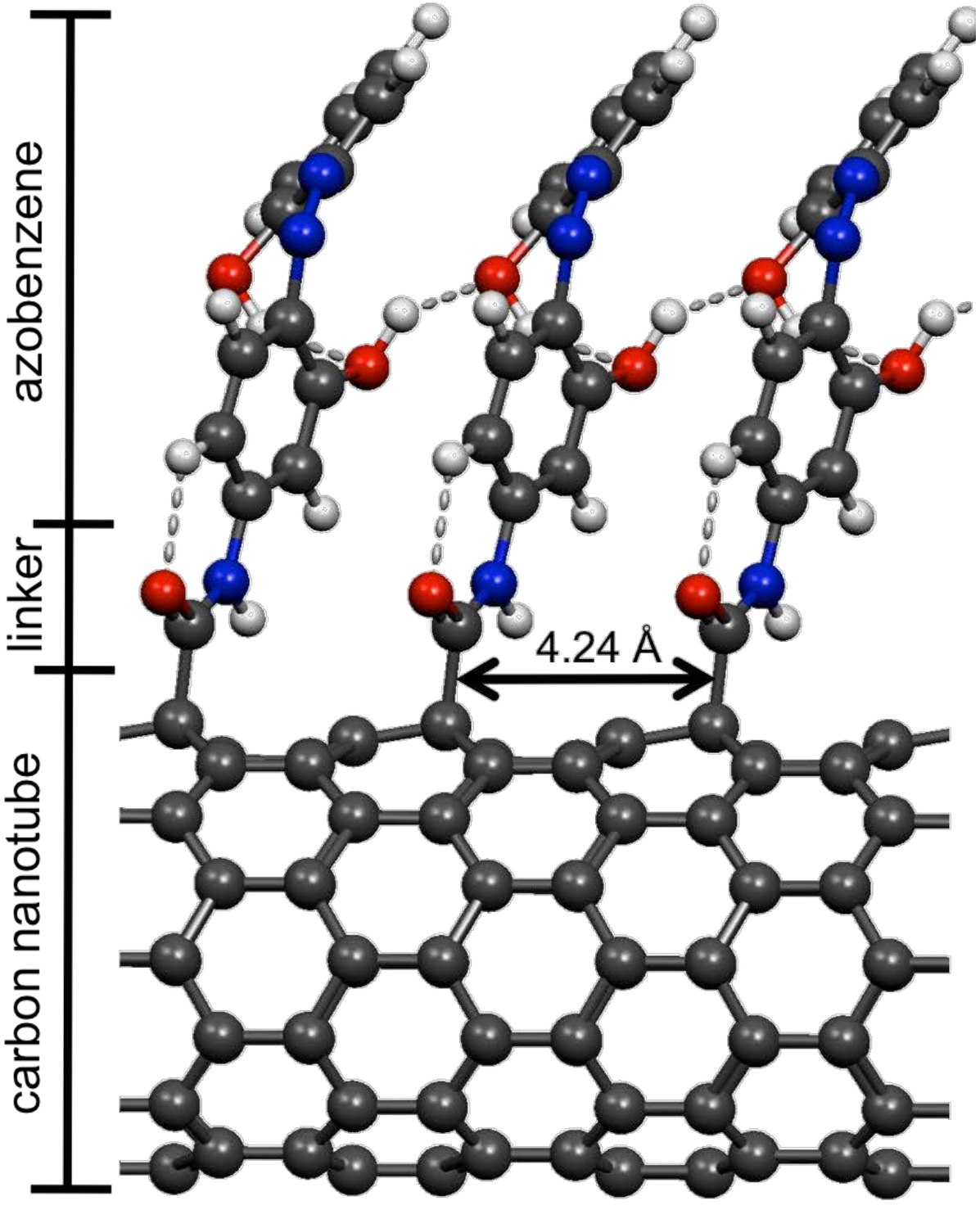
E/Z-Stilbene

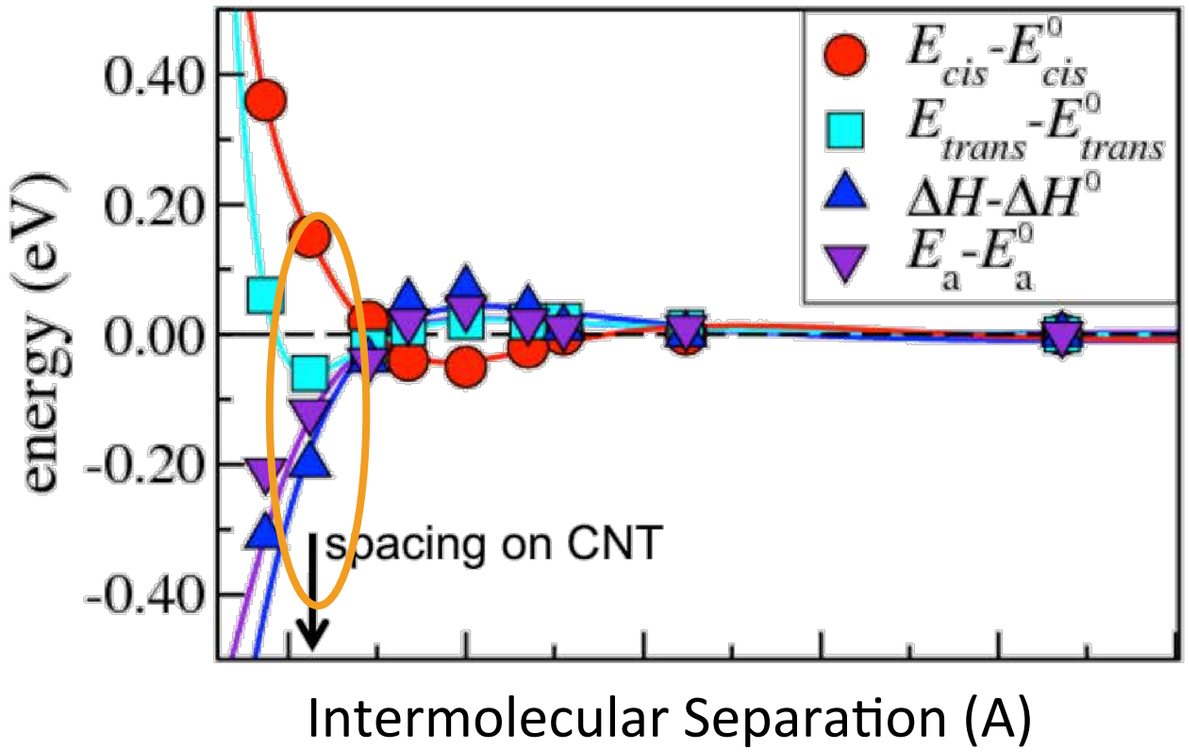


spiropyran/merocyanine

Can we turn them into good ones?

Role of the CNT template



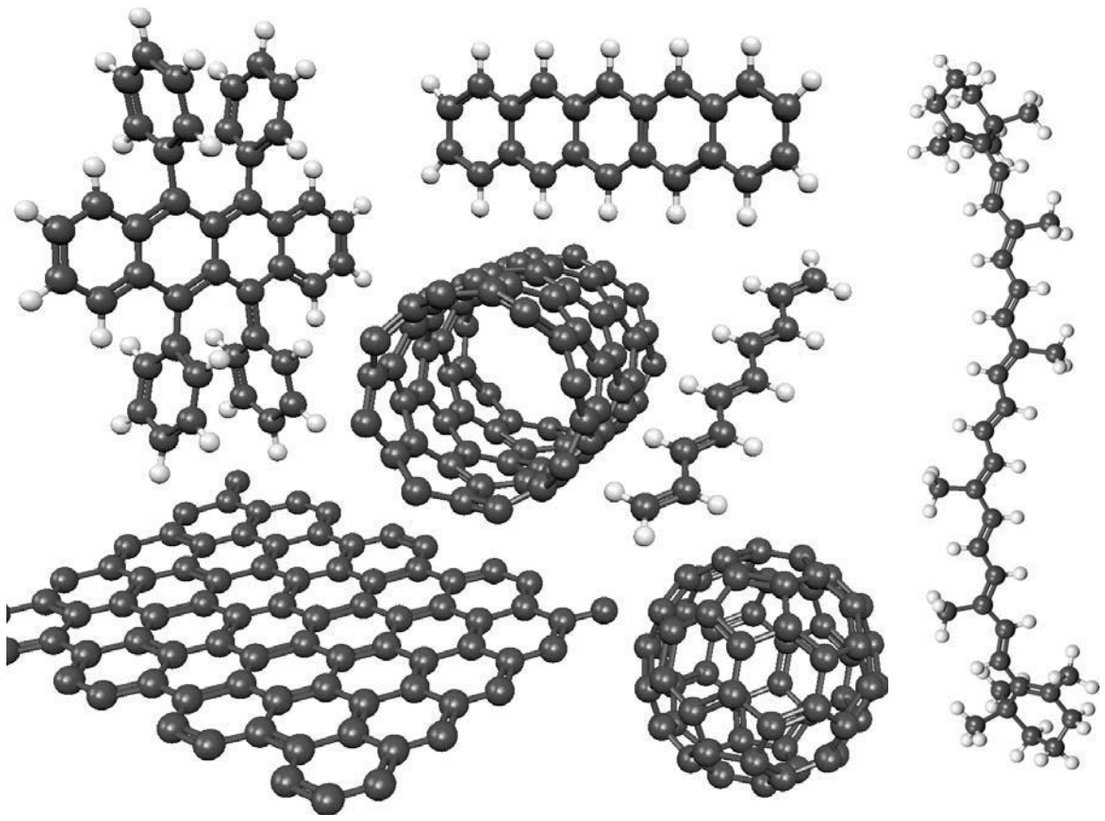


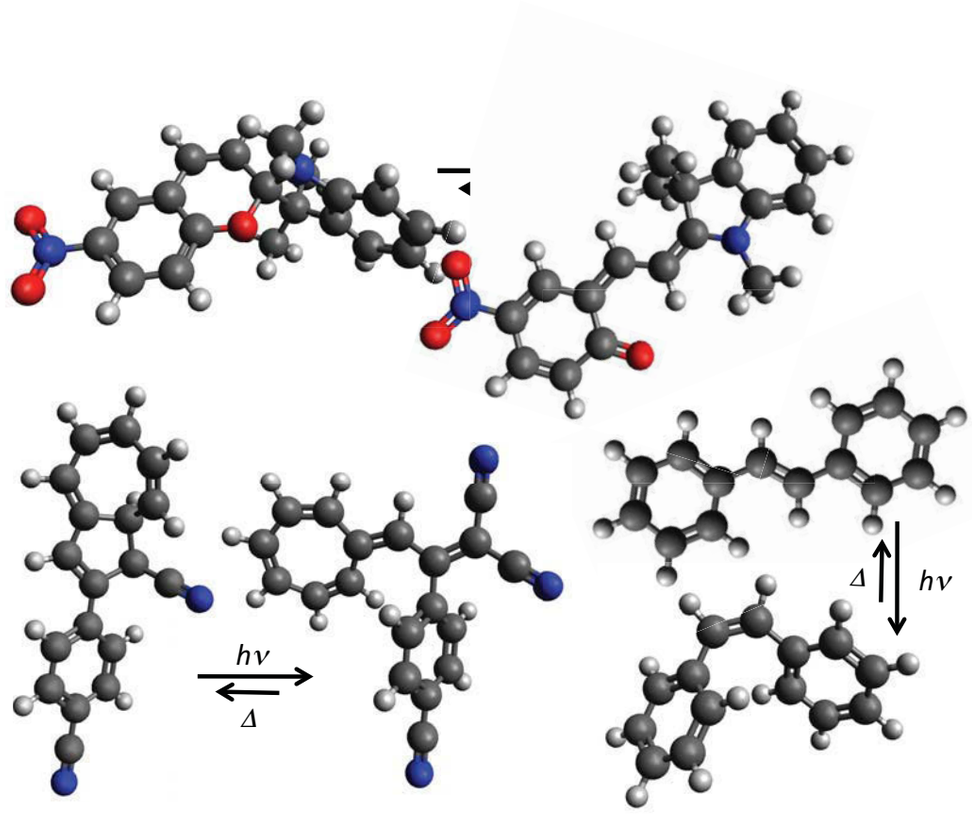
Rigid substrate – fixes inter-molecular distances over long range, enabling:

- steric inhibition
- π-stacking
- hydrophobic interactions

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

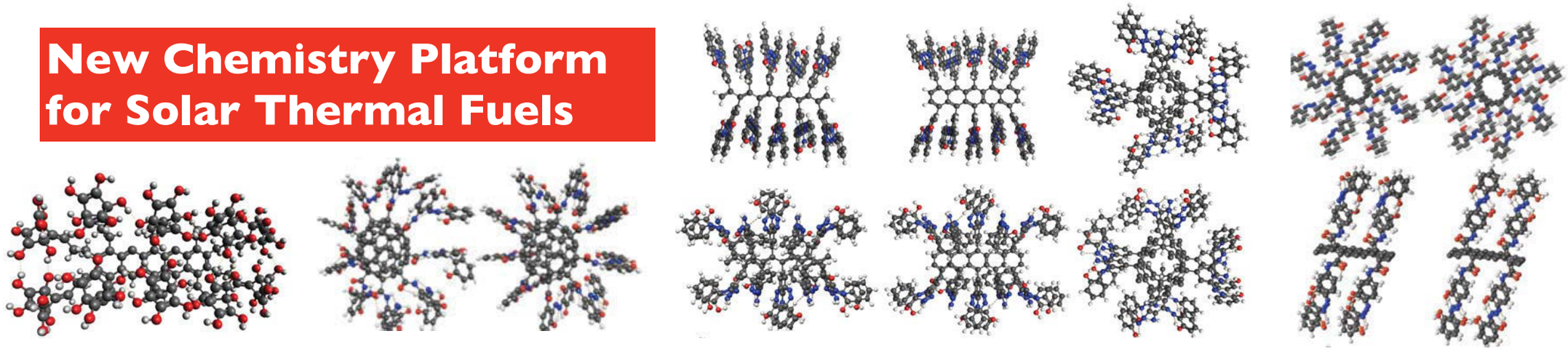
New Materials for Solar Thermal Fuels



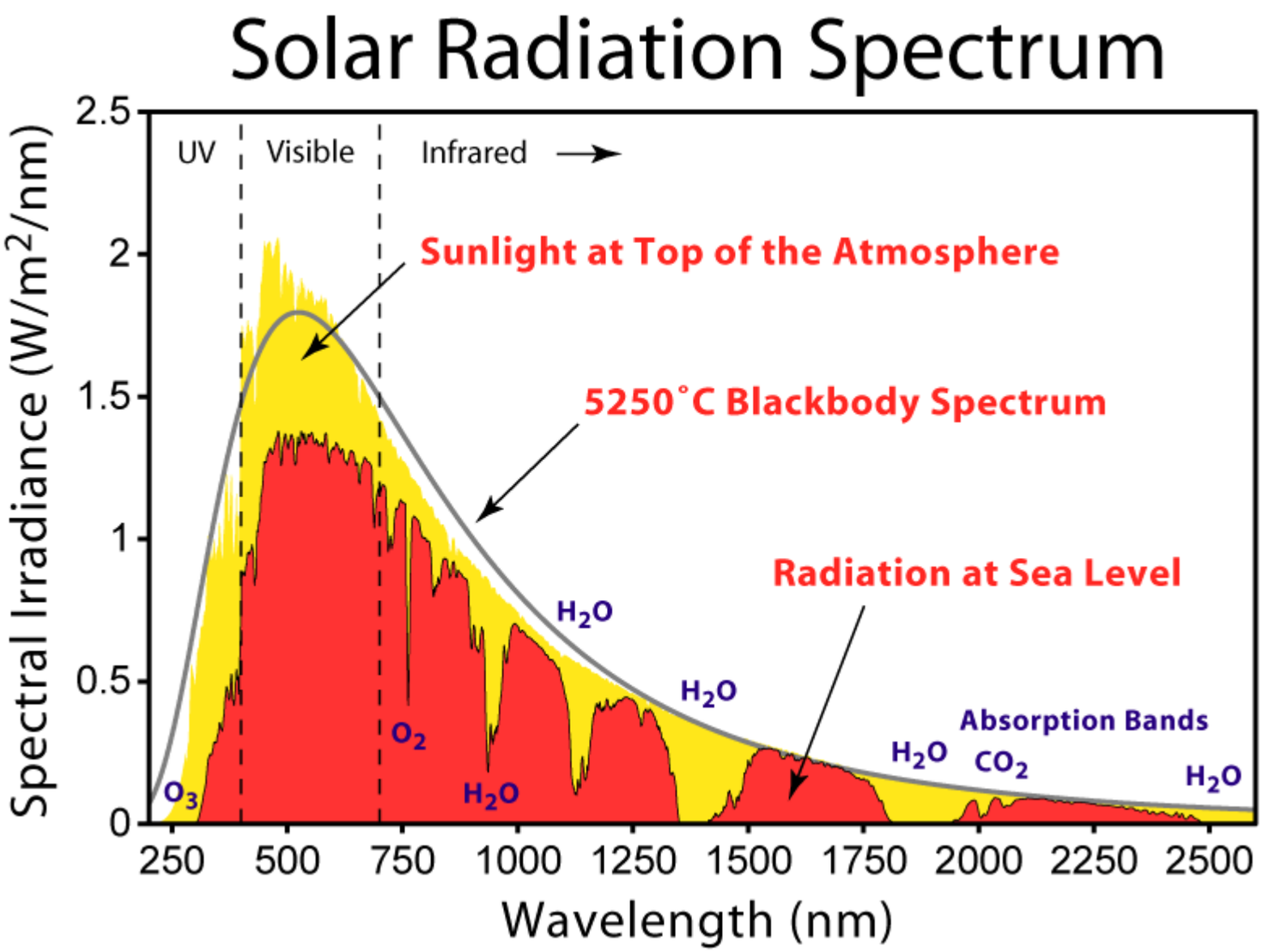


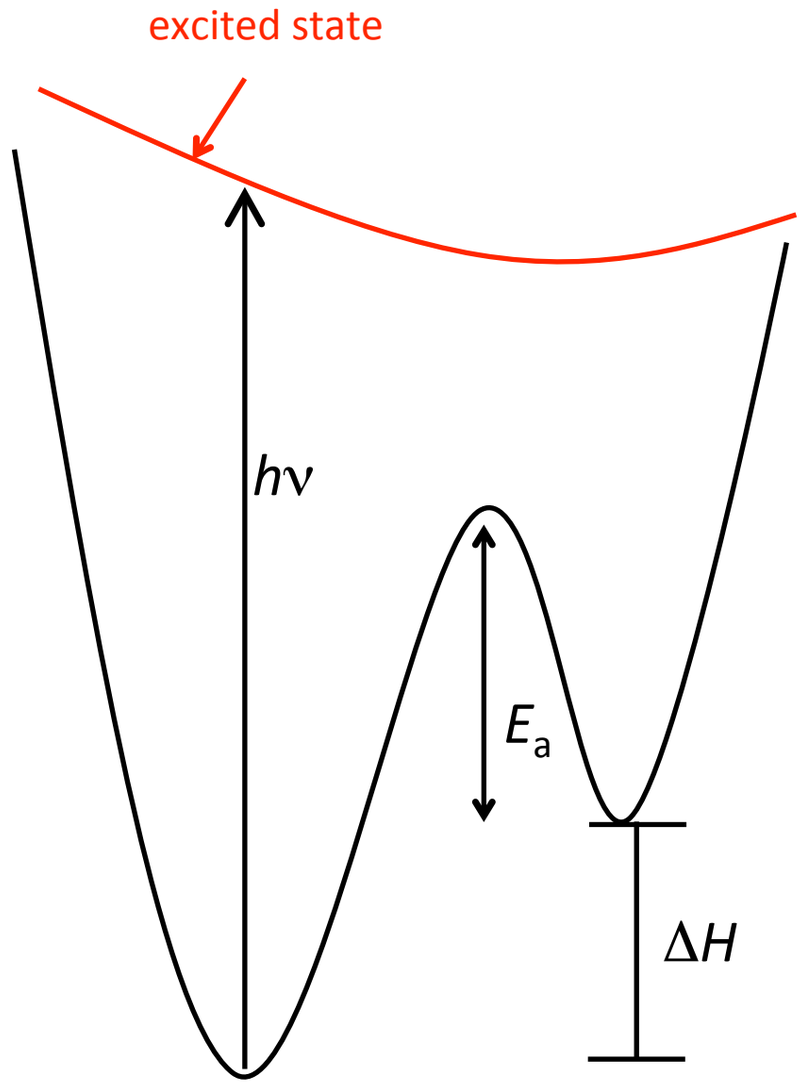
Template Materials + **Photoactive Molecules**

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



So Why do We Need QM?





In-Class Calculations of Solar Thermal Fuels

Key Concept: Density of States (DOS)

From The Band Gap to Storage Efficiency

- Assume that all photons that have higher energy than the band gap get absorbed by the molecule AND lead to photo-isomerization.
- Let the fraction of molecules in the excited state (cis state) be x.
- Then, for a solar spectrum I(lamda):

$$x \int_0^{\lambda_{max,cis}} I(\lambda) d\lambda = (1-x) \int_0^{\lambda_{max,trans}} I(\lambda) d\lambda$$

$$\lambda_{max} = \frac{hc}{E_{bandgap}}$$

From Absorption Spectra to Storage Efficiency

- Assume that all absorbed photons lead to photo-isomerization.
- Let the fraction of molecules in the excited state (cis state) be x.
- Then, for a solar spectrum I(lamda):

$$x \int abs_{cis}(\lambda) \frac{I(\lambda)}{(\frac{hc}{\lambda})} d\lambda = (1-x) \int abs_{trans}(\lambda) \frac{I(\lambda)}{(\frac{hc}{\lambda})} d\lambda$$

But how do we get this "abs" function?

--> from the energy levels!!

Summary/Reading

- What is convergence in a Quantum Mechanical Calculation?
- Feeling for what those energy levels mean!
- Connection of energy levels to light absorption, and connection of that to charging efficiency in solar fuels.
- Extra reading: google "atomic orbitals," "molecular orbital theory," etc.
- A bit on hydrogen storage.

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