

Quantum materials and devices: from organic superconductors to biomolecules

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Outline

- Big questions I would like to know answers to.
- What are quantum materials and devices?
- Focus on minimal models: quantum many-body Hamiltonians
- Resonating Valence Bond theory of organic superconductors
- Biomolecular systems as the ultimate nanoscale devices
- Spin boson model for decoherence in optically active biomolecules

Big questions

- When and how does a quantum system become classical? On what length and time scales?
- How do macroscopic properties emerge from the properties of the constituent atoms and molecules?
- To what extent is rational design and molecular engineering of functional materials possible due to the tuneability of the constituent molecules?
- When and how are quantum effects required for biological functionality?
- To what extent can we create and manipulate coherent entangled quantum states in condensed phases of matter?

What are quantum materials and devices?

- Quantum mechanics determines the structure of all materials at the atomic and molecular scale! This is because quantum properties of electrons determines inter-atomic & inter-molecular forces. But, molecular dynamics is often classical.
- But some materials and devices can ONLY be understood in terms of
- Collective quantum many-body effects
and/or
- Quantum dynamics

Quantum states of matter

Nature, last weeks issue!!

A new universality class of phase transition.

Critical exponents are determined by quantum fluctuations.

nature

Vol 436|28 July 2005|doi:10.1038/nature03806

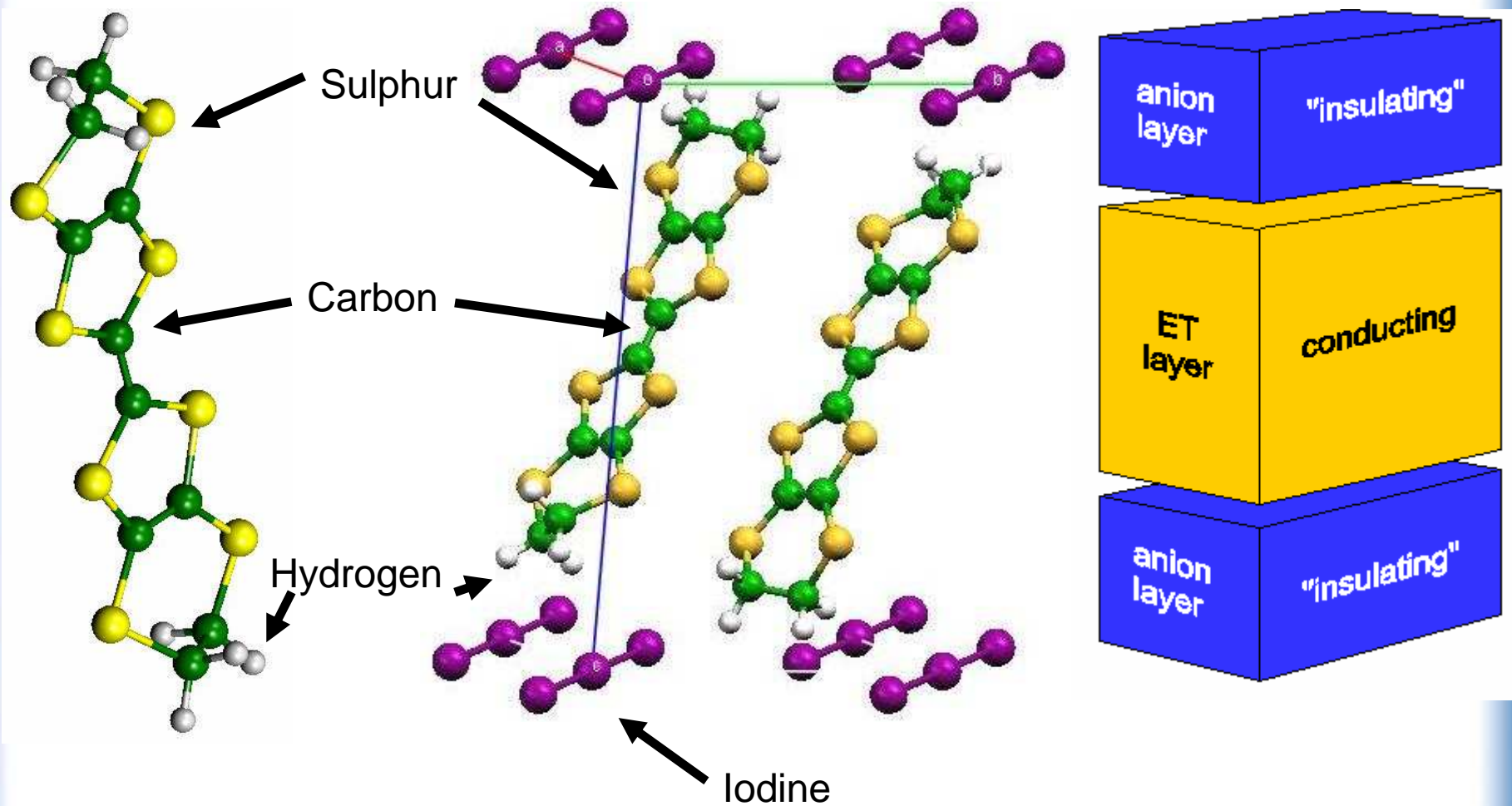
LETTERS

Unconventional critical behaviour in a quasi-two-dimensional organic conductor

F. Kagawa¹, K. Miyagawa^{1,2} & K. Kanoda^{1,2}

For a theoretical explanation see,
Imada, cond-mat/0506468

Superconducting molecular crystals, β -ET₂I₃



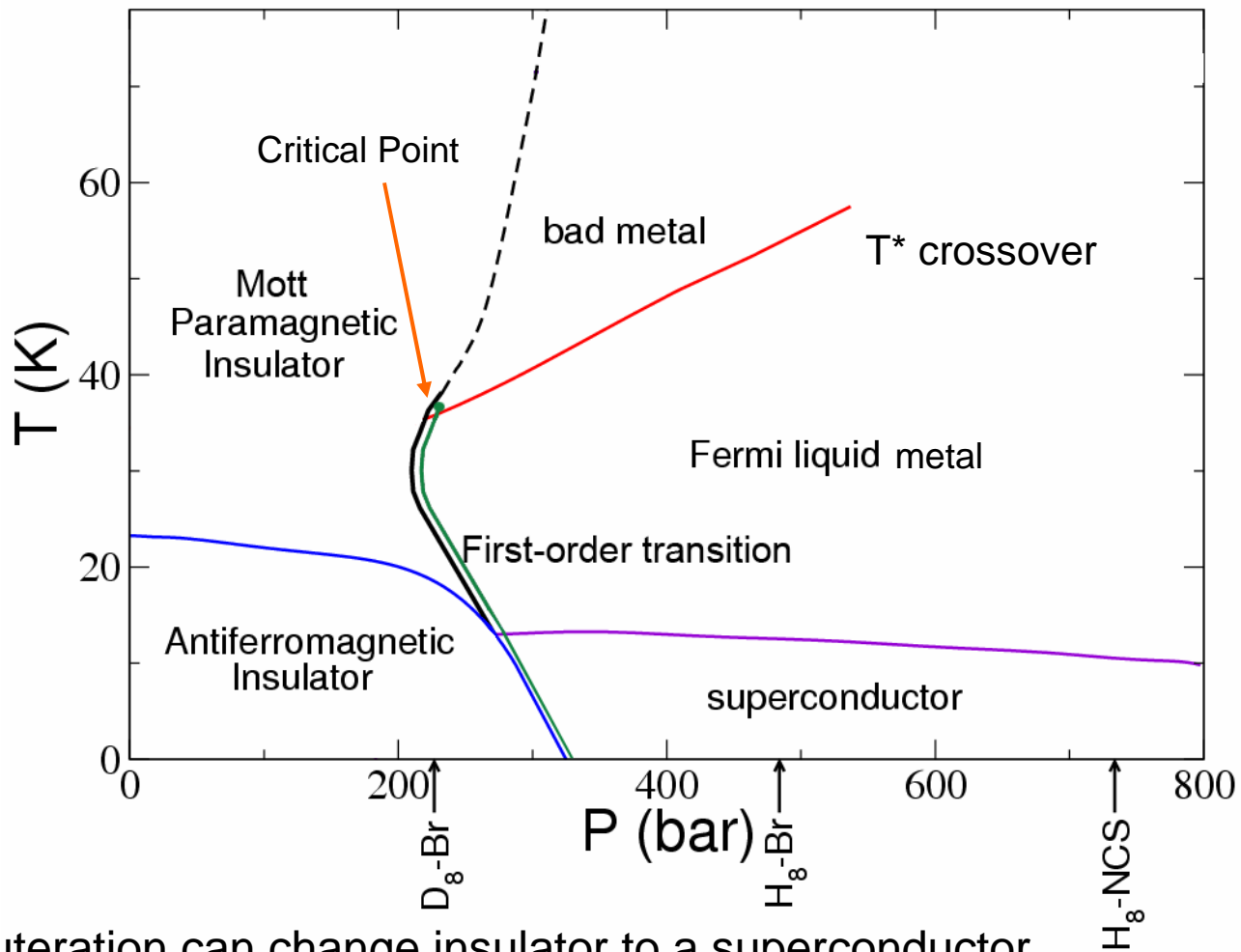
Ionic, covalent, van der Waals, and hydrogen bonding

Superconductivity: a macroscopic quantum state of electrons

- Zero electrical resistance
- Expels magnetic fields (Meissner effect) → levitation
- Quantum interference: Josephson effect
- Nobel prizes in 1972, 1975, 1987, 2002



Phase diagram: κ -ET₂Cu[N(CN)₂]Cl temperature vs. pressure



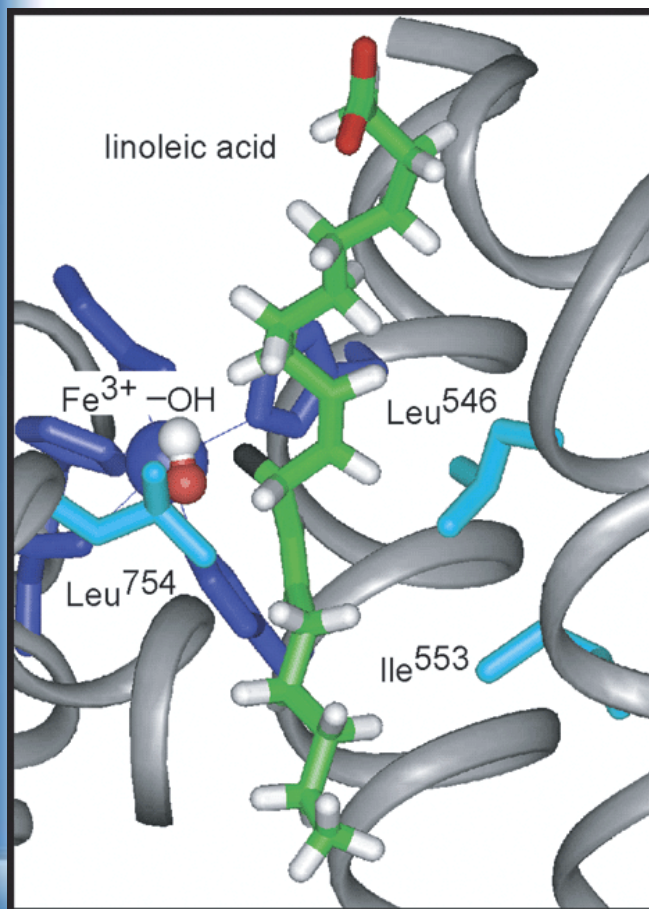
Deuteration can change insulator to a superconductor

Quantum tunneling & Enzyme kinetics

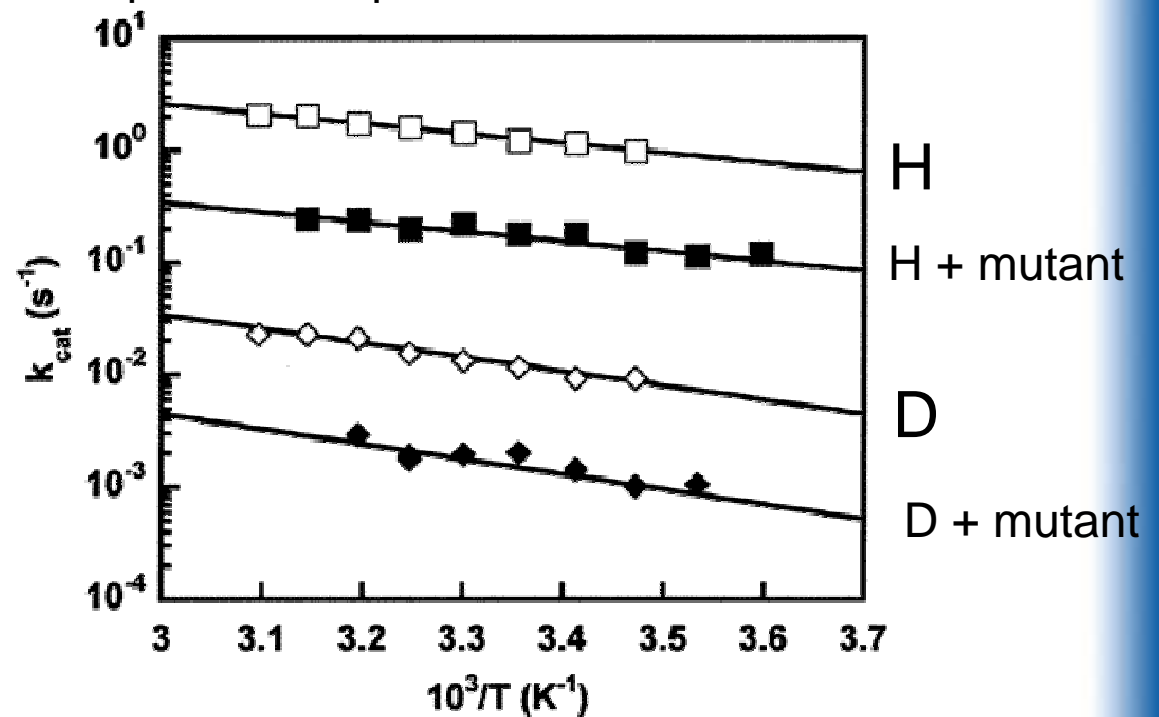
Enzymes are the ultimate catalysts. They can increase biochemical reaction rates by as many as 30 orders of magnitudes

Hydrogen atom transfer in soybean lipoxygenase.

Replacement of H with deuterium reduces reaction rate by a factor of 100.



Temperature dependence of reaction rate



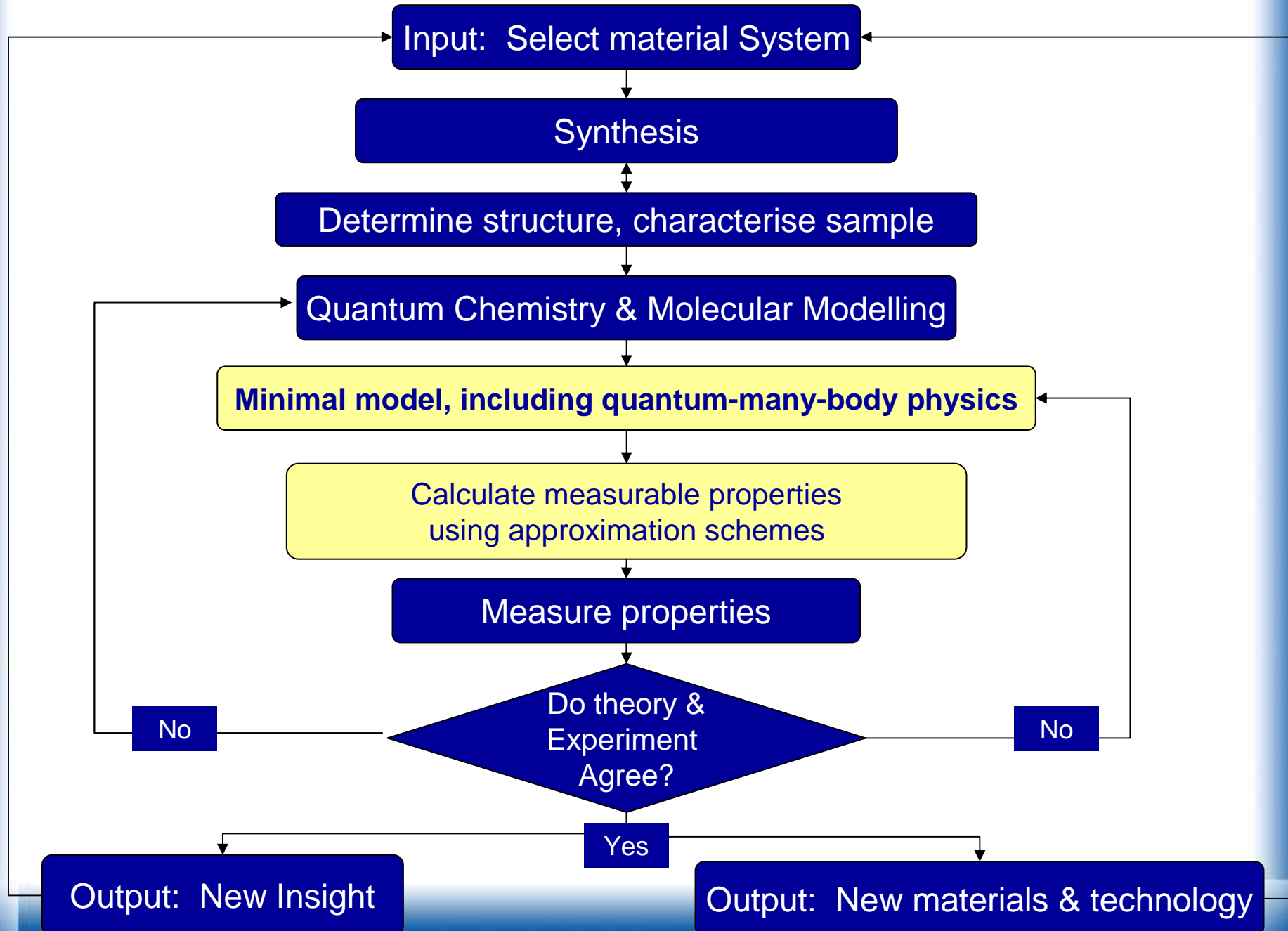
[Knapp et al., JACS 124, 3865 (2002)]

Specificity vs. universality

For complex molecular materials when do the details matter?

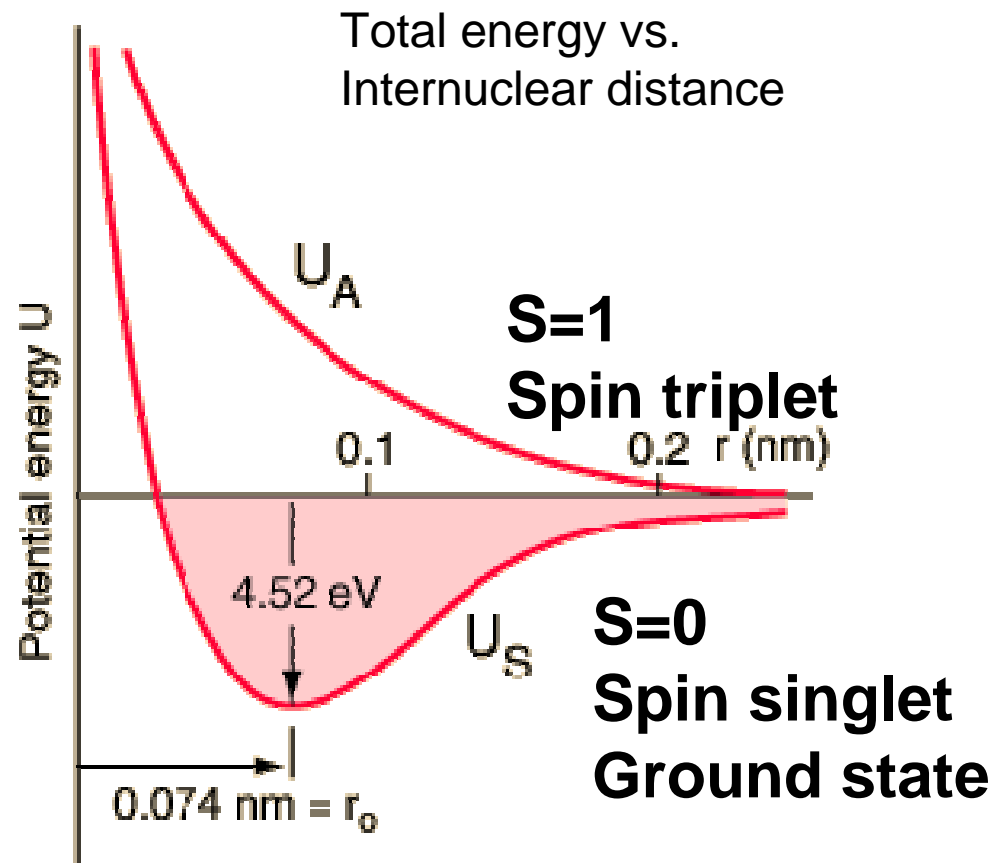
- Physicists say the details don't matter. They think cows are spherical!
- Chemists say details do matter.
- Biologists say the details are a matter of life and death!
- But the phase diagrams of κ -ET₂Cu[N(CN)₂]Cl and vanadium oxide alloys have many similarities.
- Do emergent properties challenge the structure-property-function paradigm?

An integrated iterative approach



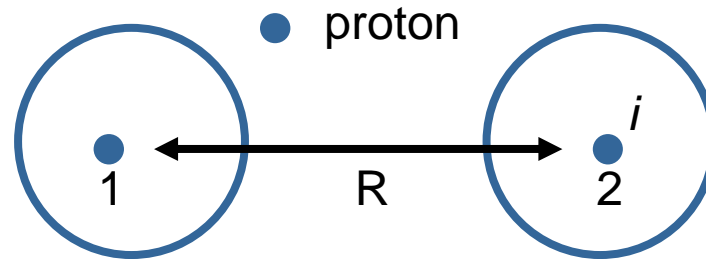
Chemical bonding

Hydrogen molecule H_2



What is the origin of
-bonding?
-energy difference
between singlet and
triplet?
-lowest $S=0$ excited
state having much
higher energy?

A minimal model for H_2^+



$N = 1$ electron

Molecular orbitals

$$\phi_{\pm}(\vec{r}) = \frac{1}{\sqrt{2}} (\phi_1(\vec{r}) \pm \phi_2(\vec{r}))$$

Notation

$$|+\uparrow\rangle = \frac{1}{\sqrt{2}} (C_{1\uparrow}^+ + C_{2\uparrow}^+) |0\rangle$$

Energy Levels

- = anti-bonding orbital $\text{---} +t$

+ = bonding orbital $\text{---} \uparrow -t$

Hamiltonian

$$H = -t (C_1^+ C_2 + C_2^+ C_1)$$

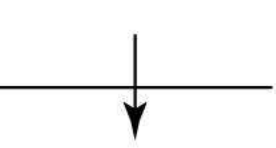
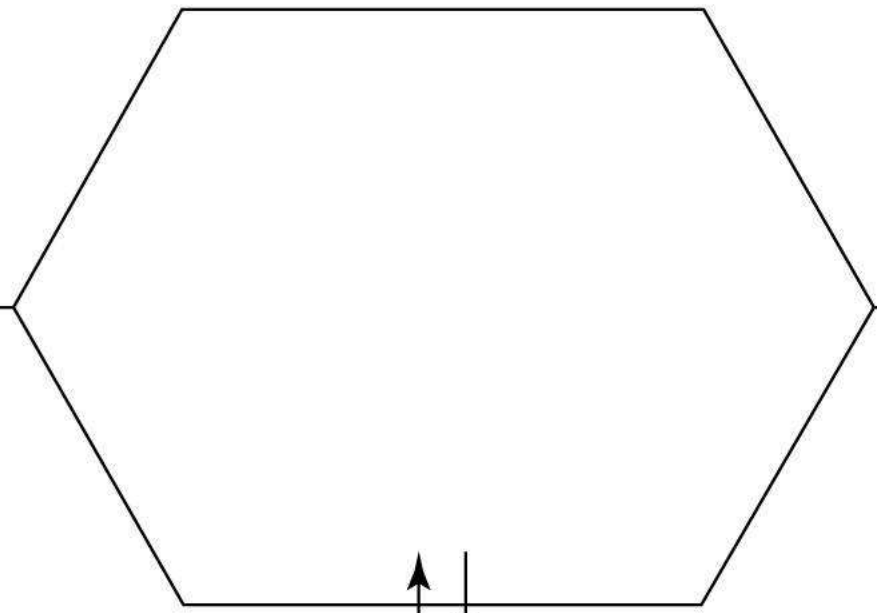
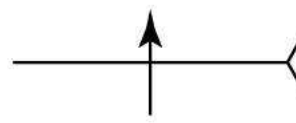
node



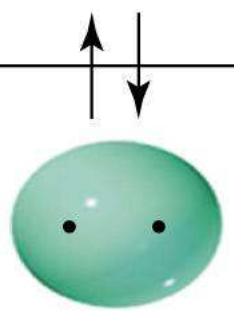
σ^* antibonding molecular orbital



1s atomic orbital

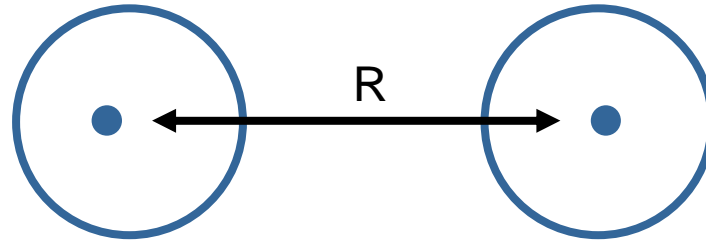


1s atom orbital



σ bonding molecular orbital

Hückel model for H₂



N = 2 electrons

$$H_0 = -t \sum_{\sigma=\uparrow,\downarrow} (C_{1\sigma}^+ C_{2\sigma} + C_{2\sigma}^+ C_{1\sigma})$$

Neglects interaction between electrons

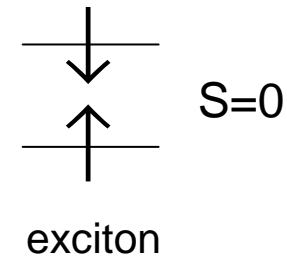
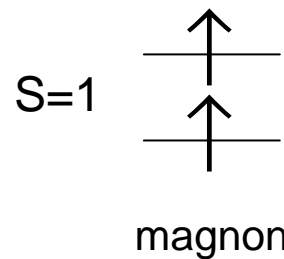
Molecular orbital theory

Charge + spin excitations are degenerate

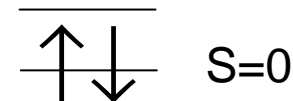
Ground State

$$|\psi\rangle = |+\uparrow\rangle |+\downarrow\rangle$$

$$= \frac{1}{2} (|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle + |\uparrow\downarrow,0\rangle + |0,\downarrow\uparrow\rangle)$$



Problem: Bond is equally covalent and ionic.
H⁺ + H⁻ is just as probable as H + H



Minimal model for H₂:

2 site Hubbard model with N=2 electrons

$$H = H_0 + u(n_{1\uparrow}n_{1\downarrow} + n_{2\uparrow}n_{2\downarrow})$$

Includes Coulomb repulsion energy u between electrons in same atomic orbital

Exact Ground state Wave function

$$|\Psi_0\rangle = \alpha(|\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle) + \beta(|\uparrow\downarrow, 0\rangle + |0, \uparrow\downarrow\rangle)$$

For $U=0$, $\alpha=\beta$

For $U \gg 4t$, $|\alpha| \gg |\beta|$

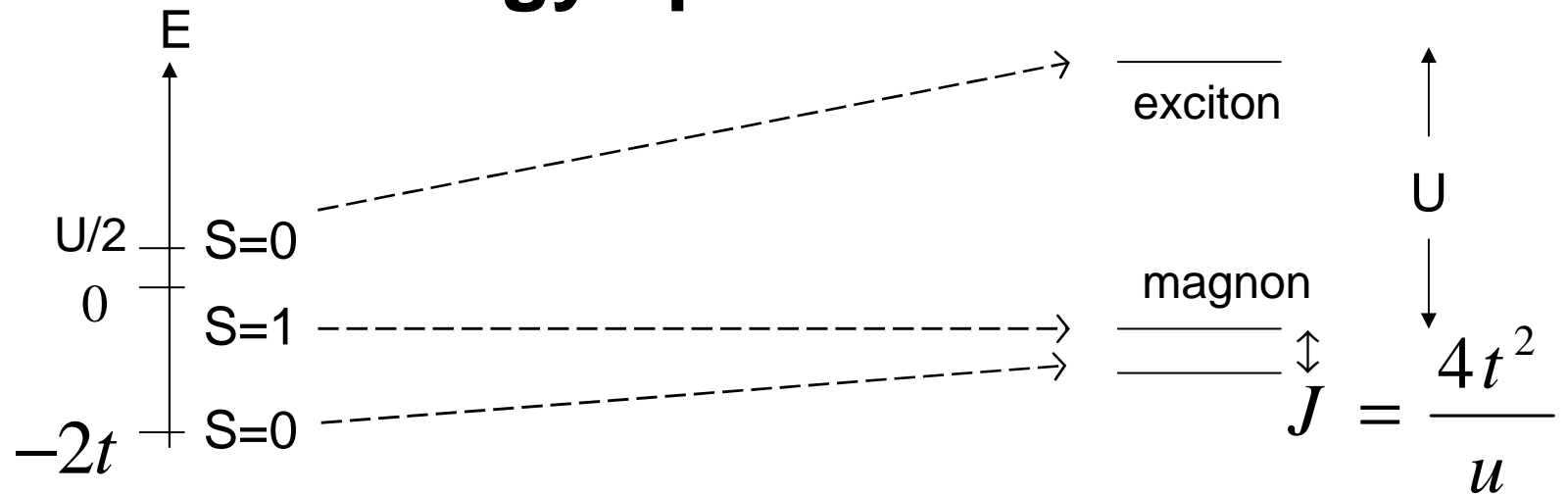
Approximate Ground State Wave Functions in Quantum chemistry

$\beta = 0$ **Valence bond theory (Pauling), Heitler – London approximation**

$\alpha = \beta$ **Molecular orbital theory; Hartree – Fock approximation**

$\alpha = 0$ **Ionic bonds**

Energy spectrum vs. U/t



$U \ll 4t$

$U \gg 4t$

Charge and spin excitations occur on very different energy scales

Effective Hamiltonian for spin degrees of freedom:

Heisenberg model

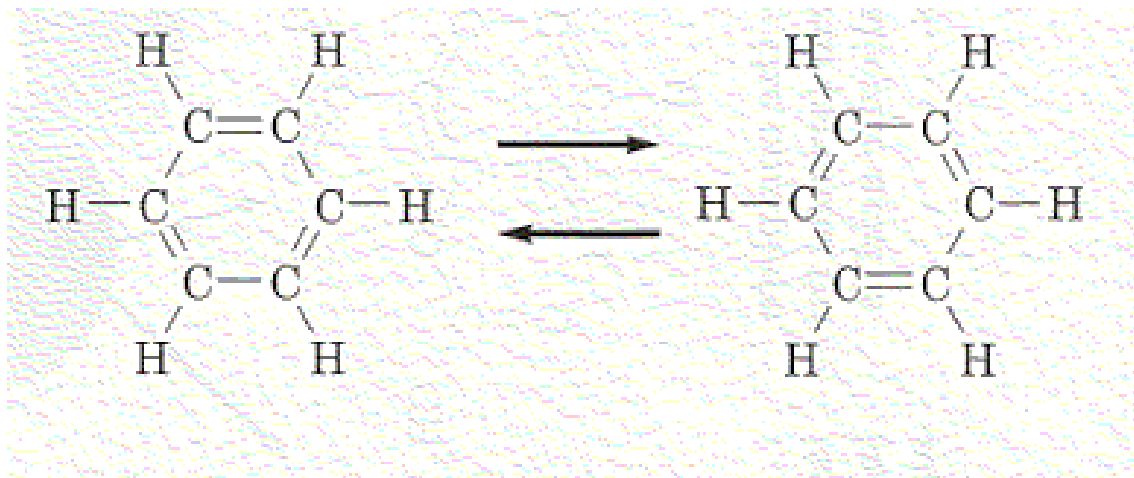
$$H = J \vec{S}_1 \cdot \vec{S}_2$$

$J > 0$ antiferromagnetic interactions

Lessons from the minimal model

- For widely separated atomic orbitals, electron-electron interactions become increasingly important, and lead to valence bonds.
- Simple models can capture qualitatively important features such as origin of chemical bonding, singlet-triplet splitting, and large difference in charge and spin excitations.
- Tendency to charge localisation (Mott insulator) and formation of local moments (antiferromagnetism).

Resonating valence bonds in benzene



Pauling (1937) proposed the ground state is a superposition of two valence bond states

$$|\Psi_0\rangle = |12\rangle|34\rangle|56\rangle + |23\rangle|45\rangle|61\rangle$$

Resonating valence bonds in quantum antiferromagnets

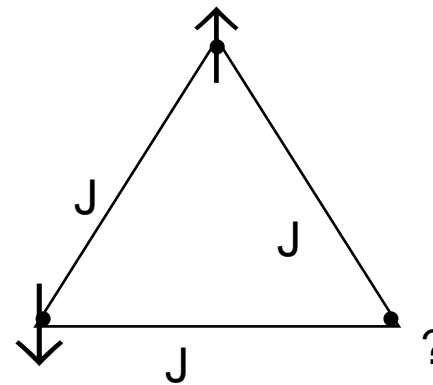
3 site Heisenberg model

$$H = J \left(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_2 \cdot \vec{S}_3 + \vec{S}_3 \cdot \vec{S}_1 \right)$$

4-fold degenerate ground state

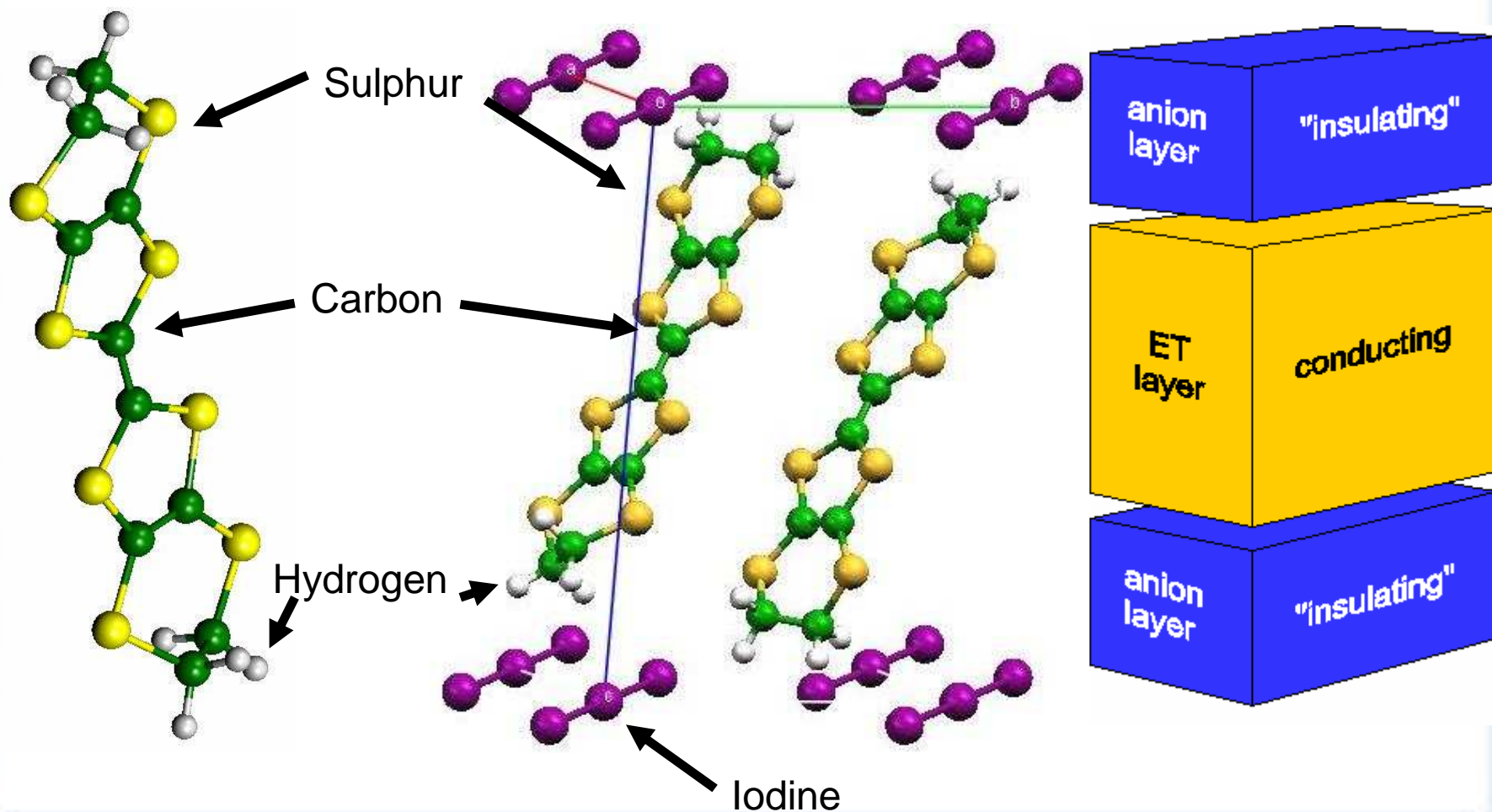
$$|\psi_1\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\uparrow\rangle - |\downarrow\uparrow\uparrow\rangle)$$

$$|\psi_3\rangle = \frac{1}{\sqrt{6}} (2|\uparrow\uparrow\downarrow\rangle - |\uparrow\downarrow\uparrow\rangle - |\downarrow\uparrow\uparrow\rangle)$$

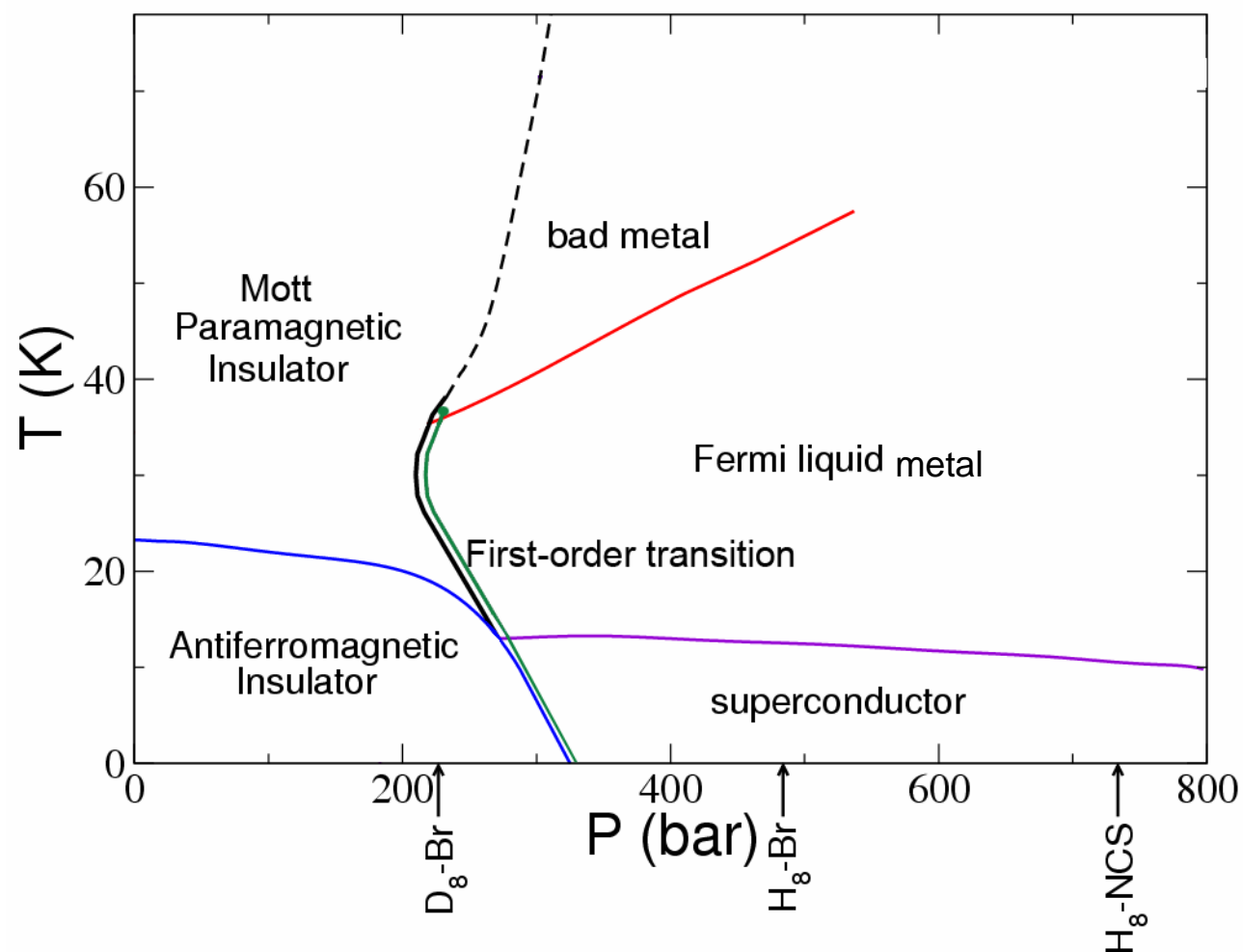


Frustration

Superconducting molecular crystals, β -ET₂I₃



Phase diagram: κ -ET₂Cu[N(CN)₂]Cl temperature vs. pressure



But Hückel theory / band theory ($U=0$) claims this material should always be a Fermi liquid metal!

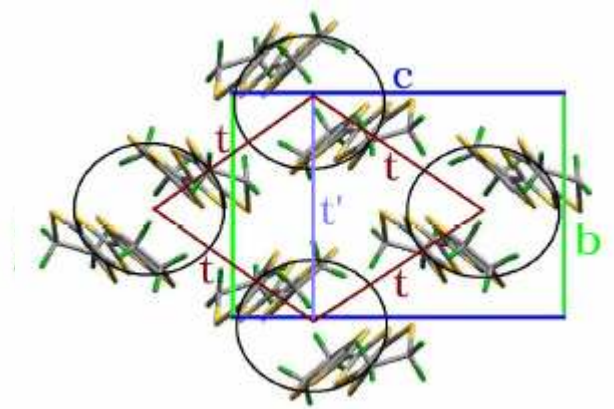
Minimal model for κ -(ET)₂X

Hubbard model on anisotropic triangular lattice

$$\hat{H} = \hat{H}_t + \hat{H}_U$$

$$\hat{H}_t = t \sum_{\langle ij \rangle \sigma} \hat{c}_{i\sigma}^+ \hat{c}_{j\sigma} + t' \sum_{\{ij\} \sigma} \hat{c}_{i\sigma}^+ \hat{c}_{j\sigma} - \mu \sum_{i\sigma} \hat{c}_{i\sigma}^+ \hat{c}_{i\sigma}$$

$$\hat{H}_U = U \sum_i \hat{c}_{i\uparrow}^+ \hat{c}_{i\uparrow} \hat{c}_{i\downarrow}^+ \hat{c}_{i\downarrow}$$

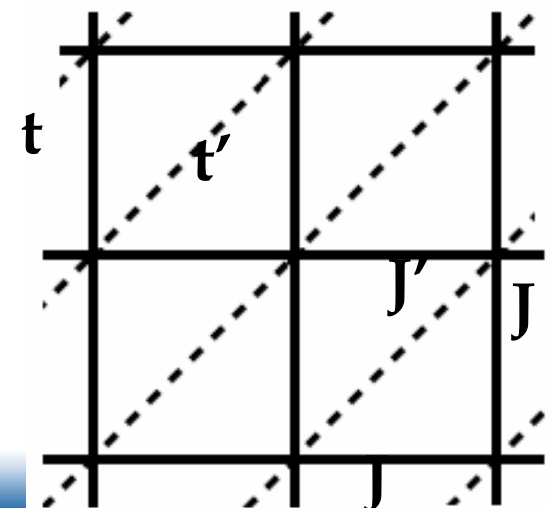


Each site corresponds to the bonding orbital of an ET dimer

t

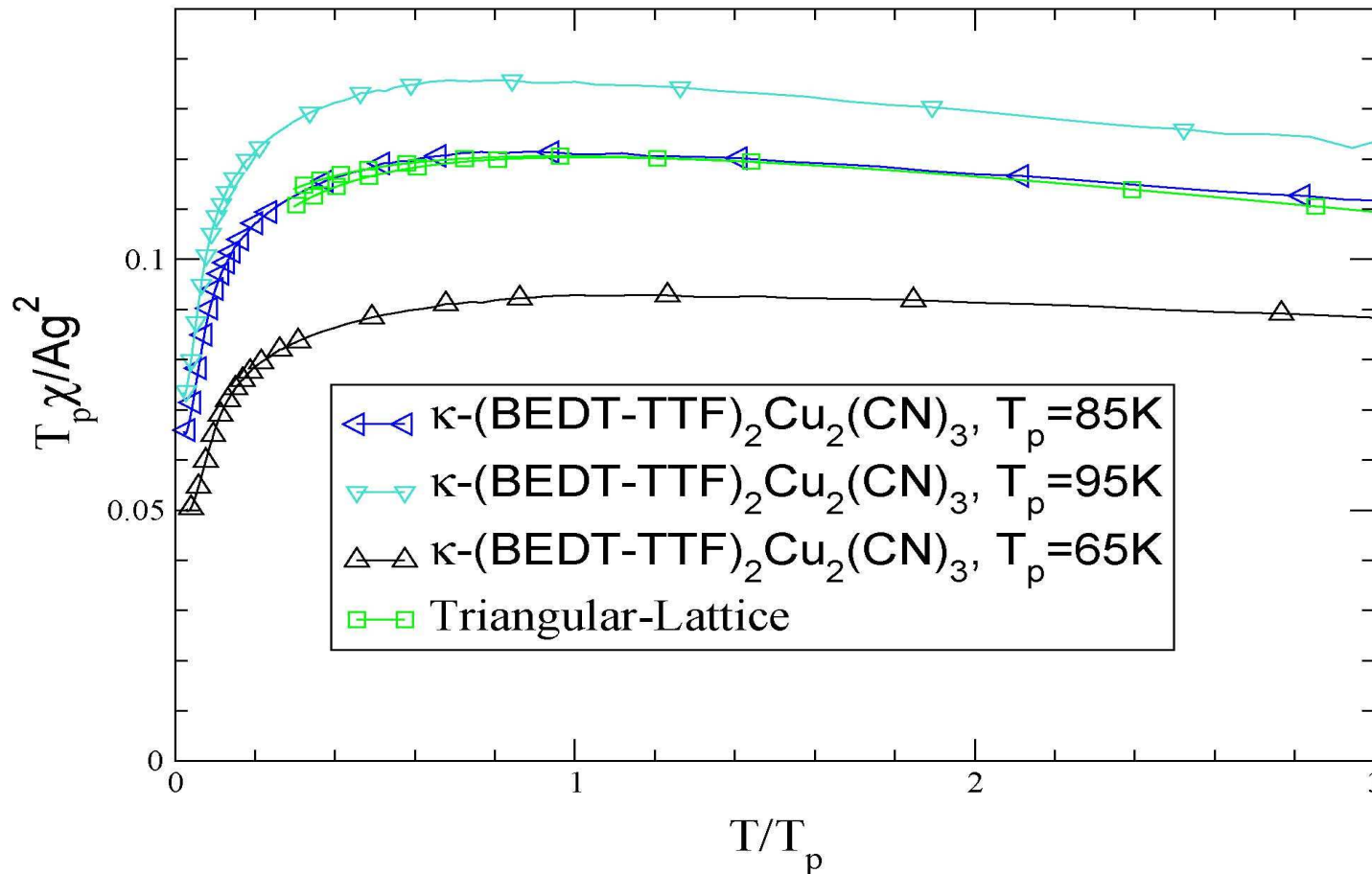
What is the ground state as a function of U/t and t'/t ?

Frustration is important.



Frustrated antiferromagnetism in Mott insulator

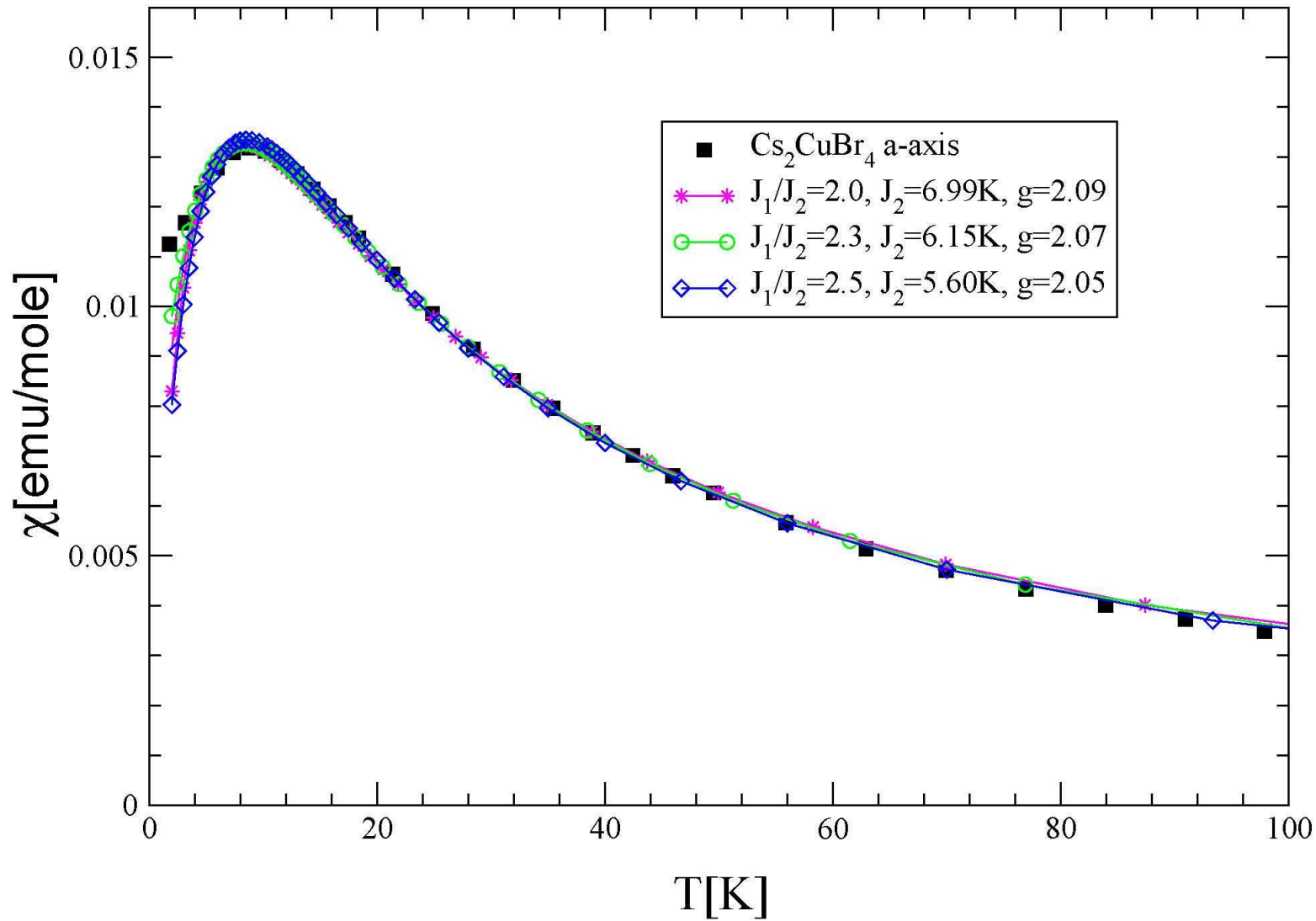
Magnetic susceptibility vs. temperature



Shimizu et al.,
PRL 91, 016401
(2003);
Zheng et al.,
PRB (2005)

Comparison with high-temperature series expansions.
 $\chi(T)$ is quite sensitive to amount of frustration (J'/J).

The theory is also applicable to a completely different material



Zheng, Singh, McKenzie, Coldea, PRB (2005)

RVB theory of superconductivity

In 1987 Anderson proposed that:

- the Hubbard model is the minimal model to understand the high- T_c cuprate superconductors.
- the ground state of the two-dimensional Heisenberg model and the doped Hubbard model may be a RVB (resonating valence bond) state.
- RVB states were most favourable for low dimensions, spin-1/2, and in the presence of frustration.



RVB ground state for Hubbard model

Variational wave function

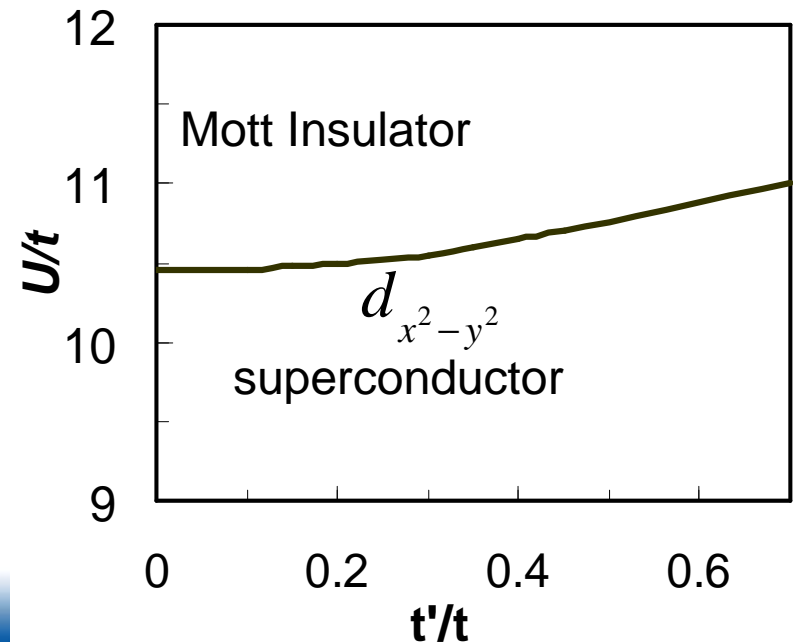
$$|\psi\rangle = \underbrace{\prod_i \left(1 - \alpha n_{i\uparrow} n_{i\downarrow}\right)}_{\text{Gutzwiller projection reduces number of doubly occupied sites required by large } U} \exp \left(\underbrace{\sum_{ij} \Delta_{ij} c_{i\uparrow}^+ c_{j\downarrow}^+}_{\text{Cooper pairing of electrons into spin singlets}} \right) |FS\rangle$$

↑
Fermi Sea

α, Δ_{ij} are variational parameters

Zero temperature phase diagram

[Powell & McKenzie PRL 94, 047004 (2005)]



Quantum devices: Technological motivations

Increasing demand for new nanoscale devices for

- Information processing and storage
- Energy conversion
- Electronic devices and displays
- Biosensors in health care
- Chemisensors for environmental monitoring

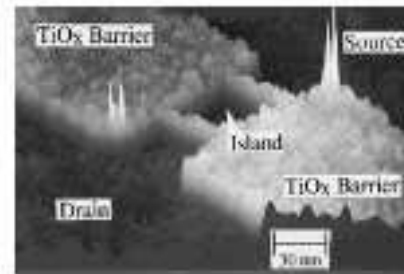
Devices based on organic materials can be tuneable, processible, and flexible like polymers.

How small can computers get?

faster → smaller → shrinking computer



1m



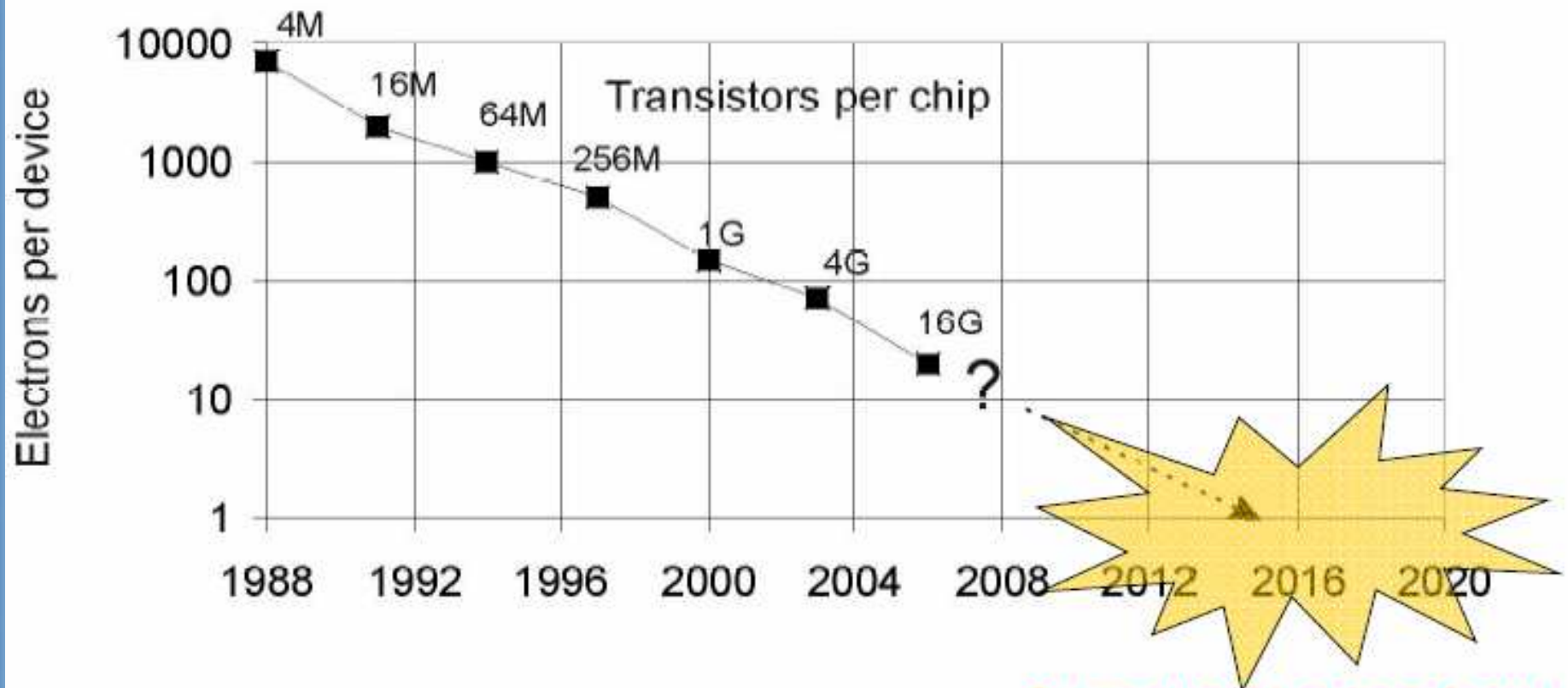
1nm



Moore's Law

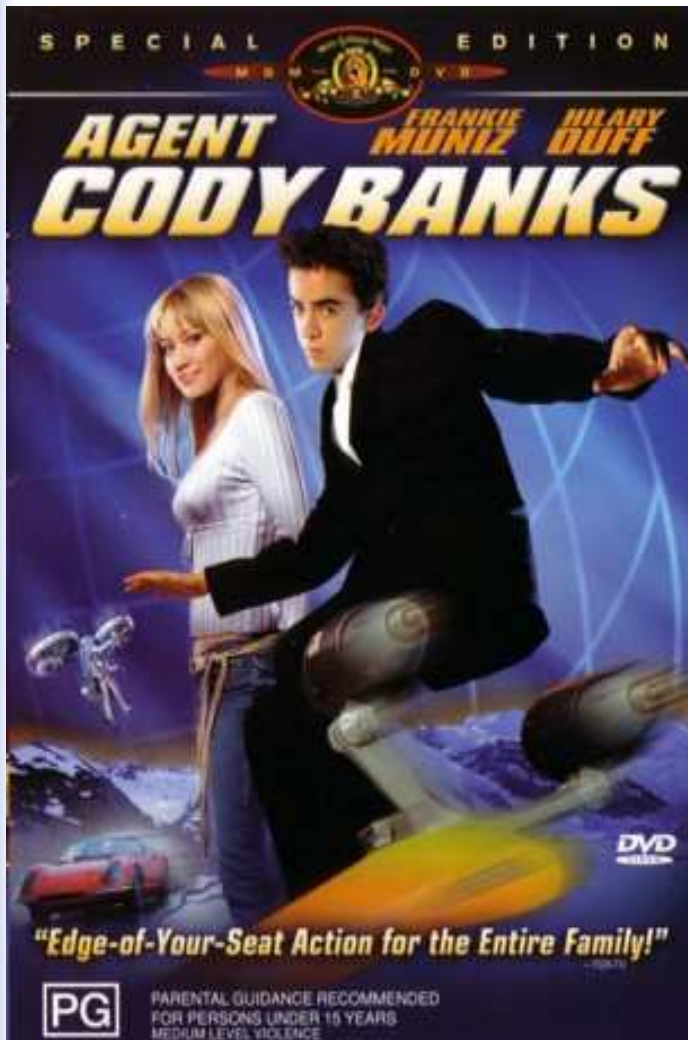
Every 18 months microprocessors double in speed
FASTER = SMALLER

Towards the quantum limit



Quantum technology
Limits or Opportunities?

Sources of confusion about nanotechnology



2003: "Agent Cody Banks"

His mission:
"befriend fellow teen Natalie in order to gain access to her father, a scientist unknowingly developing a fleet of deadly nanobots for the evil organization ERIS."



Device design by Biomimetics

Biomolecular systems have features we wish to copy:

- Synthesis and self-assembly of complex molecular nanostructures
- Fine tuning by molecular engineering
- High quantum efficiency (solar cells, single photon detectors)

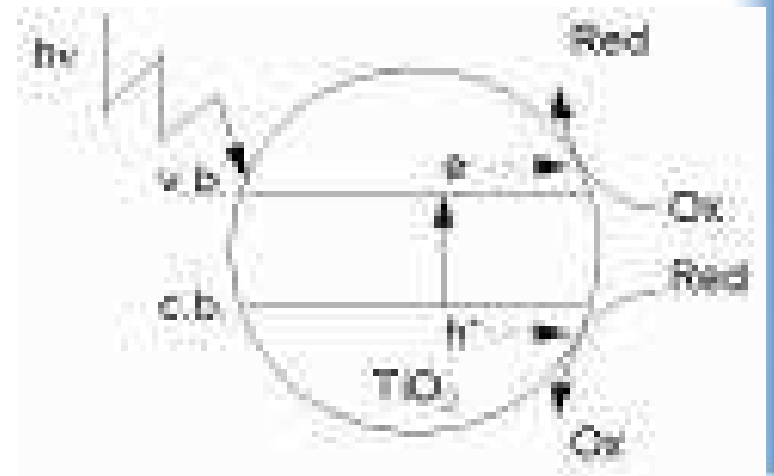
Semiconductor device basics

- Photovoltaic cells

Photon \rightarrow electron-hole pair \rightarrow charge separation

- Light emitting diode (LED)

Voltage \rightarrow spatially separated electron and hole \rightarrow electron-hole recombination



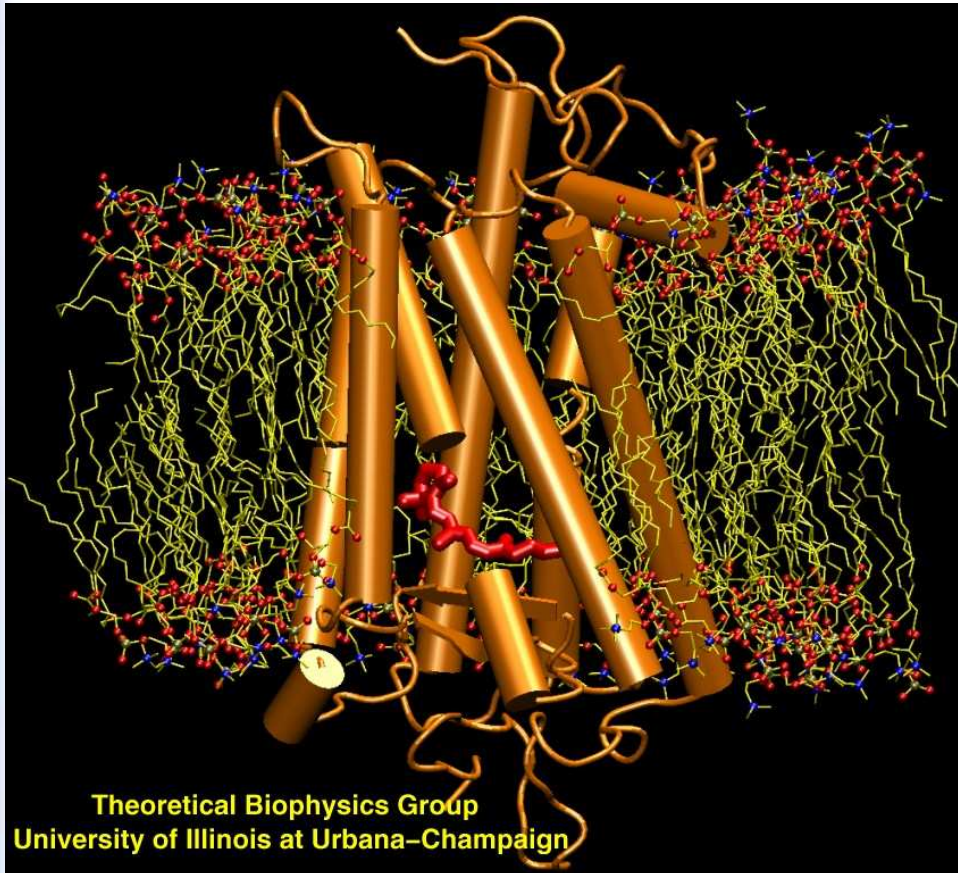
Optically active biomolecules

- Some chromophores are crucial to biological functionality:
 - retinal in rhodopsin (vision)
 - chlorophylls in photosynthesis
 - luciferase in fireflies
 - green fluorescent protein (GFP) (biological marker)
- Interact strongly with their environment (protein and solvent)

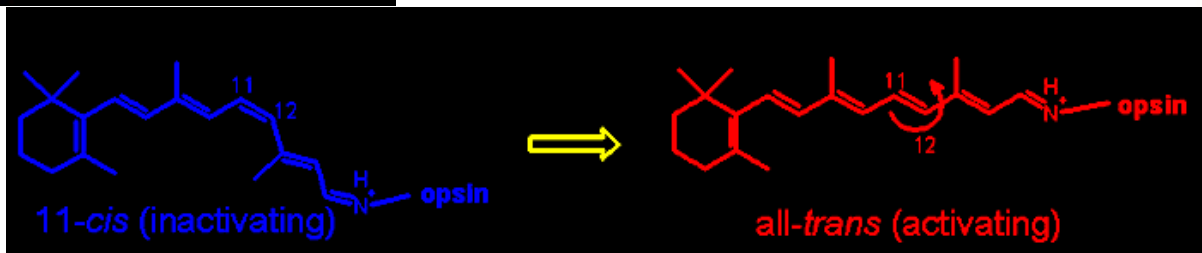
The chromophore in GFP will not fluoresce in the absence of the protein cage.



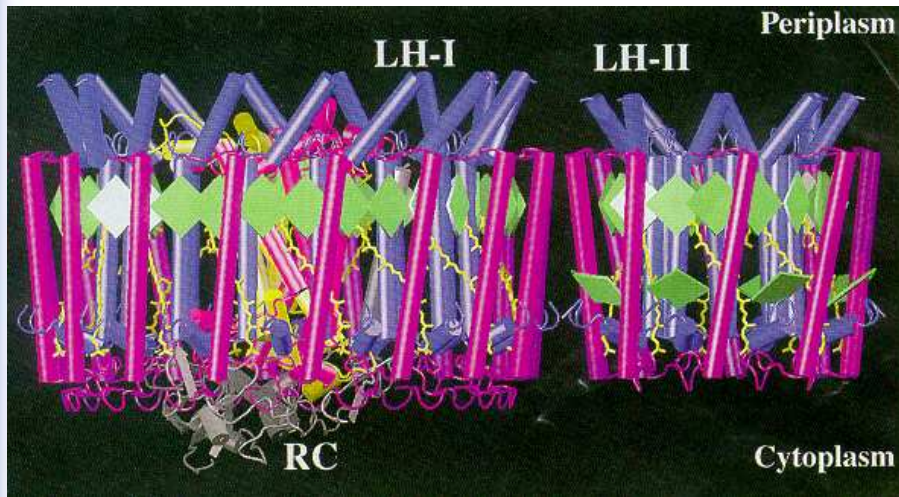
The ultimate single photon detector?



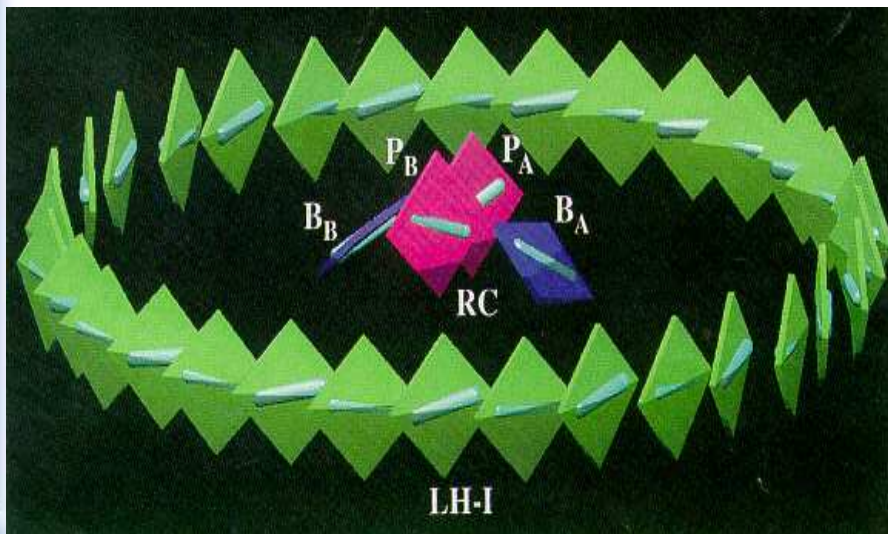
- **Retinal**, a chromophore involved in vision, undergoes ultrafast and ultra-efficient conformational (structural) change on absorbing a photon.
- This leads to charge separation and an electric potential difference
- The surrounding protein (rhodopsin) is critical for the chromophore's functioning.



The ultimate photovoltaic cell?



- Rings of chlorophyll molecules absorb photons of sunlight
- Intra-ring intermolecular transfer of excitons is **coherent**.

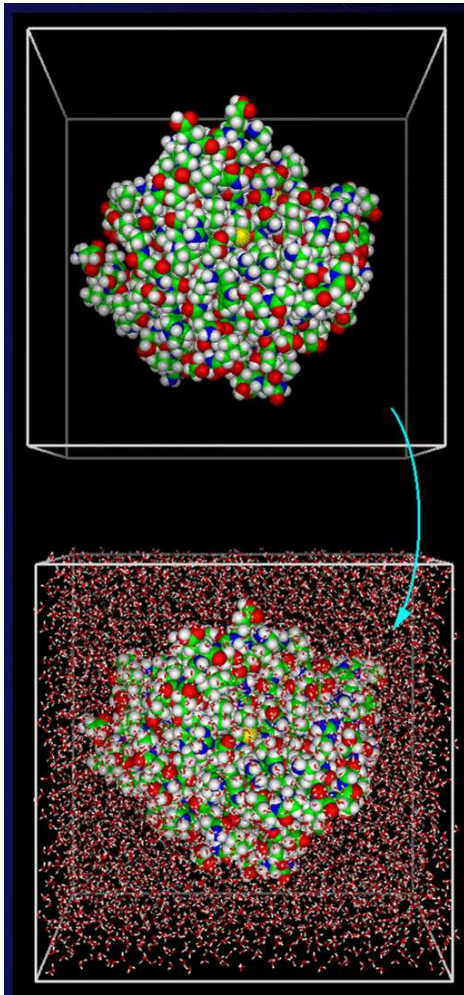


- Inter-ring exciton transfer is **incoherent**

Photosynthesis

photon -> exciton ->
separated electron hole
pair -> electric potential -
> chemical reaction

Quantum's nemesis: Decoherence



- Interaction of quantum systems with their environment can lead to decoherence and the emergence of classical behaviour.
- Biochemical processes occur in a “hot and wet” environment. Most biology happens at room temperature in water!
- The environment of a biomolecule (the solvent or surrounding protein) can “wash out” (decohere) quantum interference effects.
- This can be a very strong effect (e.g., decoherence can be a million times greater than in Josephson junction qubits!) Gilmore & McKenzie, JPCM 2005

Minimal model for decoherence

Spin-boson model

$$H = \frac{1}{2}\epsilon\sigma_z + \Delta\sigma_x + \sum_{\alpha} \omega_{\alpha} a_{\alpha}^{\dagger} a_{\alpha} + \sigma_z \sum_{\alpha} M_{\alpha} (a_{\alpha}^{\dagger} + a_{\alpha})$$

Tunneling between 2 states

ϵ is energy difference
between 2 states

Environment is a
bath of harmonic
oscillators

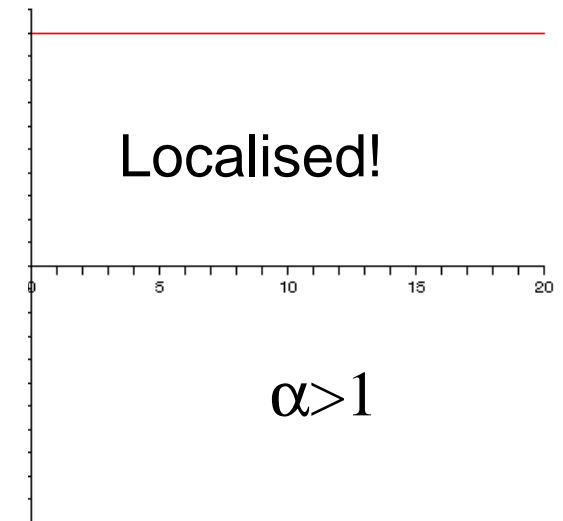
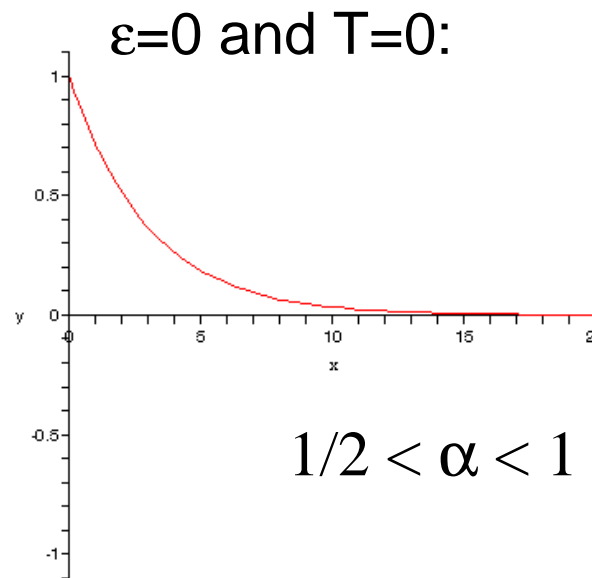
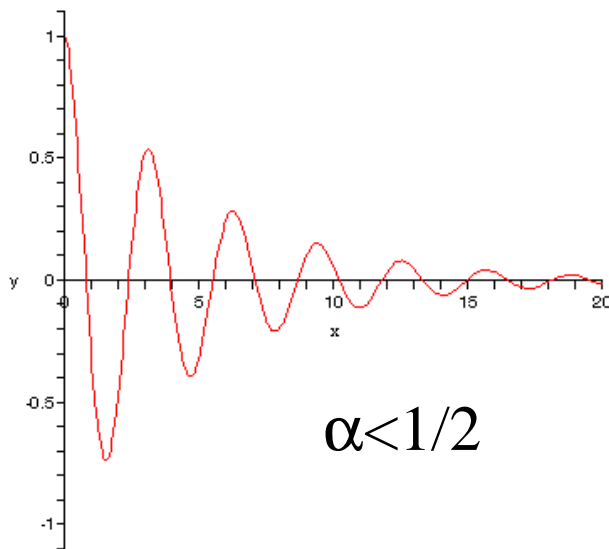
- Quantum dynamics completely determined by the **spectral density**

$$J(\omega) = \sum_{\alpha} M_{\alpha}^2 \delta(\omega - \omega_{\alpha})$$

Rich quantum many-body physics: Leggett, Weiss, Saleur,

Quantum dynamics of the spin-boson model

- When $J(\omega) \approx \alpha\omega$, and $\Delta \ll \omega_c$, then α is the dimensionless coupling constant that determines the quantum dynamics: damped Rabi oscillations, incoherent relaxation, or localisation.
- Relative population of the two states is $P(t) = \langle \sigma_z \rangle$
 - state1 $P(t) = -1$; state2, $P(t) = +1$



- Behaviour is modified by temperature and bias ($\varepsilon > 0$)

Exciton transfer between pairs of chromophores

Gilmore & McKenzie, quant-ph/0412170

Interaction of the chromophores with the environment: protein and polar solvent (water) can be described by a spin-boson model.

Provides quantitative criteria for coherent Rabi oscillations.

Can describe both coherent and incoherent energy transfer in photosynthesis.

Decoherence can improve device performance because it can ensure rapid and irreversible transfer of energy or charge separation.

Conclusions

- There are a diverse range of materials and devices which can only be understood in terms of quantum-many body physics.
- Minimal model Hamiltonians such as the Hubbard and spin-boson models can provide a semi-quantitative description of emergent properties such as competition between superconductivity and frustrated antiferromagnetism.