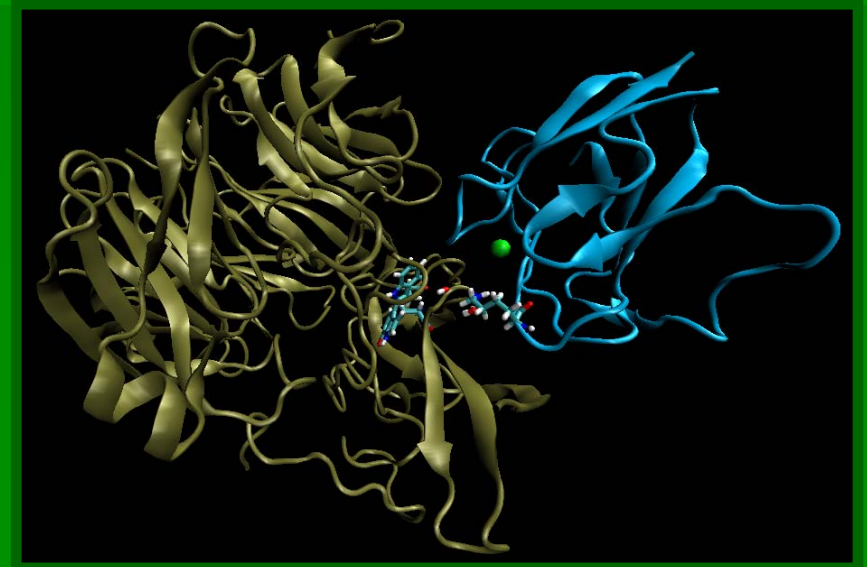




Coherent & Incoherent Electron Transfer in Biological Systems

Nathan Babcock
Aurélien de la Lande
Dennis Salahub
Barry Sanders



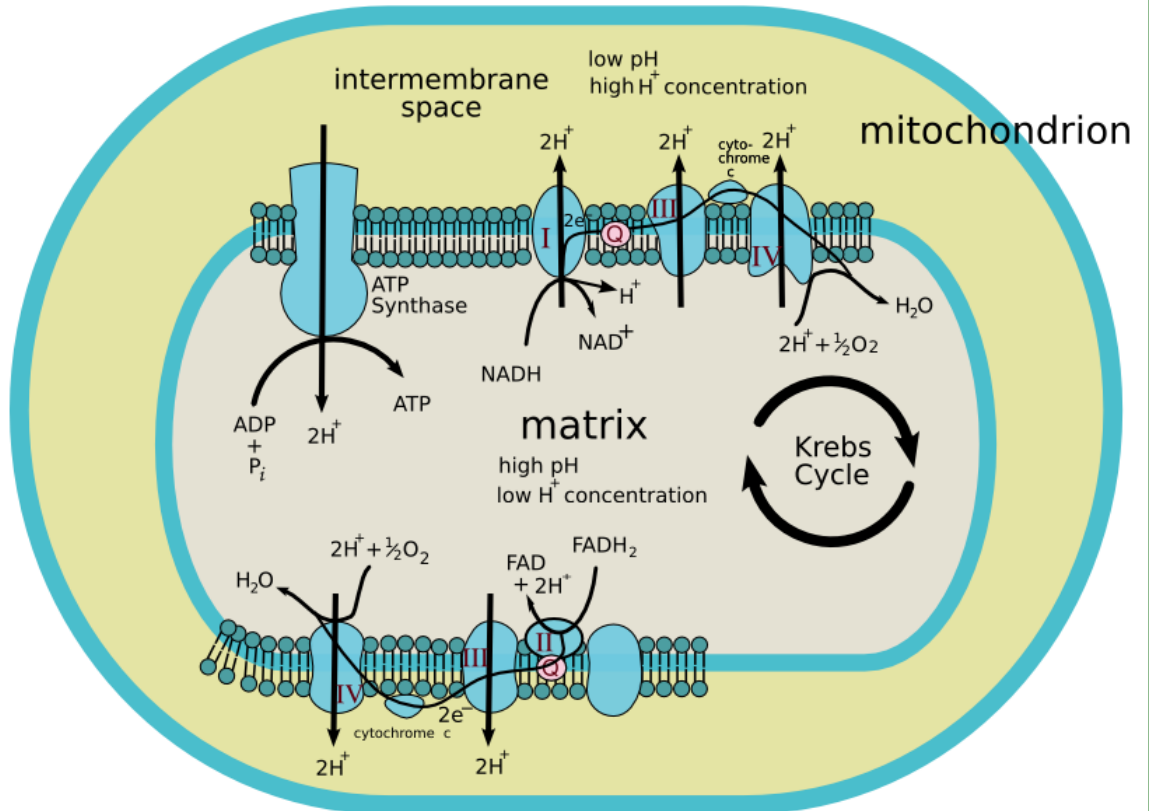
Biological Electron Transfer

All known oxygen-breathing (aerobic) life is sustained by nanoscopic electric motors!

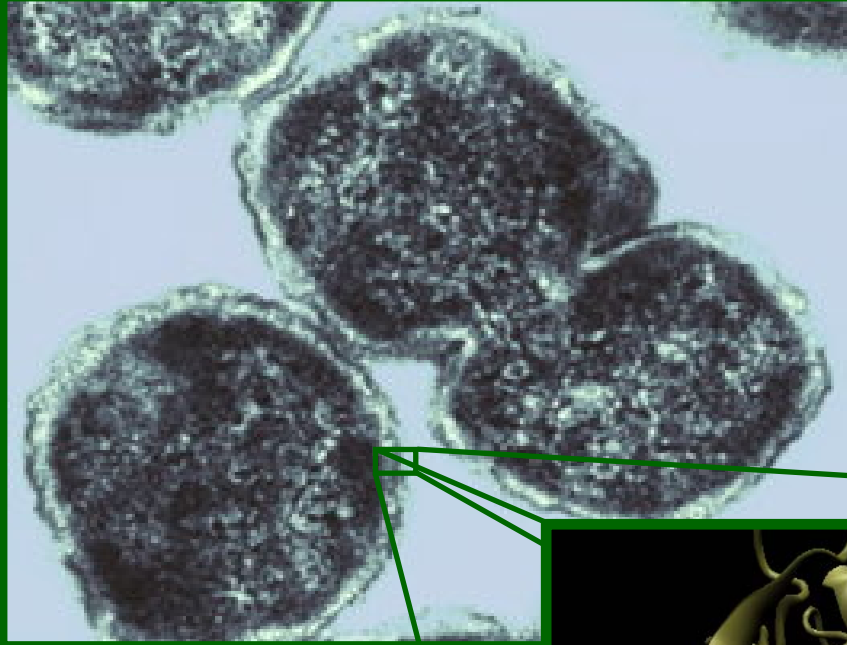
Electrical current powers a series of hydrogen pumps, creating a charge gradient to power ATP synthase.



Mitochondrial Electron Transport Chain

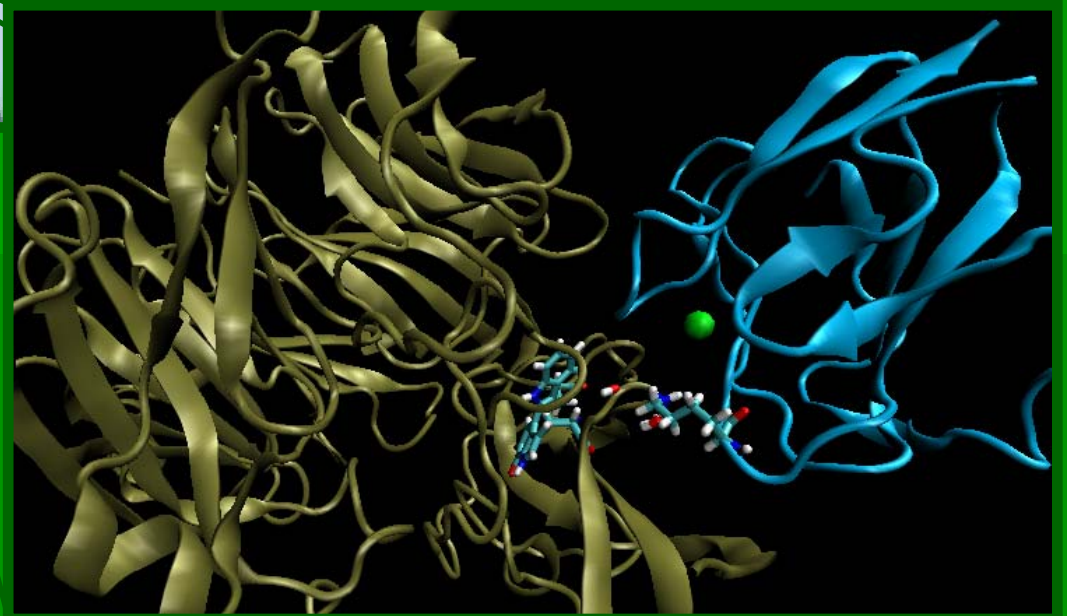


Mitochondria & Friends



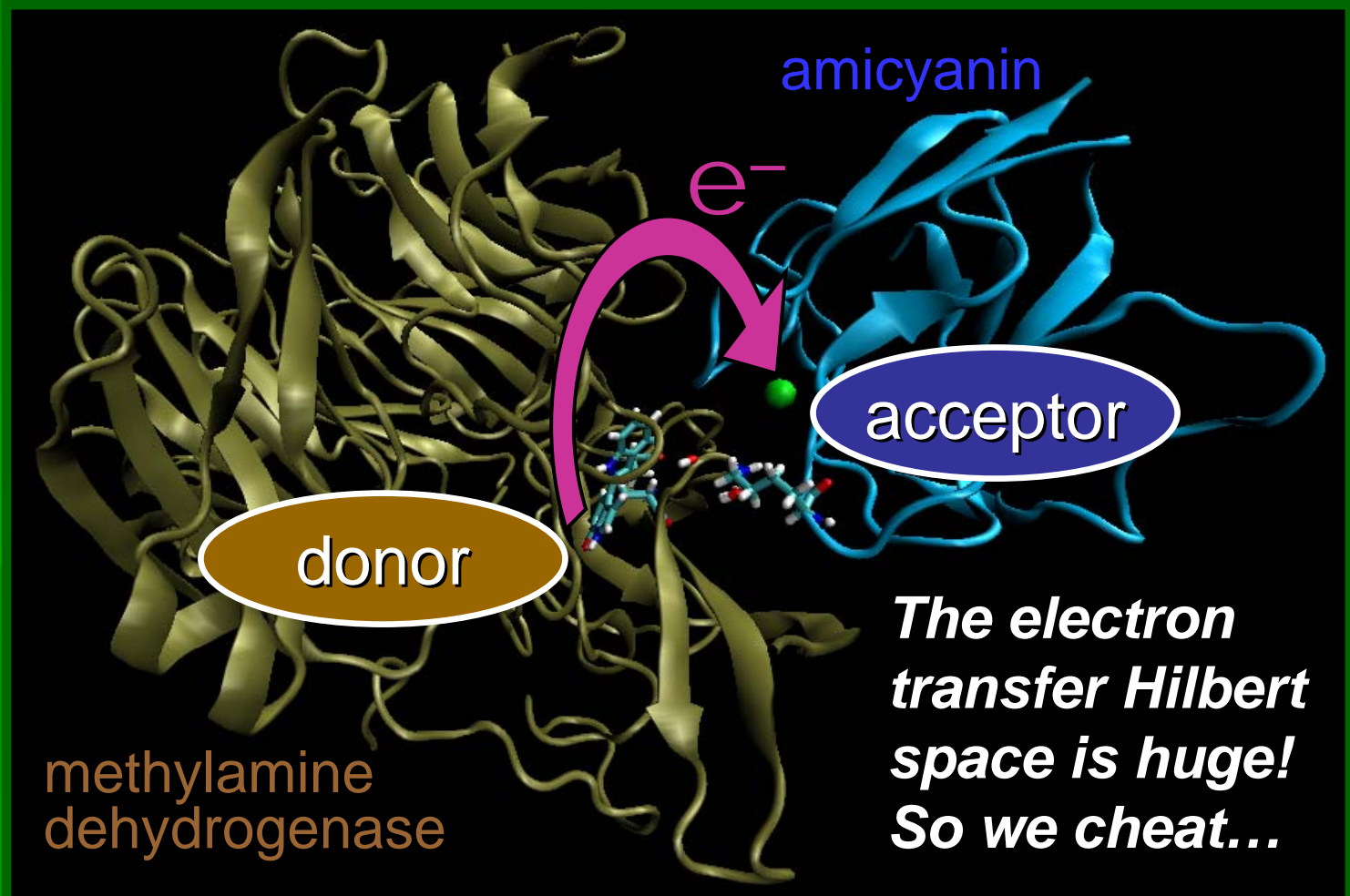
Paracoccus denitrificans is suspected to share a common ancestor with eukaryotic mitochondria (endosymbiotic theory).

Many membrane-bound molecular structures sustain respiration!



An Electron Transfer Example

Electron transport from MADH (tan) to amicyanin (cyan) is vital to cellular respiration in *Paracoccus denitrificans*.



Two State Approximation

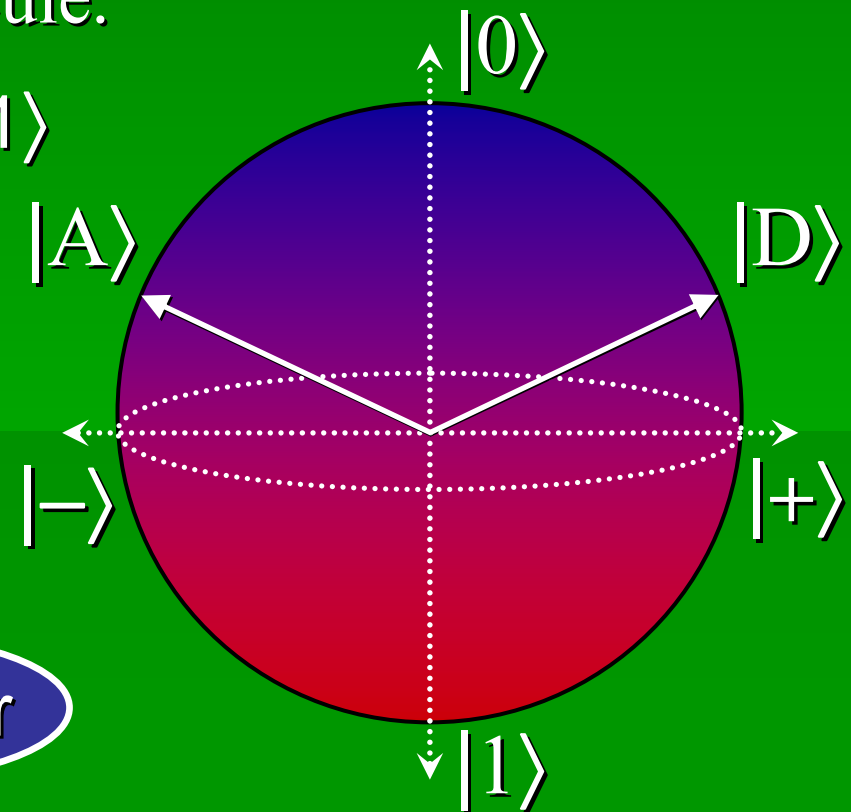
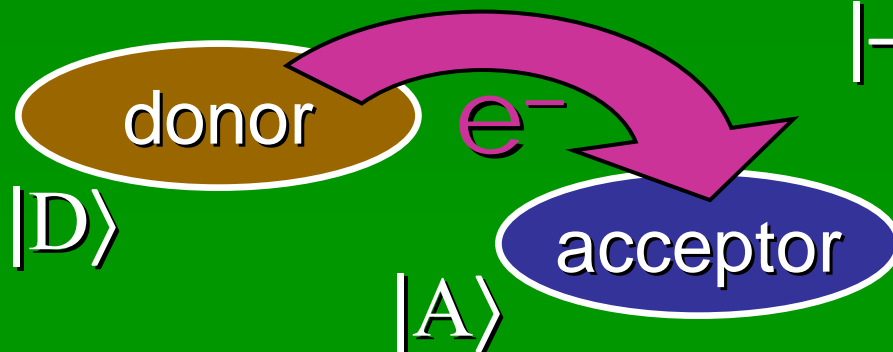
For decades, biochemists have modeled electron transfer (ET) systems as qubits!

$|D\rangle$ describes an electron at the “donor” molecule,
 $|A\rangle$ at the “acceptor” molecule.

$$\hat{H}|0\rangle = E_0|0\rangle \quad \hat{H}|1\rangle = E_1|1\rangle$$

$$H_{DA} = \langle D|\hat{H}|A\rangle$$

$$\sin\alpha = \langle D|A\rangle \ll 1$$



What are $|D\rangle$ and $|A\rangle$?

Assume $|D\rangle$ & $|A\rangle$ are real and that $\langle D|A\rangle \neq 0$.

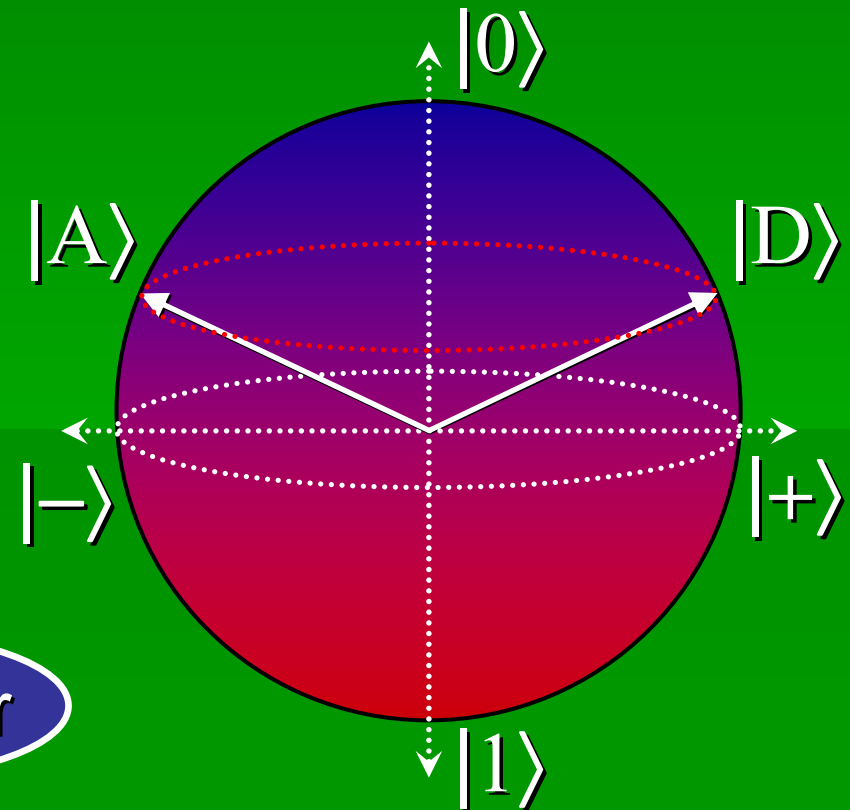
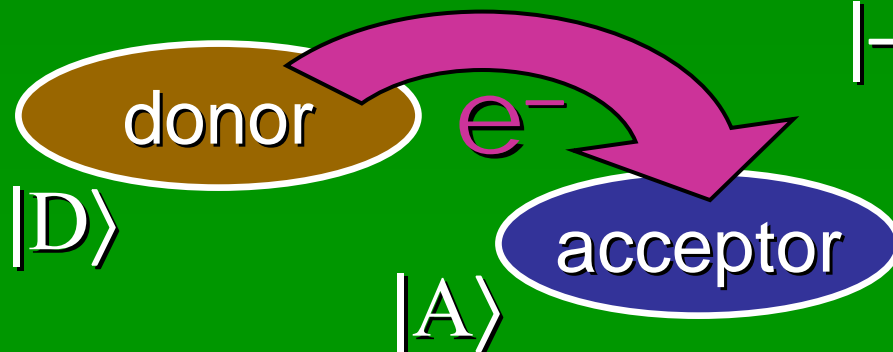
Assume resonance: $\langle E\rangle_D = \langle D|\hat{H}|D\rangle = \langle A|\hat{H}|A\rangle = \langle E\rangle_A$.

We therefore define $\alpha = \alpha^*$ such that $\sin\alpha = \langle D|A\rangle$,

$$|D\rangle = \cos\frac{\alpha}{2} |+\rangle + \sin\frac{\alpha}{2} |-\rangle,$$

$$|A\rangle = \sin\frac{\alpha}{2} |+\rangle + \cos\frac{\alpha}{2} |-\rangle,$$

without loss of generality.

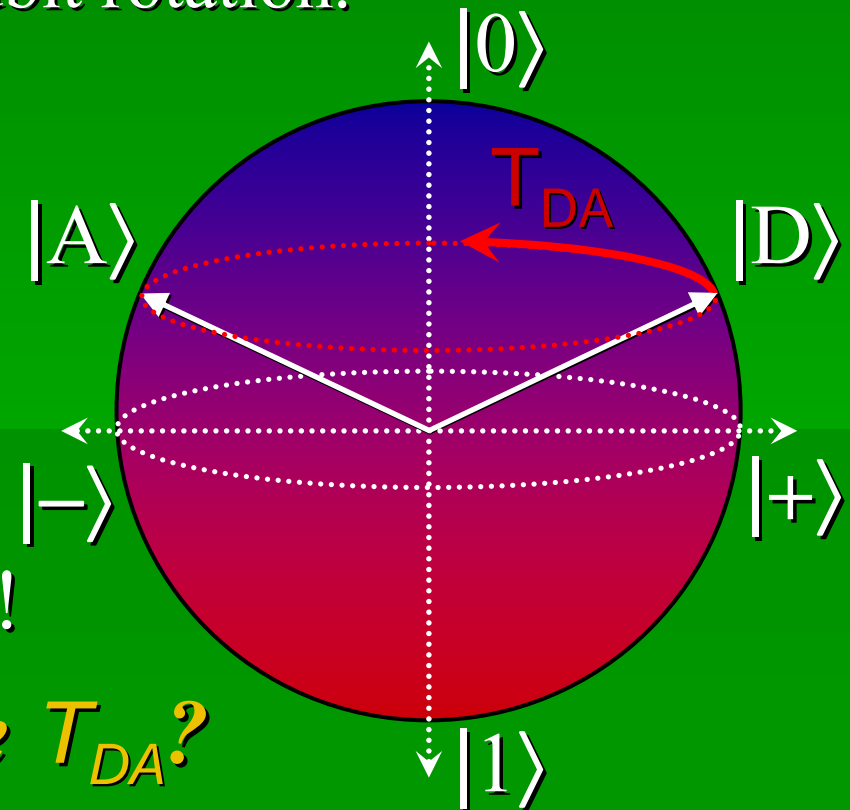


The Transfer Matrix Element

ET is usually treated as a unitary resonant tunneling (“superexchange”) event!

Define T_{DA} as the “electron transfer matrix element.”
It gives the frequency of qubit rotation.

$$f = \frac{2T_{DA}}{\hbar} = \frac{E_1 - E_0}{\hbar}$$



Diagonalizing the full
Hamiltonian is too hard!

How can we calculate T_{DA} ?

Calculating T_{DA}

$$f = \frac{2T_{DA}}{\hbar} = \frac{E_1 - E_0}{\hbar}$$

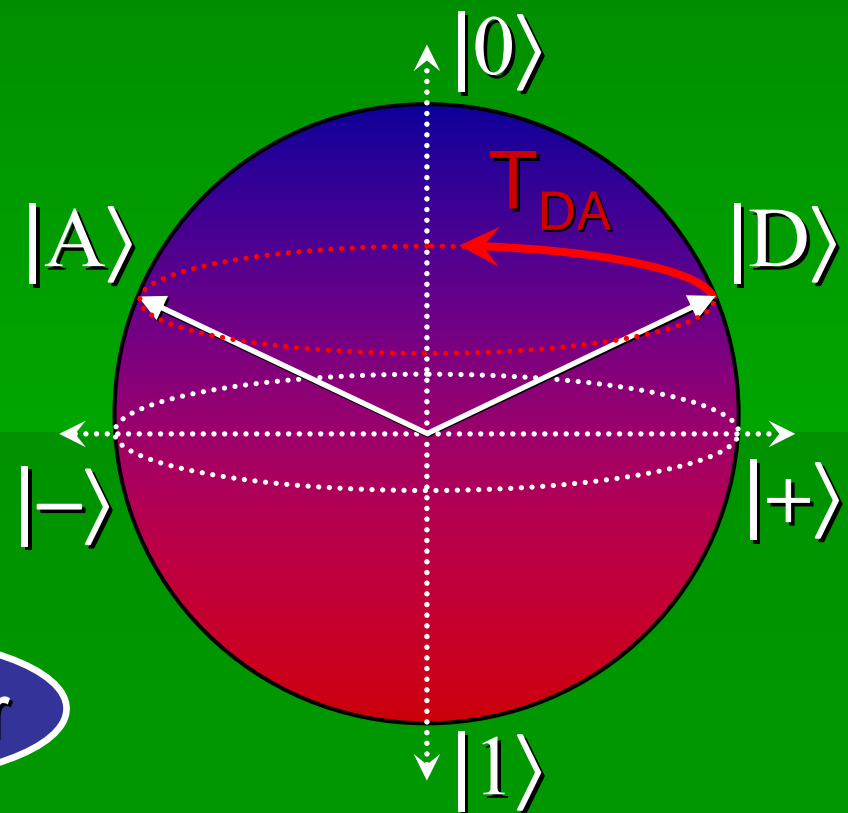
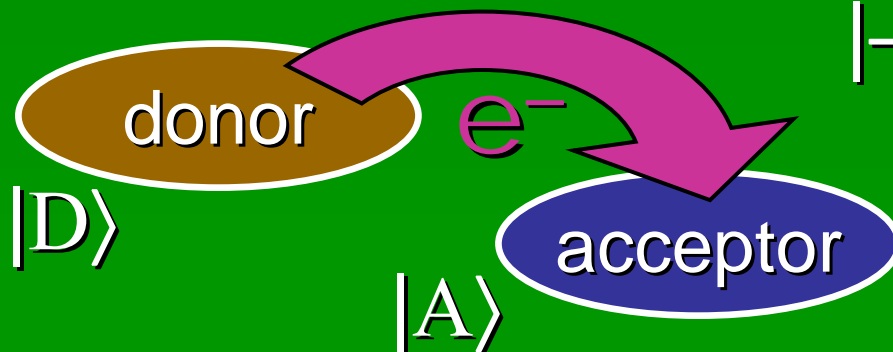
We assume $|D\rangle$ & $|A\rangle$ are real, and $\sin\alpha = \langle D|A\rangle \neq 0$.

We also assume $E_D = \langle D|\hat{H}|D\rangle = \langle A|\hat{H}|A\rangle = E_A$.

To obtain $E_1 - E_0$, we solve the eigenvalue equation

$$|\hat{H} - E\hat{1}| = 0$$

in terms of only $\{|D\rangle, |A\rangle\}$,
which is a spanning set
but not a basis!



Solving the Secular Equation

Introduce the POVM element $\hat{B} = |0\rangle\langle D| + |1\rangle\langle A|$.
 Since $\det(\hat{A}\hat{B}) = \det(\hat{A})\det(\hat{B})$, we can instead solve

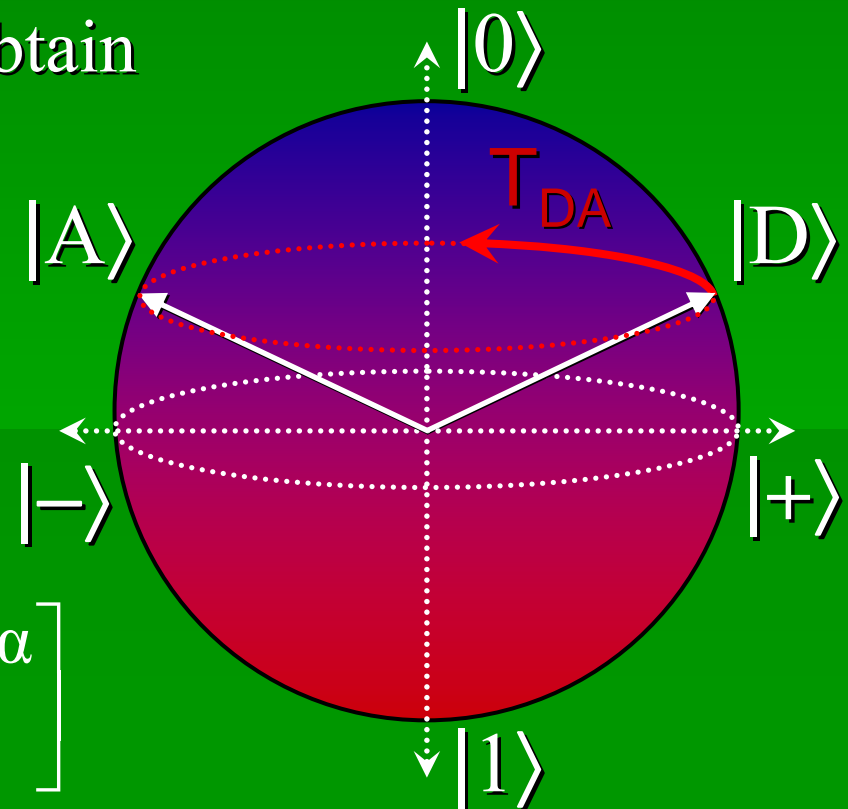
$$|\hat{B}(\hat{H} - E\hat{1})\hat{B}^\dagger| = 0, \text{ using } \langle D|A\rangle = \sin\alpha$$

with $T_{DA} = (E_1 - E_0)/2$ to obtain

$$T_{DA} = \frac{H_{DA} - E_D \sin\alpha}{1 - \sin^2\alpha}.$$

$$\hat{B}(\hat{H} - E\hat{1})\hat{B}^\dagger =$$

$$\begin{bmatrix} H_{DD} - E & H_{DA} - E \sin\alpha \\ H_{AD} - E \sin\alpha & H_{AA} - E \end{bmatrix}$$



The Electron Transfer Matrix

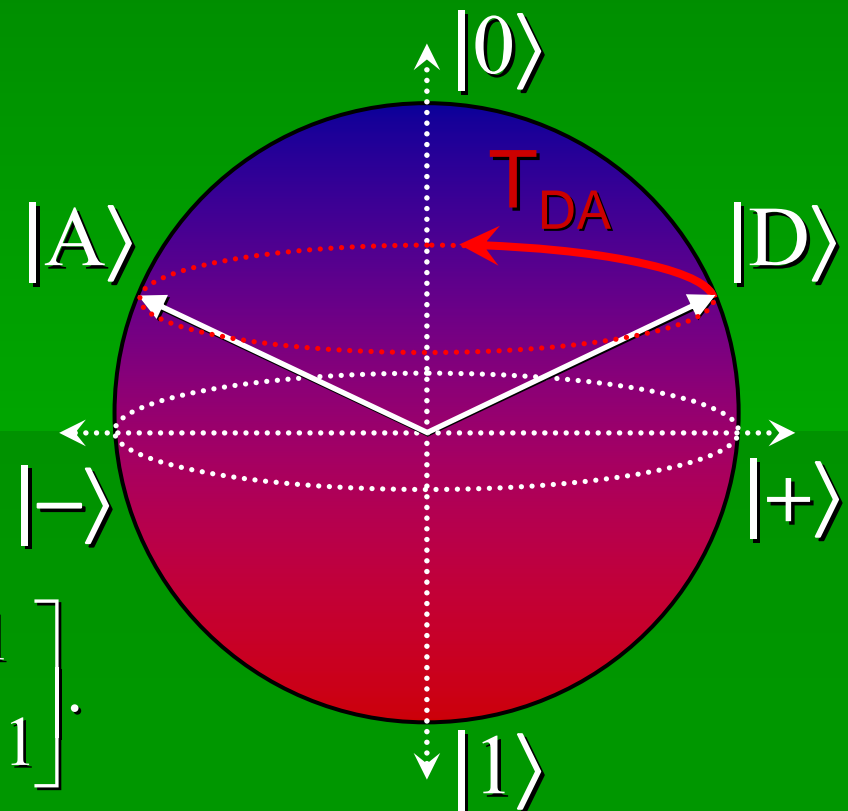
Having obtained $T_{DA} = \frac{H_{DA} - E_D \sin \alpha}{1 - \sin^2 \alpha}$, we infer that

$$\hat{T} = \frac{\hat{H} - E_D \hat{1}}{1 - \sin^2 \alpha}.$$

Thus, we represent the quantum channel as a non-linear operator...?

Also of interest:

$$\hat{B} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & \sin \alpha \\ \sin \alpha & 1 \end{bmatrix} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}.$$



Golden Rule (Marcus Theory)

Finally, to obtain the overall transfer rate, we use first order perturbation theory, replacing \hat{H} with \hat{T} in Fermi's Golden Rule:

$$k = \frac{2\pi}{\hbar} T_{DA}^2 \frac{e^{-\frac{-(\Delta G^{0'} + \lambda)^2}{4\lambda RT}}}{\sqrt{4\pi\lambda RT}}$$

Prefactor

Rate

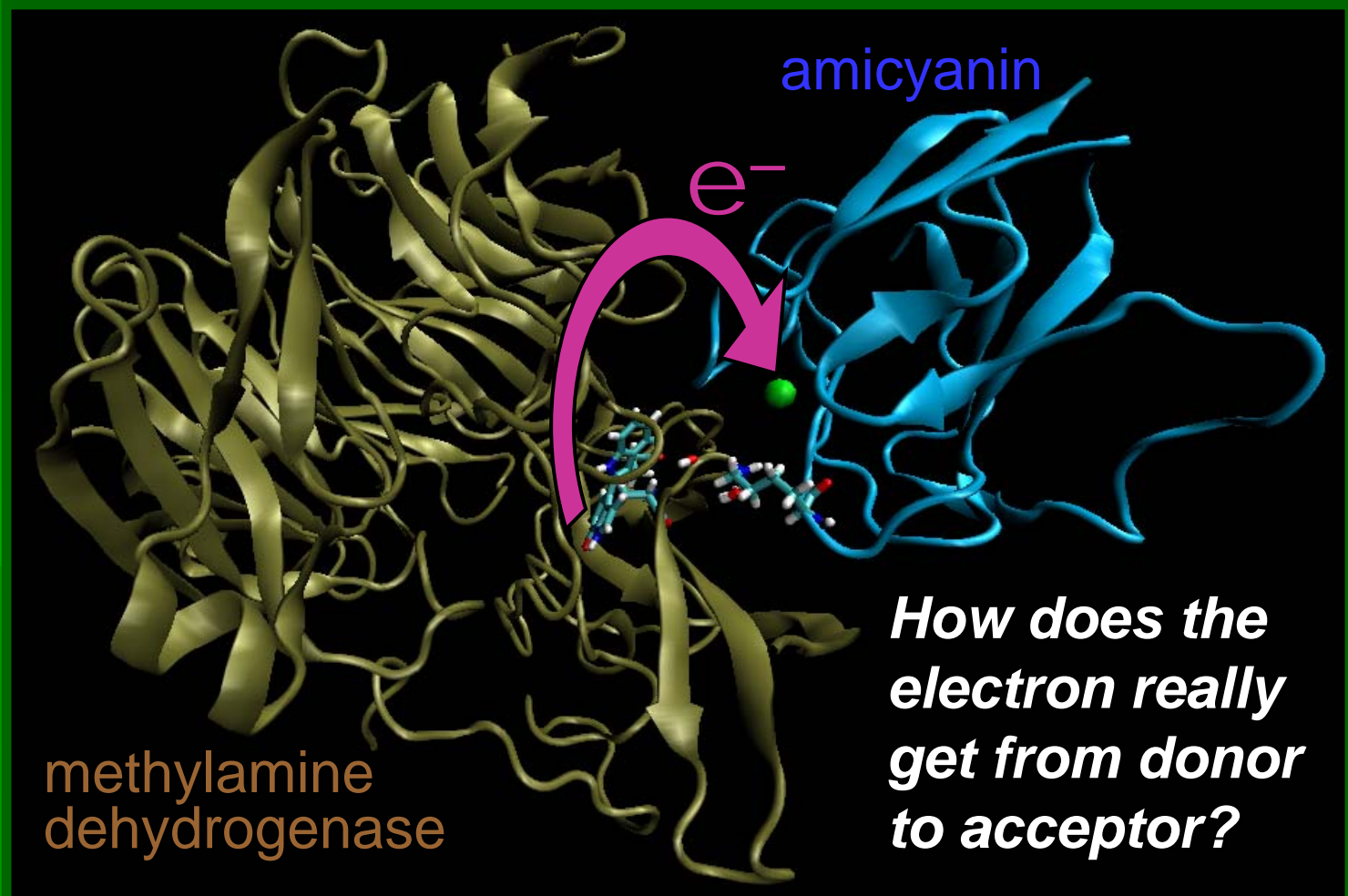
Electronic Matrix Element

Density of Nuclear States ("Frank-Condon" factor)

This is R.A. Marcus' Nobel prize equation, but it ignores electronic decoherence!

More Detailed Models of ET

We want a model of electron transfer that includes non-unitary effects (electron-nuclei entanglement)...

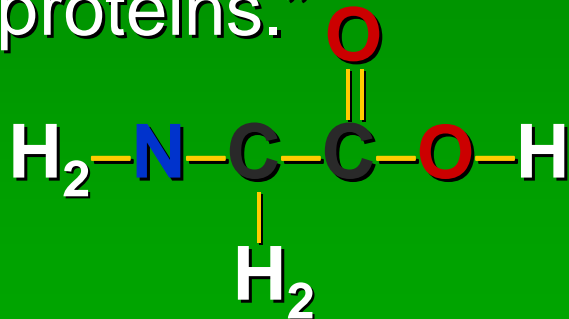


Crash Course in Biochemistry

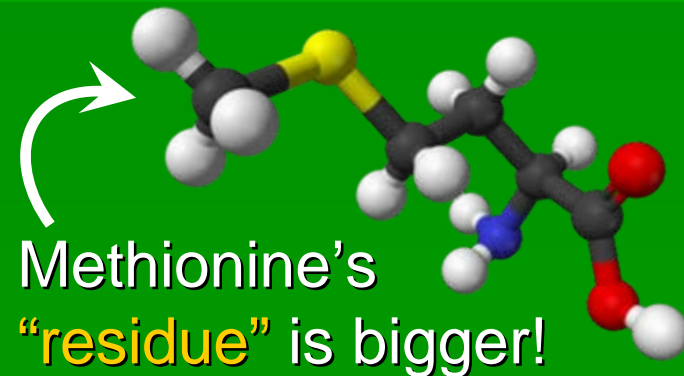
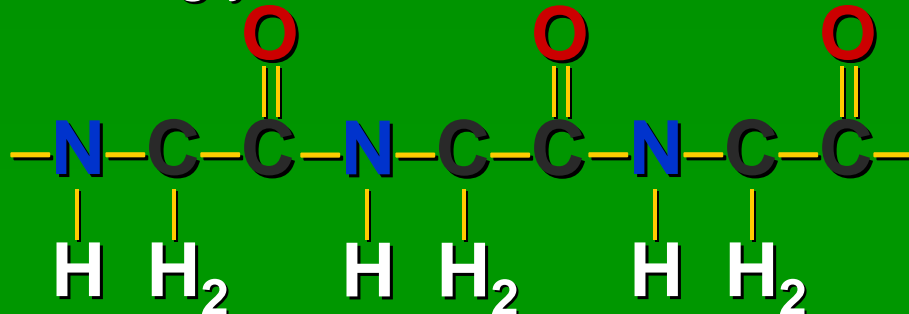
...but we must first introduce a few biochemical concepts!

“Amino Acids” are the “building blocks of life.”

These small molecules hook together to form chains called “proteins.”



Like a glycine chain:

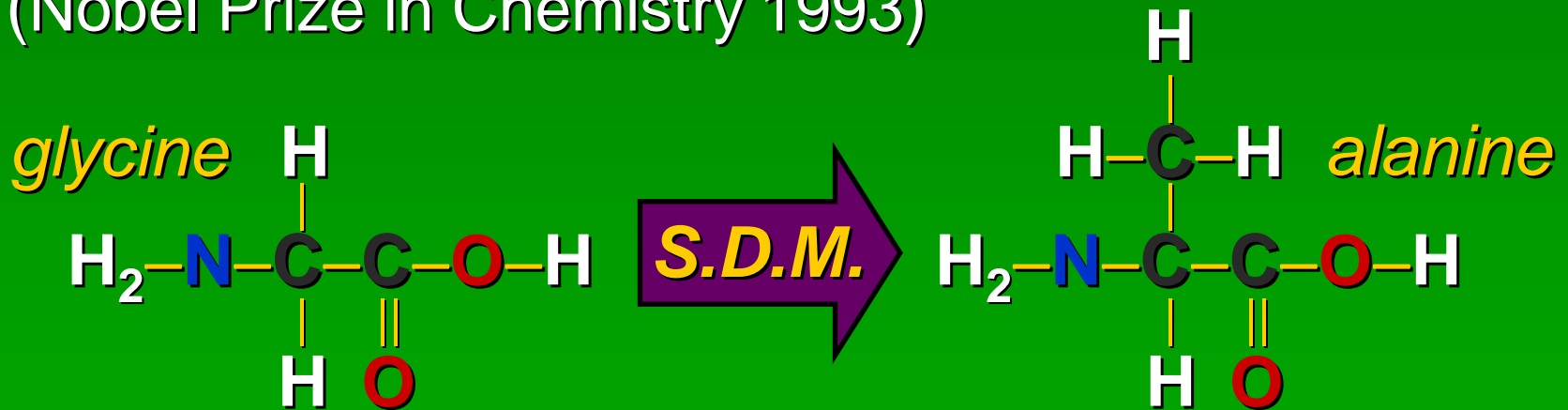


Genetic Engineering

“Site-Directed Mutagenesis”

Biochemists use this method to alter the genetic code for a protein, one amino acid at a time.

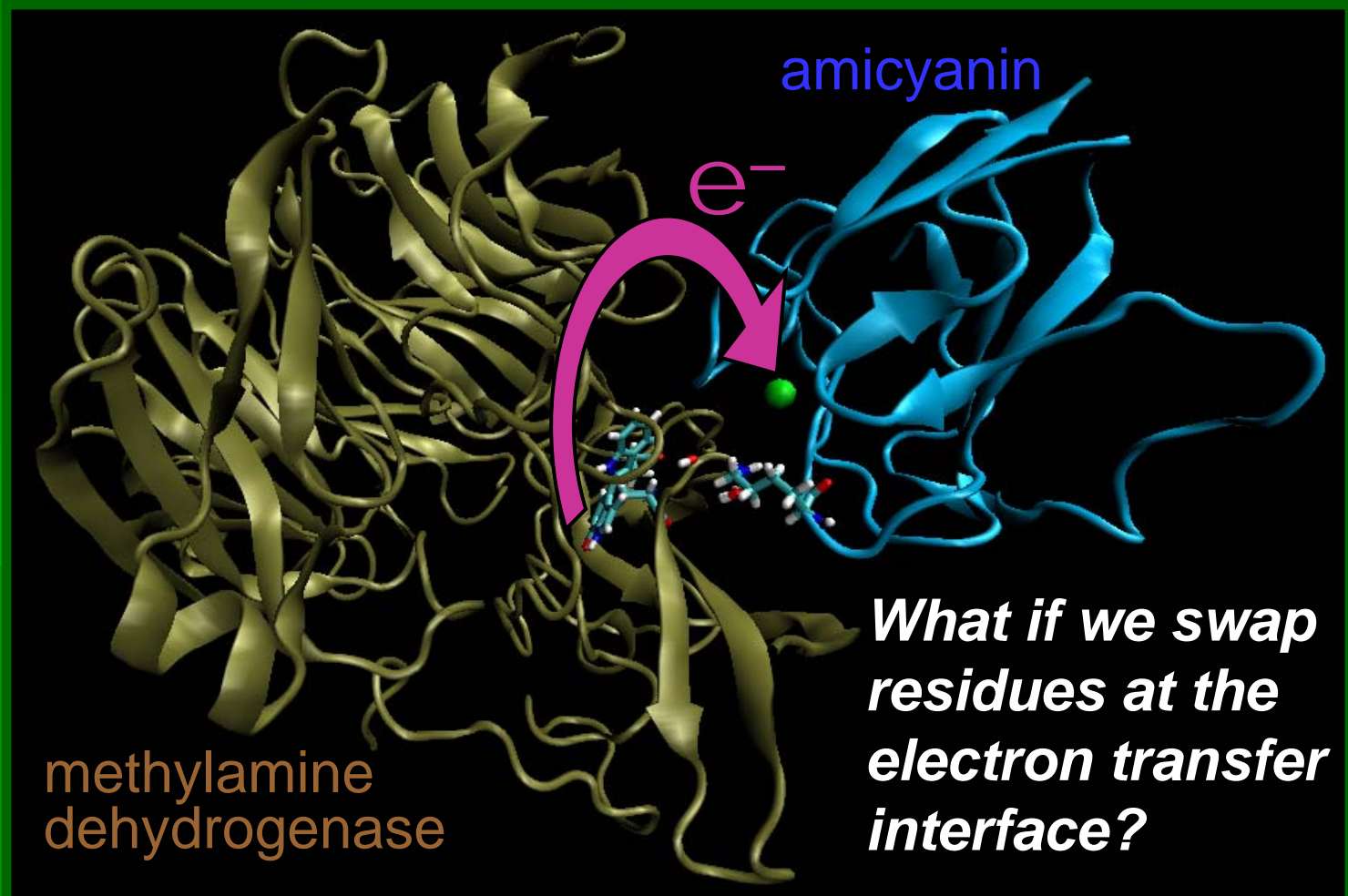
(Nobel Prize in Chemistry 1993)



This creates an incredible opportunity to study proteins at the atomic scale. E.g., swapping glycine for alanine changes only four atoms!

Investigating the Interface

How does protein-to-protein electron transfer change when we alter amicyanin by just a few atoms?



Making Mutant Amicyanin

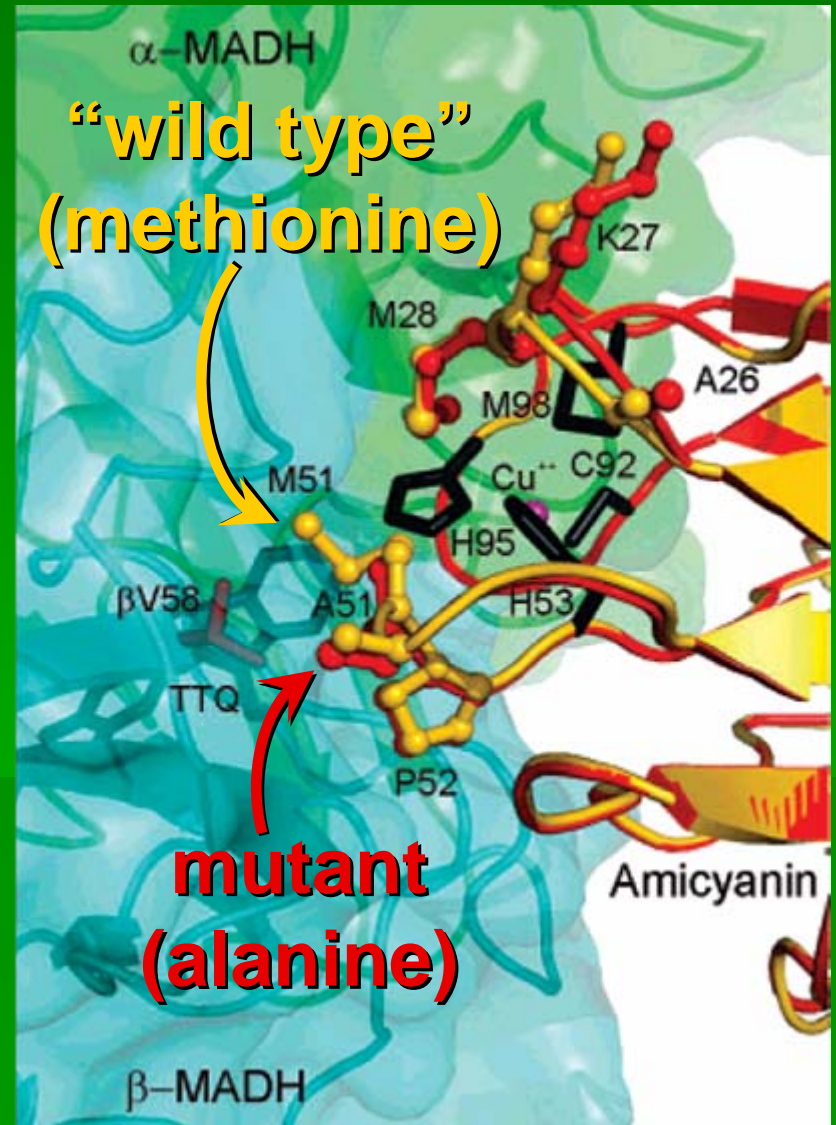
*Methionine 51 mutation
in amicyanin molecule.*

Unchanged features:

- spectra
- structure
- conformation
- equilibrium constant

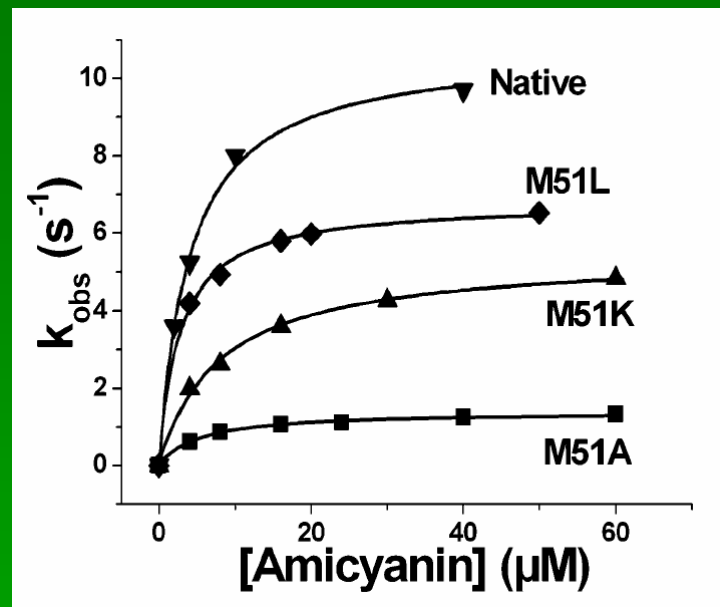
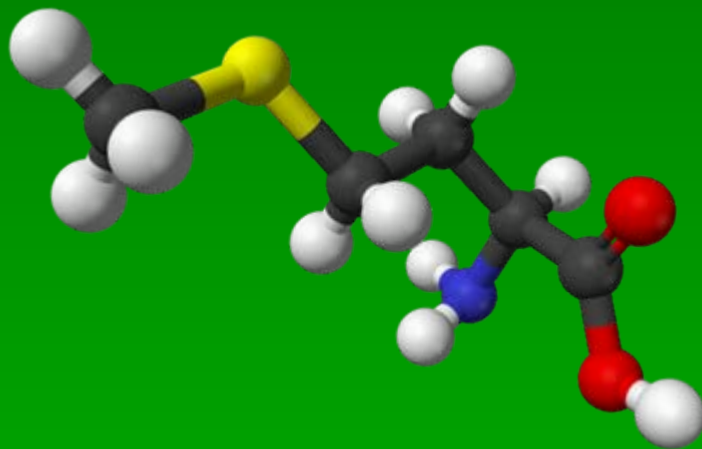
*Electron transfer rate
changes drastically!*

Biochemistry 46 11137 (2007)



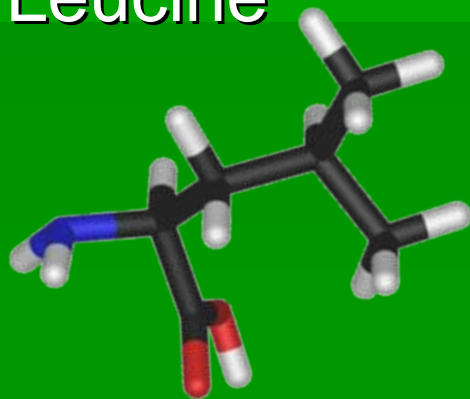
More Amino Acid Mutations

Methionine
(wild type)

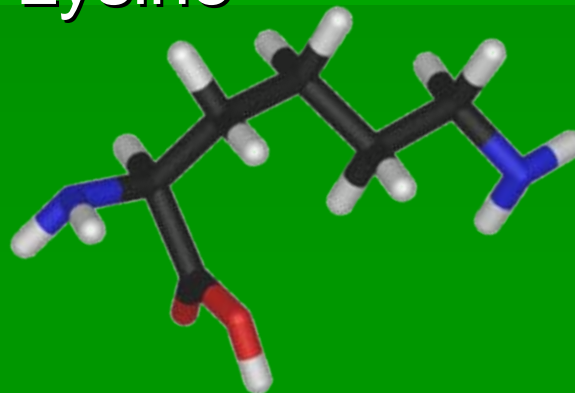


Biochemistry 46 11137 (2007)

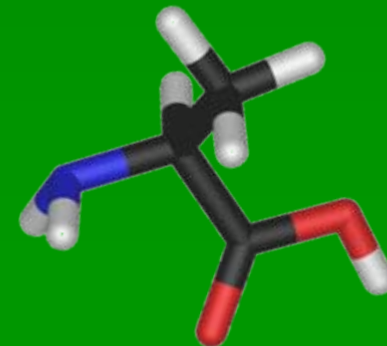
Leucine



Lysine



Alanine



Failure of Standard Theory

- Element T_{DA} exceeds “non-adiabatic” limit.
- “Reorganization energy” λ 300% too big.
- Separation r is unreasonably small.
- T_{DA} “borrowed” from very different system.

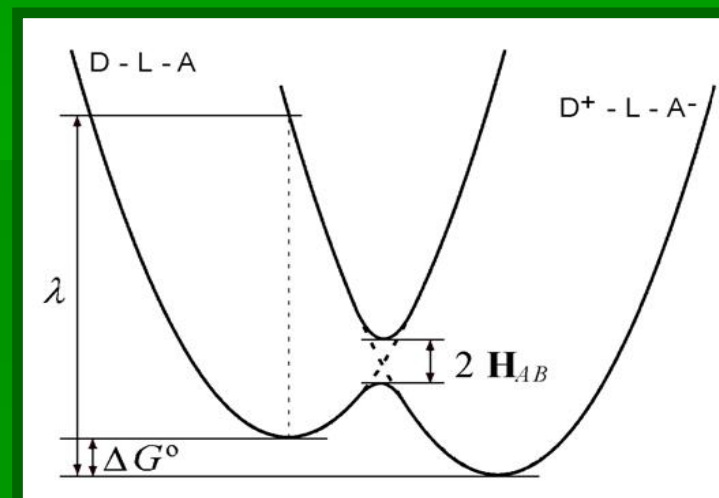
The theory used is not satisfactory!

The usual Marcus equation:

$$k = \frac{2\pi}{\hbar\sqrt{4\pi\lambda RT}} T_{DA}^2 e^{-\frac{(\Delta G^{\circ} + \lambda)^2}{4\lambda RT}}$$

$$T_{DA}^2 \approx e^{-\beta(r-r_o)}$$

empirical fudge factor!

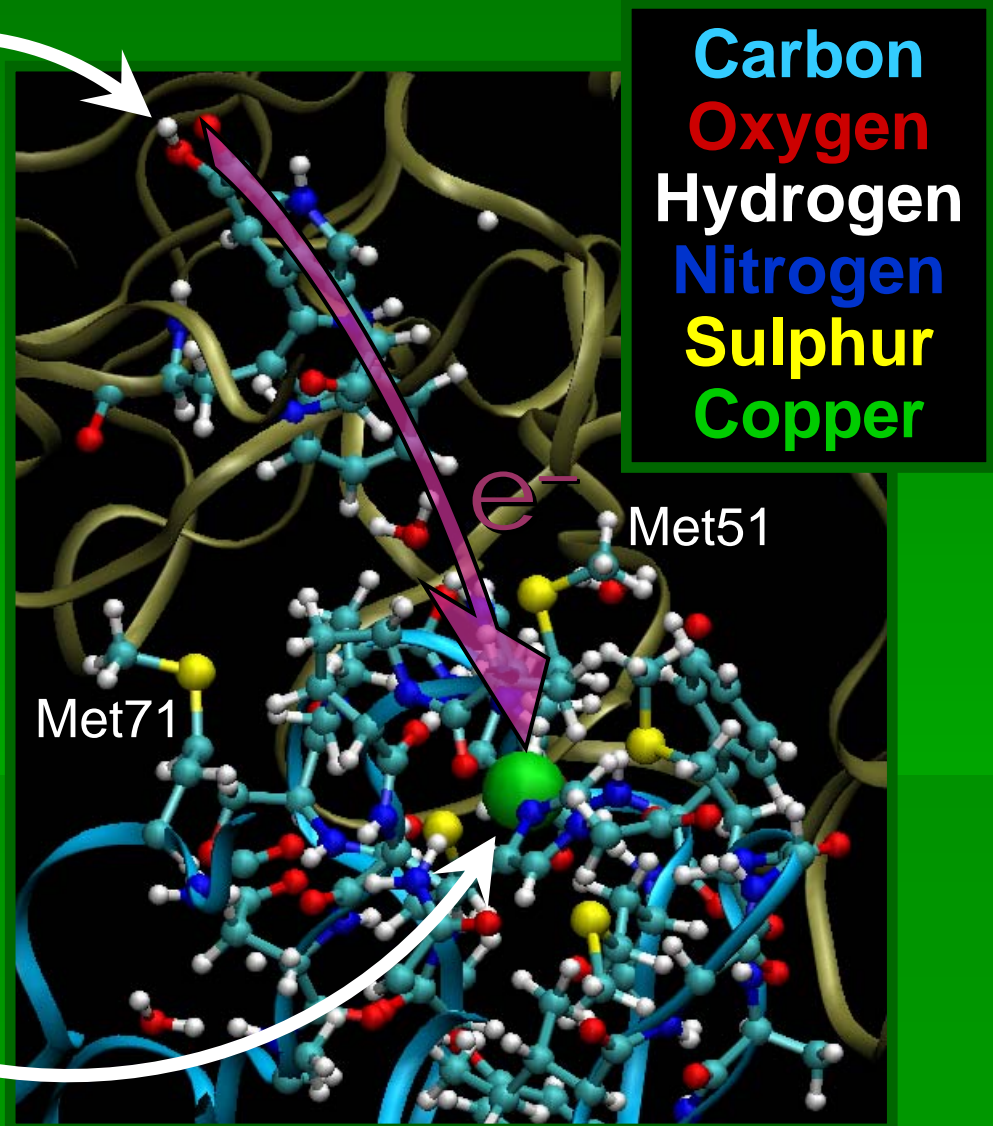


Water Bridge Hypothesis

donor

Electron transport across a stabilized water "bridge" from the hydroxide group in MADH to copper atom in amicyanin?

acceptor



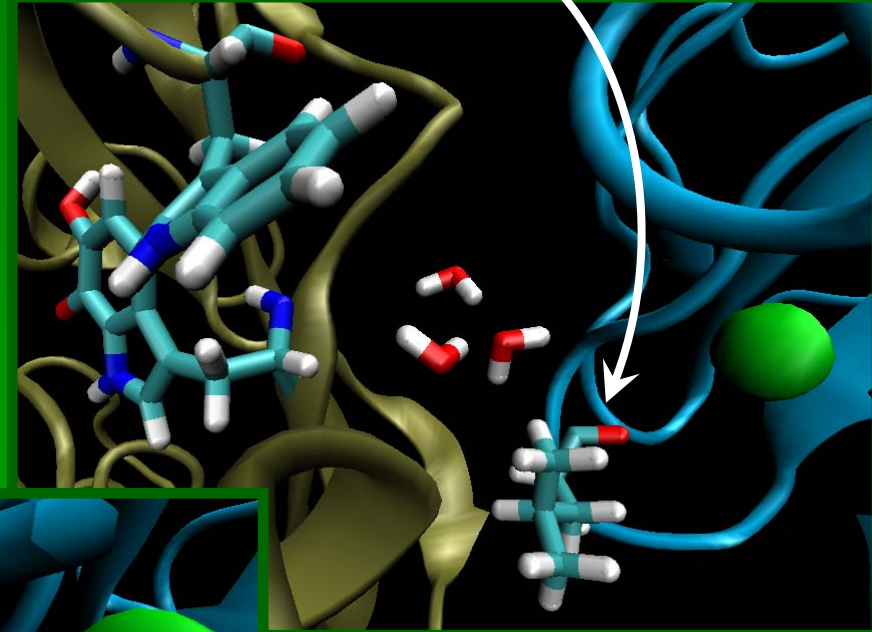
Loss of stable H₂O Bridge?

- Some special “molecular conformation” present in the wild type system is absent in mutants, *Biochemistry* **46** 11137 ('07).
- Similar phenomena discovered in PHM system due to destabilized water bridge. de la Lande *et al*, *JACS* **129** 11700 ('07).
- Is resonant tunneling (“superexchange”) being suppressed due to rotation-induced decoherence, as in *PNAS* **102** 3552 ('05)?

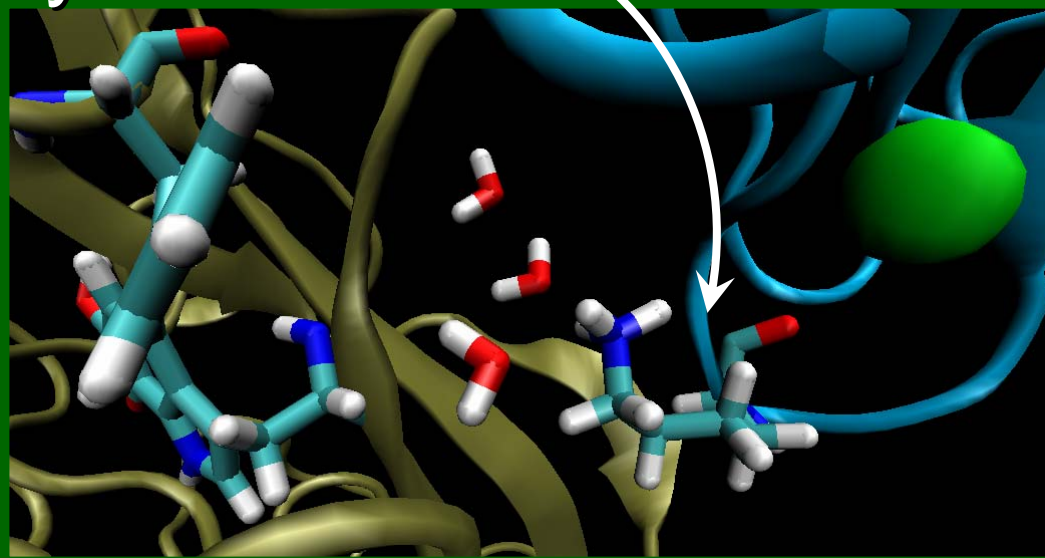
Poor Substitutes?

We hypothesize that the amino acids swapped in to replace methionine do not properly stabilize nearby water molecules.

Leucine



Lysine



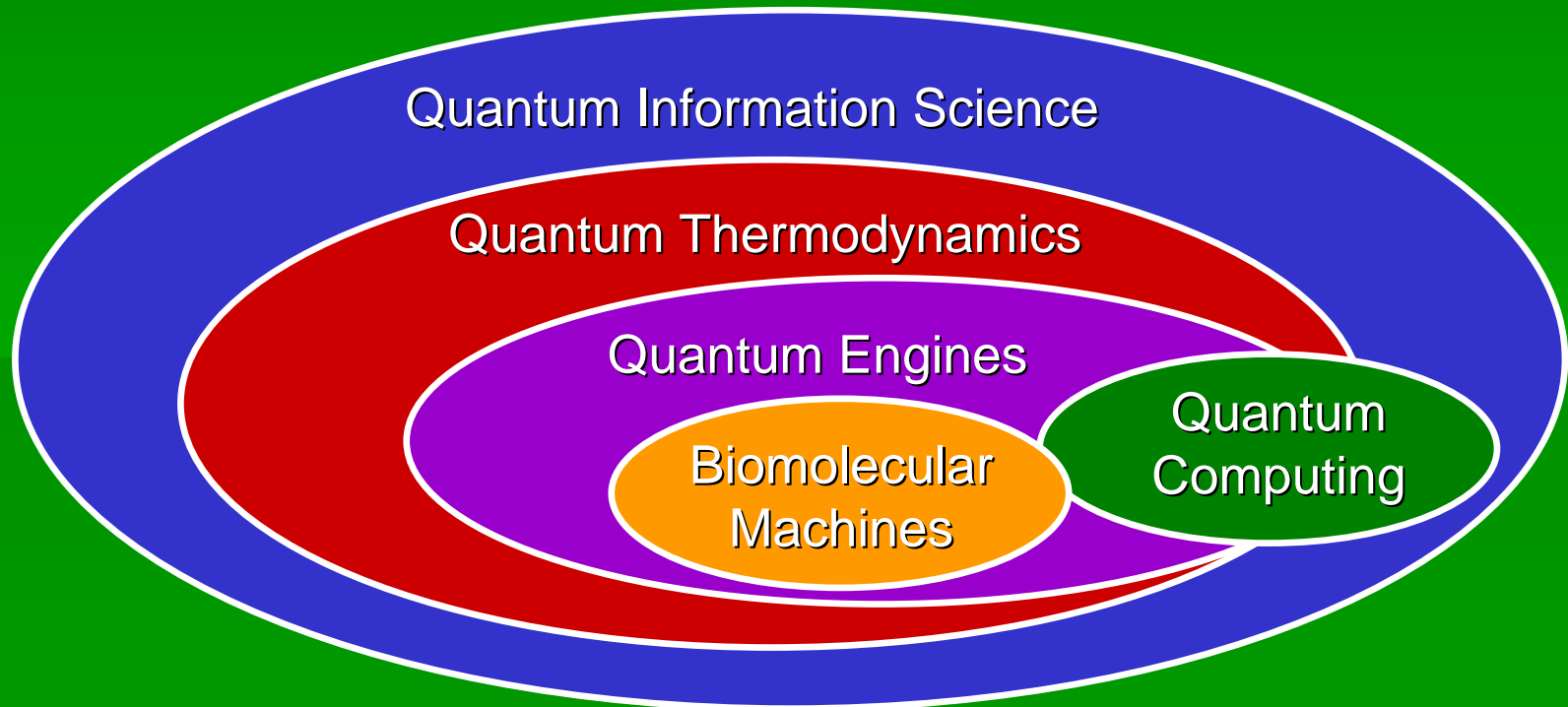
Carbon
Oxygen
Hydrogen
Nitrogen
Copper

Our Approach...

- Simulate amicyanin's molecular dynamics to determine nuclear conformations for various mutants (CHARMM).
- Use DFT to evaluate H_{AB} , ΔG^0 , and λ .
- Determine how mutations alter bridging effects during the transfer process.
- Do nuclear dynamics play a role on the timescale of the electronic coupling (i.e., tumbling water molecules)?

Outlook (Feynman's Vision)

- We can learn a lot from the quantum thermodynamic machines found in living systems.
- The advent of human-made quantum nanomachines will drastically change human life as we know it.
- *There's still "plenty of room at the bottom!"*



A Word From Our Sponsors



**NSERC
CRSNG**



ALBERTA
INGENUITY
FUND



CORE



UNIVERSITY OF
CALGARY



Institute for
Quantum Information Science
at the University of Calgary