Electron Transfer at the Cytochrome / Mineral Interface:

An Overview of the EMSL BGC Modeling Component

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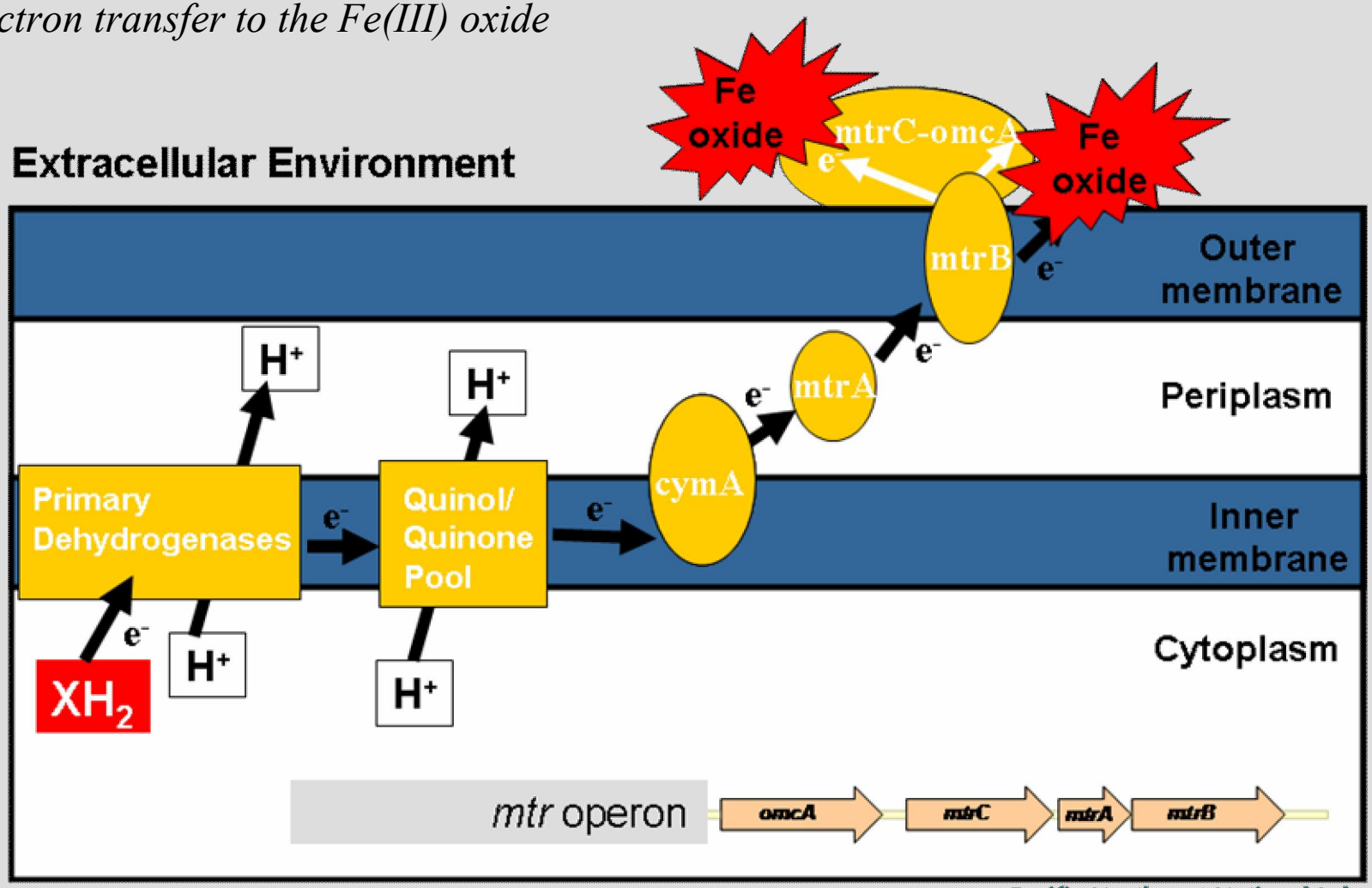
ERSD PI Meeting – April 2006

Acknowledgements: US-DOE-OBER-ERSD-EMSL
EMSL Molecular Sciences Computing Facility
EMSL NWChem Project

Current Conceptual Model for Electron Transfer to Extracellular Substrates in *Shewanella*

BGC Hypothesis: *Outer membrane cytochromes OmcA/MtrC are responsible for direct electron transfer to the Fe(III) oxide*

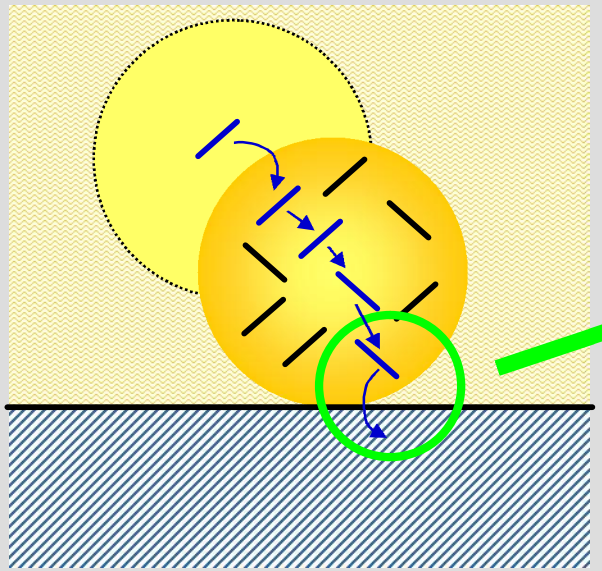


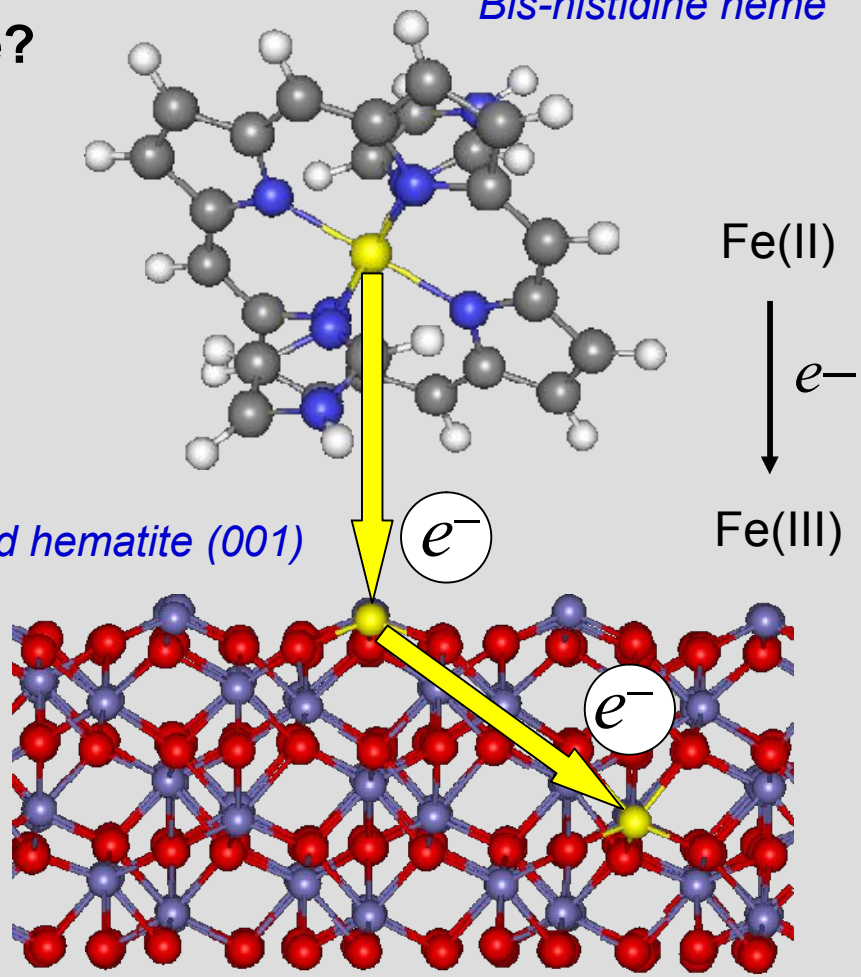
Courtesy - D. Richardson

Science Questions

What regulates the ET rate across the cytochrome/Fe(III)-oxide interface?

How are Fe(III) acceptor sites 'regenerated' and how fast?

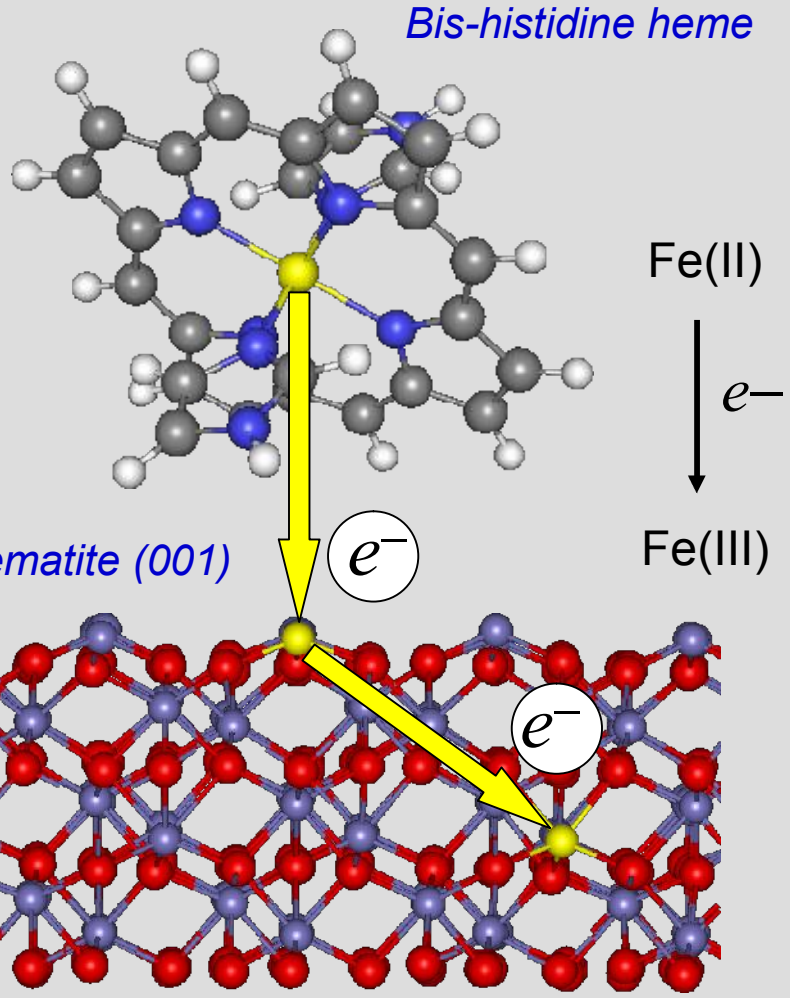




Obstacles / Challenges

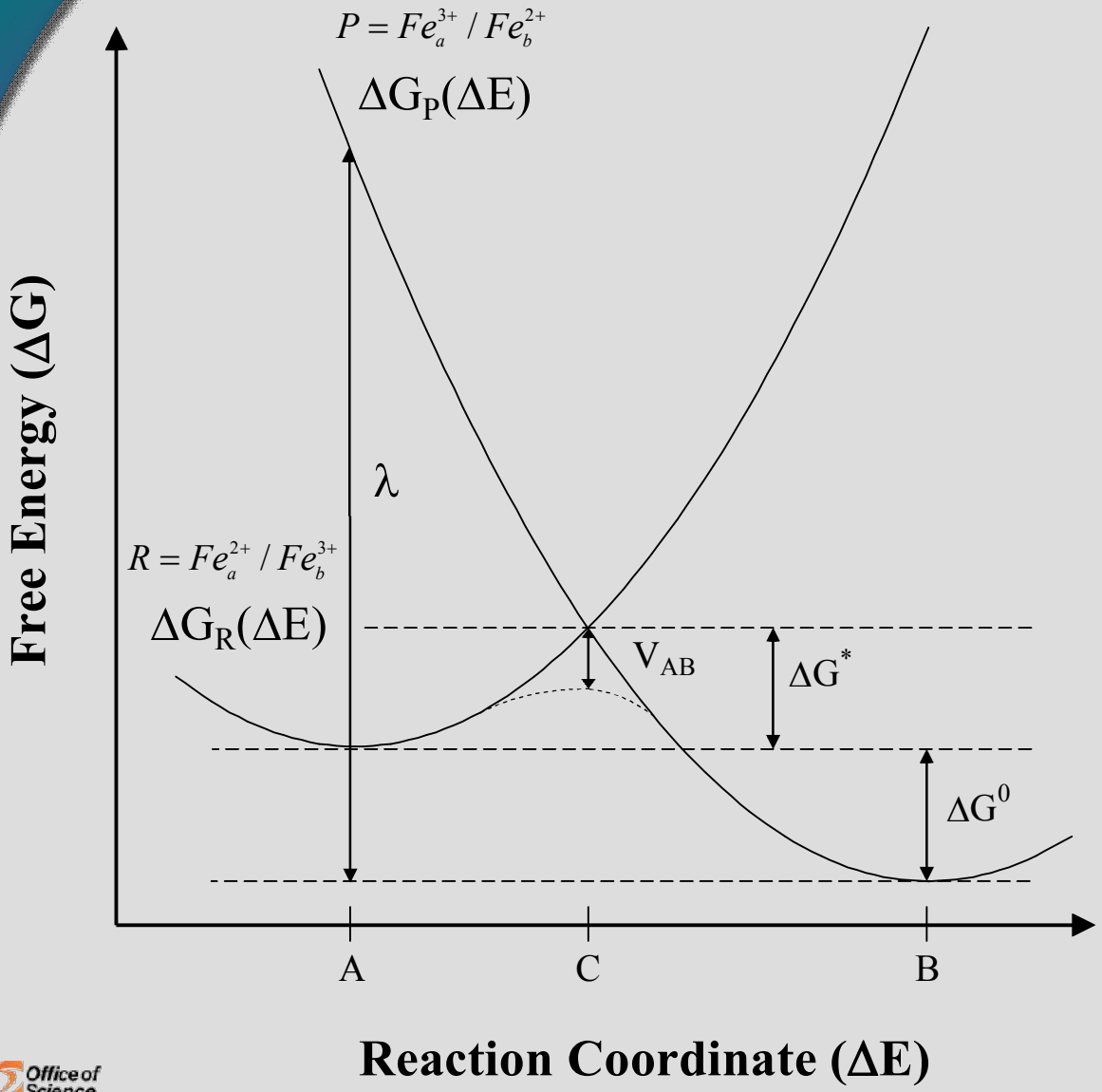
Aspects influencing the ET kinetics at the molecular scale:

electron transfer distance
heme electronic structure
axial ligand orientation
heme orientation
porphyrin distortion
intervening / bridging molecules
surface atomic structure
surface electronic structure



electron transfer distance
crystallographic direction
proximity to surface plane
surface termination
surface hydration
defects

Basic Electron Transfer Theory



ΔE: Reaction coordinate or energy gap

$$\Delta E = E_P - E_R$$

λ : Reorganization energy

V_{AB}: Electronic coupling

ΔG*: Diabatic activation free energy

ΔG^0: Free energy of ET

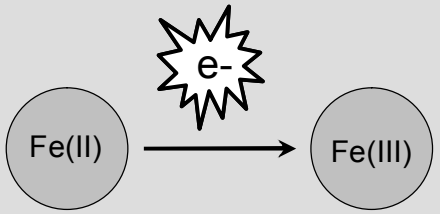
Basic Electron Transfer Theory

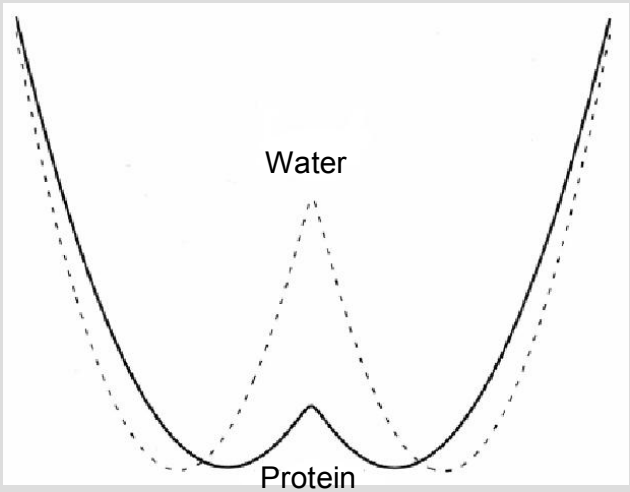
ET rate = electronic part + nuclear part

electronic

$$k_{et} = \frac{2\pi}{\hbar} V_{AB}^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp[-\frac{\Delta G^*}{k_B T}]$$

nuclear



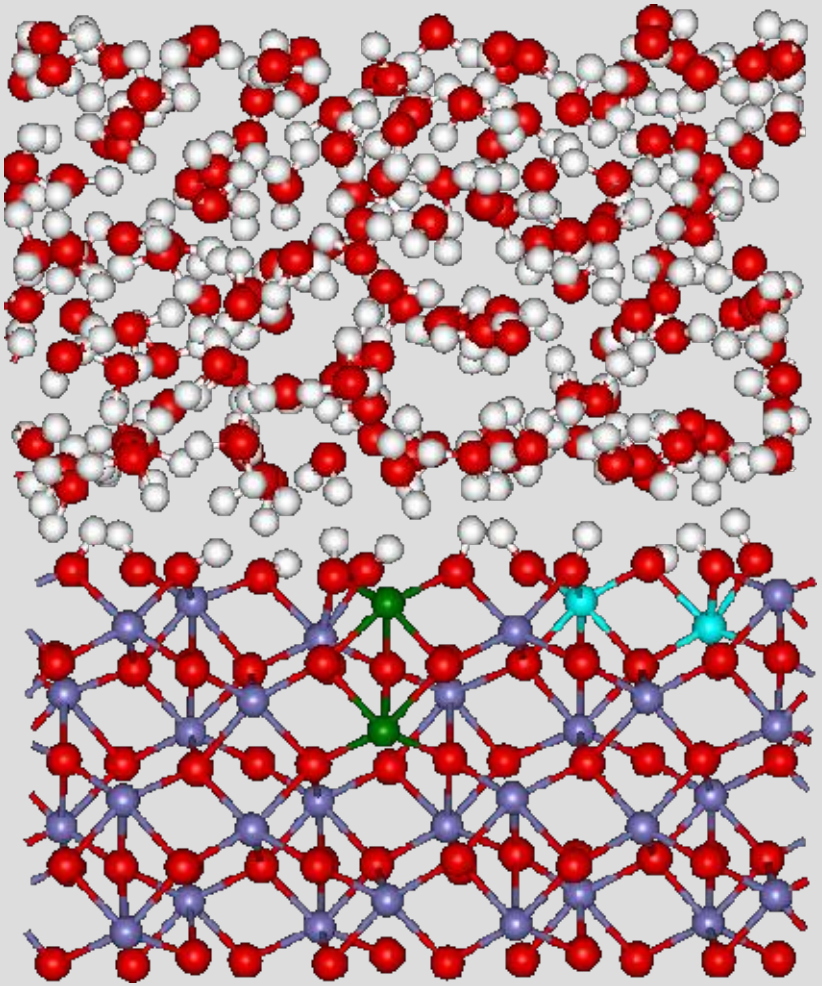


Details of the molecular environment strongly influence the PES's and electronic coupling

Electron Migration at Hematite Surfaces

Hematite surfaces examined

Fe-terminated (001)
O(H)-terminated (001)
(012)



Hydroxylated hematite (001)

Approach to Model the Interatomic Interactions

The method is based on the **Born model of solids**.

$$V(r_{ij}) = \frac{q_i q_j}{r_{ij}} + \phi(r_{ij})$$

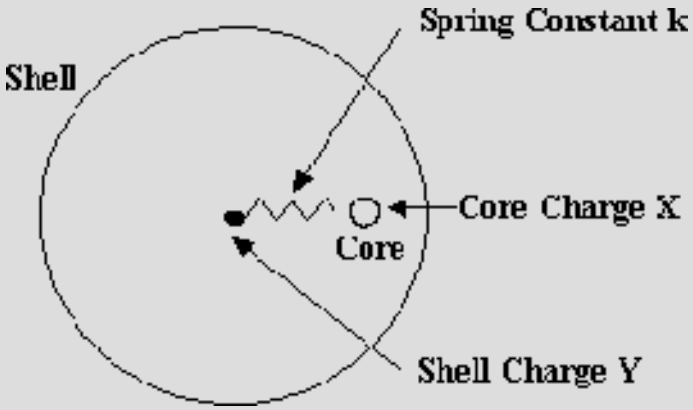
1st Term - Long range interactions

Coulombic energy

2nd Term - Short range interactions

Electron cloud repulsion,
Van der Waals, bond stretch,
angle bend, torsion…

Shell Model[1]:



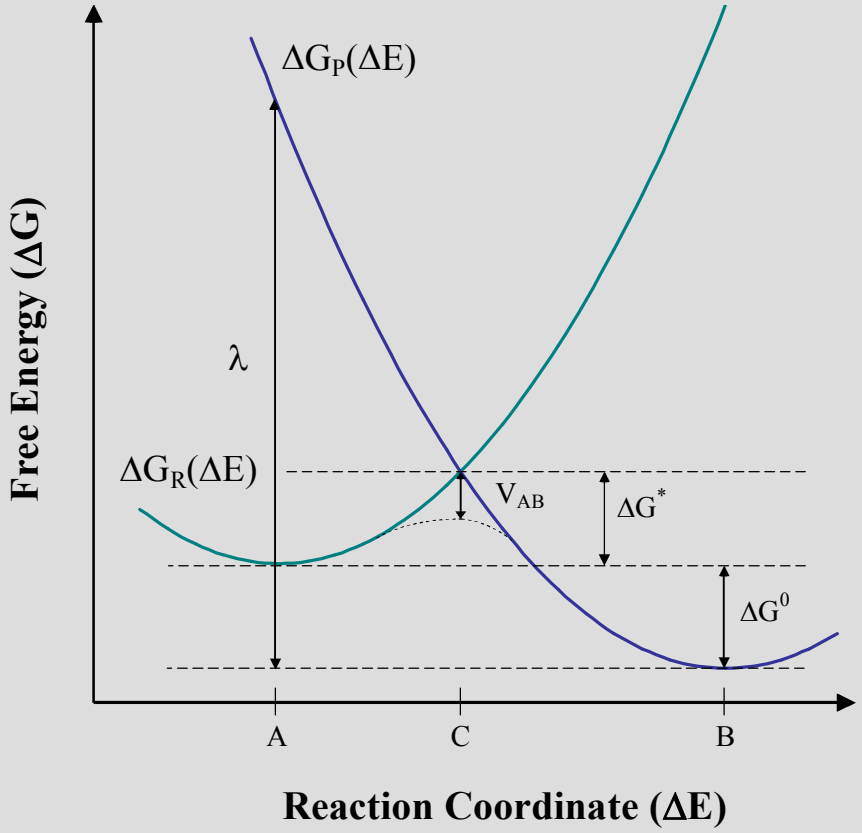
Buckingham Potential:

$$\phi(r_{ij}) = A_{ij} * \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}$$

[1]Dick and Overhauser *Phys. Rev.*, 112, 90, **1958**.

Approach to Compute the PES's: MD + Umbrella Sampling

300 Kelvin
λ_{TOTAL} is obtained directly



Run MD collecting configurations

ΔE is calculated for each configuration

$$\Delta G(\Delta E) = -RT \ln\left[\frac{P(\Delta E)}{P(\langle \Delta E \rangle)}\right]$$

As configurations with **ΔE~0 are rare**, umbrella sampling technique is used to obtained a complete distribution.

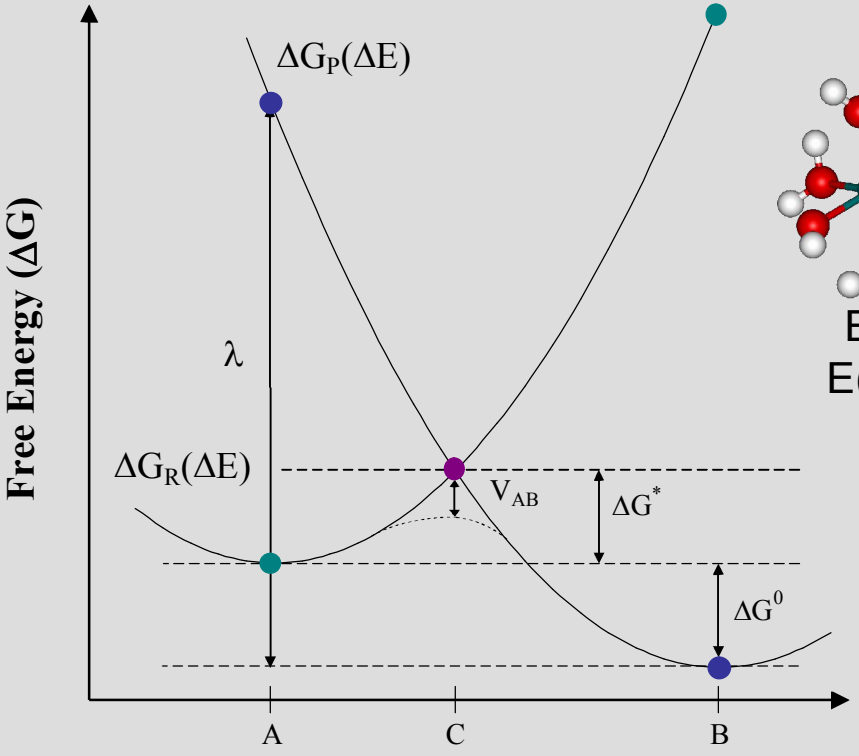
$$V_\theta = \theta V_A + (1-\theta) V_B$$

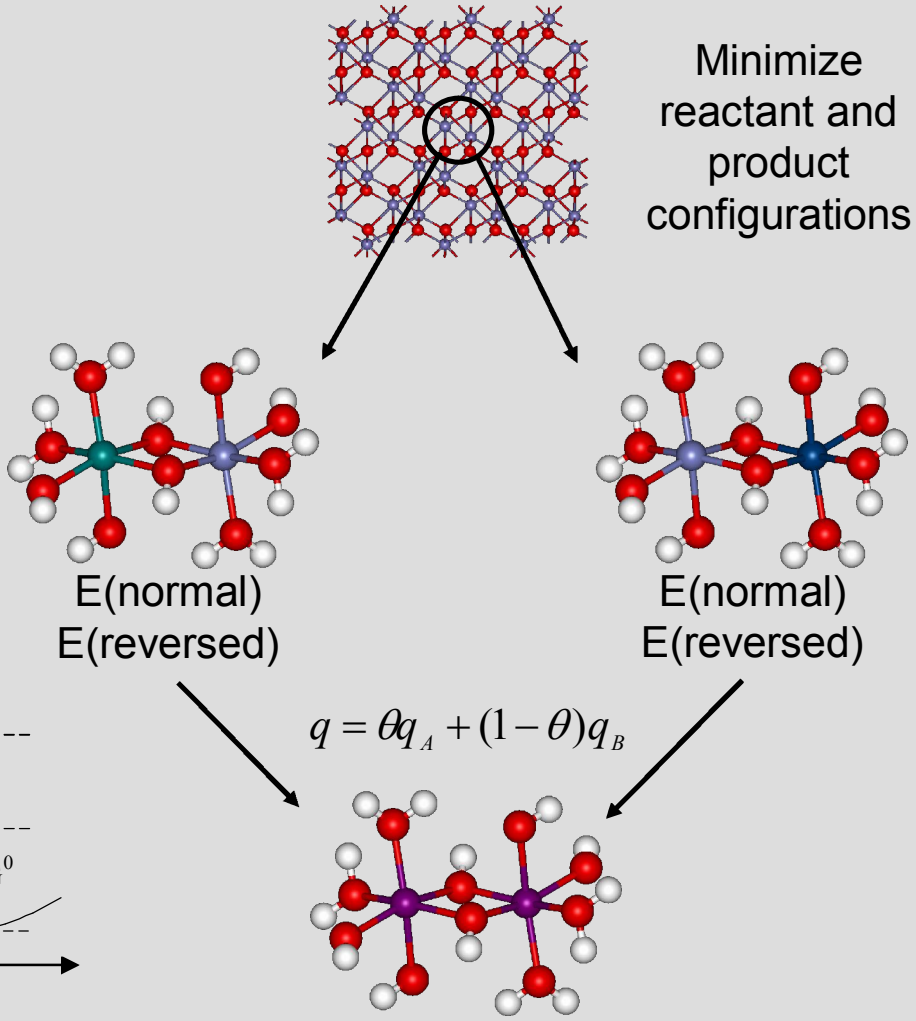
Calculations are carried out for several values of θ (from 0 to 1).

Kerisit and Rosso, JCP, *123*, 224712, **2005**

Approach for Computing the Electronic Coupling

Zero Kelvin – without ZPE
λ_I and λ_E obtained separately





{01.2} Hematite Surface - Hydrated

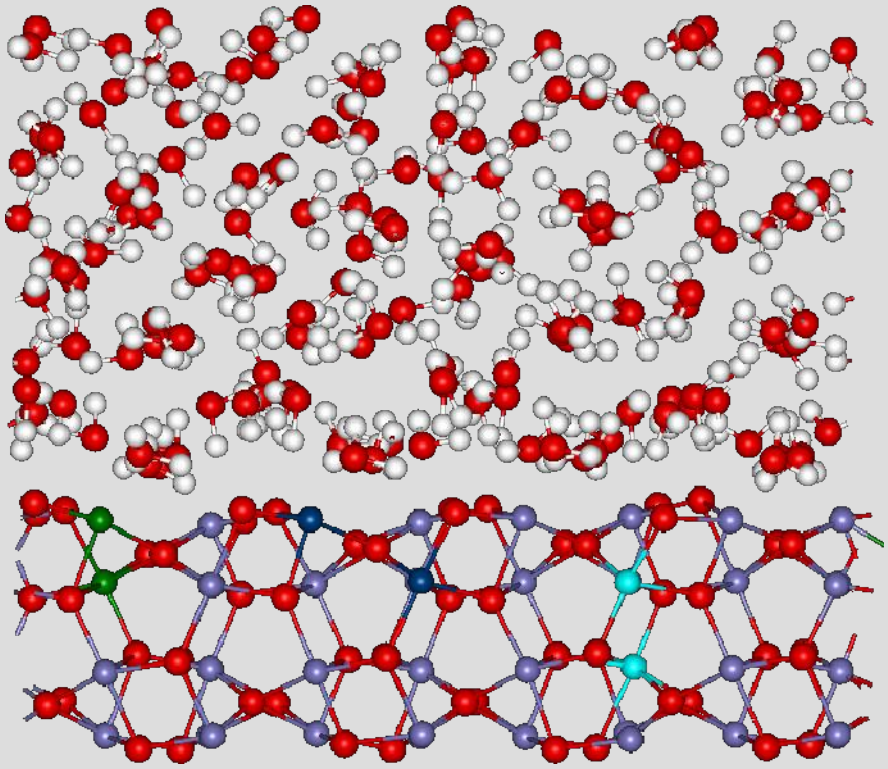
Lower activation energy at the surface

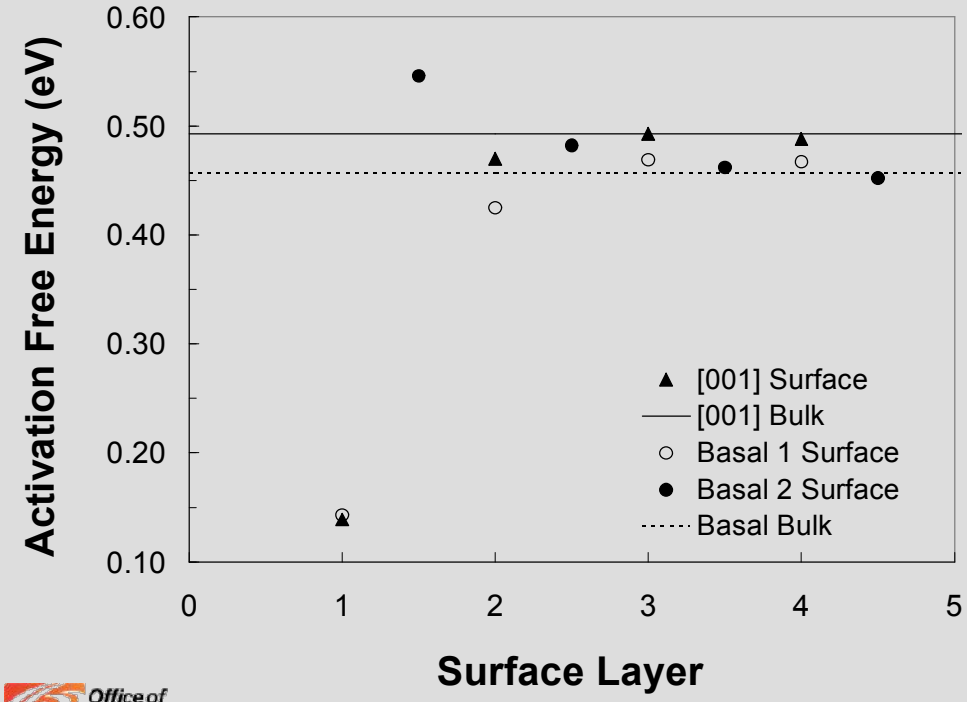
Great driving force at the surface

First interlayer transfer is uphill

Rapid convergence to bulk value

Water molecules: ~350
Water slab thickness: ~25 Å





Electron Transfer at the {01.2} Hematite Surface

LAYER 1

Direction	ΔG^0 (eV)	ΔG^* (eV)	V_{AB} (eV)	i	k_{et} (s^{-1})
Basal 1	-1.04	0.14	0.031	2	4.9E+11
Basal 2	0.20	0.55	0.184	1	1.5E+07
Basal (bulk)	0.00	0.46	0.184	3	1.5E+09
C direction	-1.07	0.14	0.028	1	2.5E+11
C dir. (bulk)	0.00	0.49	0.028	1	6.6E+07

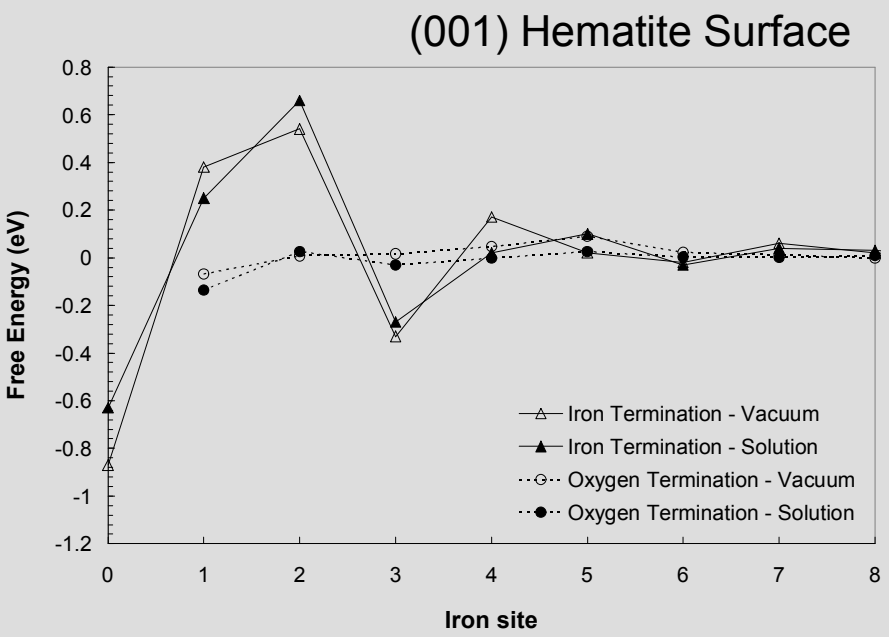
Summary of Hematite Surface Results

Water significantly affects the free energy when in direct contact with Fe(III) electron transfer centers and is able to from a short bond with the surface (*e.g.* (012) surface).

Different surfaces exhibit different behaviors due to different orientations.

Surface termination affects electron transfer some distance down into the surface.

Undercoordinated terminal iron atoms can act as electron traps at the surface.



Electrons migrate through the surface of hematite no slower than 10^7 s^{-1}.

The details of the mineral surface structure are critical for controlling the electron migration rate

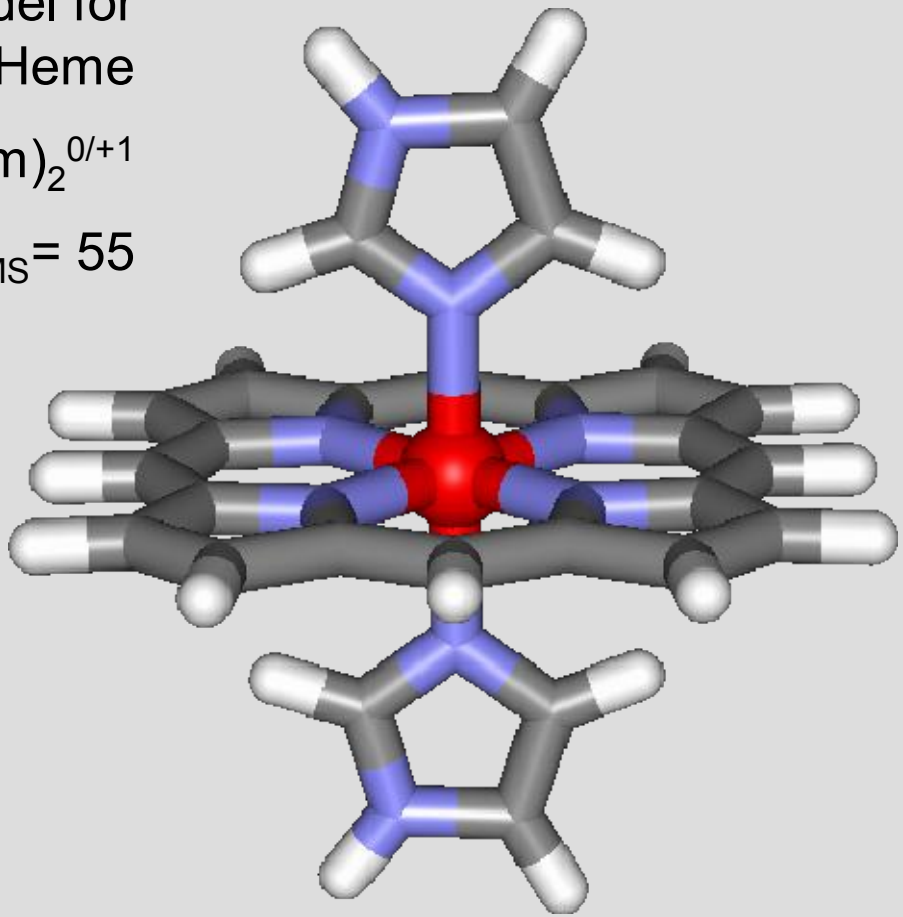
Kerisit and Rosso, GCA, in press.

Heme / Hematite Electron Transfer

Cluster model for
Bis(histidine) Heme

$FeP(Im)_2^{0/+1}$

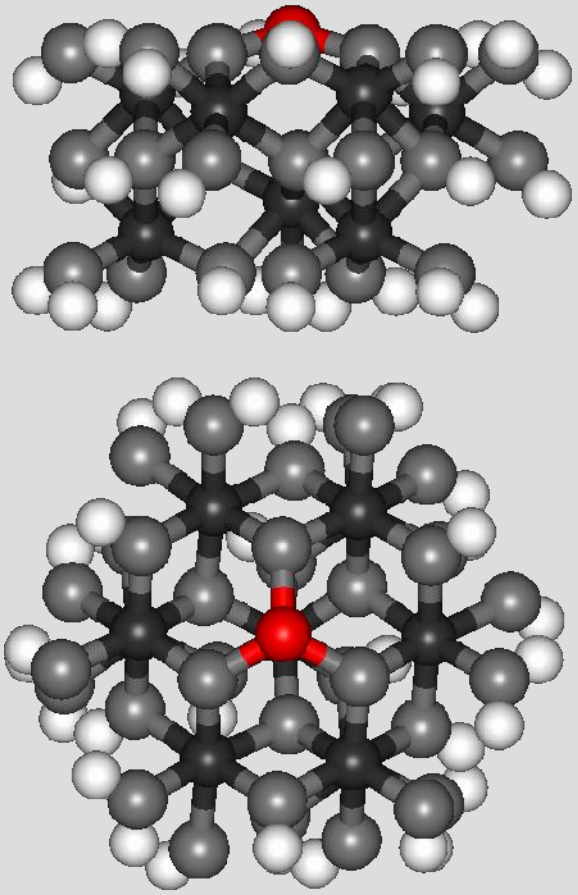
N_{ATOMS}= 55



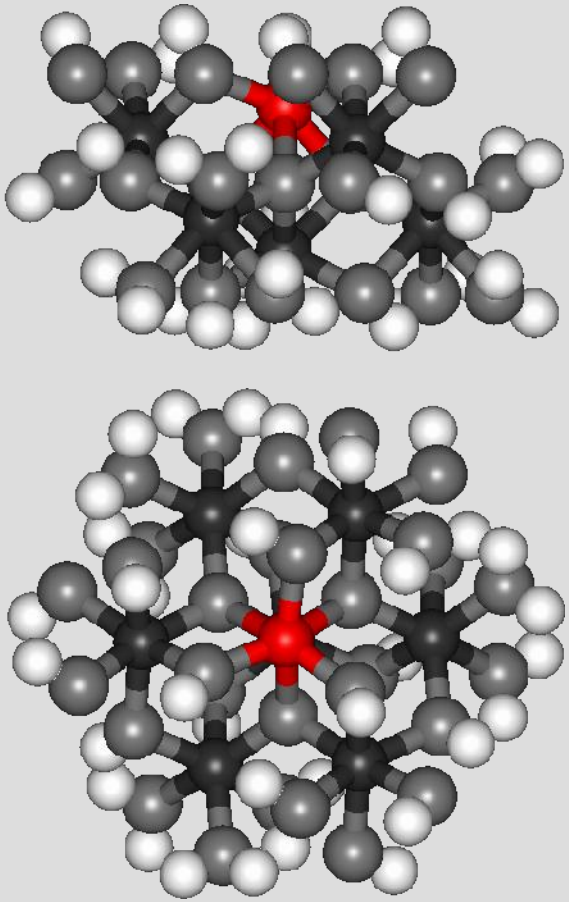
Heme / Hematite Electron Transfer

Hematite surface cluster models:

Iron Termination: $[Fe_{11}0_{33}H_{33}]^{0/-1}$

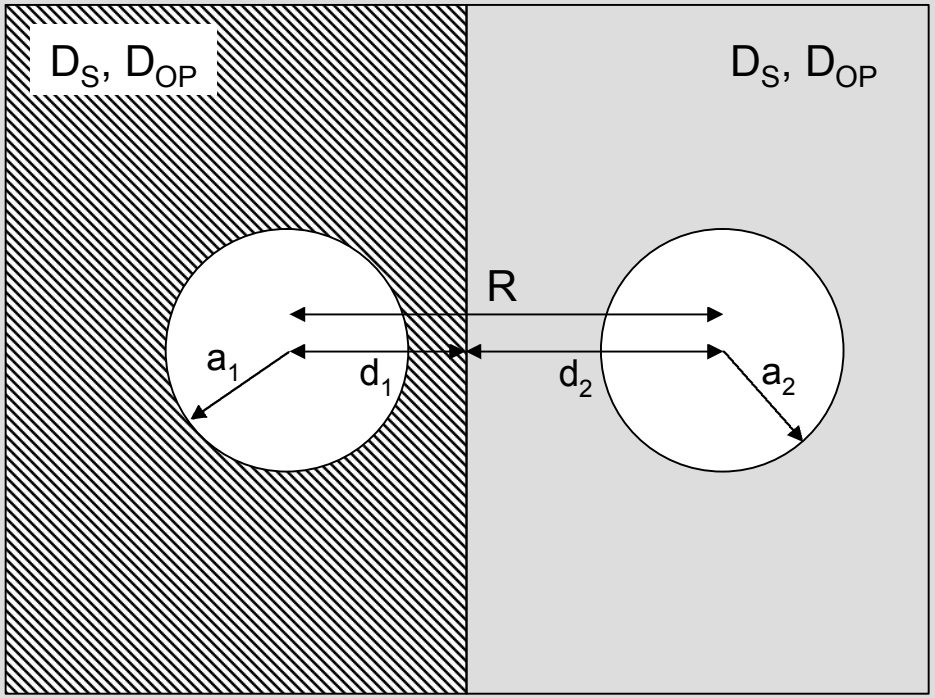


Hydroxyl Termination: $[Fe_80_{30}H_{36}]^{0/-1}$



Heme / Hematite Electron Transfer

Need a simple approach to simulate the repolarization behavior of the surrounding protein and mineral at the interface:



$$\lambda_{TOT.} = \lambda_{INT.} + \lambda_{EXT.}$$

External Part: Continuum Model

Marcus' equation for ET across interfaces*

$\lambda_{EXT.}$ = 0.46-0.71 eV (7-14 Å range)

$$\lambda_{TOT.} = 1.91\text{- }2.16 \text{ eV}$$

* Marcus JPC (1990)

Heme / Hematite Electron Transfer

Estimation of the Free Energy of Electron Transfer:

Heme operation potentials of OmcA from *S. Oneidensis*
-66 mV, -149 mV, -212 mV in 3:3:4 heme ratio
(B.J.N. Jepson et al.)

Flat band potential of hematite anodes in 2 M NaOH solution
-426 mV v NHE at pH 13.6
(Quinn et al. J. Mater. Res. Bull. *11*, 1011-1017, **1976**)

"59 mV per unit pH change"
(J.K. Leland and A.J. Bard J. Phys. Chem. *91*, 5076-5083, **1987**)

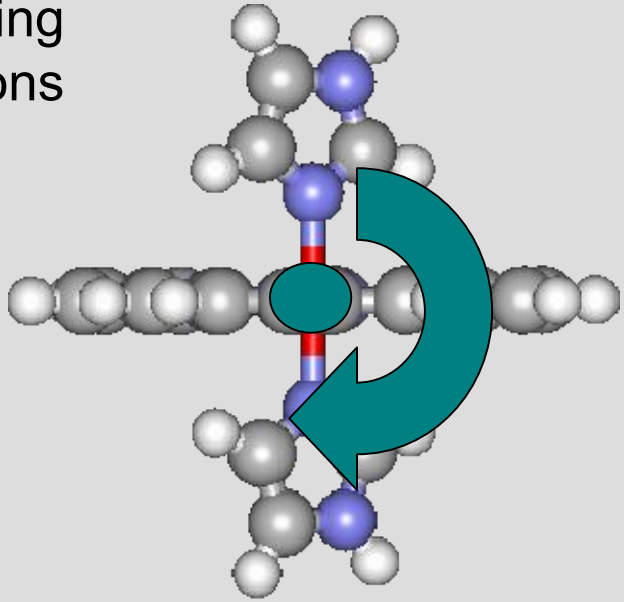
pH of point of zero charge of hematite ~ 8
(L. Cromieres et al. Colloids Surfaces A: Physicochem. Eng. Aspects *202*, 101-115, **2002**)

Hematite redox potential v NHE at pH_{PZC}= -95 mV

Free Energy of ET (Heme=>Hematite)	
Heme Potential (mV)	ΔG^0 (mV)
-66	29
-149	-54
-212	-117

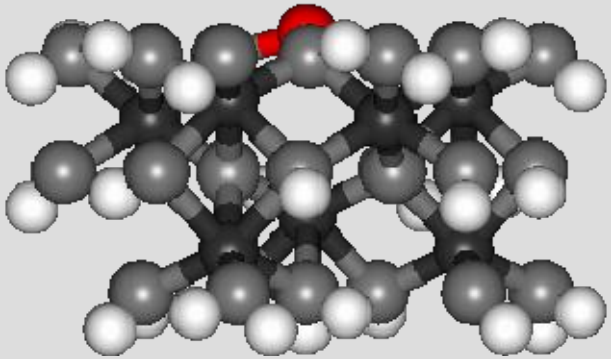
Heme / Hematite Electron Transfer

Electronic coupling calculations



0, 45 and 90°

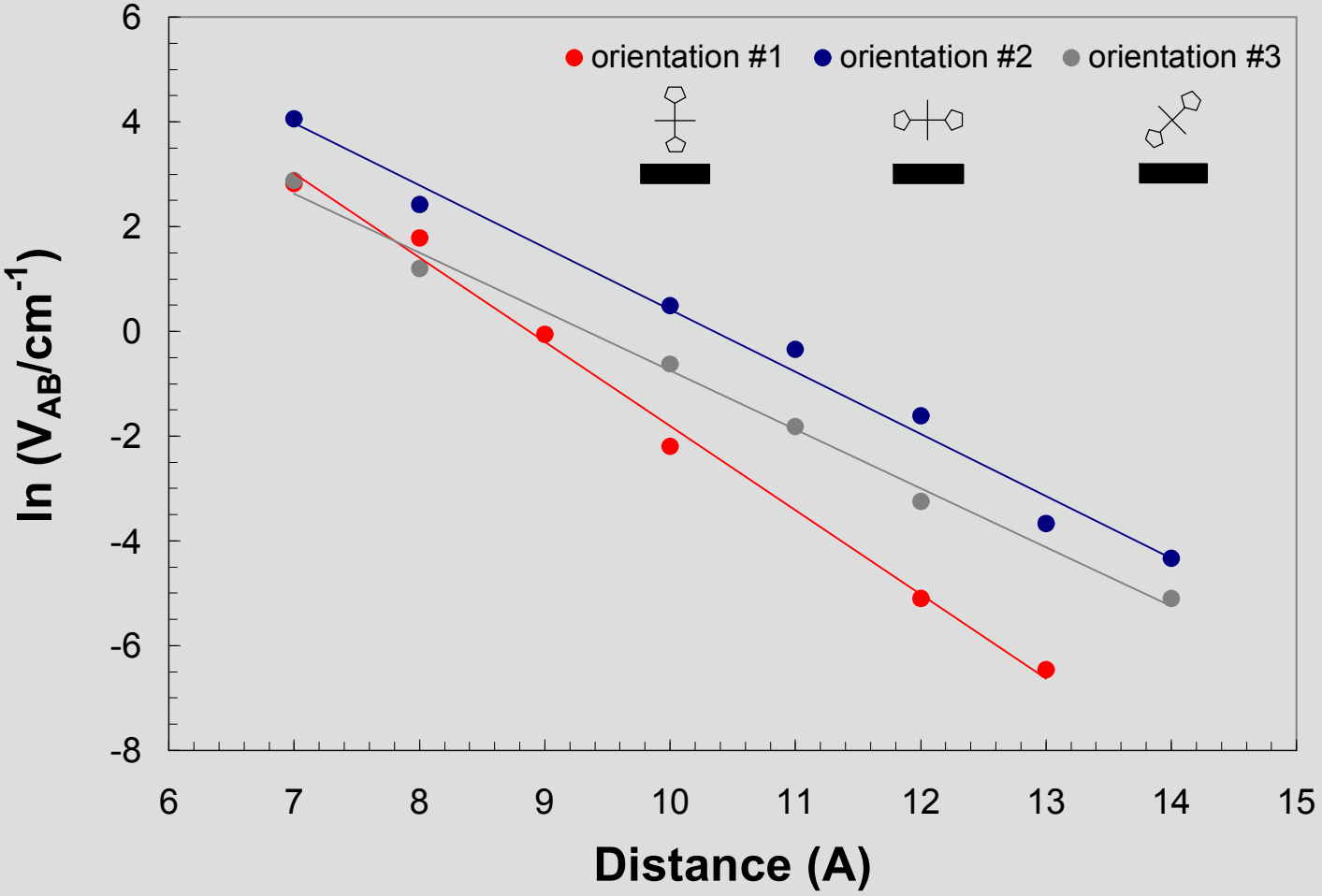
7 to 14 Å



NWChem
Unrestricted Hartree-Fock Level
Fe Ahlrichs VTZ
C,O,N,H 6-31G*
N_{ATOMS}= 129 or 132

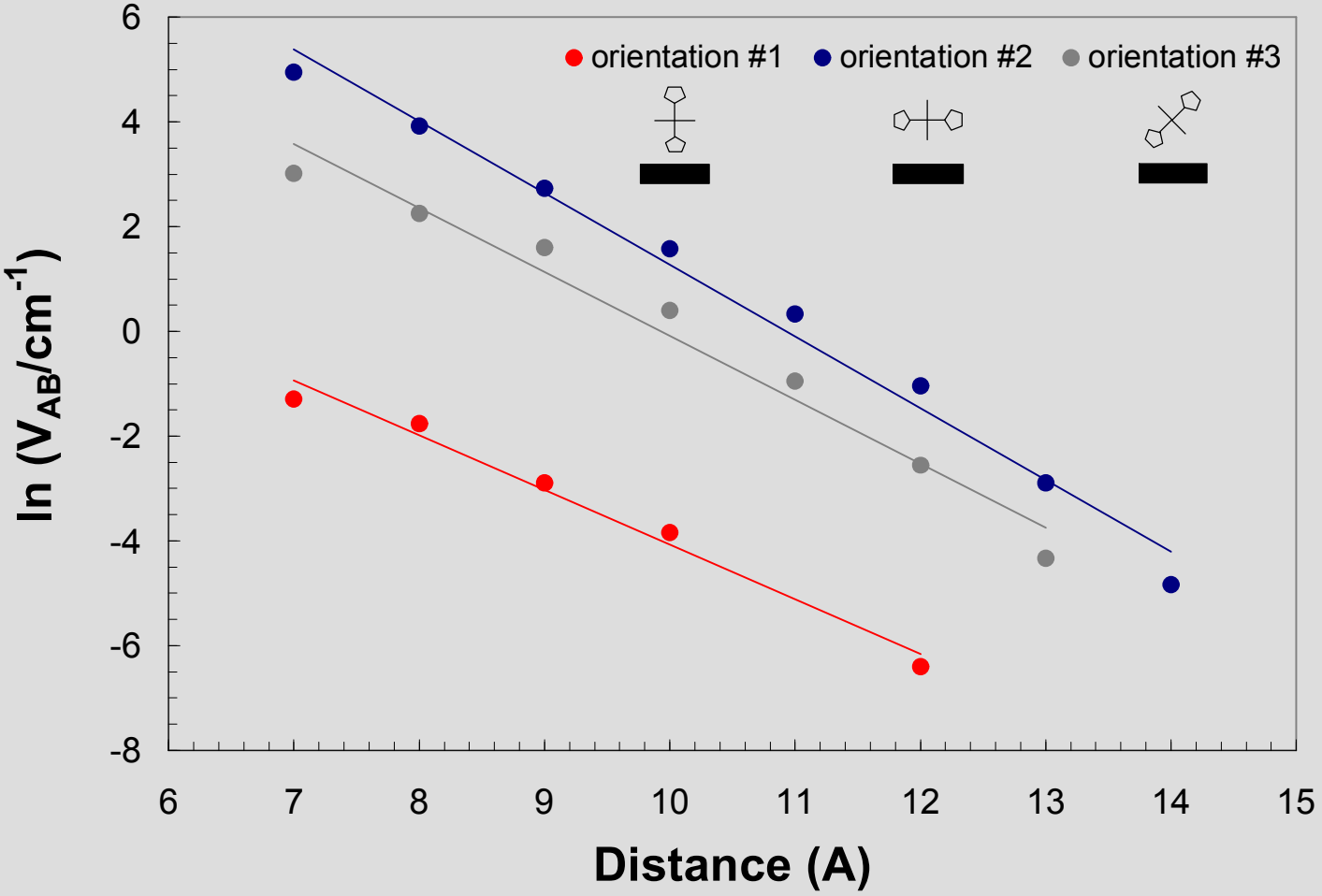
Heme / Hematite Electron Transfer

Hydroxylated hematite (001)



Heme / Hematite Electron Transfer

Fe-terminated hematite (001)



Heme / Hematite Electron Transfer

$$k_{ET} = \frac{2\pi}{\hbar}|V_{AB}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left\{-\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_B T}\right\}$$

Rate (s^{-1}) for ΔG^0 = -54 mV

Hematite (001) surface

Distance	Hydroxyl Termination			Iron Termination		
	1	2	3	1	2	3
7	1.5E+03	1.8E+04	1.7E+03	4.0E-01	**1.0E+05**	2.2E+03
8	9.8E+01	3.5E+02	3.1E+01	8.1E-02	**7.0E+03**	2.5E+02
9	1.5E+00	1.3E+01	7.6E-01	5.1E-03	**4.0E+02**	4.1E+01
10	1.4E-02	3.1E+00	3.3E-01	5.3E-04	**2.7E+01**	2.6E+00
11	-	4.3E-01	2.3E-02	-	**1.7E+00**	1.3E-01

Heme / Hematite Summary

Electronic coupling is weak except at very short distances.

Electron transfer is fastest when the edge of the porphyrin ring is orientated towards the surface.

The electron transfer rate decays an order of magnitude with every Å increase in distance.

Surface termination affects the rate: for most orientations, electron transfer is faster for Fe-termination.

Delivery of electrons to the hematite surface is slower than electron migration through the surface.

More protein-specific information is needed to select conditions appropriate for comparison with experimental results.

Current Directions – KMC Models

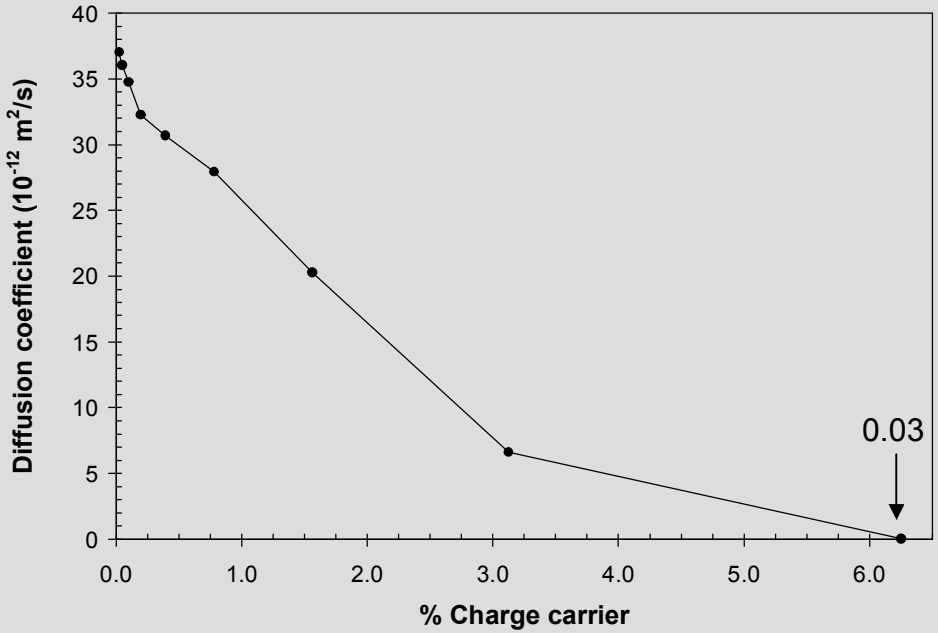
Effect of charge carrier concentration

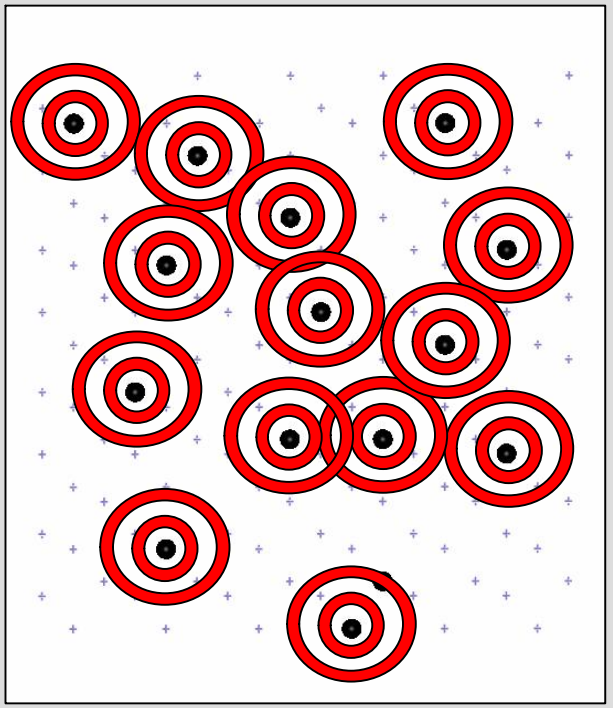
1,000,000 KMC steps - 3D periodic boundary conditions

Temperature = 300 K

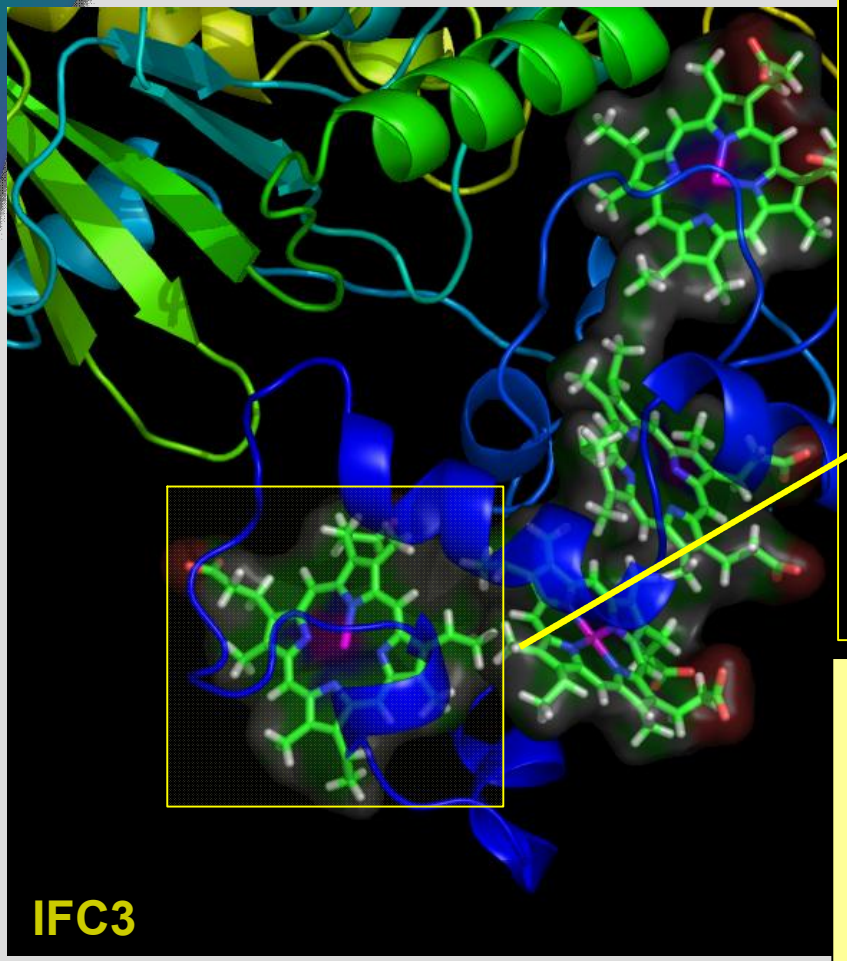
4096 iron sites: 1, 2, 4, 8, 16, 32, 64,128 and 256 charge carriers

$$k_{et} = \upsilon_n \exp\left(-\frac{(\lambda + \Delta G^0)^2 / 4\lambda - V_{AB}}{k_B T} \right)$$

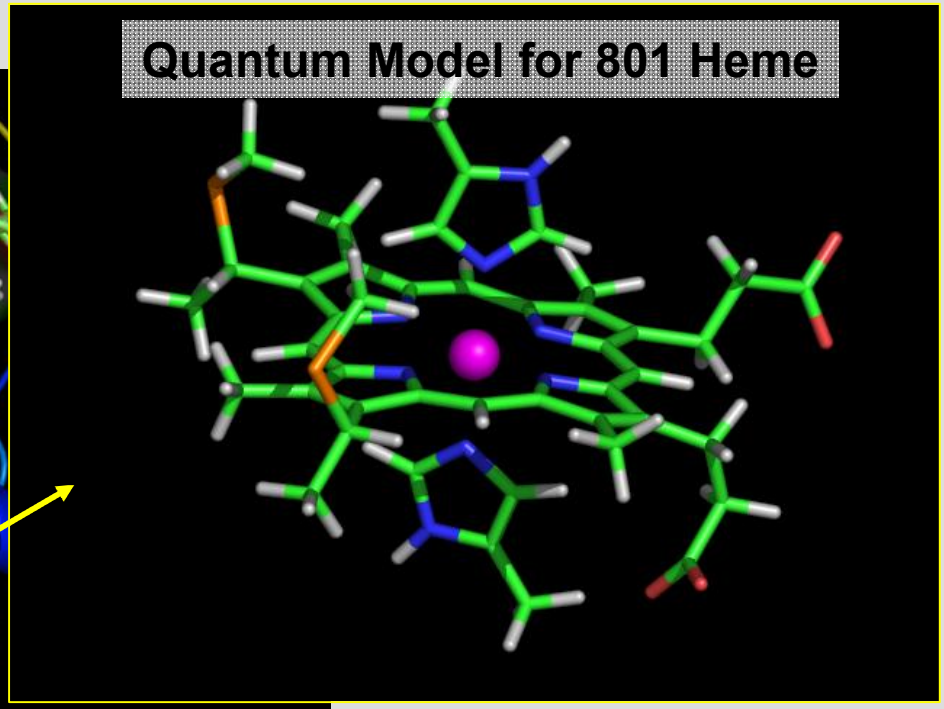




Current Directions – Heme Environment



IFC3 – flavin domain → STC



- NWChem QM/MM module (M. Valiev)
- QM region - 109 atoms (DFT/B3LYP)
- MM region ~ 77000 atoms
- Separate calculation for each of four hemes
- Structural and electronic properties
- Redox potentials
- IR spectra, ….