Non-Born-Oppenheimer Effects Between Electrons and Protons

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Key Challenge

Standard electronic structure packages
-    treat nuclei as classical point charges
-    invoke the Born-Oppenheimer separation between nuclei and electrons, where electrons respond instantaneously to nuclear motion

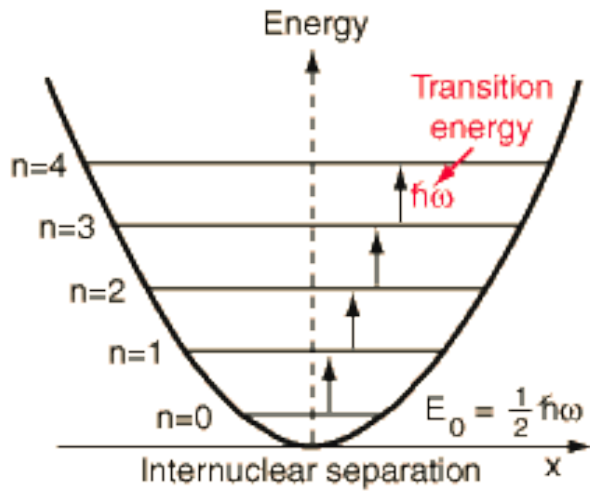$$H\Psi(\mathbf{r}^e; \mathbf{r}^c) = E(\mathbf{r}^c)\Psi(\mathbf{r}^e; \mathbf{r}^c)$$

$\mathbf{r}^e$: electron coordinates (quantum)

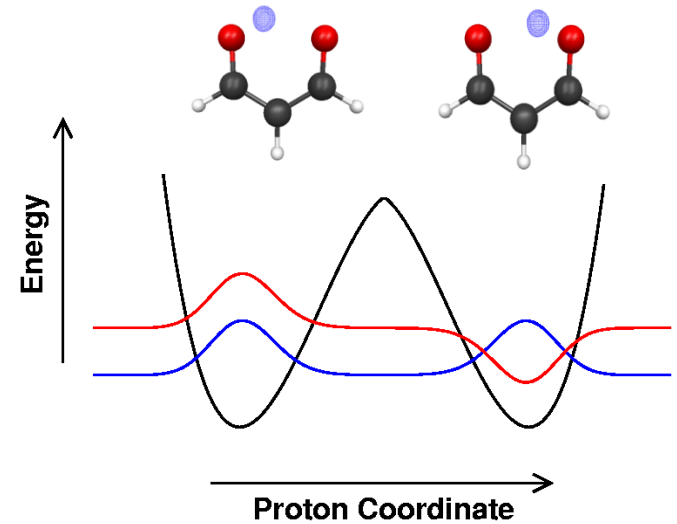$\mathbf{r}^c$: nuclear coordinates (classical point charges)

Key Challenge:
Include nuclear quantum effects and non-Born-Oppenheimer effects between select nuclei and electrons in electronic structure calculations
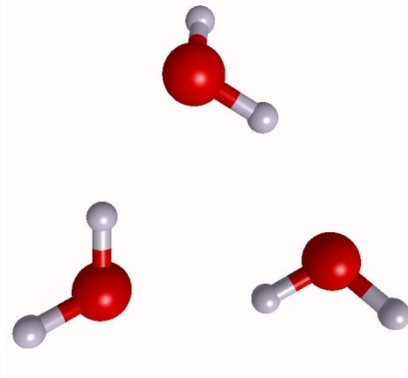
Nuclear Quantum Effects

Zero point energy
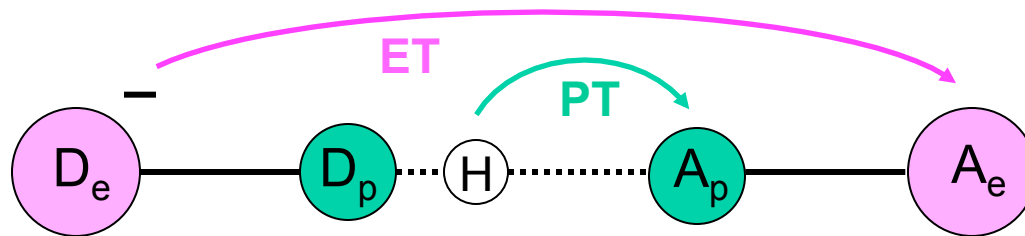Vibrationally excited states

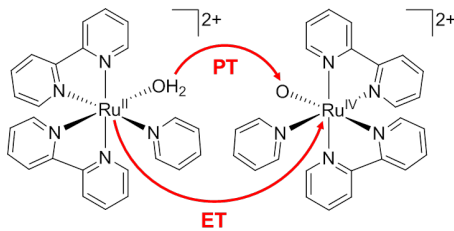Hydrogen tunneling

Hydrogen bonding

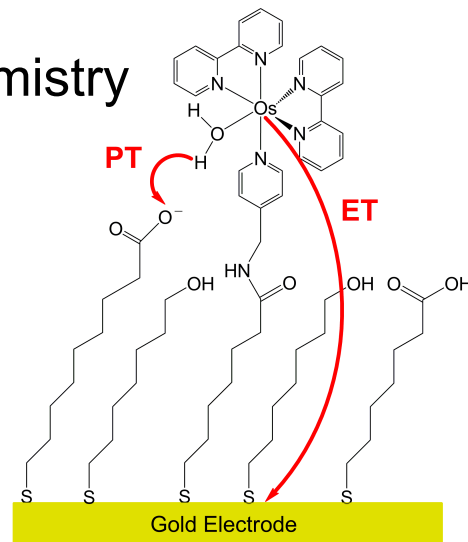# Non-Born-Oppenheimer Effects

Proton-coupled electron transfer (PCET)

- Electrons and transferring proton behave quantum mechanically
- Hydrogen tunneling important
- Non-Born-Oppenheimer effects significant (nonadiabatic)
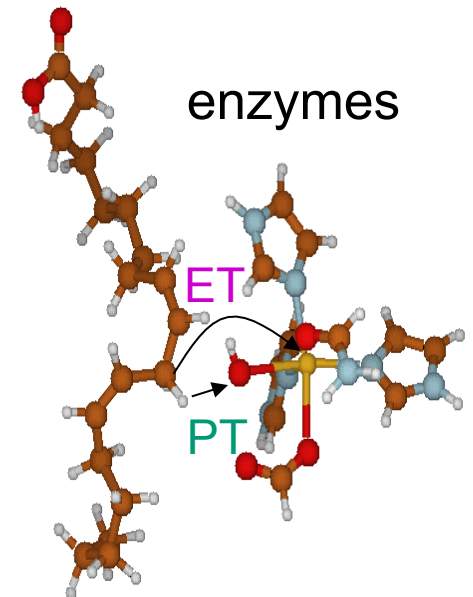- Proton tunneling time can be faster than electronic transition time

solution

electrochemistry

enzymes

Soudackov and SHS, JPC B 2008

Significance of PCET

- Biological processes: photosynthesis, respiration, enzymes
- Chemical processes: fuel cells, solar cells, energy devices

Photosynthesis
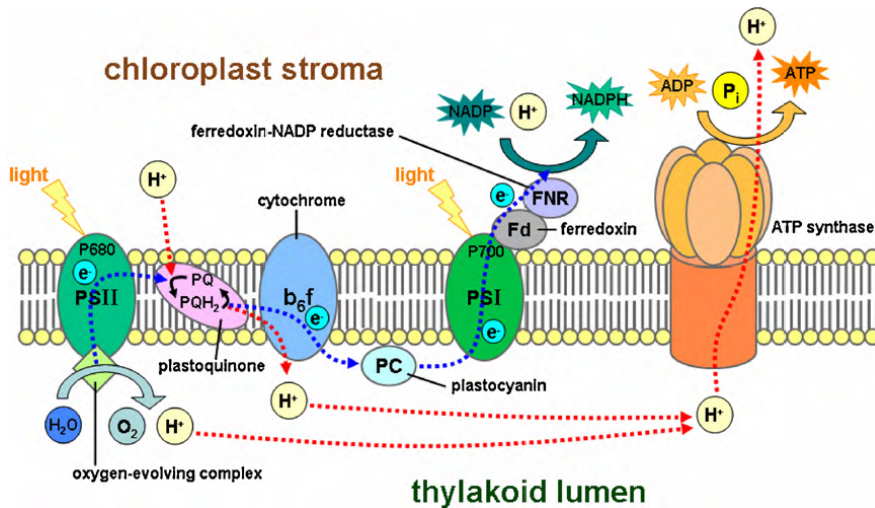
Class I Ribonucleotide Reductase

Stubbe group: http://web.mit.edu/biochemistry/research.htm
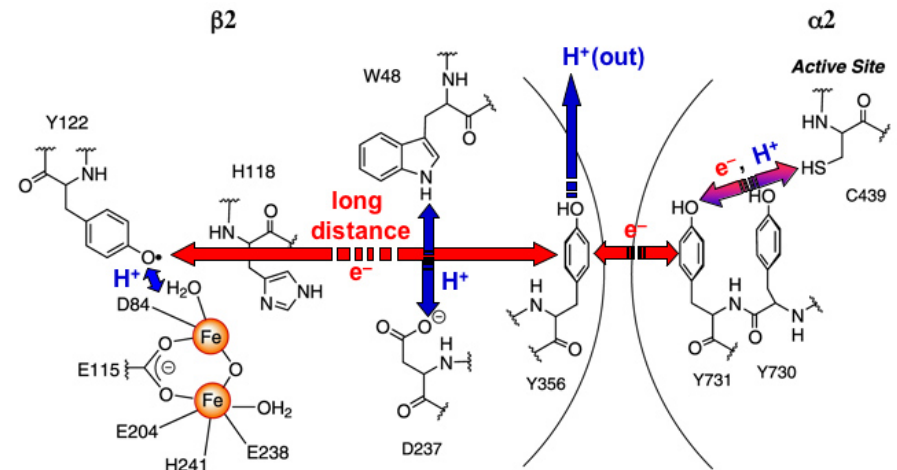
Cukier, Nocera, Meyer, Hammarström, Stuchebrukhov, Mayer, Borden, Martinez, Jordan, Batista, Costentin, Savéant, Robert, Petek, Klinman, Finklea, Sevilla, Siegbahn, Stubbe, Roth, Gray, Dubois, Bullock, Dupuis, Muckerman, Bollinger, Darensbourg, Krylov, Kubiak, Carter, Bocarsly …

Energy Storage and Delivery Systems
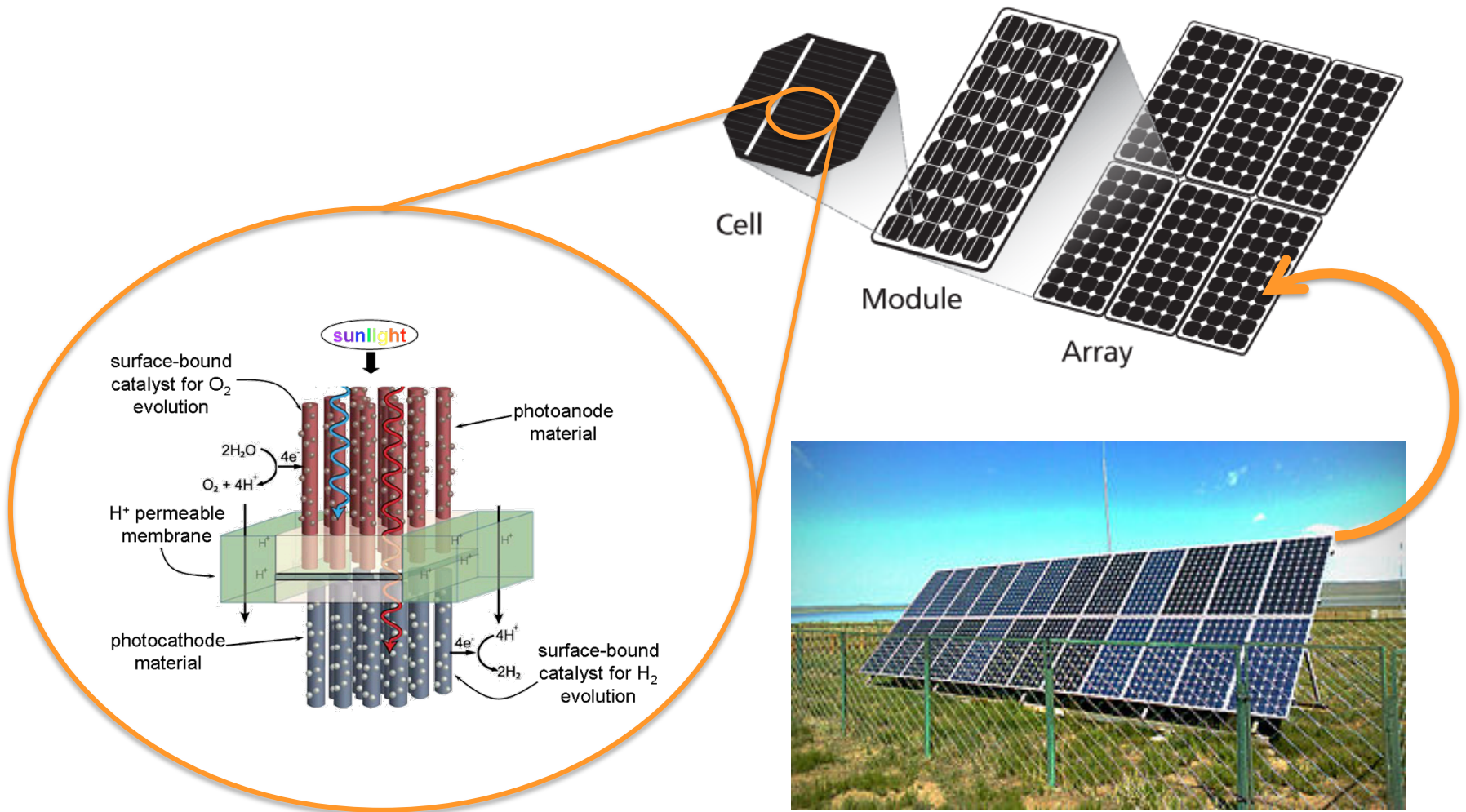
Solar Fuel Generation
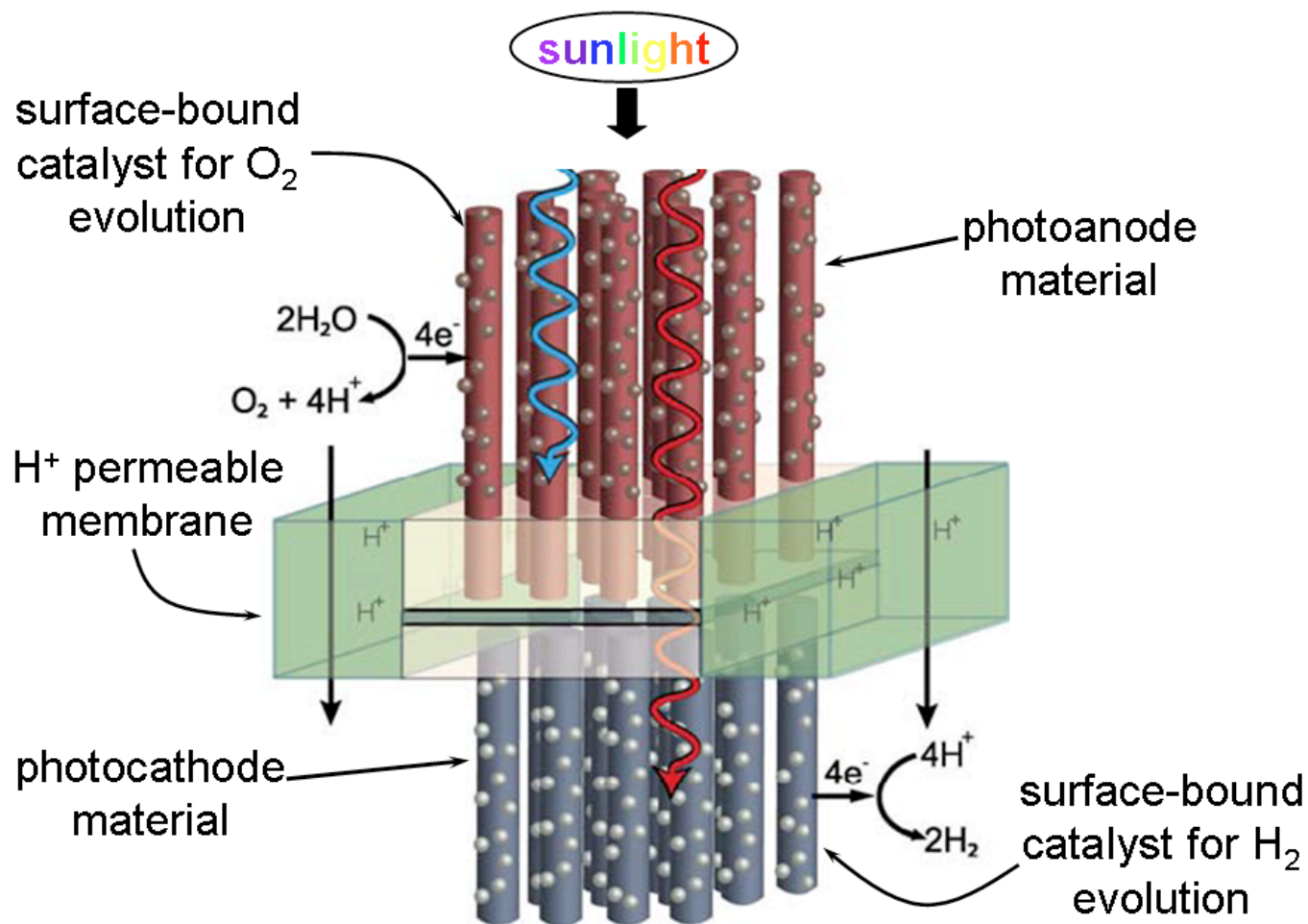
Molecular Electrocatalysis

- Design molecular electrocatalysts for H_2 production and oxidation
- Objective: high turnover frequency, low overpotential
- Environmentally friendly, cost effective, earth abundant
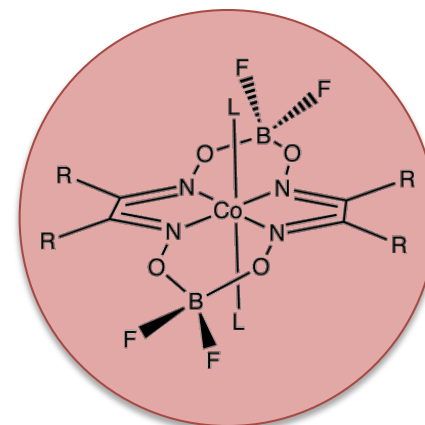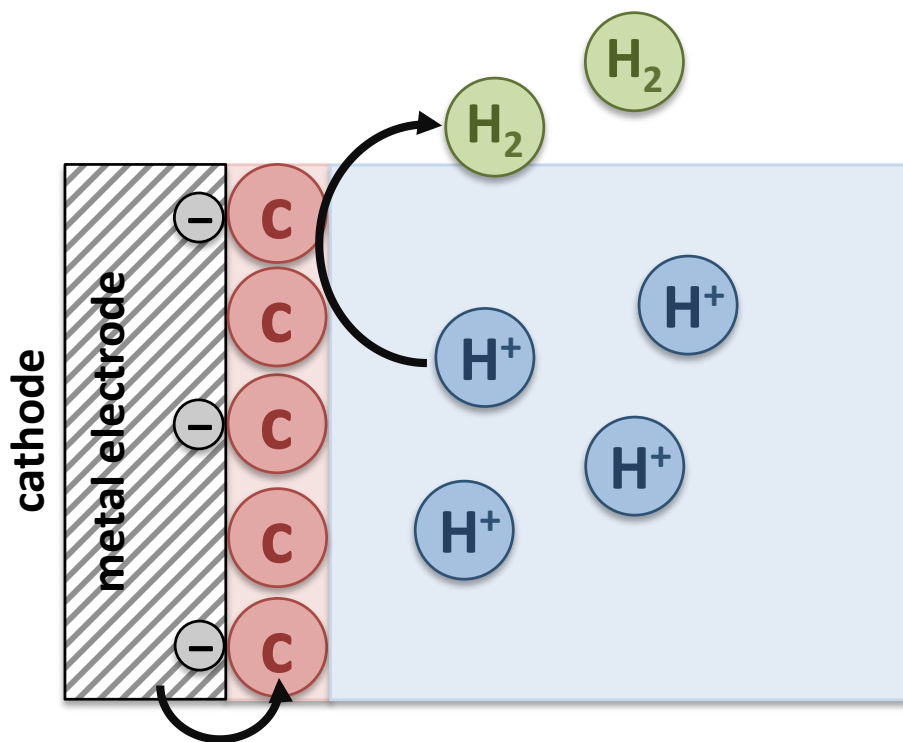
PCET Theory

Soudackov and SHS, JCP 2000; Soudackov, Hatcher, SHS, JCP 2005

Collective solvent coordinate
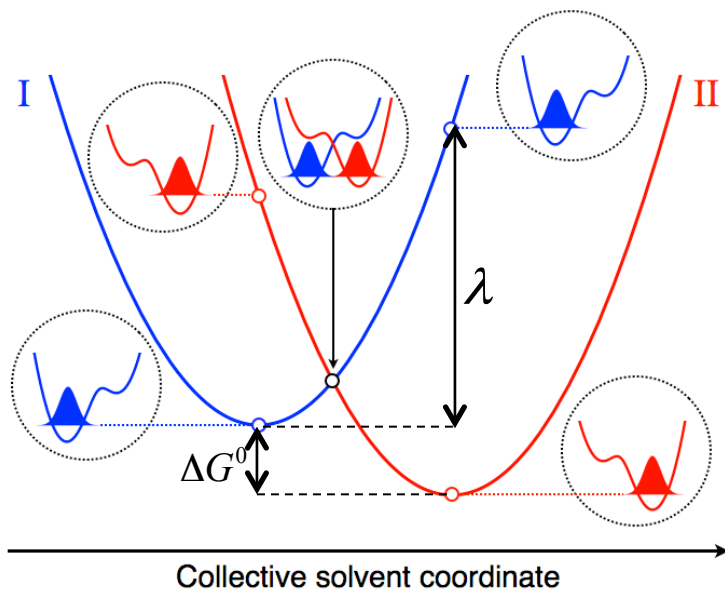
- Treat H nucleus quantum mechanically
- Typically PCET reactions nonadiabatic
- Use Golden Rule to derive rate constants

Reactant D⁻   A
Product D   A⁻
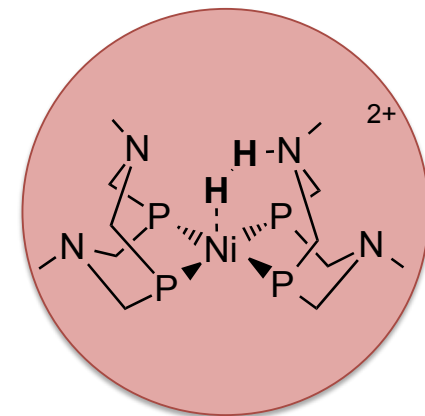
$$k = \frac{2\pi}{h} \sum_{\mu} P_{\mu}^{I} \sum_{\nu} \left(4\pi\lambda k_B T\right)^{-1/2} \left|V_{\mu\nu}\right|^2 \exp\left[-\Delta G_{\mu\nu}^{\dagger}\Big/(k_B T)\right]$$

$$\Delta G_{\mu\nu}^{\dagger} = \left(\Delta G_{\mu\nu}^0 + \lambda\right)^2 \Big/ (4\lambda) \qquad V_{\mu\nu} = \left\langle \Phi^{I}\left(\mathbf{r}^e, \mathbf{r}^p\right) \left| \hat{H} \right| \Phi^{II}\left(\mathbf{r}^e, \mathbf{r}^p\right)\right\rangle$$

Non-Born-Oppenheimer methods needed to calculate input quantities

Nuclear-Electronic Orbital (NEO) Method

- NEO method avoids Born-Oppenheimer separation between electrons and select quantum nuclei
- Treat specified nuclei quantum mechanically on same level as electrons
  - treat only key H nuclei QM
  - retain at least two classical nuclei
- Solution of mixed nuclear-electronic time-independent Schrödinger equation with molecular orbital methods

$\mathbf{r}^p$: quantum proton

$\mathbf{r}^c$: all other nuclei
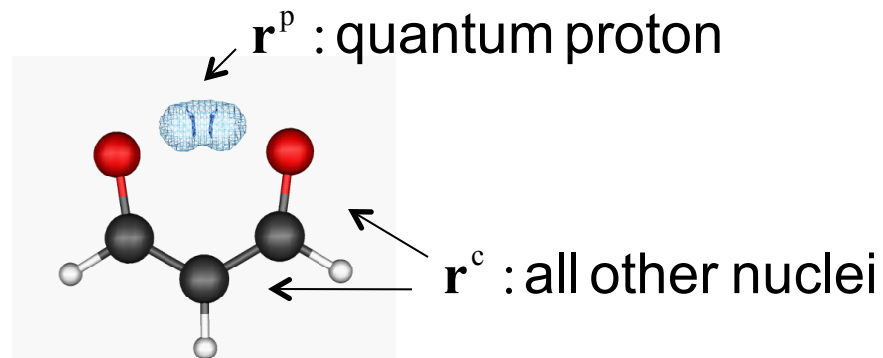
Nuclear-Electronic Hamiltonian

$$H_{\mathrm{NEO}} = -\frac{1}{2}\sum_i^{N_e}\nabla_i^2 - \sum_i^{N_e}\sum_A^{N_c}\frac{Z_A}{|\mathbf{r}_i^e - \mathbf{r}_A^c|} + \sum_{i>j}^{N_e}\frac{1}{|\mathbf{r}_i^e - \mathbf{r}_j^e|} \qquad \text{Electronic terms}$$

$$-\frac{1}{2m_p}\sum_{i'}^{N_p}\nabla_{i'}^2 + \sum_i^{N_p}\sum_A^{N_c}\frac{Z_A}{|\mathbf{r}_{i'}^p - \mathbf{r}_A^c|} + \sum_{i'>j'}^{N_p}\frac{1}{|\mathbf{r}_{i'}^p - \mathbf{r}_{j'}^p|} \qquad \text{Nuclear terms}$$

$$-\sum_{i'}^{N_p}\sum_i^{N_e}\frac{1}{|\mathbf{r}_i^e - \mathbf{r}_{i'}^p|} \qquad \text{Nuclear-Electronic interaction term}$$

N_e, N_p, N_c Number of electrons, quantum nuclei, and classical nuclei

$\mathbf{r}_i^e, \mathbf{r}_{i'}^p, \mathbf{r}_A^c$ Coordinates of electrons, quantum nuclei, and classical nuclei

$$H_{\mathrm{NEO}}\Psi_{\mathrm{tot}}(\mathbf{r}^e, \mathbf{r}^p; \mathbf{r}^c) = E_{\mathrm{NEO}}(\mathbf{r}^c)\Psi_{\mathrm{tot}}(\mathbf{r}^e, \mathbf{r}^p; \mathbf{r}^c)$$

NEO-HF (Hartree-Fock)

- HF wavefunction

$$\Psi_{tot}(\mathbf{r}^e, \mathbf{r}^p) = \Phi_0^e(\mathbf{r}^e)\Phi_0^p(\mathbf{r}^p) \qquad \Phi_0^e, \Phi_0^p : \text{Slater determinants}$$

- HF energy

$$E = \left\langle \Phi_0^e(\mathbf{r}^e)\Phi_0^p(\mathbf{r}^p) \left| H_{NEO} \right| \Phi_0^e(\mathbf{r}^e)\Phi_0^p(\mathbf{r}^p) \right\rangle$$

- Expand electronic, nuclear MO's in Gaussian basis sets
- Minimize energy with respect to electronic and nuclear MO's

  → HF-Roothaan equations for electrons and quantum protons

Problem: Inadequate treatment of electron-proton correlation
- Proton orbitals much too localized
- H vibrational frequencies much too high, impacts all properties

Electron-Proton Correlation: NEO-XCHF

Swalina, Pak, Chakraborty, SHS, JPCA 2006

$$\Psi^{\mathrm{XCHF}}\left(\mathbf{x}^{\mathrm{e}}, \mathbf{x}^{\mathrm{p}}\right) = \Phi^{\mathrm{e}}\left(\mathbf{x}^{\mathrm{e}}\right)\Phi^{\mathrm{p}}\left(\mathbf{x}^{\mathrm{p}}\right)\left\{1 + \sum_{i=1}^{N_{\mathrm{e}}}\sum_{j=1}^{N_{\mathrm{p}}} g\left(\mathbf{r}_i^{\mathrm{e}}, \mathbf{r}_j^{\mathrm{p}}\right)\right\}$$

Gaussian-type geminals: $\quad g\left(\mathbf{r}_i^{\mathrm{e}}, \mathbf{r}_j^{\mathrm{p}}\right) = \sum_{k=1}^{N_{\mathrm{gem}}} b_k \exp\left[-\gamma_k \left|\mathbf{r}_i^{\mathrm{e}} - \mathbf{r}_j^{\mathrm{p}}\right|^2\right]$

- Gaussian-type geminals for electron-proton correlation
- b_k and γ_k are constants pre-determined from models
- Variational method: minimize total energy wrt molecular orbital coefficients → Modified Hartree-Fock equations, solve iteratively to self-consistency

Advantage: provides accurate nuclear wavefunctions
Disadvantage: computationally expensive

Paradigm Shift: NEO-RXCHF

Sirjoosingh, Pak, Swalina, SHS, JCP 2013

- NEO-XCHF correlates all electrons to quantum nucleus via same set of geminal functions

- NEO-RXCHF correlates a subset of electronic orbitals
  - dramatic increase in computational tractability
  - enhanced accuracy: molecular orbitals optimized for relevant interaction

Examples
  - Positronic systems: couple positron to one electron to represent positronium → accurate densities and annihilation rates

  - PCET: couple relevant electronic orbitals on donor, acceptor, and transferring H to the transferring H nucleus
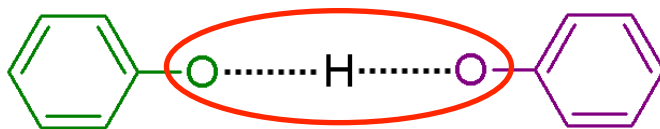
Scaling of NEO Methods

- **Bottleneck:** large number of 2-, 3-, 4-, and 5-particle integrals that are matrix elements of the explicitly correlated wavefunction over the mixed nuclear-electronic Hamiltonian

$$\left\langle \chi^p(p)\chi_a^e(1)\chi_b^e(2)\chi_1^e(3)\chi_c^e(4)\left|\frac{g(3,p)g(4,p)}{r_{12}}\right|\chi^p(p)\chi_c^e(1)\chi_a^e(2)\chi_b^e(3)\chi_1^e(4)\right\rangle$$

- N_{ebf}: number of electronic basis functions
  N_{pbf}: number of nuclear (proton) basis functions

- Scaling of NEO-XCHF: $(N_{ebf})^8(N_{pbf})^2$

- Scaling of NEO-RXCHF for two coupled orbitals: $(N_{ebf})^6(N_{pbf})^2$

- Scaling will be alleviated somewhat by using restricted basis sets for coupled electronic orbitals

- Still requires substantial computational resources

Unique Attributes of Blue Waters

- Calculations require a large number of processors and a substantial amount of memory
- Main computational expense: multiparticle integrals that must be calculated and stored in memory or on disk
- Integrals can be calculated independently from one another → embarrassingly parallelizable
- Hybrid MPI/OpenMP: obviates the need to store all integrals on a single node; instead partitions calculation and storage across nodes
- Blue Waters provides capability of splitting large number of calculations and storage requirements over **many** nodes
- Our in-house code has demonstrated excellent scaling → maximally benefit from using **large number of nodes simultaneously**
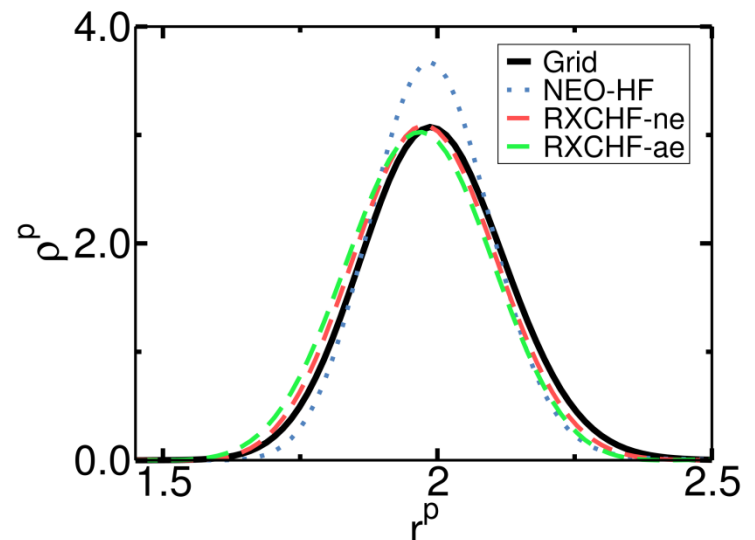
NEO-RXCHF on HCN

- Hydrogen cyanide (HCN)
  - 14 electrons, 1 quantum proton
  - 2 coupled electronic spin orbitals
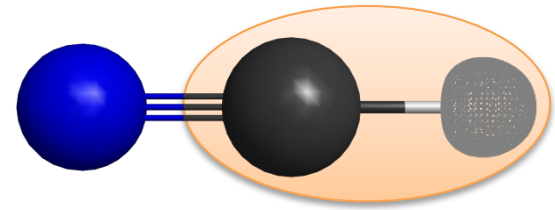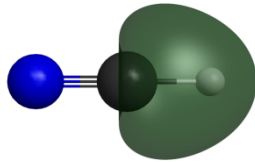
- NEO-RXCHF successfully captures nuclear density profile
  and associated CH stretching frequency

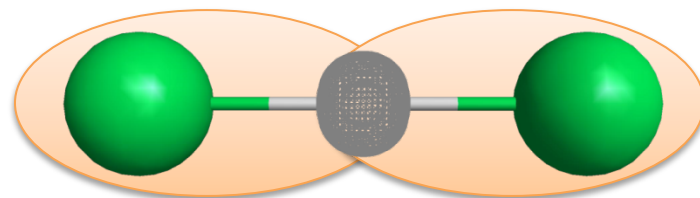|	Stretching Frequency (cm^{-1})
NEO-HF	5077
RXCHF-ne	3604
RXCHF-ae	3476
Grid	3544

Grid: benchmark
NEO-HF: Hartree-Fock, mean field
RXCHF: ne and ae denote different approximations for electron exchange

NEO-RXCHF on FHF⁻

- FHF⁻ (bihalide anion)

  - 20 electrons, 1 quantum proton

  - 4 coupled electronic spin orbitals


- Amount of integrals to calculate and store

  - 2-particle integrals: 1.9 MB

  - 3-particle integrals: 720 MB

  - 4-particle integrals: 310 GB

  - 5-particle integrals: 67 TB

- Calculations in progress on Blue Waters

  - Integral calculation and storage manageable with ~4096 MPI procs

  - Algorithmic developments to decrease cost

Summary

- NEO method incorporates nuclear quantum effects and non-Born-Oppenheimer effects between electrons and select protons
- Explicitly correlated wavefunctions with geminal functions are accurate but computationally expensive
- Bottleneck is calculation and storage of multiparticle integrals
- Blue Waters is allowing us to address this challenge
- Current applications to molecular systems with protons are in progress, and preliminary results are promising
- Algorithmic developments to decrease cost in progress
- Future directions: use multiconfigurational NEO methods to study non-Born-Oppenheimer systems, such as PCET reactions

Acknowledgments
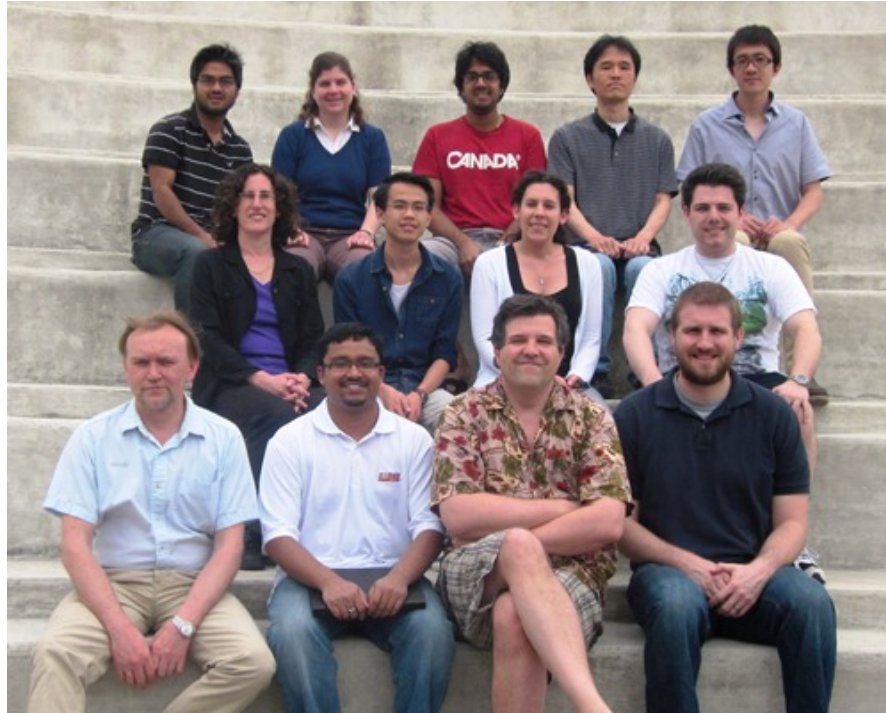
Simon Webb, Tzvetelin Iordanov, Chet Swalina, Mike Pak, Jonathan Skone, Arindam Chakraborty, Anirban Hazra, Ben Auer, Chaehyuk Ko, Andrew Sirjoosingh