

Non-Born-Oppenheimer Effects Between Electrons and Protons

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Computer time:

Blue Waters

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

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

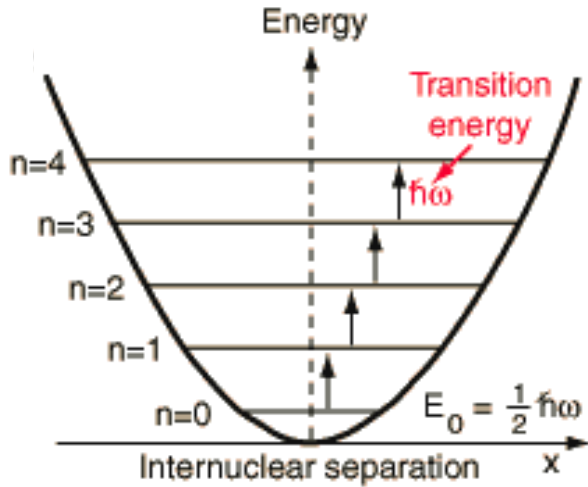
\mathbf{r}^e : electron coordinates (quantum)

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

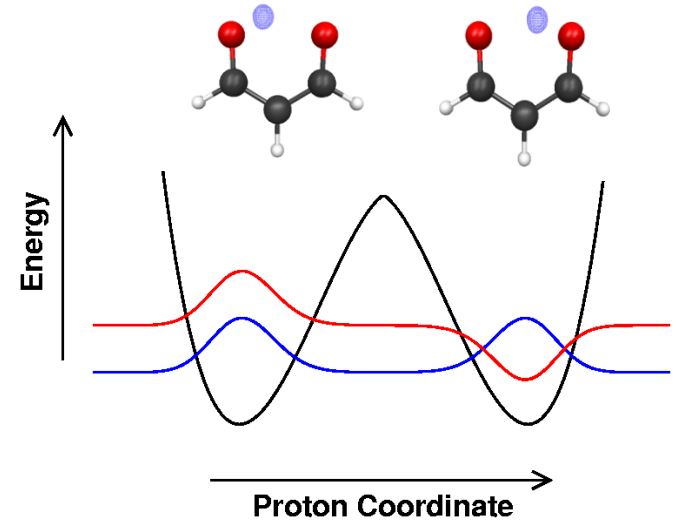
Key Challenge:

Include nuclear quantum effects and non-Born-Oppenheimer effects between select nuclei and electrons in electronic structure calculations

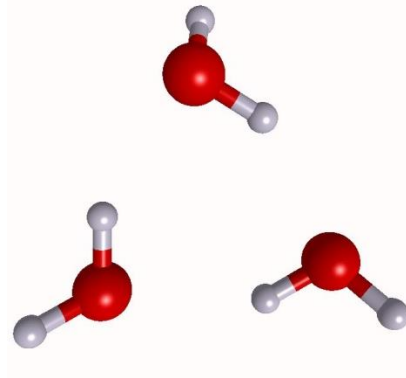
Nuclear Quantum Effects



Zero point energy
Vibrationally excited states

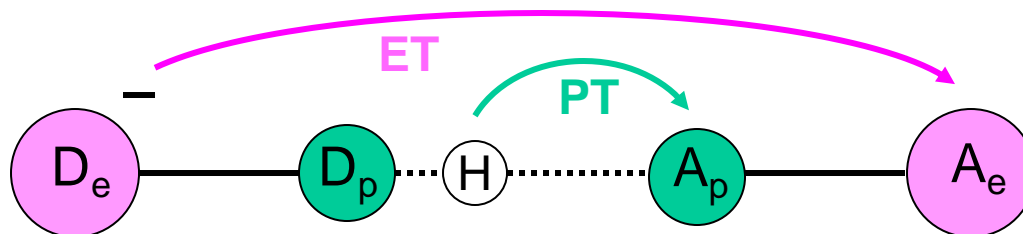


Hydrogen tunneling



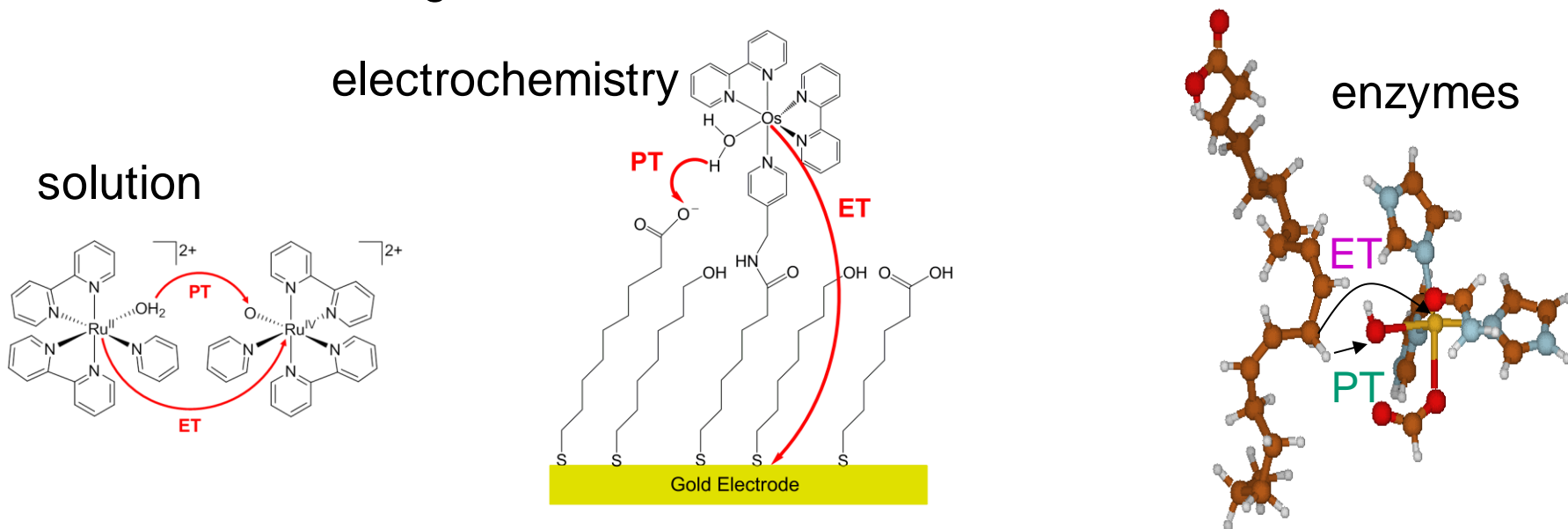
Hydrogen bonding

Non-Born-Oppenheimer Effects



Proton-coupled electron transfer (PCET)

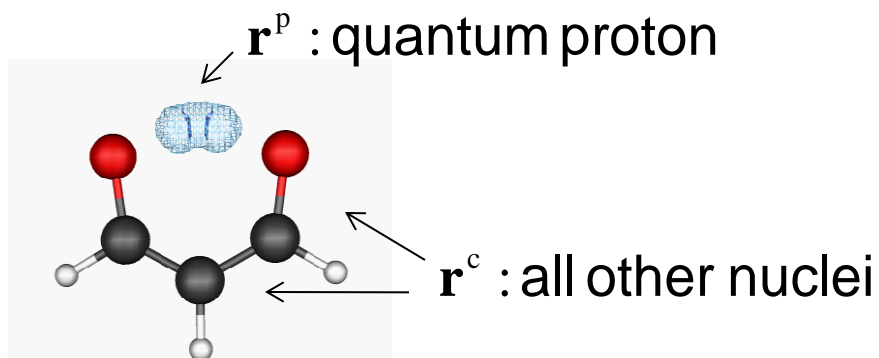
- Electrons and transferring proton behave quantum mechanically
- Hydrogen tunneling important
- Non-Born-Oppenheimer effects significant (nonadiabatic)
- Proton tunneling time can be faster than electronic transition time



Nuclear-Electronic Orbital (NEO) Method

Webb, Jordanov, and Hammes-Schiffer, JCP 117, 4106 (2002)

- 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



Nuclear-Electronic Hamiltonian

$$\begin{aligned}
 H_{\text{NEO}} = & -\frac{1}{2} \sum_i^{N_e} \nabla_i^2 - \sum_i^{N_e} \sum_A^{N_c} \frac{Z_A}{|\mathbf{r}_i^e - \mathbf{r}_A^c|} + \sum_{i>j}^{N_e} \frac{1}{|\mathbf{r}_i^e - \mathbf{r}_j^e|} && \text{Electronic terms} \\
 & -\frac{1}{2m_p} \sum_{i'}^{N_p} \nabla_{i'}^2 + \sum_{i'}^{N_p} \sum_A^{N_c} \frac{Z_A}{|\mathbf{r}_{i'}^p - \mathbf{r}_A^c|} + \sum_{i'>j'}^{N_p} \frac{1}{|\mathbf{r}_{i'}^p - \mathbf{r}_{j'}^p|} && \text{Nuclear terms} \\
 & - \sum_{i'}^{N_p} \sum_i^{N_e} \frac{1}{|\mathbf{r}_i^e - \mathbf{r}_{i'}^p|} && \text{Nuclear-Electronic interaction term}
 \end{aligned}$$

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

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

NEO-HF (Hartree-Fock)

- HF wavefunction

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

- HF energy

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

- 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, Hammes-Sciffer, JPCA 2006

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

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

- 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 \rightarrow Modified Hartree-Fock equations, solve iteratively to self-consistency

Advantage: provides accurate nuclear wavefunctions

Disadvantage: computationally expensive

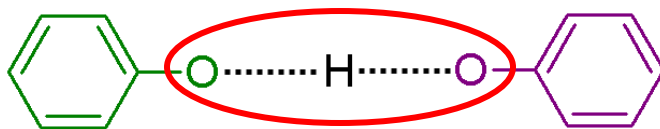
Paradigm Shift: NEO-RXCHF

Sirjoosingh, Pak, Swalina, Hammes-Schiffer, 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: $(N_{\text{ebf}})^8(N_{\text{pbf}})^2$
- Scaling of NEO-RXCHF for two coupled spin orbital: $(N_{\text{ebf}})^6(N_{\text{pbf}})^2$

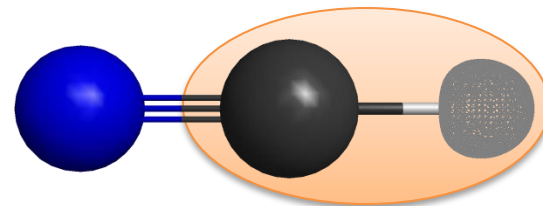
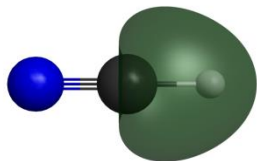
Unique Attributes of Blue Waters

- 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

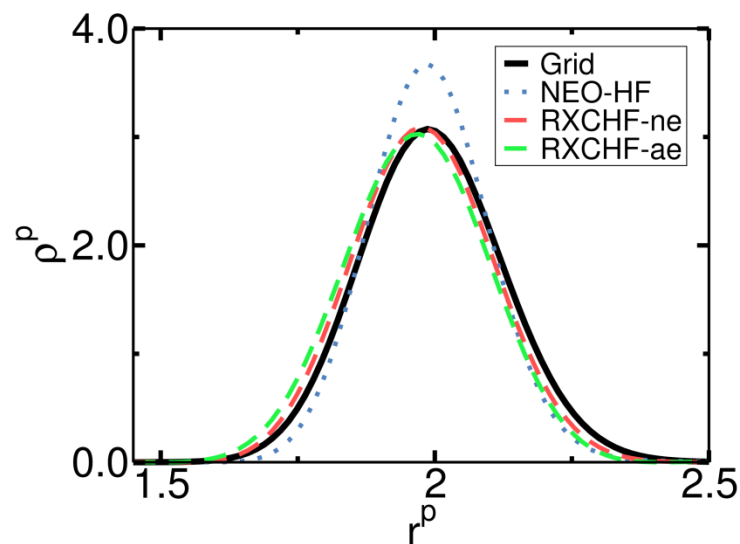
Sirjoosingh, Pak, Brorsen, Hammes-Schiffer, JCP, Accepted

- 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

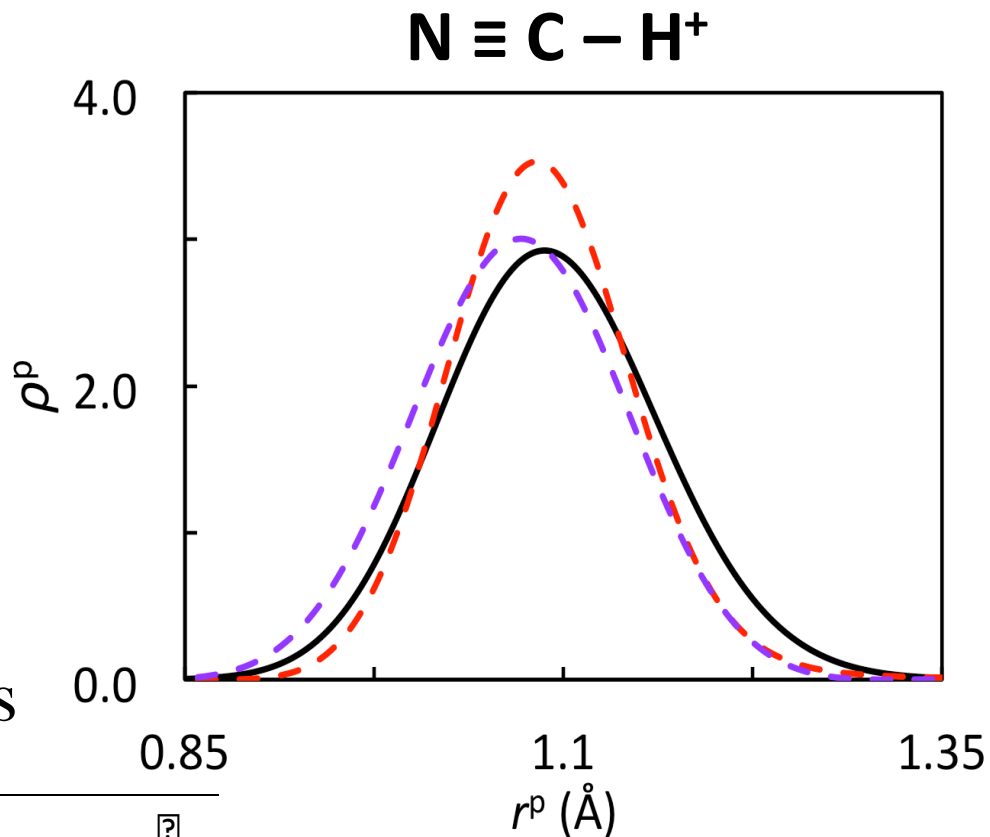
NEO-HF: Hartree-Fock, mean field

RXCHF: ne and ae denote different approximations for electron exchange

Open-shell RXCHF

Brorsen, Sirjoosingh, Pak, Hammes-Schiffer, JCP, Accepted

- Many systems which exhibit non-adiabatic effects are open-shelled
- Implemented with odd number of non-coupled electrons and even number of coupled electrons
- ROHF for regular electrons



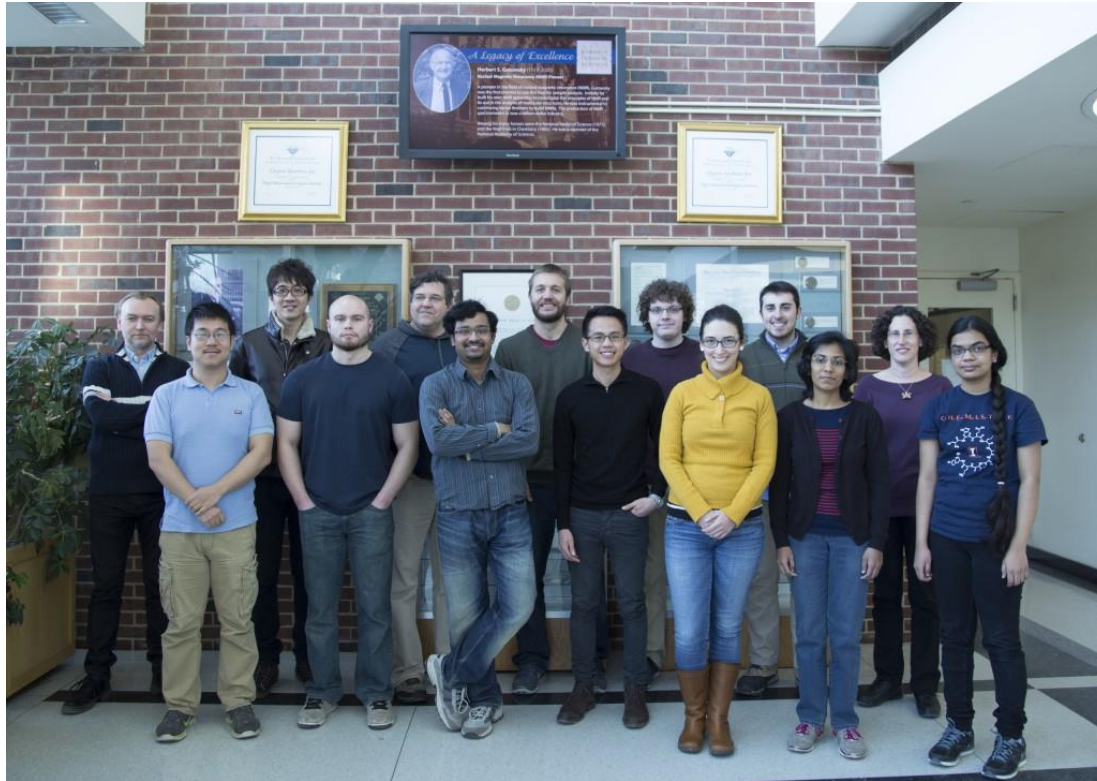
| Method | HCN ⁺ | |
|----------|-------------------------|-----------|
| | n (cm ⁻¹) | r_0 (Å) |
| NEO-HF | 4733 | 1.084 |
| RXCHF-ne | 3385 | 1.071 |
| RXCHF-ae | 3103 | 1.064 |
| 1D-FGH | 3209 | 1.090 |

— Grid
- - - NEO-HF
- - - RXCHF

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



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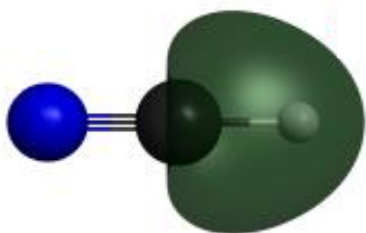
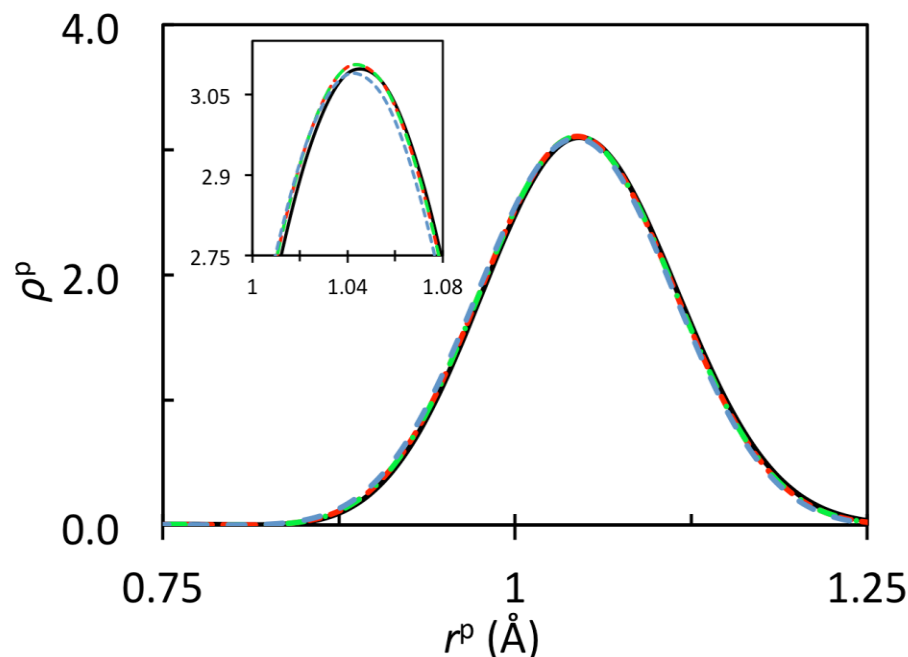
Funding: AFOSR, NSF

Computer Resources: Garnet (ERDC DoD), Blue Waters

RXCHF restricted basis

Brorsen, Sirjoosingh, Pak, Hammes-Schiffer, JCP, Accepted

- Atomic orbitals centered on atoms not bonded to the nuclear quantum atom have negligible contribution to the coupled electronic orbitals
 - Local proton density argument
- Try to restrict the coupled electronic basis to AOs that are expected to contribute.



- Full basis (21)
- AOs on C and H (12)
- AOs on C and H excluding off-axis p orbitals (8)
- AOs on C and H excluding off-axis p orbitals and C core s orbital (7)