

Accurate wavefunctions for multi-sorted quantum systems

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Multi-sorted quantum systems

- Quantum Chemistry:

$$\hat{H} = -\frac{1}{2m_e} \sum_i^{N_e} \nabla_i^2 - \sum_i^{N_e} \sum_A^{N_c} \frac{Z_A}{|\mathbf{r}_i^e - R_A^c|} + \sum_{i>j}^{N_e} \frac{1}{|\mathbf{r}_i^e - \mathbf{r}_j^e|}$$

- Multi-sorted Quantum Systems:

$$\hat{H} = -\frac{1}{2m_e} \sum_i^{N_e} \nabla_i^2 - \sum_i^{N_e} \sum_A^{N_c} \frac{Z_A}{|\mathbf{r}_i^e - R_A^c|} + \sum_{i>j}^{N_e} \frac{1}{|\mathbf{r}_i^e - \mathbf{r}_j^e|}$$

“Electronic” terms

$$-\frac{1}{2m_p} \sum_{i'}^{N_p} \nabla_{i'}^2 - \sum_{i'}^{N_p} \sum_A^{N_c} \frac{Z_A}{|\mathbf{r}_{i'}^p - R_A^c|} + \sum_{i'>j'}^{N_p} \frac{1}{|\mathbf{r}_{i'}^p - \mathbf{r}_{j'}^p|}$$

“Nuclear” terms

$$-\sum_{i'}^{N_p} \sum_i^{N_e} \frac{1}{|\mathbf{r}_i^e - \mathbf{r}_{i'}^p|}$$

“Nuclear-Electronic” interaction term

Multi-sorted quantum systems

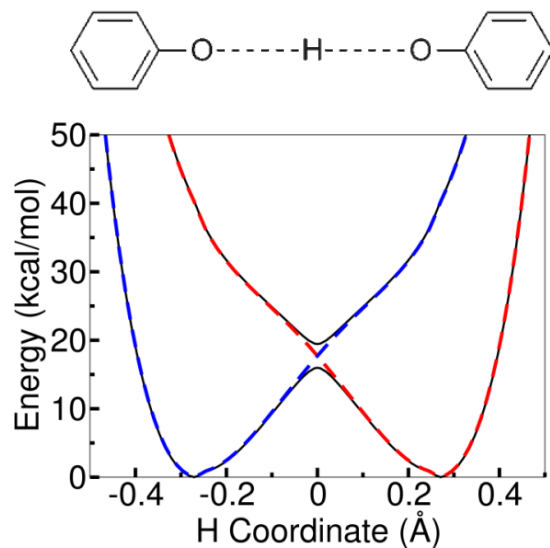
Type I: $m_e \sim m_p$

positronic chemistry, muonized atoms and molecules

e: electrons p: positron/muon/etc. $N_p = 1$

Type II: $m_e \ll m_p$

“Chemically” non-adiabatic molecular systems



e: electrons

p: quantum nuclei

$N_p = 1$

$$\Psi(\mathbf{r}_e | \mathbf{R}) \rightarrow \Psi(\mathbf{r}_e, R_p | \mathbf{R})$$

quantum classical

| | | |
|---|---|---|
| e | p | n |
|---|---|---|

“Imitating” Quantum Chemistry: mean-field based approaches

- Mean-field (HF) wavefunction:

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

$$\text{HF energy: } E^{HF} = \left\langle \Phi_0^e(\mathbf{r}^e)\Phi_0^p(\mathbf{r}^p) \left| \hat{H} \right| \Phi_0^e(\mathbf{r}^e)\Phi_0^p(\mathbf{r}^p) \right\rangle$$

- Configuration interaction (CI) / MCSCF

$$\Psi^{CI}(\mathbf{r}^e, \mathbf{r}^p) = \sum_I^{N_{CI}^e} \sum_{I'}^{N_{CI}^p} C_{II'} \Phi_I^e(\mathbf{r}^e)\Phi_{I'}^p(\mathbf{r}^p)$$

$$\text{CI/MCSCF energy: } E^{CI} = \left\langle \Psi^{CI}(\mathbf{r}^e, \mathbf{r}^p) \left| \hat{H} \right| \Psi^{CI}(\mathbf{r}^e, \mathbf{r}^p) \right\rangle$$

- Perturbation theory (MP2)

$$E^{MP2} = E^{HF} + E_{ee}^{(2)} + E_{ep}^{(2)}$$

Use 2nd-order perturbation theory to calculate
electron-electron and electron-proton corrections

Testing electron-positron wavefunctions

- Good reference points:
 - experimental: e⁺ binding energies and annihilation rates
 - computational: high accuracy results for small few-electron systems (QMC, SVM, SVM+ECG, etc.)

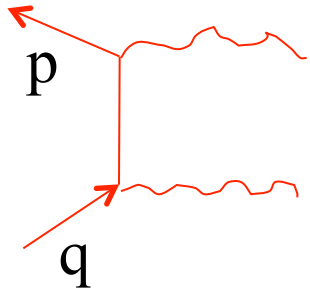
$$\Psi(r_1, r_2, r_p) = \hat{A}_{12} \sum_{i,j,k,l,m,n} C_{ijklmn} r_1^i r_2^j r_p^k r_{1p}^l r_{2p}^m r_{12}^n e^{\sum_v (-\alpha_{12}^v r_{12} - \alpha_{1p}^v r_{1p} - \alpha_{2p}^v r_{2p})}$$

$$\Psi(r_1, r_2, r_p) = \hat{A}_{12} \exp\left(\frac{a_1 r_1 + c_1 r_1^2}{1 + b_1 r_1} + \frac{a_2 r_2 + c_2 r_2^2}{1 + b_2 r_2} + \frac{a_p r_p + c_p r_p^2}{1 + b_p r_p} + \frac{a_{12} r_{12} + c_{12} r_{12}^2}{1 + b_{12} r_{12}} + \frac{a_{1p} r_{1p} + c_{1p} r_{1p}^2}{1 + b_{1p} r_{1p}} + \frac{a_{2p} r_{2p} + c_{2p} r_{2p}^2}{1 + b_{2p} r_{2p}}\right)$$

- Positron binding energies
 - no binding predicted for most systems: e.g., Li, Be, Na, Mg atoms, LiH molecule etc.
 - accounting for the Ps dissociation channel is problematic
- Positron annihilation rate
 - direct measure of quality of e/e⁺ wavefunctions

$$\Psi(\mathbf{r}_1^e, \mathbf{r}_2^e, \mathbf{r}^p) \rightarrow \rho^{ep}(\mathbf{r}) = \left\langle \Psi(\mathbf{r}_1^e, \mathbf{r}_2^e, \mathbf{r}^p) \left| \sum_{i=1}^N \delta(\mathbf{r}_i^e - \mathbf{r}) \delta(\mathbf{r}^p - \mathbf{r}) \right| \Psi(\mathbf{r}_1^e, \mathbf{r}_2^e, \mathbf{r}^p) \right\rangle \rightarrow \lambda^{2\gamma} = C \int \rho^{ep}(\mathbf{r}) d\mathbf{r}$$

Bound Positrons – Annihilation Rate



$$|\Psi_i\rangle = \hat{b}^+(p)\hat{a}^+(q)|\Omega_0\rangle$$

$$\sigma_{2\gamma} = \langle \Psi_f | \hat{H} | \Psi_i(0,0) \rangle \rightarrow 4\pi r_0^2 c$$

$$|\Psi_f\rangle = \hat{c}^+(k)\hat{c}^+(p+q-k)|\Omega_0\rangle$$

$$r_0 = \alpha\hbar / m_e c$$

$$|\Psi_i\rangle = \Psi(x_1, x_2, x_3) = \hat{A}_{23} f(r_1, r_2, r_3) [\alpha(1)(\alpha(2)\beta(3) - \beta(2)\alpha(3))]$$

$$|\Psi_i\rangle = \int dp_1 dp_2 dp_3 \bar{f}(p_1, p_2, p_3) \hat{b}^+(p_1, \uparrow) [\hat{a}^+(p_2, \uparrow)\hat{a}^+(p_3, \downarrow) - \hat{a}^+(p_2, \downarrow)\hat{a}^+(p_3, \uparrow)] |\Omega_0\rangle$$

$$|\Psi_f\rangle = \int dp' \bar{\chi}(p') \hat{a}^+(p', \uparrow) \hat{c}^+(k, e_1) \hat{c}^+(p+q-k, e_2) |\Omega_0\rangle$$

$$\lambda = \sum_{\chi} \langle \Psi_f(\chi) | \hat{H} | \Psi_i \rangle = 1/2 \sigma_{2\gamma} \hat{A}_{23} \int dp_1 dp_2 dp_3 dp' \bar{f}(p_1, p_2, p_3) \bar{\chi}(p') [\delta(p'-p_3)\delta(p-p_1-p_2)]$$

$$\lambda = 1/2 \sigma_{2\gamma} \int dr \rho(r_1, r_2) \Big|_{r_1=r_2=r}$$

$$\lambda = 4\pi r_0^2 c \langle \Psi | \sum_{i=1}^{N_e} \hat{S}_{ep}^S \delta(\mathbf{r}_i^e - \mathbf{r}^p) | \Psi \rangle = \pi r_0^2 c \langle \Psi | \sum_{i=1}^{N_e} \delta(\mathbf{r}_i^e - \mathbf{r}^p) | \Psi \rangle$$

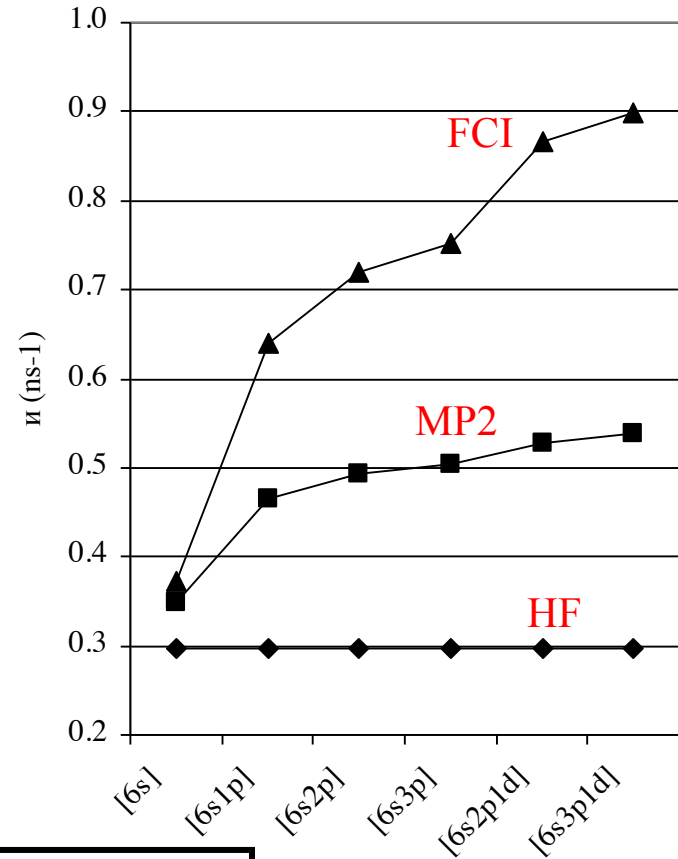
PsH Annihilation Rate

HF $\lambda^{HF} = 2\pi r_0^2 c \sum_{i=1}^N S_{ii'l'1'}$

$$S_{ijij'} = \int \phi_i(\mathbf{r})\phi_j(\mathbf{r})\phi_{i'}(\mathbf{r})\phi_{j'}(\mathbf{r})d\mathbf{r}$$

MP2 $\lambda^{(1)} = -4\pi r_0^2 c \sum_{arr'} \frac{\langle a1'|rr'\rangle}{\epsilon_a + \epsilon_{1'} - \epsilon_r - \epsilon_{r'}} S_{ar1'r'}$

FCI $\lambda^{FCI} = 2\pi r_0^2 c \left[\sum_{II'} \sum_{IJ'} C_{II'} C_{IJ'} \sum_{i=1}^N S_{I_i I_i' J_i' J_i'} + 2 \sum_{II' < JJ'} C_{II'} C_{JJ'} S_{I_i J_i J_i' I_i'} \right]$



| | 6s | 6s1p | 6s2p1d | 6s3p1d |
|-----------------|--------|--------|--------|--------|
| λ^{HF} | 0.2972 | 0.2976 | 0.2978 | 0.2977 |
| λ^{MP2} | 0.3490 | 0.4018 | 0.5287 | 0.5376 |
| λ^{FCI} | 0.3723 | 0.6304 | 0.8662 | 0.8993 |

Dynamical correlation

- Electron-electron dynamical correlation:
 - defined as difference between exact and mean-field answers

E.g. for the energy:
$$E^{corr} = \langle \Psi^{exact} | \hat{H} | \Psi^{exact} \rangle - \langle \Psi^{HF} | \hat{H} | \Psi^{HF} \rangle$$

- mathematically is (mostly) due to deviation of Ψ^{exact} from Ψ^{HF} when $|\mathbf{r}_i^e - \mathbf{r}_j^e| \rightarrow 0$
 - typically is ‘icing on the cake’: e-e Coulomb interaction is repulsive...
- Electron-proton correlation is the cake!
 - *qualitatively important*: e-p Coulomb interaction is attractive



Explicitly correlated wavefunctions

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

$$\Psi^{\text{RXCHF-fe}}(\mathbf{x}^e, \mathbf{x}^p) = \frac{\chi^p(\mathbf{x}^p)}{\sqrt{N!}} \begin{vmatrix} \chi_1^e(\mathbf{x}_1^e) g(\mathbf{r}_1^e, \mathbf{r}^p) & \chi_2^e(\mathbf{x}_1^e) & \cdots & \chi_N^e(\mathbf{x}_1^e) \\ \chi_1^e(\mathbf{x}_2^e) g(\mathbf{r}_2^e, \mathbf{r}^p) & \chi_2^e(\mathbf{x}_2^e) & \cdots & \chi_N^e(\mathbf{x}_2^e) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1^e(\mathbf{x}_N^e) g(\mathbf{r}_N^e, \mathbf{r}^p) & \chi_2^e(\mathbf{x}_N^e) & \cdots & \chi_N^e(\mathbf{x}_N^e) \end{vmatrix}$$

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-positron 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

PsH Annihilation Rate from NEO XCHF

$$\Psi(\mathbf{r}_e, \mathbf{r}_p) = \Psi_e(\mathbf{r}_e) \Psi_p(\mathbf{r}_p) \left\{ 1 + \sum_{i=1}^{N_e} \sum_{j=1}^{N_p} \sum_{k=1}^{N_{\text{gem}}} b_k \exp \left[-\gamma_k (\mathbf{r}_{e,i} - \mathbf{r}_{p,j})^2 \right] \right\}$$

$$\lambda: \int \rho_{ep}(x_e, x_p) |_{x_e=x_p=x} dx = \int \sum_{i=1}^{N_e} \delta(\mathbf{r}_{e,i} - \mathbf{r}_p) |\Psi_0(\mathbf{r}_e, \mathbf{r}_p)|^2 d\mathbf{r}_e =$$

$$\sum_{i=1}^{N_e} \langle \Psi | \Omega_1(x_i, x_p) | \Psi \rangle + \sum_{i \neq j}^{N_e} \langle \Psi | \Omega_2(x_i, x_j, x_p) | \Psi \rangle + \sum_{i \neq j \neq k}^{N_e} \langle \Psi | \Omega_3(x_i, x_j, x_k, x_p) | \Psi \rangle$$

$$\Omega_1(x_i, x_p) = \delta_{ip} + 2g_{ip} \delta_{ip} + g_{ip}^2 \delta_{ip}$$

$$\Omega_2(x_i, x_j, x_p) = 2g_{ip} \delta_{jp} + g_{ip}^2 \delta_{jp} + 2g_{ip} g_{jp} \delta_{jp}$$

$$\Omega_3(x_i, x_j, x_k, x_p) = g_{ip} g_{jp} \delta_{kp}$$

| Method | E | $\lambda_{2\gamma}(\text{ns}^{-1})$ |
|----------|-----------|-------------------------------------|
| HF | -0.664337 | 0.3189 |
| XCHF-1G | -0.693216 | 0.6883 |
| XCHF-2G | -0.705863 | 1.1402 |
| XCHF-3G | -0.712496 | 2.0122 |
| XCHF-4G* | 0.716097 | 2.0443 |
| FCI | -0.758965 | 0.8993 |
| SVM | -0.789198 | 2.4714 |

Basis sets:

HF, XCHF: **6s**

FCI: **6s2p1d**

Two-Photon Annihilation Rates

| | e ⁺ Li | LiPs | e ⁺ LiH |
|----------|---------------------------|--------------------------|-------------------------|
| NEO-HF | 3.3556×10 ⁻⁴ | 0.0512 | 0.03 |
| XCHF | 1.7361 | 0.566 | 0.62 |
| RXCHF-ne | 1.6759 | 1.940 | 1.08 |
| RXCHF-ae | 1.6657 | 1.940 | 1.11 |
| SVM/ECG | 1.7512^a | 2.107^b | 1.26^c |

Units: ns⁻¹

- HF very inaccurate
- XCHF better but still inaccurate
- RXCHF-ne/ae perform similarly and agree well with highly accurate ECG/SVM results
- Electronic and positronic densities are also in decent agreement
- RXCHF is 235 (25) times faster than XCHF for e⁺Li (LiPs)

^aMitroy, *Phys. Rev. A* **70**, 024502 (2004).

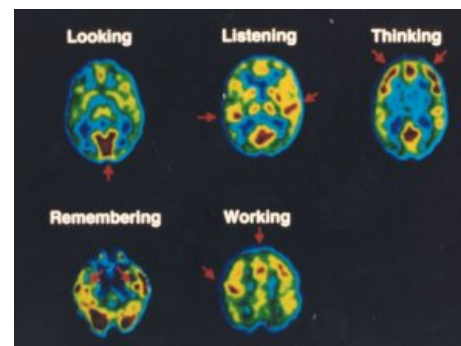
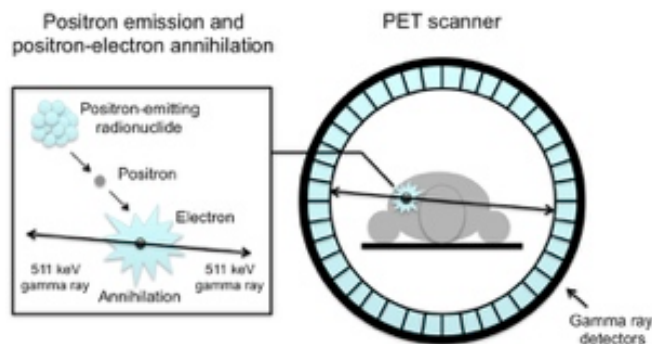
^bRyzhikh, Mitroy, Varga, *J. Phys. B* **31**, 3965 (1998).

^cStrasburger, *J. Chem. Phys.* **111**, 10555 (1999).

Conclusions:

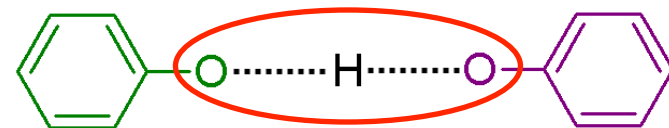
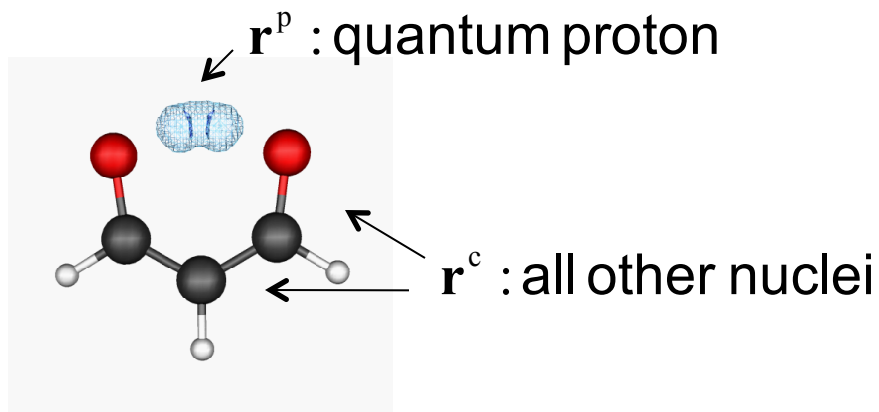
Electron-positron wavefunctions

- No usable method for computing accurate wavefunctions is available:
 - highly accurate methods of ECG+SVM type are not practical for systems with more than 5-10 electrons. ((NEO-XCHF/RXCHF is perhaps in the same class))
 - methods easily applied to larger positronic molecules (HF, MP2, CI) are utterly unreliable even for systems with 3 electrons or less.
 - trivial example: experimentally, e^+ binds to propane. No known theoretical method can predict this binding...
- The field is wide open, and in need of new ideas...
- PET applications



Multi-sorted quantum systems: electron-nuclear wavefunctions

- Solution of mixed nuclear-electronic time-independent Schrödinger equation with molecular orbital methods
- Treat specified nuclei quantum mechanically on same level as electrons
 - treat only key H nuclei QM
 - retain at least two classical nuclei
- Easy access to 'exact' answer is available for benchmarking electron-nuclear orbital methods



Electron-proton wavefunctions: how accurate is BO approximation?

- Expand exact solution in double-adiabatic basis

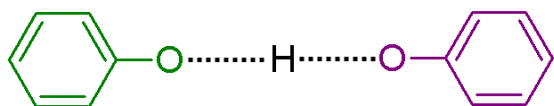
$$\Psi_k^{\text{tot}}(\mathbf{r}_e, \mathbf{r}_p | \mathbf{R}) = \sum_{i,\mu} c_{i\mu}^k \Psi_i^{\text{elec}}(\mathbf{r}_e | \mathbf{r}_p, \mathbf{R}) \Psi_{i\mu}^{\text{prot}}(\mathbf{r}_p | \mathbf{R})$$

- Need to evaluate non-adiabatic coupling terms:

$$H_{i\mu, j\nu} = \delta_{ij} \delta_{\mu\nu} \varepsilon_{\mu}^{(i)}(\mathbf{R}) - \frac{\hbar^2}{m_p} \left\langle \Psi_{i\mu}^{\text{prot}} | \mathbf{d}_{ij}^{(\text{ep})} \cdot \nabla_{\mathbf{r}_p} | \Psi_{j\nu}^{\text{prot}} \right\rangle_p - \frac{\hbar^2}{2m_p} \left\langle \Psi_{i\mu}^{\text{prot}} | g_{ij}^{(\text{ep})} | \Psi_{j\nu}^{\text{prot}} \right\rangle_p$$

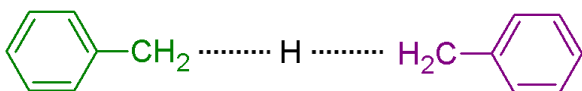
$$\mathbf{d}_{ij}^{(\text{ep})} = \left\langle \Psi_i^{\text{elec}} | \nabla_{\mathbf{r}_p} | \Psi_j^{\text{elec}} \right\rangle_e \quad g_{ij}^{(\text{ep})} = \left\langle \Psi_i^{\text{elec}} | \nabla_{\mathbf{r}_p}^2 | \Psi_j^{\text{elec}} \right\rangle_e$$

Phenoxy-phenol: electronically non-adiabatic

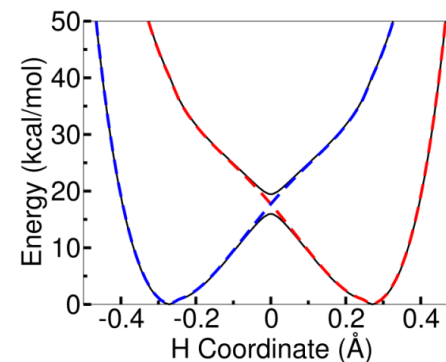


$$C_{00}^0 = .9973$$

Benzyl-toluene: electronically adiabatic



$$C_{00}^0 = .9997$$

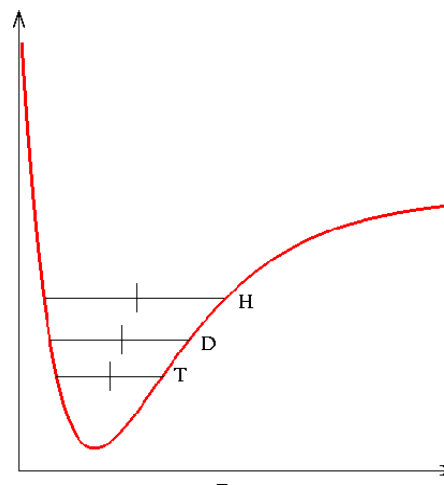


Electron-proton wavefunctions: what is 'accurate'?

- Isotope Effects on Geometries

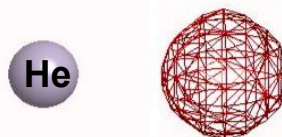
Bond lengths in Å

| X | HX | DX | TX |
|----|--------|--------|--------|
| F | 0.9186 | 0.9134 | 0.9110 |
| Cl | 1.2884 | 1.2815 | 1.2785 |
| Br | 1.4235 | 1.4165 | 1.4134 |

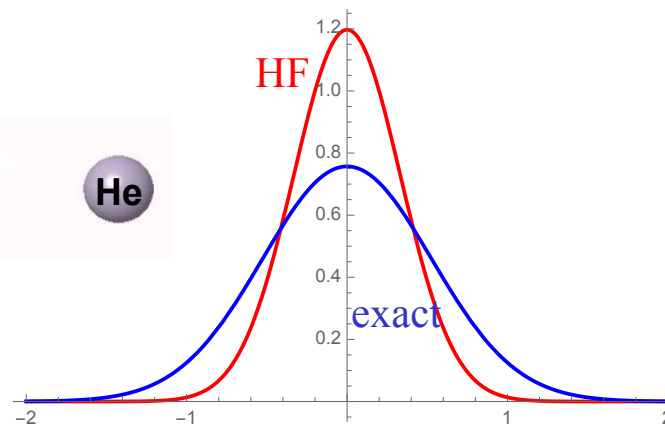


- NEO-HF → As mass increases,
 - bond length decreases
 - magnitude of negative partial charge on X decreases
- Same trends observed for H₂O, NH₃, H₃O⁺

- Proton density distribution:

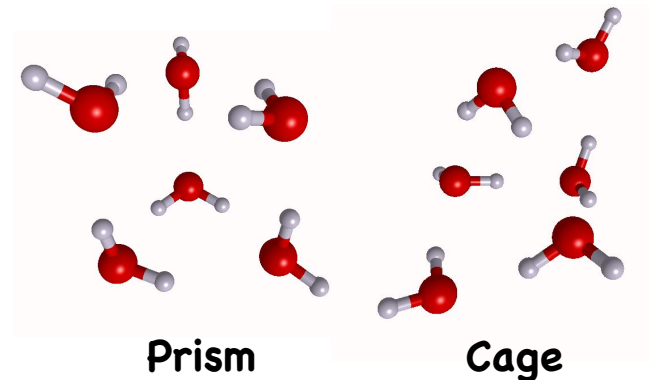
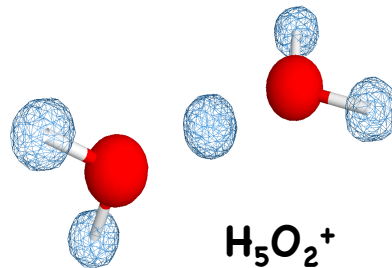
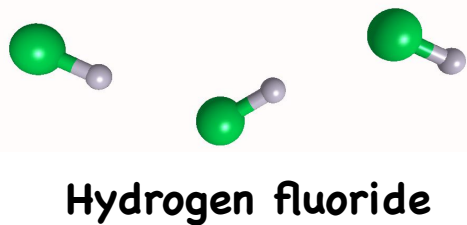


typically, HF frequency is off by 200% or more



Nuclear Quantum Effects and H-bonding

- Large amplitude, anharmonic zero-point motion
- Zero point energy effects:
 - bending-type modes
→ increase D–A distance
 - stretching modes
→ decrease D–A distance



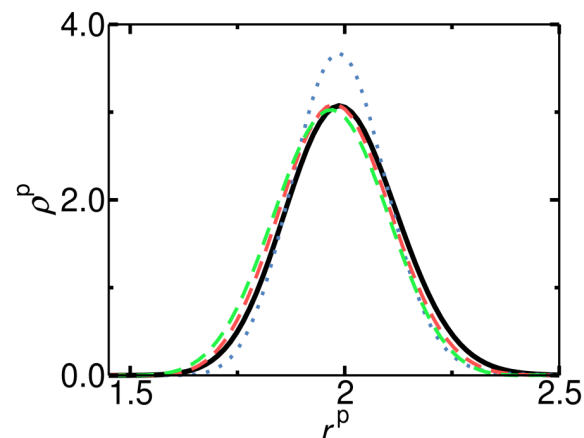
- **Clusters: increase H-bond donor–acceptor distances**
 - $(\text{H}_2\text{O})_{n=2-6}$ → QDMC: *Clary, CR 2000*
 - $(\text{HF})_2$ → Experiment: *Klemperer, JCP 1984*
- **Liquids: decrease H-bond donor–acceptor distances**
 - H_2O , HF → PICPMD: *Klein, JACS 2003, PRL 2004*

Proton-Containing Systems with RXCHF



- 14-electron system
- Explicitly correlate two electronic orbitals to proton (CH bond orbital)

| | Frequency (cm^{-1}) |
|--------------|--------------------------------|
| HF | 5077 |
| NEO-RXCHF-ne | 3604 |
| NEO-RXCHF-ae | 3476 |
| 3D grid | 3544 |

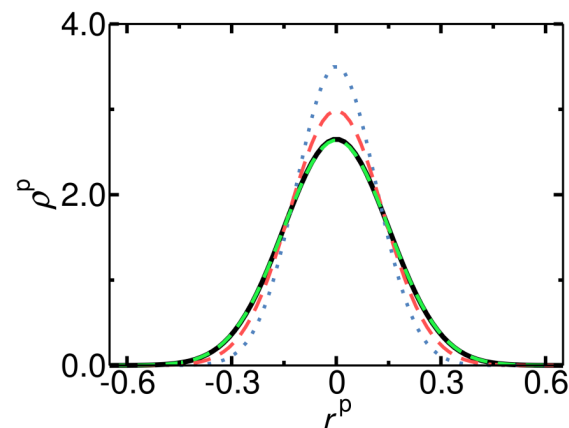


black: grid (adiabatic)
 blue: NEO-HF
 red: RXCHF-ne
 green: RXCHF-ae



- 20-electron system
- Explicitly correlate four electronic orbitals to proton (FH bond orbitals)

| | Frequency (cm^{-1}) |
|--------------|--------------------------------|
| NEO-HF | 4614 |
| NEO-RXCHF-ne | 3348 |
| NEO-RXCHF-ae | 2616 |
| 3D grid | 2639 |

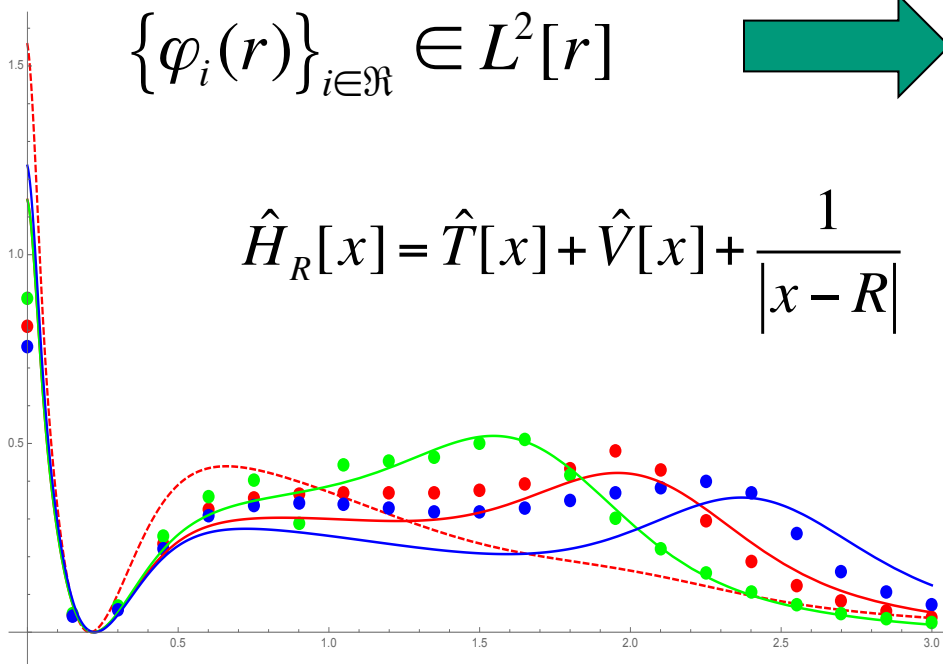


Problems with explicitly correlated methods for BO systems

$$\Psi(r_1, r_2) \begin{cases} \rightarrow \phi(r_1)\chi(r_2) & |r_1 - r_2| \gg 0 \\ \rightarrow Ce^{-\gamma|r_1 - r_2|} & |r_1 - r_2| \rightarrow 0 \end{cases} \longrightarrow \Phi^e(\mathbf{x}^e)\Phi^p(\mathbf{x}^p) \left\{ 1 + \sum_{i=1}^{N_e} \sum_{j=1}^{N_p} g(\mathbf{r}_i^e, \mathbf{r}_j^p) \right\}$$

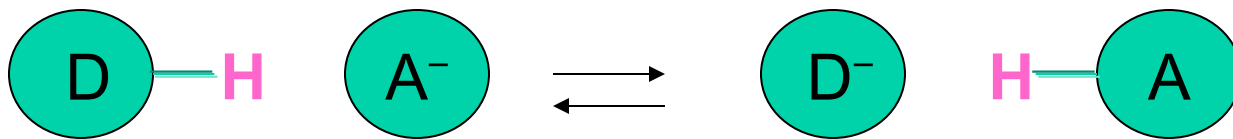
$$\{\varphi_i(r)\}_{i \in \mathfrak{R}} \in L^2[r] \longrightarrow \varphi(r, R) \in L^2[r \otimes R]$$

$$\hat{H}_R[x] = \hat{T}[x] + \hat{V}[x] + \frac{1}{|x - R|} \longrightarrow \Psi_R(x)$$

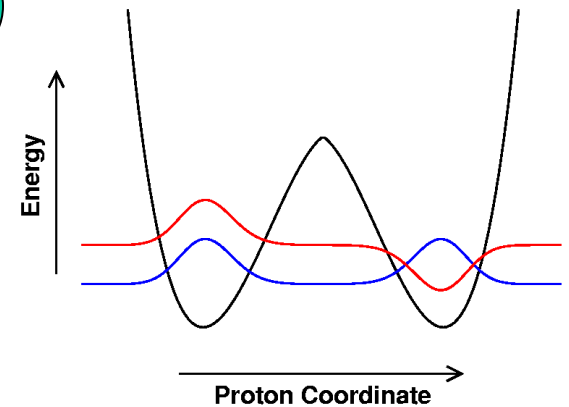
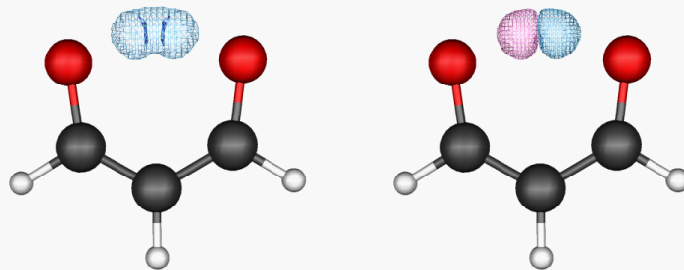


electron density: BO(solid line) vs. RXCHF (dotted line)

Description of Bilobal Wavefunctions



- TS for H transfer reactions corresponds to equal H probability near donor and acceptor



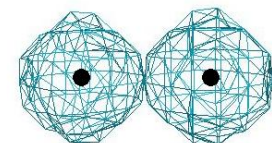
Model system studies (analytical proof)

Pak and SHS, PRL 2004

HF: variational solution is always localized

In practice, so is CI/CASSCF

Delocalization: at least FCI in a very large basis set



Conclusions

- Electron-positron correlation is too large to make HF a viable reference.
 - Post-HF (CI,MP2) methods fail to produce reasonably accurate electron-positron wavefunctions.
 - Explicitly correlated methods do somewhat better, but are very expensive.
 - New approaches are needed to describe positron behavior in large molecules.
-
- BO ground state electron-nuclear wavefunctions are almost exact even for chemically non-adiabatic systems.
 - Orbital-based methods fail to reproduce the shape and size of exact nuclear density. This is true, to some extent, even for explicitly-correlated approaches.
 - This basic failure probably implies that the functional dependence of electronic wavefunction on nuclear coordinate is described incorrectly.
 - Producing bilobal proton wavefunctions (in a double-well potential) with nuclear-electron orbital methods is essentially an unsolved problem.

Acknowledgments

Sharon Hammes-Schiffer (PSU, UIUC)

Simon Webb

Andrès Reyes

Arindam Chakraborty

Kurt Brorsen

Tzvetelin Iordanov

Chet Swalina

Jonathan Skone

Andrew Sirjoosingh

Tanner Culpitt

Funding: **AFOSR, NSF**

NEO method is incorporated into GAMESS

Extra: Topology of nodal surfaces

- Diffusion MC (DMC) depends on the fixed-node approximation.
- Topology of the nodal surface of multi-sorted wavefunctions responds to the level of correlation in an unknown way.
- Nodal surface of an $N+M$ -particle system is an embedded manifold (in \mathbb{R}^{3N+3M}).
- Alternatively, after a polynomial approximation, it is an algebraic variety over \mathbb{R} .
- We need a computable pathway from the embedding function to some suitable topological characteristic (e.g. Betti numbers for some cohomology theory) of the surface.
- Example: de Rham cohomology groups for (a complement to) an affine variety over \mathbb{C} can be computed from the polynomial coefficients of the variety.

Toshinori Oaku, Nobuki Takayama, Journal of Pure and Applied Algebra, 139 (1999) 201

Multicomponent DFT

Hohenberg-Kohn theorem has been proven for multi-component systems:
functional exists for electronic and nuclear 1-particle densities

Parr, JCP1982

$$\rho_e(r), \rho_N(r) \longleftrightarrow V_{ext}(r)$$

Kreibich, Gross, PRL 2001

$$\rho_e(r), \Gamma(R_1, \dots, R_N) \longleftrightarrow V_{ext}(r)$$

Strategy for Developing e-p Functional

Chakraborty, Pak, SHS, PRL 2008

$$\Psi_{\text{gem}} = (1 + G) \underbrace{\Phi^e \Phi^p}_{\text{auxiliary densities}}$$

←

$\rho^{\text{ep}}, \rho^e, \rho^p$
geminal densities

$\tilde{\rho}^e, \tilde{\rho}^p, \dots$
auxiliary densities

- Geminal ansatz defines **map** from **auxiliary** to **geminal** densities
- Use this map to obtain a **functional relationship** between 1- and 2-particle geminal densities

$$\begin{array}{l}
 \rho^{\text{ep}}[\tilde{\rho}^e, \tilde{\rho}^p, \dots] \\
 \rho^e[\tilde{\rho}^e, \tilde{\rho}^p, \dots] \\
 \rho^p[\tilde{\rho}^e, \tilde{\rho}^p, \dots]
 \end{array}
 \xrightarrow{?}
 \rho^{\text{ep}} = F[\rho^e, \rho^p]$$

- Obtain geminal densities by integration of geminal wavefunction
- Truncate expressions for geminal densities
- Make a well-defined approximation that satisfies sum rules

Electron-Proton Functional

Contribution to total energy:

$$E_{\text{epc}} [\rho^e, \rho^p] = -\int d\mathbf{r}^e d\mathbf{r}^p r_{\text{ep}}^{-1} \rho^{\text{ep}} + \int d\mathbf{r}^e d\mathbf{r}^p r_{\text{ep}}^{-1} \rho^e \rho^p$$

Expression for ep pair density in terms of 1-particle densities:

$$\Psi_{\text{gem}} = (1 + G) \Phi^e \Phi^p \quad \longrightarrow \quad \begin{aligned} \rho^{\text{ep}} &= \rho^e \rho^p + \rho^e \rho^p \langle \rho^e \rho^p g N_e^{-1} N_p^{-1} \rangle_{\text{ep}} \\ &+ \frac{\rho^e \rho^p g + \rho^e \rho^p N_e^{-1} N_p^{-1} \langle \rho^p g \rangle_p \langle \rho^e g \rangle_e}{1 + N_e^{-1} N_p^{-1} \langle \rho^e \rho^p g \rangle_{\text{ep}}} \\ &- \rho^e \rho^p \langle \rho^e g N_e^{-1} \rangle_e - \rho^e \rho^p \langle \rho^p g N_p^{-1} \rangle_p \end{aligned}$$

Geminal function:

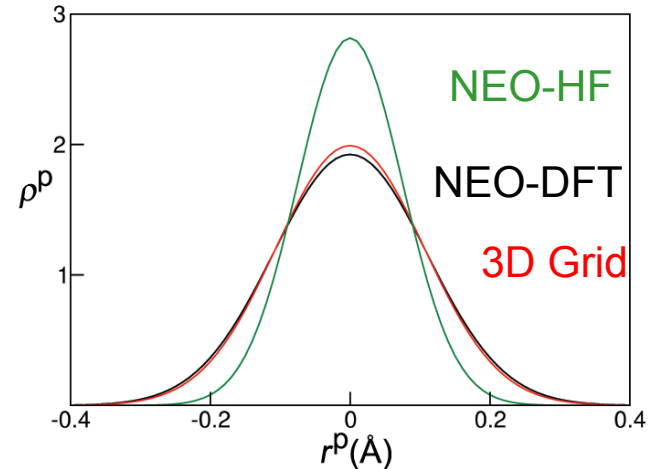
$$g(\mathbf{r}^e, \mathbf{r}^p) = \sum_{k=1}^{N_{\text{gem}}} b_k \exp \left[-\gamma_k |\mathbf{r}^e - \mathbf{r}^p|^2 \right]$$

Motivating work: Colle and Salvetti, 1975, developed an electronic functional

NEO-DFT for $[\text{He-H-He}]^+$



He nuclei classical, H nucleus quantum
Electronic basis set: STO-2G
Nuclear basis set: 5s



Frequencies in cm^{-1} with H, D, and T for the central nucleus

| Isotope | NEO-HF | NEO-XCHF | 3D Grid | NEO-DFT |
|---------|--------|----------|---------|-------------|
| H | 3759 | 1030 | 1107 | 1072 |
| D | 2738 | 725 | 783 | 770 |
| T | 2274 | 558 | 639 | 630 |

- NEO-DFT agrees well with NEO-XCHF and grid method
- NEO-DFT ~1400 times faster than NEO-XCHF for this system

Frequencies determined by fitting nuclear density along He-He axis to Gaussian

XCHF vs. RXCHF: Physical Assumptions

- **XCHF** correlates all electrons with positron using same geminal parameters
 - geminal functions are used to account for interactions other than short-ranged electron-positron dynamical correlation
 - wavefunction is not optimized to accurately describe this specific interaction but rather is more globally optimized
- **RXCHF** correlates only one electron with positron using geminal parameters optimized for a single e^-/e^+ interaction
 - geminal functions are used to account mainly for the short-ranged electron-positron dynamical correlation
 - wavefunction produces highly accurate description of this interaction, although overall wavefunction is not optimal

NEO-DFT for [He-H-He]⁺

Sirjoosingh, Pak, SHS, JCTC 2011; JCP 2012



- He nuclei classical (fixed)
- H quantum mechanical

Nuclear basis set: 1s exponent optimized variationally

2 Gaussian-type geminals, scaled with single scaling factor to fit H cc-pVDZ result

Frequencies in cm⁻¹ with H, D, T for central nucleus

| Isotope | NEO-HF cc-pVDZ | NEO-DFT cc-pVDZ | 3D Grid cc-pVDZ | NEO-DFT cc-pVTZ | 3D Grid cc-pVTZ |
|---------|-------------------|--------------------|--------------------|--------------------|--------------------|
| H | 3098 | 1191 | 1191 | 1103 | 1111 |
| D | 2284 | 820 | 801 | 782 | 740 |
| T | 1903 | 660 | 633 | 646 | 581 |

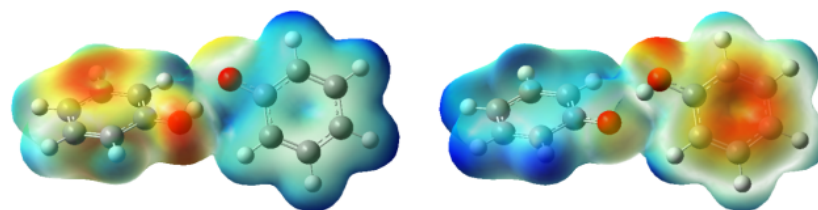
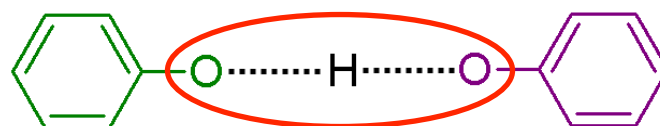
- **NEO-DFT provides accurate nuclear densities at low cost!**
- Electron-electron and electron-proton correlation predominantly additive

PCET: Multiconfigurational RXCHF

- Two-configuration SCF approach for O-H bond on left or right
- Only explicitly correlate 2 electronic orbitals to proton orbital (O-H bond)
- Restricted basis set: only expand explicitly correlated orbitals in terms of valence basis functions on donor, acceptor, and H
- Includes static and dynamical electron-proton correlation
- Substantial computational savings → allows applications to larger systems

$$\Psi^I = C_1^I \Psi_1^{\text{RXCHF}} + C_2^I \Psi_2^{\text{RXCHF}}$$

$$\Psi^{\text{II}} = C_1^{\text{II}} \Psi_1^{\text{RXCHF}} + C_2^{\text{II}} \Psi_2^{\text{RXCHF}}$$



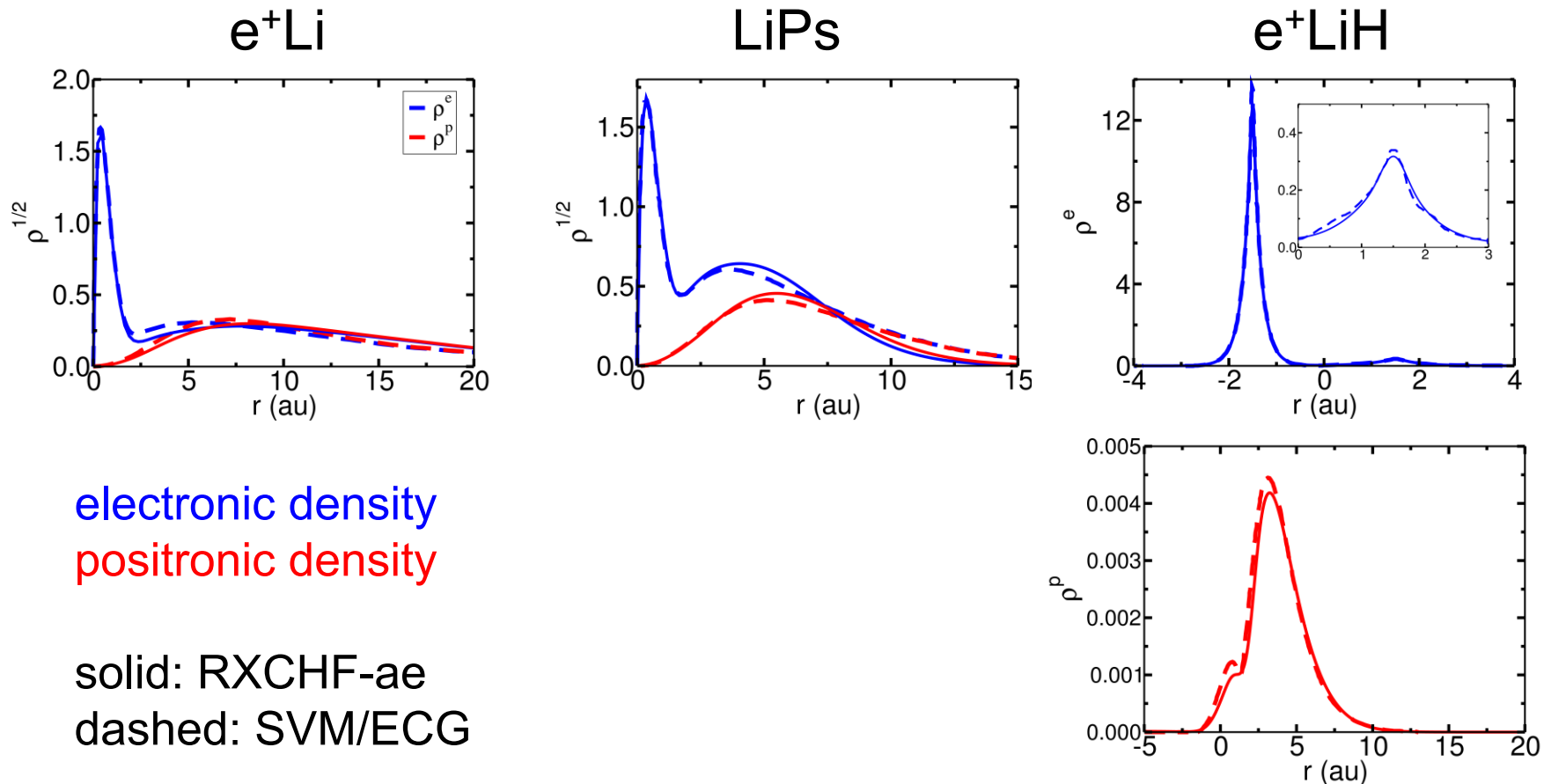
O-H O

State 1

O H-O

State 2

Electronic and Positronic Densities



RXCHF-ne and RXCHF-ae perform similarly and agree well with highly accurate SVM/ECG results

SVM data (dashed lines): Ryzhikh, Mitroy, Varga, *J. Phys. B* **31**, 3965 (1998).
ECG data (dashed lines): Strasburger, *J. Chem. Phys.* **111**, 10555 (1999).

Multicomponent DFT

Chakraborty, Pak, SHS, PRL 2008; Sirjoosingh, Pak, SHS, JCTC 2011; JCP 2012

$$E[\rho^e, \rho^p] = E_{\text{ext}}[\rho^e, \rho^p] + E_{\text{ref}}[\rho^e, \rho^p] \leftarrow \begin{array}{l} \text{kinetic energy of} \\ \text{noninteracting system,} \\ \text{"classical" Coulomb} \end{array} \\ + E_{\text{exc}}[\rho^e] + E_{\text{pxc}}[\rho^p] + E_{\text{epc}}[\rho^e, \rho^p]$$

Strategy for designing electron-proton functionals:

- Define e-p functional as

$$E_{\text{epc}}[\rho^e, \rho^p] = -\int d\mathbf{r}^e d\mathbf{r}^p r_{\text{ep}}^{-1} \rho^{\text{ep}}(\mathbf{r}^e, \mathbf{r}^p) + \int d\mathbf{r}^e d\mathbf{r}^p r_{\text{ep}}^{-1} \rho^e(\mathbf{r}^e) \rho^p(\mathbf{r}^p)$$

- Use an explicitly correlated wavefunction to obtain expression for electron-proton pair density $\rho^{\text{ep}}(\mathbf{r}^e, \mathbf{r}^p)$ in terms of one-particle electron and proton densities $\rho^e(\mathbf{r}^e)$ and $\rho^p(\mathbf{r}^p)$

Advantages: provides accurate nuclear densities, consistent treatment of el-el & el-proton correlation

Disadvantages: inherent DFT approximations, still expensive

Parr, JCP1982; Kreibich, Gross, PRL 2001; Chakraborty, Pak, SHS, JCP 2009

Electron-Proton Functional

Contribution to total energy:

$$E_{\text{epc}} [\rho^e, \rho^p] = -\int d\mathbf{r}^e d\mathbf{r}^p r_{\text{ep}}^{-1} \rho^{\text{ep}} + \int d\mathbf{r}^e d\mathbf{r}^p r_{\text{ep}}^{-1} \rho^e \rho^p$$

Expression for ep pair density in terms of 1-particle densities:

$$\Psi_{\text{gem}} = (1 + G) \Phi^e \Phi^p \quad \longrightarrow \quad \begin{aligned} \rho^{\text{ep}} &= \rho^e \rho^p + \rho^e \rho^p \langle \rho^e \rho^p g N_e^{-1} N_p^{-1} \rangle_{\text{ep}} \\ &+ \frac{\rho^e \rho^p g + \rho^e \rho^p N_e^{-1} N_p^{-1} \langle \rho^p g \rangle_p \langle \rho^e g \rangle_e}{1 + N_e^{-1} N_p^{-1} \langle \rho^e \rho^p g \rangle_{\text{ep}}} \\ &- \rho^e \rho^p \langle \rho^e g N_e^{-1} \rangle_e - \rho^e \rho^p \langle \rho^p g N_p^{-1} \rangle_p \end{aligned}$$

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

Satisfies sum rules:

$$\rho^e(\mathbf{r}^e) = N_p^{-1} \left\langle \rho^{\text{ep}}(\mathbf{r}^e, \mathbf{r}^p) \right\rangle_p \quad \rho^p(\mathbf{r}^p) = N_e^{-1} \left\langle \rho^{\text{ep}}(\mathbf{r}^e, \mathbf{r}^p) \right\rangle_e$$

Motivating work: Colle and Salvetti, 1975, developed an electronic functional

Born-Oppenheimer Approximation

- Schrödinger equation for electrons and protons

$$(T_p + T_e + V(\mathbf{r}_e, \mathbf{r}_p, \mathbf{R})) \Psi_k^{\text{tot}}(\mathbf{r}_e, \mathbf{r}_p; \mathbf{R}) = E_k(\mathbf{R}) \Psi_k^{\text{tot}}(\mathbf{r}_e, \mathbf{r}_p; \mathbf{R})$$

- Fix proton position and solve electronic part

$$(T_e + V(\mathbf{r}_e, \mathbf{r}_p, \mathbf{R})) \Psi_i^{\text{elec}}(\mathbf{r}_e; \mathbf{r}_p, \mathbf{R}) = \varepsilon_i(\mathbf{r}_p, \mathbf{R}) \Psi_i^{\text{elec}}(\mathbf{r}_e; \mathbf{r}_p, \mathbf{R})$$

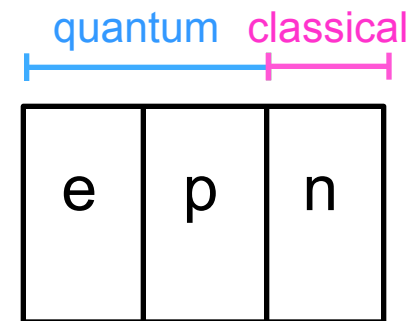
- For each electronic state, solve proton part

$$(T_p + \varepsilon_i(\mathbf{r}_p, \mathbf{R})) \Psi_{i\mu}^{\text{prot}}(\mathbf{r}_p; \mathbf{R}) = \varepsilon_{i\mu}^{(i)}(\mathbf{R}) \Psi_{i\mu}^{\text{prot}}(\mathbf{r}_p; \mathbf{R})$$

- Born-Oppenheimer approximation

$$\Psi_k^{\text{tot}}(\mathbf{r}_e, \mathbf{r}_p; \mathbf{R}) \approx \Psi_i^{\text{elec}}(\mathbf{r}_e; \mathbf{r}_p, \mathbf{R}) \Psi_{i\mu}^{\text{prot}}(\mathbf{r}_p; \mathbf{R})$$

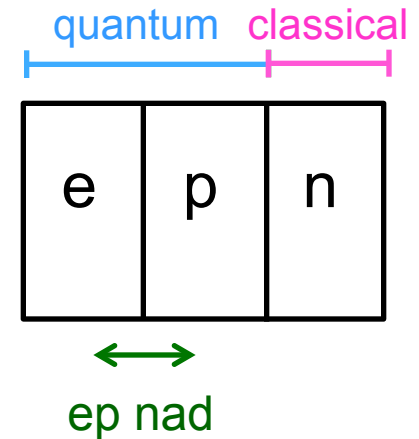
$\mathbf{r}_e, \mathbf{r}_p, \mathbf{R}$: electrons, protons, and other nuclei



Non-Born-Oppenheimer Effects

- Expand exact solution in double-adiabatic basis

$$\Psi_k^{\text{tot}}(\mathbf{r}_e, \mathbf{r}_p; \mathbf{R}) = \sum_{i, \mu} c_{i\mu}^k \Psi_i^{\text{elec}}(\mathbf{r}_e; \mathbf{r}_p, \mathbf{R}) \Psi_{i\mu}^{\text{prot}}(\mathbf{r}_p; \mathbf{R})$$



- Express Hamiltonian in matrix form

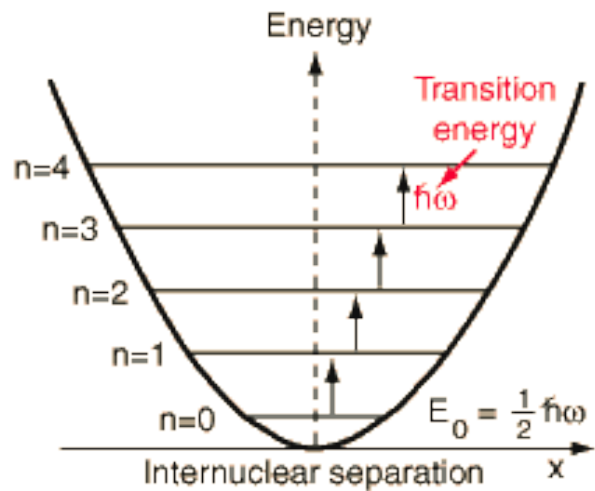
$$H_{i\mu, j\nu} = \delta_{ij} \delta_{\mu\nu} \varepsilon_{\mu}^{(i)}(\mathbf{R}) - \frac{\hbar^2}{m_p} \langle \Psi_{i\mu}^{\text{prot}} | \mathbf{d}_{ij}^{(\text{ep})} \cdot \nabla_{\mathbf{r}_p} | \Psi_{j\nu}^{\text{prot}} \rangle_p - \frac{\hbar^2}{2m_p} \langle \Psi_{i\mu}^{\text{prot}} | g_{ij}^{(\text{ep})} | \Psi_{j\nu}^{\text{prot}} \rangle_p$$

- Nonadiabatic couplings provide a measure of nonadiabaticity

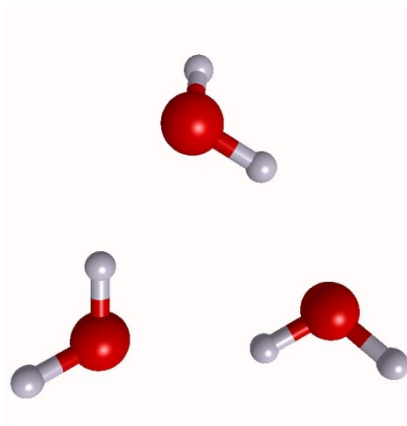
$$\mathbf{d}_{ij}^{(\text{ep})} = \langle \Psi_i^{\text{elec}} | \nabla_{\mathbf{r}_p} | \Psi_j^{\text{elec}} \rangle_e$$

$$g_{ij}^{(\text{ep})} = \langle \Psi_i^{\text{elec}} | \nabla_{\mathbf{r}_p}^2 | \Psi_j^{\text{elec}} \rangle_e$$

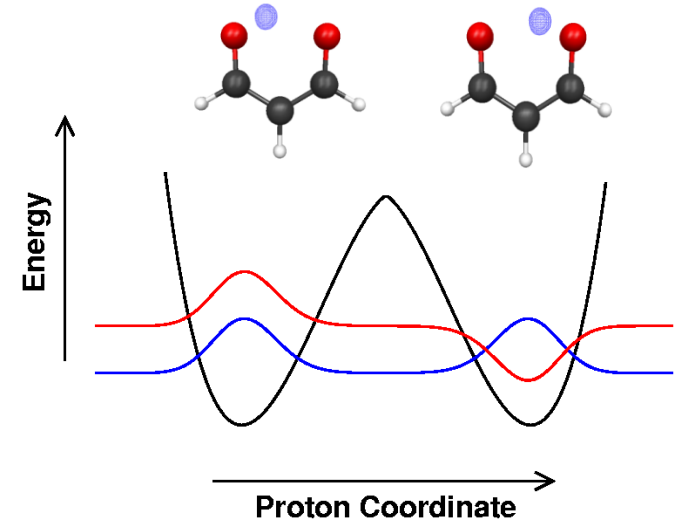
Nuclear Quantum Effects



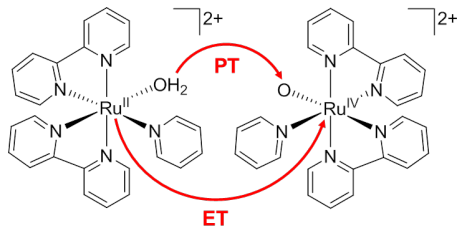
Zero point energy
Vibrationally excited states



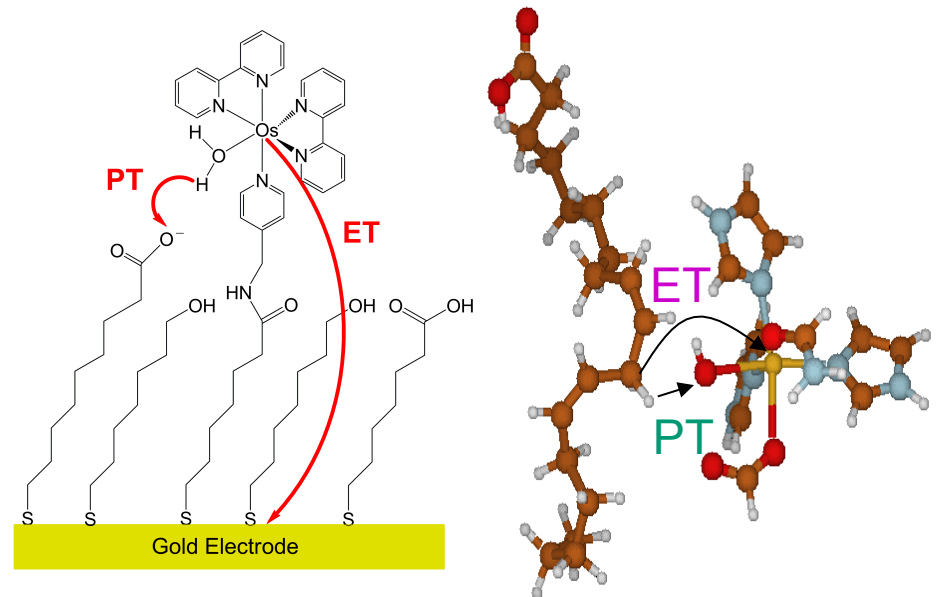
Hydrogen bonding



Hydrogen tunneling



Proton-coupled electron transfer in solution, proteins, electrochemistry



Nuclear Quantum vs. Non-Adiabatic Effects

$$\Psi(r, R) = \Phi(r | R)X(R)$$

$$\hat{H}(r, R) = \hat{H}_R + \hat{H}_r + \hat{V}(r, R)$$

$$\hat{T}_R \Phi(r, R) \approx 0$$

$$\hat{H}(r, R)\Psi(r, R) = E\Psi(r, R) \longrightarrow \begin{cases} [\hat{H}_r + \hat{V}(r, R)]\Phi(r | R) = W(R)\Phi(r | R) \\ [\hat{H}_R + \hat{W}(R)]X(R) = EX(R) \end{cases}$$

$$\hat{T}_{R_1} \Phi(r, R) \neq 0 \quad \hat{T}_R \Phi(r, R) \approx 0$$

$$\Psi(r, R) = \Phi(r, R_1 | R)X(R)$$

$$\begin{cases} [\hat{H}_r + \hat{H}_{R_1} + \hat{V}(r, R_1) + \hat{V}(r, R)]\Phi(r, R_1 | R) = W(R)\Phi(r, R_1 | R) \\ [\hat{H}_R + \hat{W}(R)]X(R) = EX(R) \end{cases}$$