Constrained density-functional theory configuration-interaction

Benjamin Kaduk

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Electronic Structure in Chemistry

Electrons (and molecules) obey the Schrodinger equation:

$$\hat{H}\Psi\left(\mathbf{r}_1,\cdots,\mathbf{r}_N\right)=E\Psi\left(\mathbf{r}_1,\cdots,\mathbf{r}_Ni\right)$$

The Born-Oppenheimer approximation gives focus to electrons.

Density-Functional Theory

Hohenberg-Kohn theorem:

$$E_{\text{exact}} = E[\rho_{\text{exact}}(\mathbf{r})]$$

Existence only, not constructive.
Approximations?

Hartree-Fock

Hartree-Fock approximation of orbitals;

$$\Psi \approx \Phi$$

$$\Phi = \mathcal{A}\left(\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_N(\mathbf{r}_N)\right)$$

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$$\Psi \approx \Phi$$

$$\Phi = \mathcal{A}\left(\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_N(\mathbf{r}_N)\right)$$

$$\hat{F}\phi_i = \epsilon_i\phi_i$$

$$\hat{F} = \hat{h} + \hat{J} - \hat{K}$$

$$\hat{h} = -\frac{1}{2}\nabla^2 + \hat{v}_{\mathrm{nuc}}$$

$$\hat{J}\phi_i(\mathbf{r}_1) = \sum_j \int d\mathbf{r}_2 \phi_j(\mathbf{r}_2)\frac{1}{\hat{r}_{12}}\phi_j(\mathbf{r}_2)\phi_i(\mathbf{r}_1)$$

$$\hat{K}\phi_i(\mathbf{r}_1) = \sum_j \int d\mathbf{r}_2 \phi_j(\mathbf{r}_2)\frac{1}{\hat{r}_{12}}\phi_i(\mathbf{r}_2)\phi_j(\mathbf{r}_1)$$

Orbital Equations

The Hartree-Fock equations for the orbitals and energies:

$$\left(\hat{h} + \hat{J} - \hat{K}\right)\phi_i = \epsilon_i \phi_i$$

Still using a determinantal wavefunction:

$$\Phi = \mathcal{A}\left(\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_N(\mathbf{r}_N)\right)$$

Kohn-Sham DFT introduces orbitals as well:

$$\left(\hat{h} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' + v_{xc}(\mathbf{r})\right)\phi_i = \epsilon_i \phi_i$$

Constrained DFT

Kohn-Sham DFT uses orbitals from a fictitious system to get the real density:

$$\rho(\mathbf{r}) = \Phi(\mathbf{r})\Phi(\mathbf{r})^\dagger$$

Pushing that density around would make charge-transfer states...

$$\left|\mathrm{D}^0\mathrm{A}^0\right\rangle \Rightarrow \left|\mathrm{D}^+\mathrm{A}^-\right\rangle$$

Specify an atomic charge so that

$$\int \rho(\mathbf{r})W(\mathbf{r})d\mathbf{r} = N$$

Constrained DFT

A standard energy functional with added constraint Lagrange multiplier term.

$$E[\rho, V_k; N_k] \equiv E[\rho] + \sum_k V_k \left(\sum_\sigma \int W_k^\sigma(\mathbf{r}) \rho^\sigma(\mathbf{r}) d^3 r - N_k \right)$$

$$E(N_k) = \min_\rho \max_{V_k} E[\rho, V_k; N_k]$$

Leading to orbital equations:

$$\left(\hat{h} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r' + v_{xc}^\sigma(\mathbf{r}) + \sum_k V_k W_k^\sigma(\mathbf{r}) \right) \phi_{i\sigma} = \epsilon_{i\sigma} \phi_{i\sigma}$$

Coupling CDFT states together

CDFT states are neither the ground state nor (formally) an excited state, but rather the ground state of a system with an extra potential. Yet we have

$$\left|\mathrm{D}^0\mathrm{A}^0\right\rangle$$

and

$$\left|\mathrm{D}^+\mathrm{A}^-\right\rangle$$

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$$\left|\mathrm{D}^0\mathrm{A}^0\right\rangle$$

and

$$\left|\mathrm{D}^+\mathrm{A}^-\right\rangle$$

Electron-transfer theory (and other applications) need a coupling between these states:

$$H_{12} = \left\langle \Psi_1 \middle| \hat{H} \middle| \Psi_2 \right\rangle$$

Coupling CDFT states together

Desired coupling is:

$$H_{12} = \left\langle \Psi_1 \middle| \hat{H} \middle| \Psi_2 \right\rangle$$

requires $|\Psi_i\rangle$... CDFT only gives $|\Phi_i\rangle$.

$$\begin{aligned}
H_{12} &= \left\langle \Psi_1 \middle| \hat{H} \middle| \Psi_2 \right\rangle \\
&= \left\langle \Psi_1 \middle| \frac{\hat{H} + V_1\hat{W}_1(\mathbf{r}) + \hat{H} + V_2\hat{W}_2(\mathbf{r})}{2} - \frac{V_1\hat{W}_1(\mathbf{r}) + V_2\hat{W}_2(\mathbf{r})}{2} \middle| \Psi_2 \right\rangle \\
&= \left\langle \Psi_1 \middle| \frac{F_1 + F_2}{2} - \frac{V_1\hat{W}_1(\mathbf{r}) + V_2\hat{W}_2(\mathbf{r})}{2} \middle| \Psi_2 \right\rangle \\
&= \frac{F_1 + F_2}{2} S_{12} - \left\langle \Psi_1 \middle| \frac{V_1\hat{W}_1(\mathbf{r}) + V_2\hat{W}_2(\mathbf{r})}{2} \middle| \Psi_2 \right\rangle
\end{aligned}$$

CDFT-Configuration Interaction

We have:

- Constrained states
- Couplings between them

. . . the Hamiltonian in a basis of (non-orthogonal) CDFT states.

CDFT-CI: theory

Basis of N states generated by arbitrary constraints:

$$\begin{pmatrix} H_{11} & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22} & & H_{2N} \\ \vdots & & \ddots & \vdots \\ H_{N1} & H_{N2} & \cdots & H_{NN} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{pmatrix} = E \begin{pmatrix} 1 & S_{12} & \cdots & S_{1N} \\ S_{21} & 1 & & S_{2N} \\ \vdots & & \ddots & \vdots \\ S_{N1} & S_{N2} & \cdots & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{pmatrix}$$

CDFT-CI: promolecules

Atomic charge in molecules is not defined.

$$\text{(exact)} \qquad \mathrm{H^{+}H} \neq \mathrm{H^{+}H} \qquad \text{(“measured”)}$$

Many approximations to choose from (Becke, Mulliken, Löwdin, Hirshfeld, . . .).

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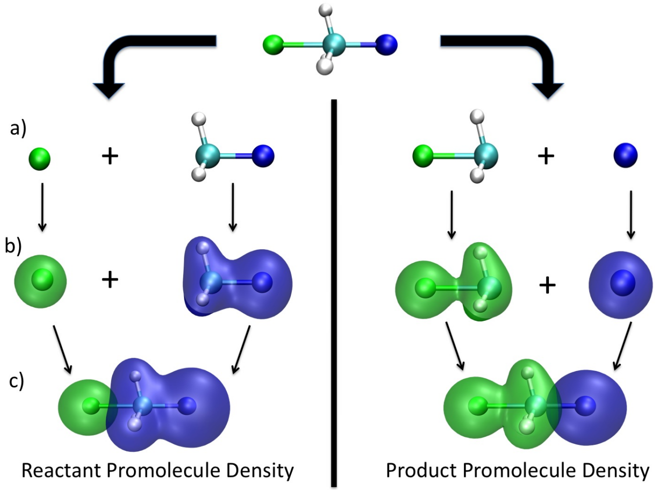
$$N_{\mathrm{new}} = \int \left(\rho_{\mathrm{H}}(\mathbf{r}-\mathbf{r}_1) + \rho_{\mathrm{H}^+}(\mathbf{r}-\mathbf{r}_2)\right) \hat{W}(\mathbf{r}) d\mathbf{r}$$

CDFT-CI: promolecules

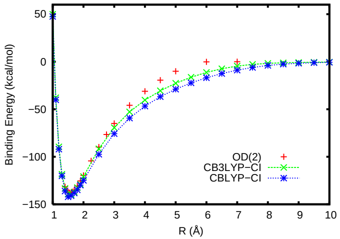


Reactant Promolecule Density

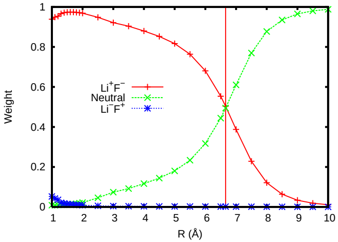
Product Promolecule Density

CDFT-CI: application

Bond dissociation:



LiF energies

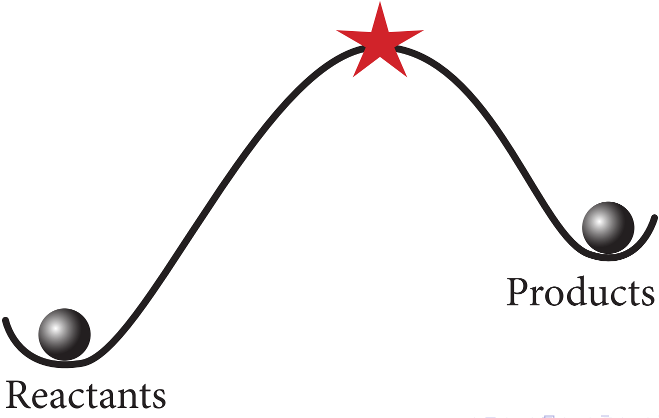


Contributions from CDFT states

- Background
- Transition States
  - Reference Set
  - CDFT-CI Gradients
  - Optimized Geometries
- Excited States
  - Conical Intersections
  - Optimized Geometries
- Conclusions

Reaction barriers

$$\mathrm{AX} + \mathrm{B} \leftrightarrow \mathrm{A} + \mathrm{XB}$$



Geometries from theory

- Experiments for transition-state geometries are often unavailable
- High-level theory gives reference states/energies
- Use reference sets to benchmark new methods
- How good is the reference?

Transition-state test set

Truhlar's group has lots of reference sets.

- intramolecular reactions are hard for CDFT/CDFT-CI
- Reactions from the HTBH38/04 and NHTBH38 databases, which used the QCISD/MG3 level of theory
- 18 hydrogen transfer (HT) reactions
- 6 heavy atom transfer (HAT) reactions
- 8 nucleophilic substitution (SN) reactions
- Forward and backward reactions are usually different

Hydrogen transfer

$$\mathrm{H} + \mathrm{HCl} \leftrightarrow \mathrm{Cl} + \mathrm{H}_2$$

$$\mathrm{OH} + \mathrm{H}_2 \leftrightarrow \mathrm{H} + \mathrm{H}_2\mathrm{O}$$

$$\mathrm{CH}_3 + \mathrm{H}_2 \leftrightarrow \mathrm{H} + \mathrm{CH}_4$$

$$\mathrm{OH} + \mathrm{CH}_4 \leftrightarrow \mathrm{CH}_3 + \mathrm{H}_2\mathrm{O}$$

$$\mathrm{H} + \mathrm{H}_2 \leftrightarrow \mathrm{H}_2 + \mathrm{H}$$

$$\mathrm{OH} + \mathrm{NH}_3 \leftrightarrow \mathrm{H}_2\mathrm{O} + \mathrm{NH}_2$$

$$\mathrm{HCl} + \mathrm{CH}_3 \leftrightarrow \mathrm{Cl} + \mathrm{CH}_4$$

$$\mathrm{OH} + \mathrm{C}_2\mathrm{H}_6 \leftrightarrow \mathrm{H}_2\mathrm{O} + \mathrm{C}_2\mathrm{H}_5$$

$$\mathrm{F} + \mathrm{H}_2 \leftrightarrow \mathrm{H} + \mathrm{HF}$$

Hydrogen transfer

$$O + CH_4 \leftrightarrow OH + CH_3$$

$$H + PH_3 \leftrightarrow PH_2 + H_2$$

$$H + HO \leftrightarrow H_2 + O$$

$$H + H_2S \leftrightarrow H_2 + HS$$

$$O + HCl \leftrightarrow OH + Cl$$

$$NH_2 + CH_3 \leftrightarrow CH_4 + NH$$

$$NH_2 + C_2H_5 \leftrightarrow C_2H_6 + NH$$

$$C_2H_6 + NH_2 \leftrightarrow NH_3 + C_2H_5$$

$$NH_2 + CH_4 \leftrightarrow CH_3 + NH_3$$

Heavy atom transfer

$$H + N_2O \leftrightarrow OH + N_2$$

$$H + FH \leftrightarrow FH + H$$

$$H + ClH \leftrightarrow HCl + H$$

$$H + FCH_3 \leftrightarrow HF + CH_3$$

$$H + F_2 \leftrightarrow HF + F$$

Nucleophilic substitution

$$CH_3 + FCl \leftrightarrow CH_3F + Cl$$

$$F^- + CH_3F \leftrightarrow FCH_3 + F^-$$

$$F^- \cdots CH_3F \leftrightarrow FCH_3 \cdots F^-$$

$$Cl^- + CH_3Cl \leftrightarrow ClCH_3 + Cl^-$$

$$Cl^- \cdots CH_3Cl \leftrightarrow ClCH_3 \cdots Cl^-$$

$$F^- + CH_3Cl \leftrightarrow FCH_3 + Cl^-$$

$$F^- \cdots CH_3Cl \leftrightarrow FCH_3 \cdots Cl^-$$

$$OH^- + CH_3F \leftrightarrow HOCH_3 + F^-$$

$$OH^- \cdots CH_3F \leftrightarrow HOCH_3 \cdots F^-$$

CDFT-CI barrier heights

How does CDFT-CI improve on regular DFT?

	LSDA		PBE		B3LYP		B97-2	
				hydrogen transfer (36)				
ME	-18.2	**-9.3**	-9.7	**-2.6**	-4.6	**2.3**	-3.4	**3.7**
MAE	18.2	**10.9**	9.7	**3.8**	4.6	**3.0**	3.6	**4.0**
				heavy atom transfer (12)				
ME	-23.5	**-15.1**	-14.9	**-7.6**	-8.5	**-1.2**	-3.1	**4.3**
MAE	23.5	**15.1**	14.9	**7.6**	8.5	**2.3**	3.4	**4.7**
				nucleophilic substitution (16)				
ME	-8.4	**-3.4**	-6.9	**-2.2**	-3.4	**0.6**	-1.4	**2.9**
MAE	8.4	**4.2**	6.9	**2.3**	3.4	**1.3**	1.4	**2.9**
				all (64)				
ME	-16.7	**-8.9**	-10.0	**-3.4**	-5.0	**1.2**	-2.8	**3.6**
MAE	16.7	**10.0**	10.0	**4.2**	5.1	**2.5**	3.0	**3.9**

Roman type is DFT, **bold is CDFT-CI**.

CDFT-CI Gradients

This benchmarking strategy is not perfect:

- reference geometry
- not necessarily critical point for CDFT-CI
- uncontrolled error
- remove error by re-optimization

We need CDFT-CI gradients (derivatives with respect to nuclear coordinates).

CDFT-CI refresher

Recalling the definition of (two-state) CDFT-CI:

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \mathcal{E} \begin{pmatrix} 1 & S_{12} \\ S_{21} & 1 \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

More simply:

$$\mathbf{H} C = \mathcal{E} \mathbf{S} C$$

Structure of approach

Take the derivative with respect to a nuclear coordinate x and write

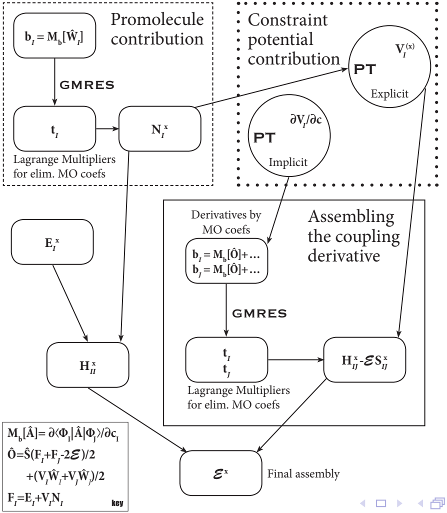
$$\mathbf{H}^x C + \mathbf{H} C^x = \mathcal{E}^x \mathbf{S} C + \mathcal{E} \mathbf{S}^x C + \mathcal{E} \mathbf{S} C^x$$

Solve for $\mathcal{E}^x$:

$$\mathcal{E}^x = C^\dagger \left(\mathbf{H}^x - \mathcal{E} \mathbf{S}^x \right) C$$

$\mathcal{E}$ and C are known; need $\mathbf{H}^x$ and $\mathbf{S}^x$.

Structure of approach



Promolecule contribution

$b_I = M_b[\hat{W}_I]$

GMRES

t_I

N_I^x

Lagrange Multipliers for elim. MO coefs

Constraint potential contribution

PT $V_I^{(x)}$ Explicit

PT $\partial V_I/\partial c$ Implicit

E_I^x

H_{II}^x

Derivatives by MO coefs

$b_I = M_b[\hat{O}]+\ldots$
$b_J = M_b[\hat{O}]+\ldots$

Assembling the coupling derivative

GMRES

t_I
t_J

Lagrange Multipliers for elim. MO coefs

$H_{IJ}^x - \mathcal{E}S_{IJ}^x$

$\mathcal{E}^x$

Final assembly

$M_b[\hat{A}] = \partial\langle\Phi_I|\hat{A}|\Phi_J\rangle/\partial c_I$
$\hat{O} = \hat{S}(F_I + F_J - 2\mathcal{E})/2$
$+(V_I\hat{W}_I + V_J\hat{W}_J)/2$
$F_I = E_I + V_I N_I$

key

Same transition states

- 18 hydrogen transfer (HT) reactions.[1]
- 6 heavy atom transfer (HAT) reactions
- 8 nucleophilic substitution (SN) reactions

$$\mathrm{H} + \mathrm{PH_3} \leftrightarrow \mathrm{PH_2} + \mathrm{H_2}$$

$$\vdots$$

$$\mathrm{H} + \mathrm{FCH_3} \leftrightarrow \mathrm{HF} + \mathrm{CH_3}$$

$$\vdots$$

$$\mathrm{OH^-} \cdots \mathrm{CH_3F} \leftrightarrow \mathrm{HOCH_3} \cdots \mathrm{F^-}$$

$$\vdots$$

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[1] Actually, only 16.

Barrier height comparison

Geometries are optimized. Quality of energies?
CDFT-CI at the reference geometry versus CDFT-CI optimized geometry.

	ME, ref	ME, opt	MAE, ref	MAE, opt
HT	1.00	0.96	2.27	2.18
HAT	-1.94	-1.82	3.03	3.22
SN	-0.07	-0.10	0.88	0.82
All reactions	0.20	0.19	2.10	2.07

Energies in kcal/mol.

- Background
- Transition States
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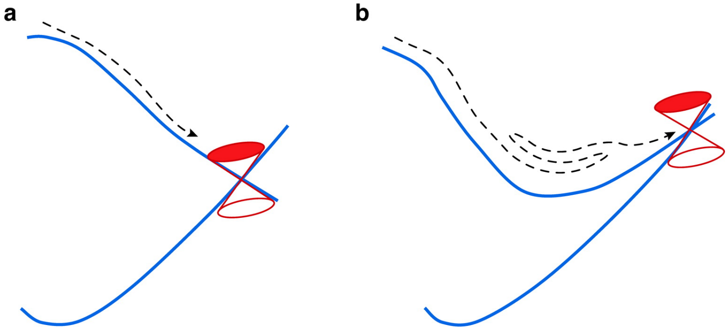
Motivation

Photoexcitation. . . then what?



Levine BG, Martínez TJ. 2007.
Annu. Rev. Phys. Chem. 58:613–34

Obtaining excited-state energies and forces

Recall the Hartree-Fock orbital equations:

$$\hat{F}\phi_i = \epsilon_i \phi_i$$

for a Slater determinant wavefunction

$$\Psi_0 = \mathcal{A}\left(\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_N(\mathbf{r}_N)\right)$$

Not the only possible wavefunction...

$$\Psi_i^a = \mathcal{A}\left(\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_{i-1}(\mathbf{r})\phi_a(\mathbf{r})\phi_{i+1}(\mathbf{r})\cdots\phi_N(\mathbf{r}_N)\right)$$

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$$\Psi = C_0\Psi_0 + \sum_{ia} C_{ia}\Psi_i^a \left[+\sum_{ij}^{ab} C_{ijab}\Psi_{ij}^{ab} + \cdots\right]$$

Use to build CIS, CISD, CASSCF, . . .

DFT isn't left out — linear-response time-dependent DFT (TDDFT)!

Conical Intersections

Consider a two-state system:

$$\mathcal{H} = \begin{pmatrix} E_1 & V \\ V & E_2 \end{pmatrix}$$

When $E_1 - E_2 = 0$, the coupling V splits the adiabats.
If V is also zero, there is true degeneracy.

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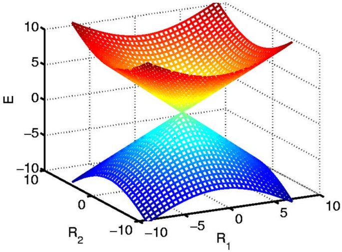
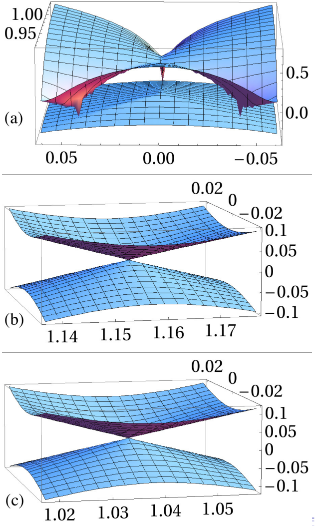
If V is also zero, there is true degeneracy.



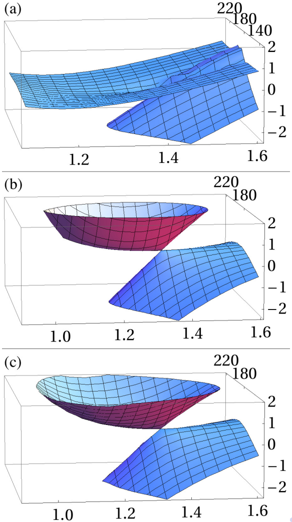
Trihydrogen

TD-DFT (a), Full CI (a), and CDFT-CI (c). The intersection is around an equilateral geometry, holding two nuclei fixed in the x-y plane while varying (x, y) of the third.



Linear water

TD-DFT (a), CASSCF (b), and CDFT-CI (c). Symmetric water, $R(\mathrm{OH}_1) = R(\mathrm{OH}_2)$. Axes are symmetric stretch, and bend.



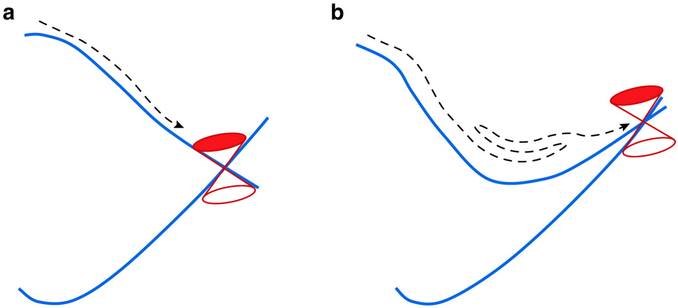
Excited-state geometry optimization

A tough choice to make.
Methods with excited-state gradients:

- CASSCF/CASPT2
- CIS
- TDDFT
- CC2

In general, slow and/or unreliable.

Where are we going?



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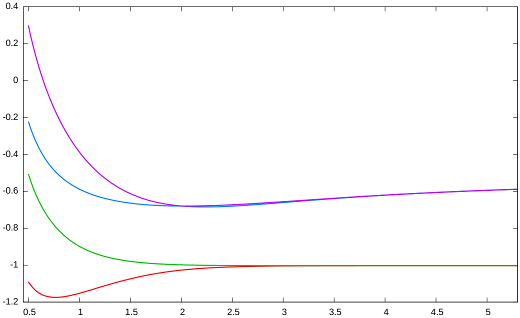
A humble beginning

H_2 is the simplest test for most electronic structure methods.



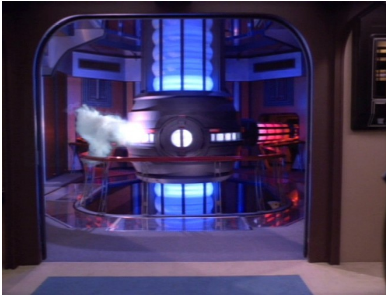
Geometry optimization finds a minimum at 2.235 Å, comparable to the reference value 2.275 Å, given the small basis set used for CDFT-CI (cc-pvdz).

Engage the warp core. . .

A slightly more engaging molecule is dilithium.

Furche has reference excited-state geometries[a] including Li_2. CDFT-CI configurations: $\mathrm{Li}^+\mathrm{Li}^-$, $\mathrm{Li}^-\mathrm{Li}^+$, $\mathrm{Li}^\uparrow\mathrm{Li}^\downarrow$, and $\mathrm{Li}^\downarrow\mathrm{Li}^\uparrow$.

	$R(\mathrm{Li}-\mathrm{Li})$ (Å)
reference	3.11
CDFT-CI	3.17



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[a] JCP 122, 064105 (2005).

Ethane

Analytical gradients become useful for polyatomics, where there is more than a single degree of freedom.

- C_2H_6 has a nice single bond we like
- Standard four-state basis becomes $CH_3^+CH_3^-$, $CH_3^-CH_3^+$, $CH_3^\uparrow CH_3^\downarrow$, and $CH_3^\downarrow CH_3^\uparrow$.
- Carbon-carbon separation doubles from 1.5 Å to 3.0 Å!
- $C-C-H$ angle of 94°
- $H-C-H$ angle of 119.4°

Results

CDFT-CI has:

- Robust performance for barrier heights
- Reasonable, efficient-scaling treatment of excited states
- Ability to produce challenging topological features
- Reliance on chemical intuition

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \mathcal{E} \begin{pmatrix} 1 & S_{12} \\ S_{21} & 1 \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

Acknowledgements

Thanks go out to:

- Troy Van Voorhis
- all of my committee
- Tim Kowalczyk
- All the residents of the theory zoo

FIN.