Gentlest Ascent Dynamics for Calculating First Excited State and Exploring Energy Landscape of Density Functionals

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Outline

- Review of Kohn-Sham Eq. (SCF)
- Δ SCF[1]
- Gentlest ascent dynamics[2] (GAD)
- GAD in KS-DFT[3]

1. T. Ziegler, A. Rauk, and E. J. Baerends, Theor. Chim. Acta **43**, 261 (1977).
2. 2. W. E and X. Zhou, Nonlinearity 24, 1831 (2011) .
3. C. Li, J. Lu, and W. Yang, J. Chem. Phys. 143, 224110 (2015).

Kohn-Sham Equation

Given density functional $E[\rho]$, with ρ coming from $\det(\varphi_1, \varphi_2, \ldots \varphi_N)$,

$$\min_{\{\psi_i\}} E[\rho] - \sum_{ij} \lambda_{ij} \left(\left\langle \varphi_i \middle| \varphi_j \right\rangle - \delta_{ij} \right)$$

gives the ground state density and energy. This leads to Euler-Lagrange equation

$$h_s \varphi_i = \sum_j \lambda_{ij} \varphi_j,$$

where $h_s \varphi_i = \dfrac{\delta E}{\delta \varphi_i^*} = \dfrac{\delta E}{\delta \rho_s} \varphi_i$. By a unitary transformation, we can rewrite above Eq. as

$$h_s \psi_i = \varepsilon_i \psi_i,$$

where $\{\psi_i\}$ is a rotation of $\{\varphi_i\}$, and are called canonical orbitals; ε_i is the orbital energy.

One solves the above Kohn-Sham equation to obtain ground state, through iterative procefure, the SCF procedure.

SCF procedure

SCF iteration procedure:

at iteration step k:

given $\rho_s^{in} = \sum_{i=1}^{occ} |\psi_i^{in}\rangle\langle\psi_i^{in}|$, compute $h_s^{out} = \frac{\delta E}{\delta \rho_s^{in}}$.

Diagonalize $h_s^{out} = \sum_{i=1}^{\infty} \varepsilon_i^{out} |\psi_i^{out}\rangle\langle\psi_i^{out}|$,

form $\rho_s^{out} = \sum_{i=1}^{occ} |\psi_i^{out}\rangle\langle\psi_i^{out}|$.

Check $\rho_s^{out} = \rho_s^{in}$?

Yes: solution found, iteration ended.

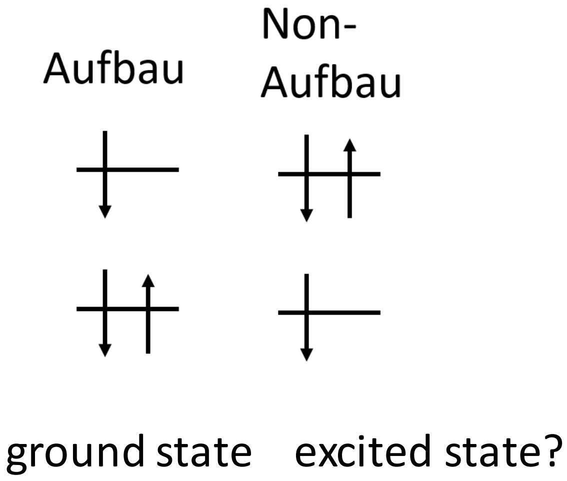
No: set $\rho_s^{in} = \rho_s^{out}$, start next iteration step.

Question: How to choose orbital to form density matrix?

ΔSCF-DFT

- Aufbau and non-Aufbau solutions

- Δ SCF
  - Two SCF calculations:



  - Both solutions are stationary
  - Question: are non-Aufbau solutions meaningful?

Equivalently: if ρ_i is non-ground state stationary density, is $E[\rho_i]$ excited state energy?

ΔSCF-DFT

- Stationary solutions of the exact density functionals $E[\rho]$[1]

  Stationary state density $\bar{\rho}_i \longrightarrow \bar{\Psi}_i$, excited state wavefunction,

  $E[\bar{\rho}_i]$ is the excited state energy.

  - Implicit assumption: ρ_i is excited state v-representable
  - Numerically give reasonable results, accuracy~TDDFT[2−4]
  - merit: low computational cost

1. M. Levy and J. P. Perdew, Phys. Rev. A 32, 2010 (1985).
2. C.-L. Cheng, Q. Wu, and T. Van Voorhis, J. Chem. Phys. **129**, 124112 (2008).
3. T. Kowalczyk, S. R. Yost, and T. V. Voorhis, J. Chem. Phys. **134**, 054128 (2011).
4. S. R. Yost, T. Kowalczyk, and T. Van Voorhis, J. Chem. Phys. **139**, 174104 (2013).

ΔSCF-DFT

- Problem:
  - No guarantee to converge
  - Possible scenario: frontier orbitals switch back and forth
- Other approach
  - Contricted DFT[1]
  - Maximum overlap method (MOM)[2]
  - Meta-dynamics related methods[3]
- Our approach: an alternative perspective
  - Use stationary nature
  - Target saddle point of energy functional

1. T. Ziegler, M. Seth, M. Krykunov, J. Autschbach, and F. Wang, J. Chem. Phys. **130**, 154102 (2009).
2. N. A. Besley, A. T. B. Gilbert, and P. M. W. Gill, J. Chem. Phys. **130**, 124308 (2009).
3. A. J. W. Thom and M. Head-Gordon, Phys. Rev. Lett. **101**, 193001 (2008).

GAD formalism

- Gentlest ascent dynamics[1] Index-1 saddle point dynamics

Given function $F(x)$ $\qquad x = (x^1, x^2, \cdots, x^n).$

Recall steepest descent

$$\frac{d}{dt}x(t) = -\frac{\partial F}{\partial x}$$

$$\frac{d}{dt}v(t) = -\frac{\partial^2 F}{\partial x^2}v, \qquad \|v\| = 1$$

$$\frac{d}{dt}x(t) = -\frac{\partial F}{\partial x} + 2\left\langle \frac{\partial F}{\partial x}, v \right\rangle v$$

1. W. E and X. Zhou, Nonlinearity 24, 1831 (2011)

GAD formalism

- Gentlest ascent dynamics in DFT
  - Energy functional $E = E[\mathbf{\Psi}]$ $\mathbf{\Psi} = (\psi_1, \psi_2, \cdots, \psi_N)^T \in \mathcal{W}$
  - admissible set $\mathcal{W} = \{\mathbf{\Psi} \mid (\psi_i, \psi_j) = \delta_{ij}\}$
  - Define inner product

$$\langle \mathbf{\Psi}, \mathbf{\Phi} \rangle = \sum_{i=1}^{N} (\psi_i, \varphi_i)$$

  - Define derivatives

$$\frac{\partial E}{\partial \mathbf{\Psi}} \mathbf{\Phi} = \left\langle \frac{\partial E}{\partial \mathbf{\Psi}}, \mathbf{\Phi} \right\rangle = \sum_{i=1}^{N} (\frac{\delta E}{\delta \psi_i}, \varphi_i)$$

$$\left(\frac{\partial^2 E}{\partial \mathbf{\Psi}^2} \mathbf{\Phi} \right)_i = \sum_{j=1}^{N} (\frac{\delta^2 E}{\delta \psi_i \delta \psi_j}, \varphi_j)$$

GAD formalism

- Energy functional expansion

note if $\mathbf{\Psi} \in \mathcal{W}$, $\mathbf{\Psi} + t\mathbf{\Phi} \notin \mathcal{W}$! define $\hat{\mathbf{F}}$, *s.t.* $\hat{\mathbf{F}}(\mathbf{\Psi} + t\mathbf{\Phi}) \in \mathcal{W}$.

$$L[\mathbf{\Psi} + t\mathbf{\Phi}] = E[\hat{\mathbf{F}}(\mathbf{\Psi} + t\mathbf{\Phi})]$$

$$= L[\mathbf{\Psi}] + t\frac{\partial L}{\partial \mathbf{\Psi}}[\mathbf{\Phi}] + \frac{1}{2}t^2 \left\langle \mathbf{\Phi}, \hat{\mathbf{H}}\mathbf{\Phi} \right\rangle$$

$\frac{\partial L}{\partial \mathbf{\Psi}}$: effective gradient, $\hat{\mathbf{H}} = \frac{\partial^2 L}{\partial \mathbf{\Psi}^2}$: effective Hessian.

By some calculation,

$$\frac{\partial L}{\partial \mathbf{\Psi}} = \frac{\partial E}{\partial \mathbf{\Psi}} \qquad \hat{\mathbf{H}} = \frac{\partial^2 E}{\partial \mathbf{\Psi}^2} - 2\hat{\mathbf{\Gamma}}$$

$$\left(\hat{\mathbf{\Gamma}}\mathbf{\Phi}\right)_i = \sum_j (\hat{h}_s \psi_i, \psi_j)\varphi_j = \sum_j \gamma_{ij}\varphi_j$$

GAD formalism

- Gentlest ascent dynamics in DFT

$$\frac{d}{dt}\mathbf{\Psi} = -\frac{\partial E}{\partial \mathbf{\Psi}} + 2\left\langle \frac{\partial E}{\partial \mathbf{\Psi}}, \mathbf{\Phi} \right\rangle \mathbf{\Phi} + \mathbf{\Lambda}\mathbf{\Psi}$$

$$\frac{d}{dt}\mathbf{\Phi} = -\hat{\mathbf{H}}\mathbf{\Phi} + \mu\mathbf{\Phi} + \mathbf{K}\mathbf{\Psi}$$

Lagrange Multipliers		Constraints
μ		$\|\mathbf{\Phi}\| = 1$
$\mathbf{\Lambda}$	→	$\mathbf{\Psi} \in \mathcal{W}$
$\mathbf{K}$		$(\psi_i, \varphi_j) = 0$ for all i and j

GAD formalism

- Gentlest ascent dynamics in KS-orbitals
- Remove Lagrange multipliers

$$\frac{d\psi_i^\sigma(\mathbf{r})}{dt} = -\hat{h}_s^\sigma \psi_i^\sigma(\mathbf{r}) + 2\sum_{j\sigma'} (\hat{h}_s^{\sigma'} \psi_j^{\sigma'}, \varphi_j^{\sigma'}) \varphi_i^\sigma(\mathbf{r})$$

$$\frac{d\varphi_i^\sigma(\mathbf{r})}{dt} = -\hat{h}_s^\sigma \varphi_i^\sigma(\mathbf{r}) - \sum_{\sigma'} \hat{V}^{\sigma\sigma'}[2\sum_j \psi_j^{\sigma'} \varphi_j^{\sigma'}] \psi_i^\sigma(\mathbf{r}) + \sum_j \gamma_{ij}^\sigma \varphi_j^\sigma(\mathbf{r})$$

With constraints

$$\begin{cases} (\psi_i^\sigma, \psi_j^\sigma) = \delta_{ij}, \\ \sum_{i\sigma} (\varphi_i^\sigma, \varphi_i^\sigma) = 1, \\ (\psi_i^\sigma, \varphi_j^\sigma) = 0. \end{cases}$$

$$\hat{V}^{\sigma\sigma'}[f] = \int \frac{\delta v_{\text{eff}}^\sigma(\mathbf{r})}{\delta \rho^{\sigma'}(\mathbf{r}')} f(\mathbf{r}') d\mathbf{r}'$$

- Direct implementation cost $O(N^4)$
- Using density fitting, reduce cost to $O(N^3)$
- Can be modified to target index-2 or higher saddle points

Results

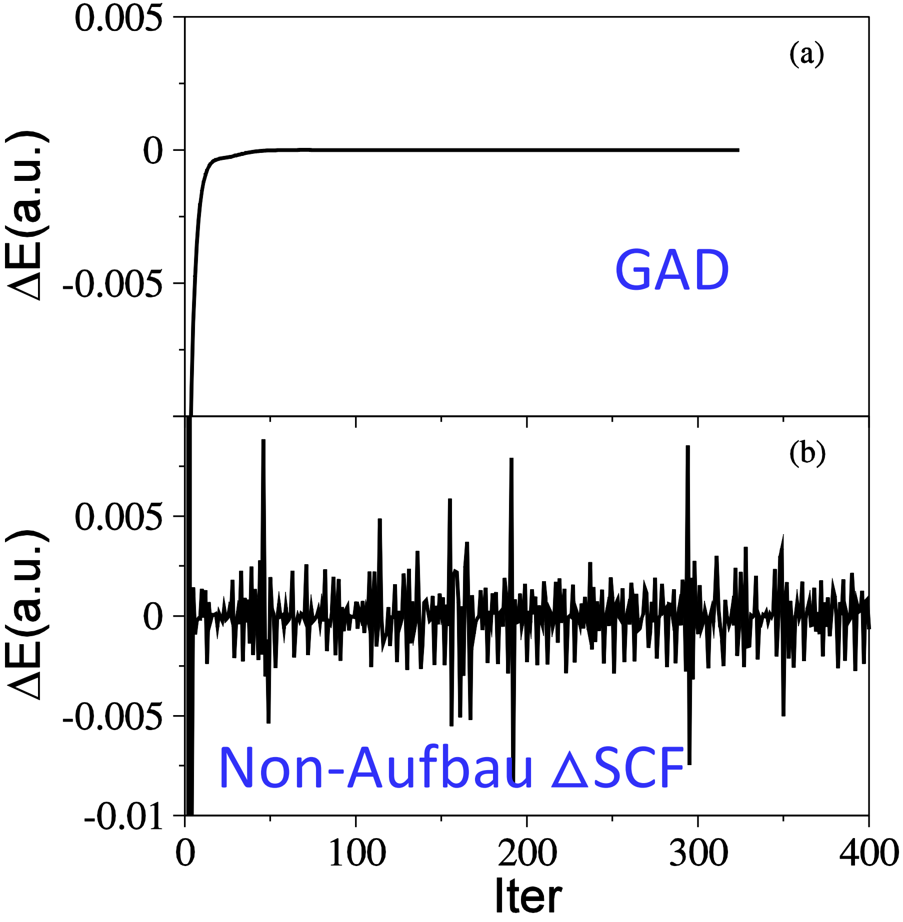
- Comparison between non-Aufbau ΔSCF and GAD
-

	Configuration	$E_{\Delta\text{SCF}}$ (a.u.)	E_{diff} (10^{-8} a.u.)
H	$2s$	-0.12530541	0.4
He	$(1s)^1(2s)^1$	-1.96025338	0.0
Li	$(1s)^2(2p)^1$	-7.27816628	-108
	$(1s)^1(2s)^2$	-5.22918853	4.9
Be	$(1s)^2(2s)^1(2p)^1$	-14.31663987	-1.1
H_2	$(1\sigma)^1(1\sigma^*)^1$	-0.77725246	-1.9
Li_2	1st.	-14.67364711	0.5
CO	1st.	-112.15621160	1.4
OH	1st.	Does not converge	converged
HF	1st.	Does not converge	Converged
H_2O	1st.	-75.55256992	-6.8

Results

- Comparison between non-Aufbau ΔSCF and GAD

first excited state calculation of HF



GAD for Exploring Landscapes

- At stationary states

$$L[\mathbf{\Psi}+t\mathbf{\Phi}] = E[\hat{\mathbf{F}}(\mathbf{\Psi}+t\mathbf{\Phi})]$$

$$= L[\mathbf{\Psi}] + t\frac{\partial L}{\partial \mathbf{\Psi}}[\mathbf{\Phi}] + \frac{1}{2}t^2\left\langle \mathbf{\Phi}, \hat{\mathbf{H}}\mathbf{\Phi} \right\rangle$$

$$\frac{\partial L}{\partial \mathbf{\Psi}} = \mathbf{0} \qquad \left\langle \mathbf{\Phi}, \hat{\mathbf{H}}\mathbf{\Phi} \right\rangle = \left\langle \mathbf{\Phi}, \varepsilon\mathbf{\Phi} \right\rangle = \varepsilon$$

$\mathbf{\Psi}$ is local minimum if $\varepsilon > 0$

$\mathbf{\Psi}$ is saddle point if $\varepsilon < 0$

- Two ways to determine ε
  - Using GAD evolution
  - Diagonalizing projected Hessian $(\hat{\mathbf{I}}-\hat{\mathbf{P}})\hat{\mathbf{H}}(\hat{\mathbf{I}}-\hat{\mathbf{P}})$

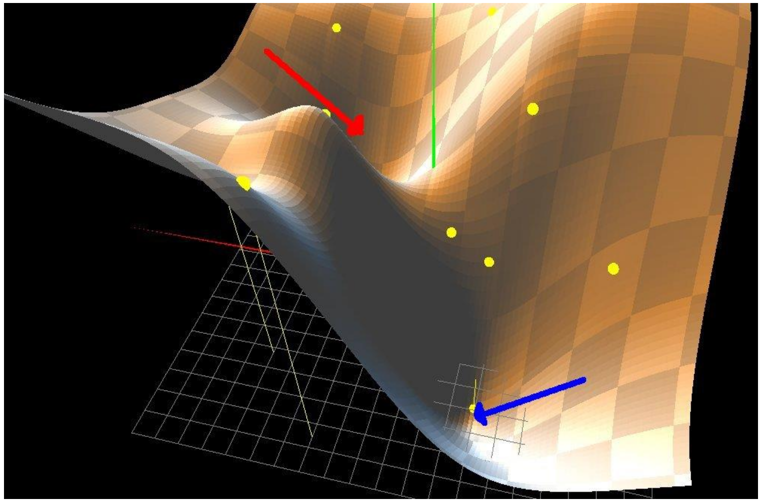
Results

- Eigenvalues of Hessian by direct diagonalization

	Configuration	Eigenvalue (a.u.)				
		1	2	3	4	5
H	1s	0.0000	0.3120	0.4773	0.4773	0.4773
	2s	-0.4417	0.0000	0.1340	0.1340	0.1340
	3s	-0.4315	-0.1084	0.0000	0.0008	0.0027
He	$(1s)^2$	0×2	0.7594	0.7594	0.7594	0.8340
	$(1s)^1(2s)^1$	-0.8715	0×2	0.0033	0.0035	0.6250
Li	$(1s)^2(2s)^1$	0×5	0.0831	0.0831	0.0831	0.1802
	$(1s)^2(2p)^1$	-0.0285	0×5	0.0004	0.0010	0.1279
	$(1s)^1(2s)^2$	-2.402	0×5	0.0341	0.0341	0.0341
Be	$(1s)^2(2s)^2$	0×8	0.0574	0.0574	0.0574	0.2779
	$(1s)^2(2s)^1(2p)^1$	-0.1074	0×8	0.0002	0.0010	0.1536

Results

- 1^{st} excited state
  - Index-1 saddle point
  - Due to the manifold constraint
- Contrast to free dynamics
  - 2^{nd} smallest stationary state given by local minimum



Results

- Eigenvalues of Hessian by direct diagonalization

	Configuration	Eigenvalue (a.u.)				
		1	2	3	4	5
H_2	$(1\sigma)^2$	0×2	0.2215	0.5593	0.8388	1.033
	$(1\sigma)(1\sigma^*)$	-0.3054	0×2	0.5188	0.5993	0.7674
	$(1\sigma^*)^2$	-0.5135	-0.1142	0×2	0.5161	0.6166
Li_2	gs.	0×18	0.0224	0.0369	0.0369	0.0516
	1^{st}.	-0.0292	0×18	0.0211	0.0211	0.0534
CO	gs.	0×98	0.1889	0.1889	0.2628	0.3167
	1^{st}.	-0.2439	0×98	0.000005	0.0896	0.0899
HF	gs.	0×50	0.3231	0.3231	0.3717	0.3717
	1^{st}.	-0.4834	0×50	0.00001	0.1263	0.5764
H_2O	gs.	0×50	0.2490	0.2982	0.3166	0.3339
	1^{st}.	-0.3402	0×50	0.0858	0.1373	0.2026

Summary

- Gentlest ascent captures the index-1 saddle point of KS density functionals
- First excited state is an index-1 saddle point
- An alternative to non-Aufbau occupation approach, convergence guaranteed
- GAD useful for scanning energy landscapes

Thank you!