Free energy barriers for local H diffusion in sodium alanates

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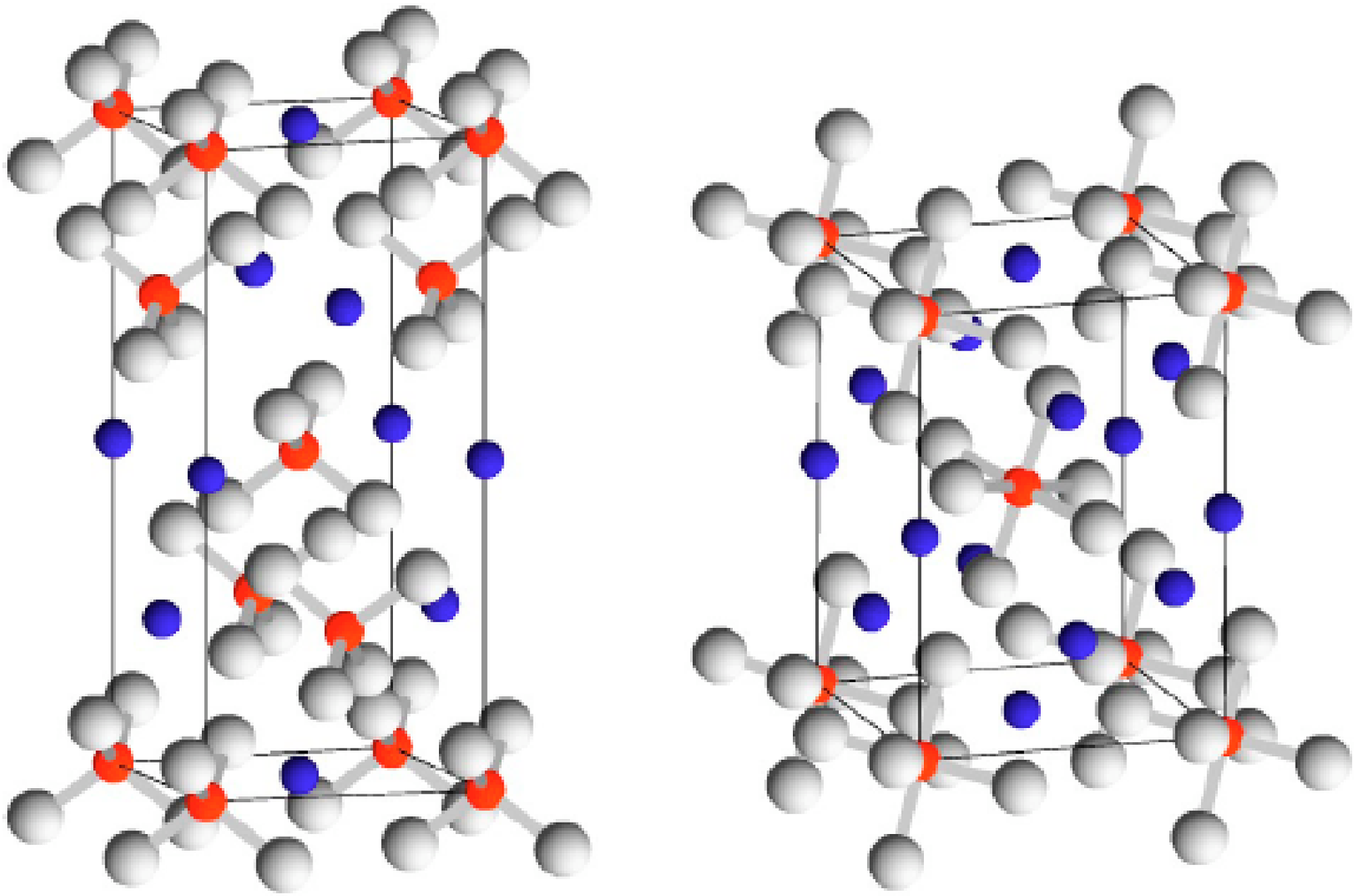
Sodium alanates are prototypical materials for solid state hydrogen storage.



$$3\mathrm{NaAlH_4} \Leftrightarrow \mathrm{Na_3AlH_6} + 2\mathrm{Al} + 3\mathrm{H_2}$$

$T = 350K \,\mathrm{and}\, 3.7\mathrm{wt}\%$

$$2\mathrm{Na_3AlH_6} \Leftrightarrow 6\mathrm{NaH} + 2\mathrm{Al} + 3\mathrm{H_2}$$

$T = 423K \,\mathrm{and}\, 1.9\mathrm{wt}\%$

$$2\mathrm{NaH} \Leftrightarrow 2\mathrm{Na} + \mathrm{H_2}$$

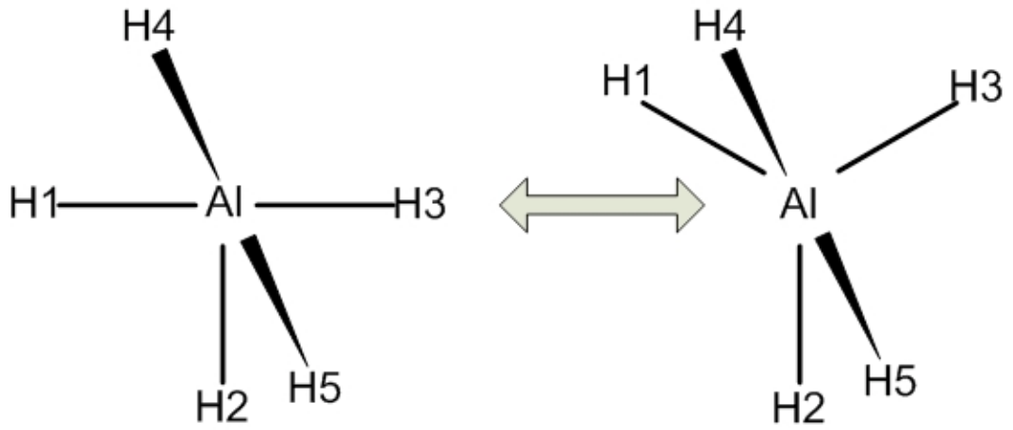
$T = 698K \,\mathrm{and}\, 1.9\mathrm{wt}\%$

$$3NaAlH_4 \Leftrightarrow Na_3AlH_6 + 2Al + 3H_2$$

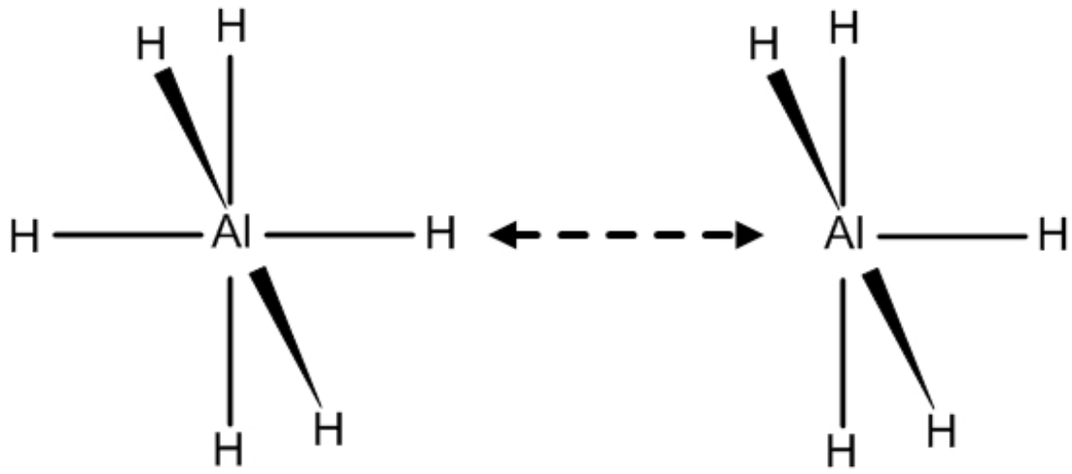
Experiments cannot identify activated mobility mechanism, barrier of 0.126 eV (~4K_BT)

Hypothesis:

Local H diffusion



Short range H diffusion

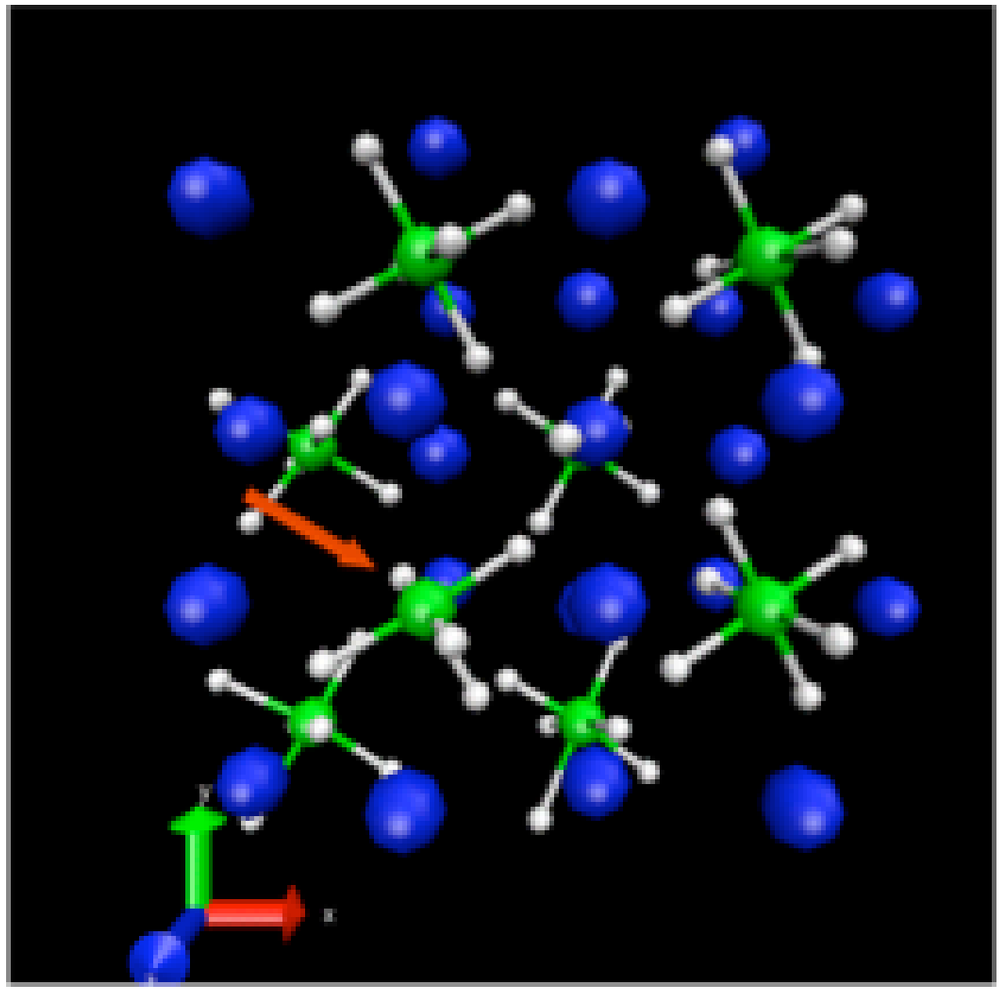


Na vacancy diffusion

1 Voss, J., Shi, Q., Jacobsen, H.S., Zamponi, M., Lefmann, K., Vegge, T., J. Phys. Chem. B **111** (2007), 3886
2 Palumbo, O., Paoloni, A., Cantelli R., Jensen A. J. Phys. Chem. B **110** (2008), 9105

Atomistic Model

- 2x2x1 supercell (bulk)
  - 7 AlH_6^{3-} and 1 AlH_5^{2-} units
  - 286 e^-
- BLYP
- E_{cut} = 80Ry
- Trouiller-Martins PP
  - Na: 9 electrons in the valence states
- dt = 0.1fs
- CPMD

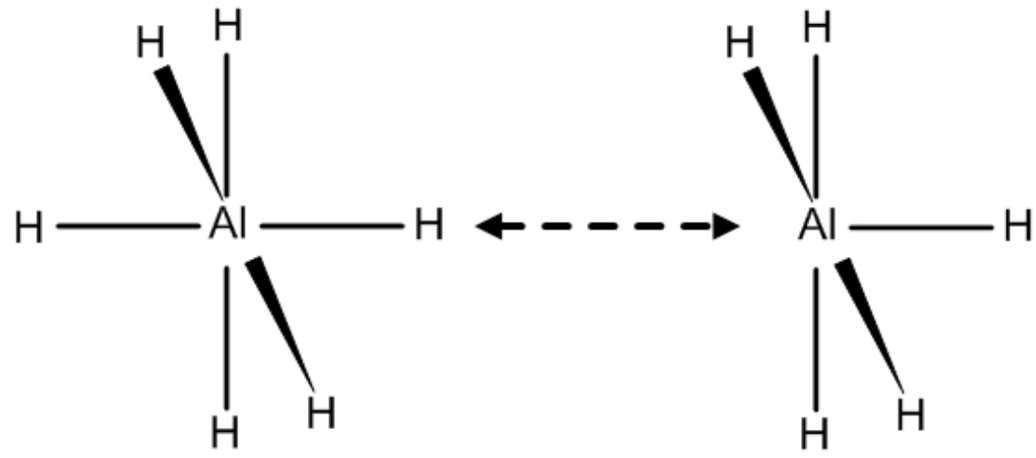


$P2_{1/m}$	a(Å)	b(Å)	c(Å)	β
Exp*	5.39	5.514	7.725	89.86
this work	5.43	5.55	7.65	89.59

* E. Ronnebro, D. Noreus, K. Kadir, A. Reiser, B. Bogdanovic, J. Alloys and comp. 299 (2000), 101

Preliminary ab initio MD run shows that the local diffusion process is not activated

Short range diffusion

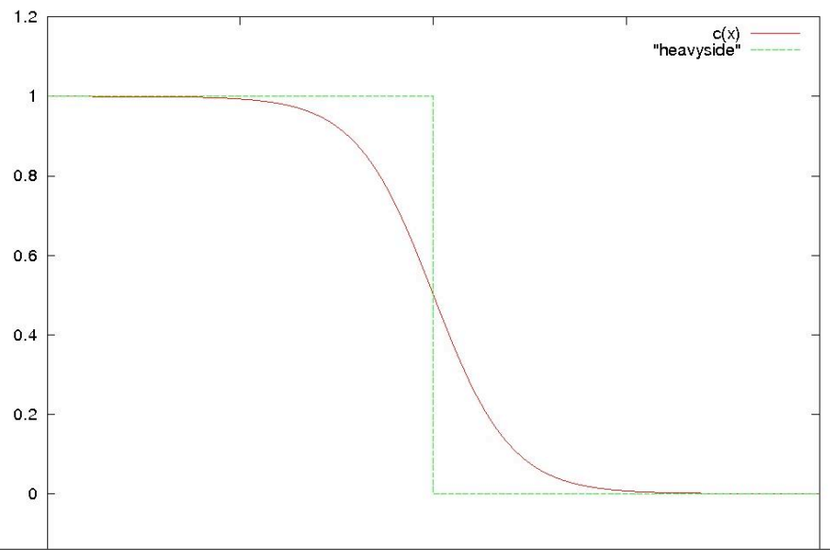


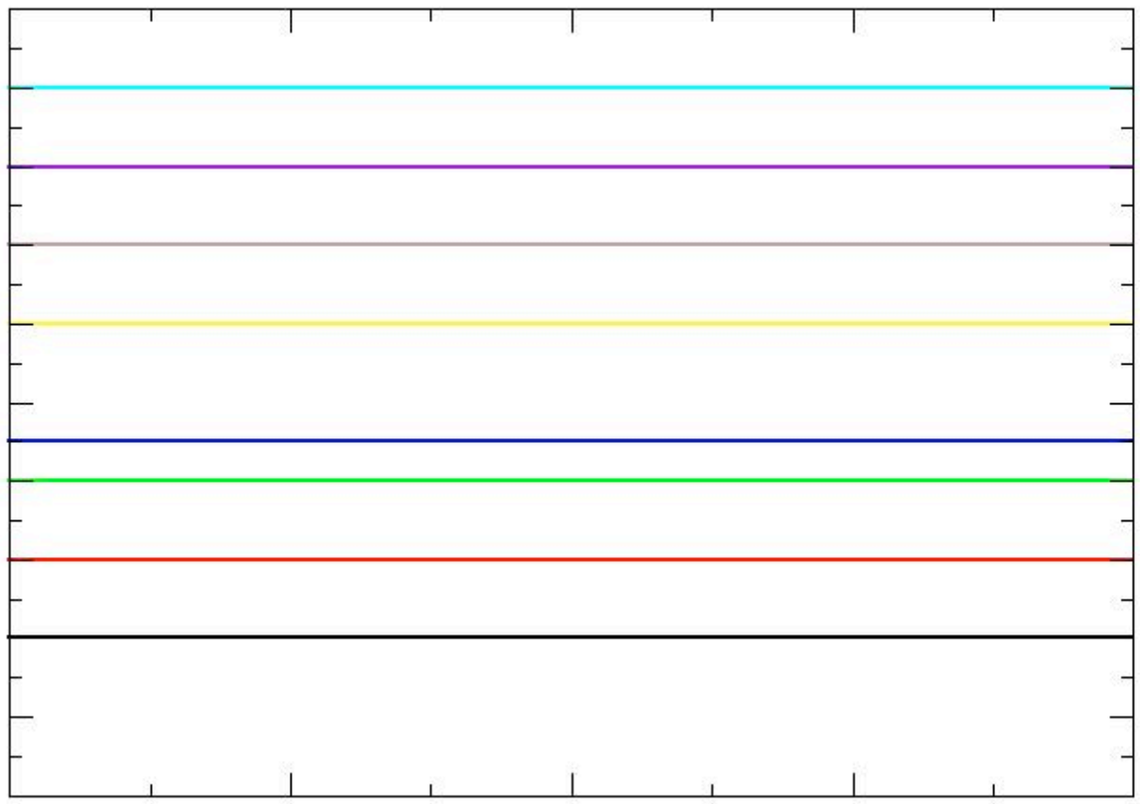
Collective variable: Al-H coordination number

$$\theta_\alpha = \sum_{i=1}^{N_H} \frac{1}{1 + e^{k(r_{i\alpha} - r_0)}}$$

$$r_{i\alpha} = |r_i - r_\alpha|$$

$$\alpha = 1, ..., 8$$





$$F(z) = -\beta^{-1} \ln Z^{-1} \int dx \; e^{-\beta V(x)} \prod_{j=1}^{m} \delta(\theta_j(x) - z_j)$$

Run a long MD trajectory to explore the configuration space of the system, histogram of the values of the CV to reconstruct F(z), and compute the free energy barriers

(a) Metastabilities

(b) Exponential scaling of the number of grid point with dimensions

Single sweep method

L. Maragliano, E. Vanden Eijnden, J. Chem. Phys., 128 (2008) 184110

(a) Use Temperature Accelerated MD to generate a trajectory in the space of the collective variables that efficiently explores relevant regions of the free energy even in the presence of significant barriers

(b) Points along the trajectory are chosen as centers for an interpolation grid and the free energy is represented as an optimized linear combination of radial basis functions centered on the grid

Temperature Accelerated MD (TAMD)

L. Maragliano L., E. Vanden-Eijnden Chem. Phys. Letters 426 168-175
U. Roethlisberger et al. (Canonical Adiabatic Free Energy Sampling)
J.Abrams, M. Tuckerman (Adiabatic Free Energy Dynamics)

Consider the extended system $x = (x_1, ..., x_N) \qquad z = (z_1, ..., z_l)$

new potential $$U_k(x, z) = V(x) + \frac{k}{2} \sum_{j=1}^{l} (\theta_j(x) - z_j)$$

coupled evolution equations:

$$m\ddot{x}_i = -\frac{\partial V(x)}{\partial x_i} - k \sum_{j=1}^{l} (\theta_j(x) - z_j) \frac{\partial \theta_j(x)}{\partial x_i} + \text{thermostat@T}$$

$$M\ddot{z}_j = k(\theta_j(x) - z_j) + \text{thermostat@}\bar{\text{T}}$$

(any dynamics that generates the canonical distribution will do)

TAMD

Adiabatic separation of the motions can be induced via the parameters associated to the evolution of the z-variables. E.g. Langevin dynamics $M >> m \qquad \bar{\gamma} >> \gamma$

The z-variables then evolve according to the effective force

$$M\ddot{z}_j = k \int dx(\theta_j(x) - z_j) \frac{e^{-\beta U_k(x,z)}}{\mathcal{Z}_k(z)} + \text{thermostat@}\bar{\text{T}}$$
$$= -\frac{\partial F_k(z)}{\partial z_j} + \text{thermostat@}\bar{\text{T}}$$

where

$$F_\kappa(z) = -\beta^{-1} \ln \mathcal{Z}_\kappa^{-1} \int dx e^{-\beta U_\kappa(x,z)}$$
$$= -\beta^{-1} \ln \mathcal{Z}_\kappa^{-1} \int dx e^{-\beta V(x)} e^{-\frac{\beta\kappa}{2} \sum_{\alpha=1}^{\nu} (\theta^\alpha(x) - z^\alpha)^2}$$

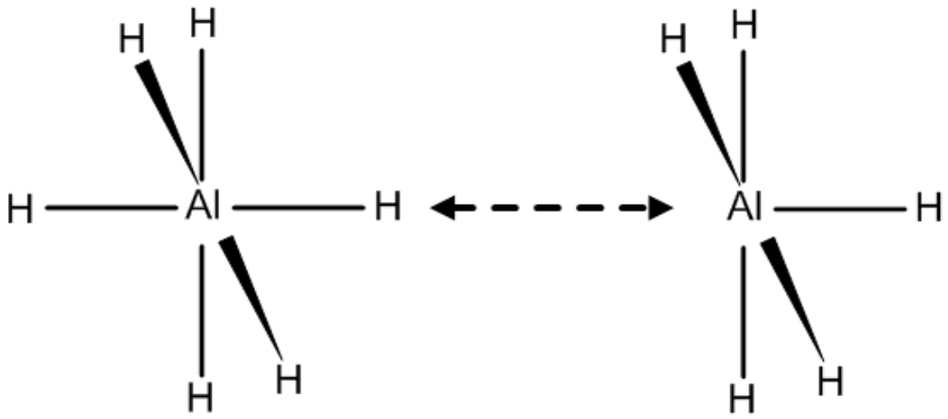
$$M\ddot{z}_j = -\frac{\partial F_k(z)}{\partial z_j} + \text{thermostat@}\bar{\text{T}}$$

Holds for all values of fictitious temperature

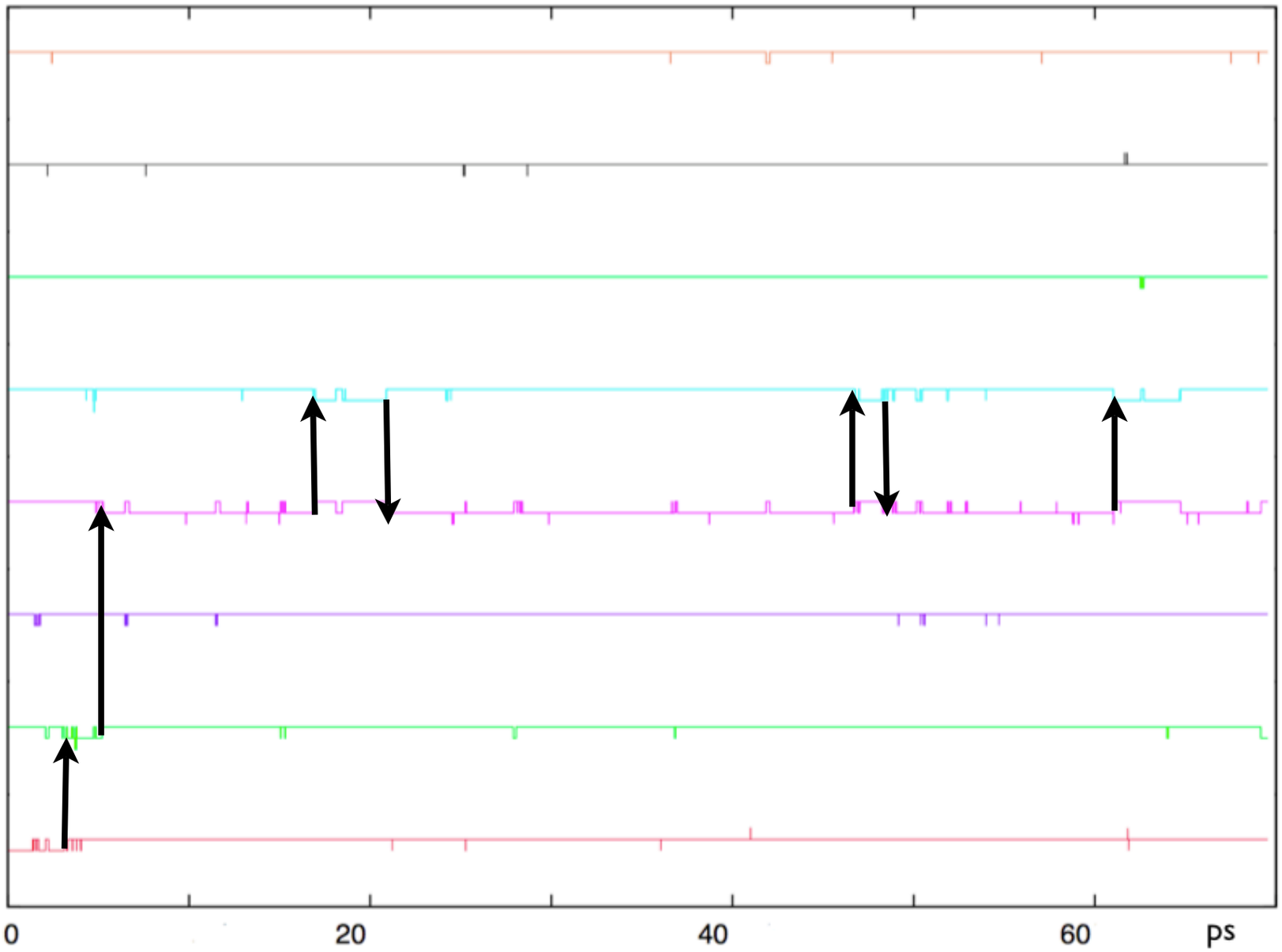
If $\bar{T} >> T$ the trajectory of the auxiliary variables can overcome barriers and quickly sweep the relevant regions of the original free energy landscape

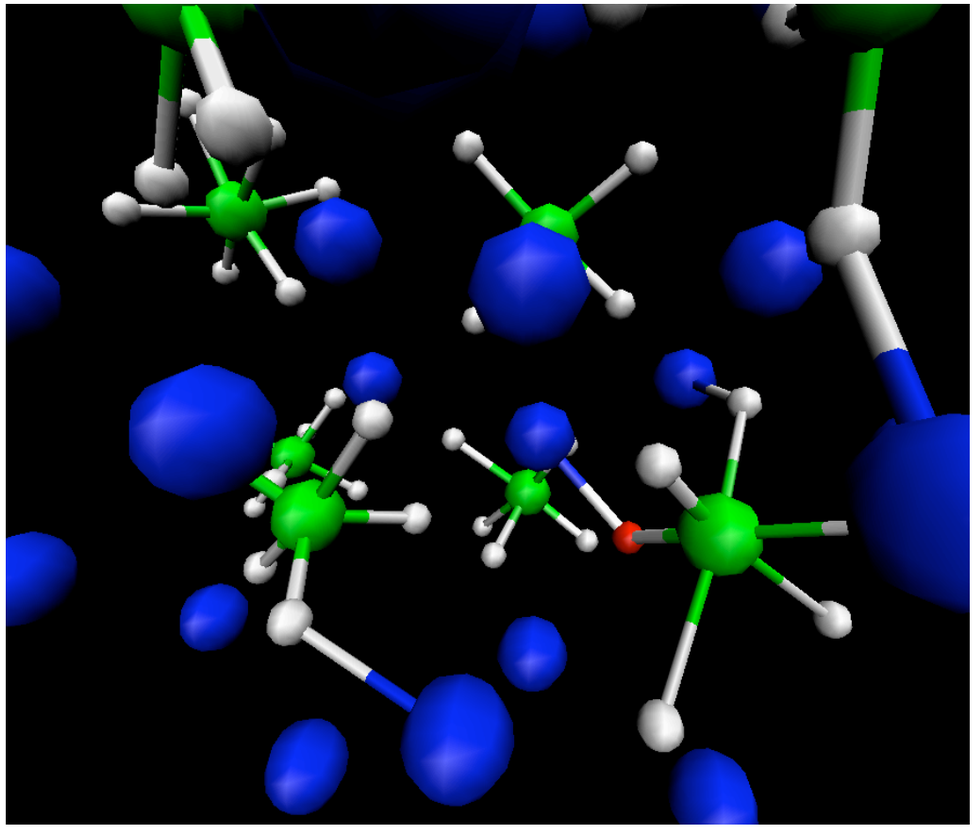
Explore the free energy (find the metastable states), many collective variables

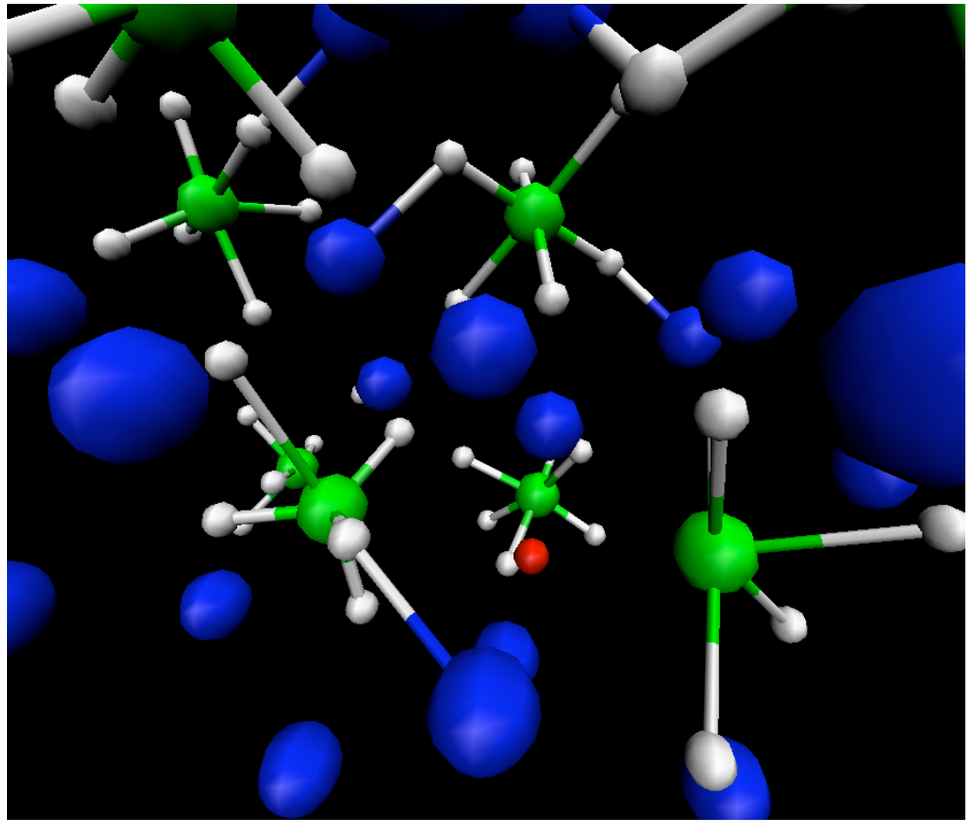
Points along the trajectory can be used as centers for an interpolation grid

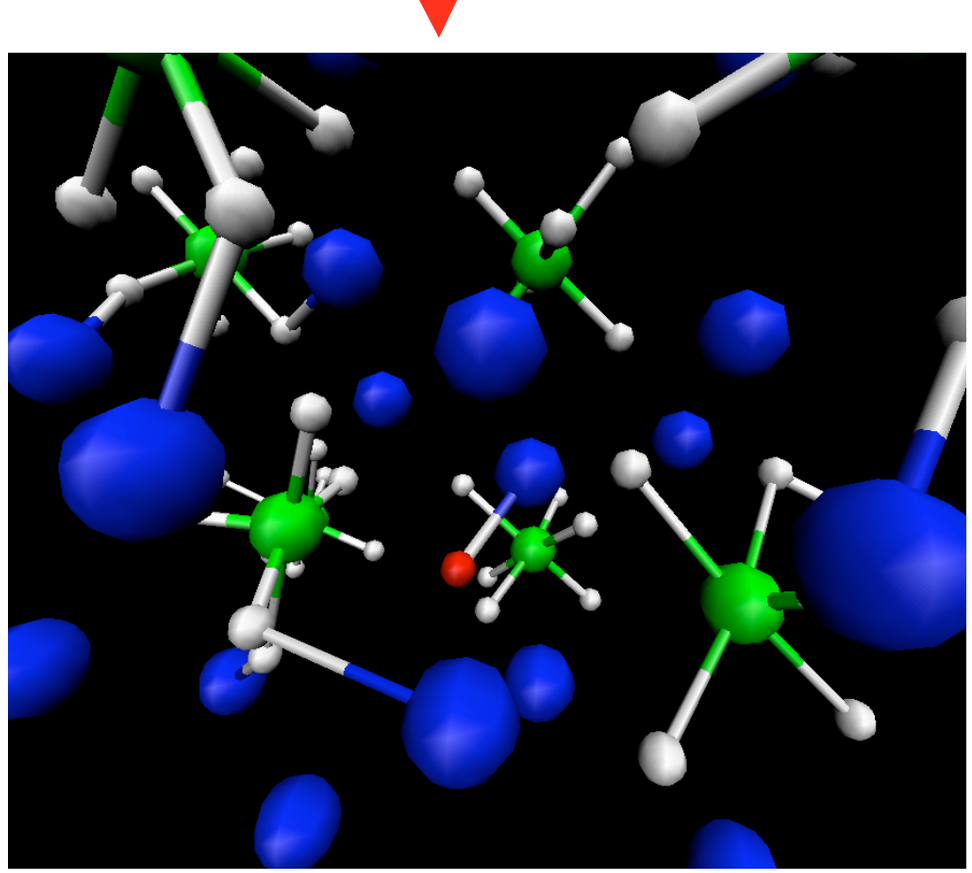


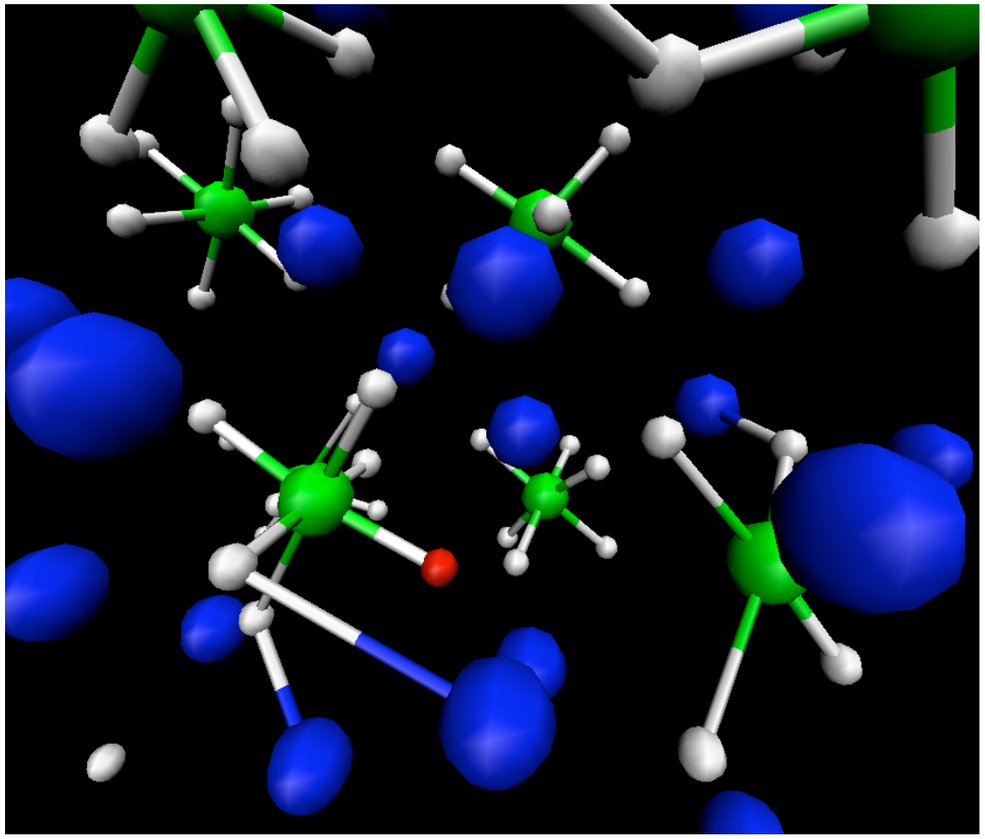
$$\theta_\alpha = \sum_{i=1}^{N_H} \frac{1}{1 + e^{k(r_{i\alpha} - r_0)}}$$











Radial basis reconstruction

$$\tilde{F}(z) = \sum_{j=1}^{J} a_j \phi_\sigma(|z - z_j|)$$

e.g. $\phi_\sigma(u) = e^{-\frac{u^2}{2\sigma^2}}$

Coefficients and variance can be determined by minimizing the object function

$$E(a, \sigma) = \sum_{j=1} |\sum_{j'=1}^{J} a_{j'} \nabla_z \phi_\sigma(|z_j - z_{j'}|) + f_j|^2$$

Input:

(a) location of the centers, distance criterion along the TAMD trajectory

(b) $f_j = -\nabla_{z_j} F(z)$ mean force at the centers, local conditional average

$$f_j = \frac{k}{\mathcal{T}} \int_0^{\mathcal{T}} (z_j - \theta_j(x(t)))dt$$

Minimization of the object function

(a) For fixed value of the variance, solve

$$\sum_{j'=1}^{J} B_{j,j'}(\sigma) a_{j'} = c_j(\sigma)$$

where

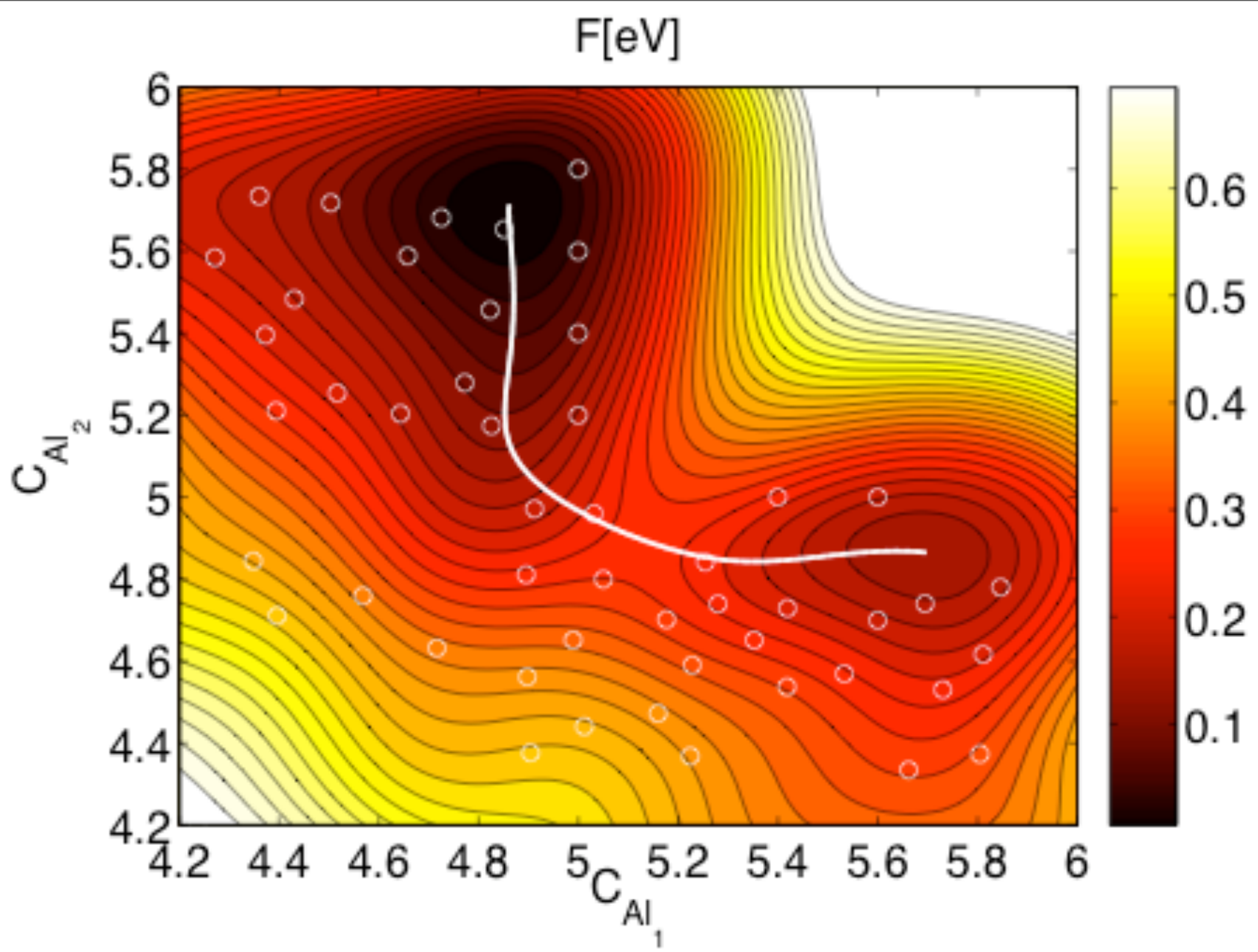
$$B_{j,j'}(\sigma) = \sum_{j''=1}^{J} \nabla_z \phi_\sigma(|z_j - z_{j''}|) \nabla_z \phi_\sigma(|z_{j''} - z_{j'}|)$$

$$c_j(\sigma) = \sum_{j'=1}^{J} \nabla_z \phi_\sigma(|z_j - z_{j'}|) f_{j'}$$

(b) The optimal value of the variance, satisfies

$$\underline{E(a^*(\sigma^*), \sigma^*) = \min_\sigma E(a^*(\sigma), \sigma)}$$

and is found by computing the residual for a (1d) grid of values of the variance



d	Centers	$C^*_{Al_1}$	$C^*_{Al_2}$	SP	$\Delta F_1[eV]$	$\Delta F_2[eV]$
0.2	25	(5.68,4.84)	(4.85,5.68)	(5.17,4.94)	0.14	0.26
0.15	37	(5.72,4.86)	(4.86,5.73)	(5.11,4.93)	0.13	0.24
0.1	55	(5.69,4.86)	(4.86,5.71)	(5.14,4.89)	0.13	0.27

Variations on single sweep

Modify definition of the basis elements

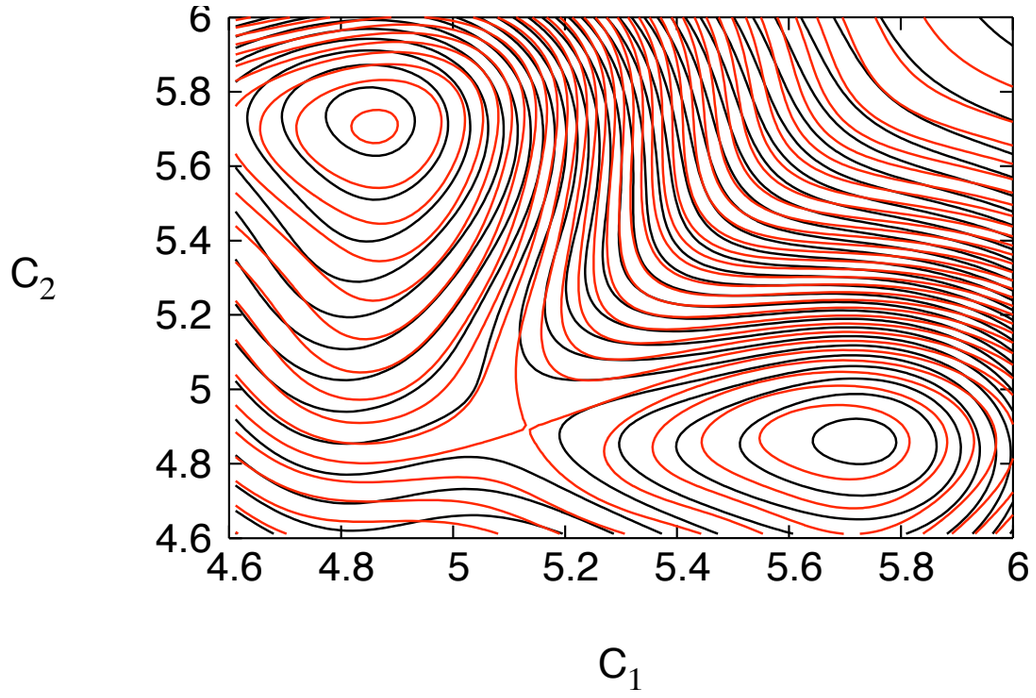
$$\Phi_{\Sigma_k}(|z - z_k|) = e^{-\frac{1}{2}(z-z_k)^T \Sigma_k^{-1}(z-z_k)}$$

$$(\Sigma_k)_{\alpha,\beta} = E[(z^\alpha - \bar{z}_k^\alpha)(z^\beta - \bar{z}_k^\beta)] = \sigma_{k,\alpha}\sigma_{k,\beta}(\delta_{\alpha,\beta} + \rho_{k,\alpha,\beta})$$

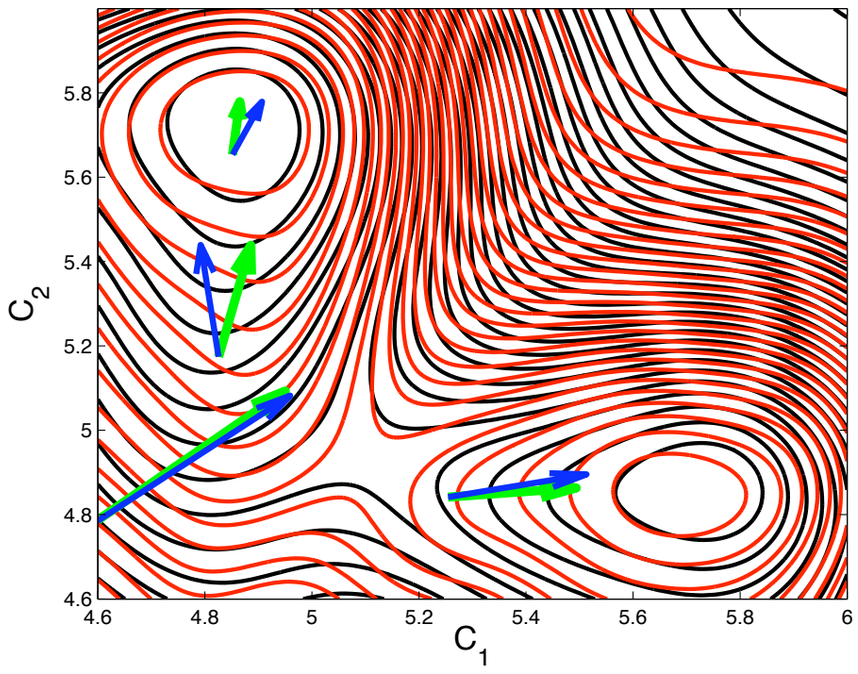
Modify definition of the object function

$$E_r(a, \Sigma) = \sum_{k=1}^{K} \sum_{\alpha=1}^{\nu} \epsilon_k^\alpha [f_k^\alpha + \nabla_\alpha \tilde{F}(z_k)]^2$$

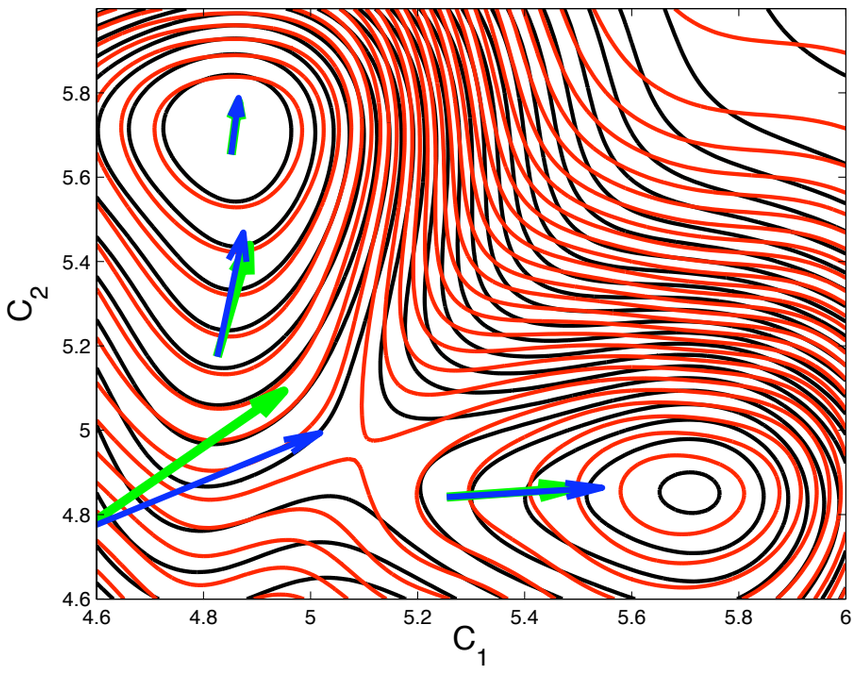
$$\epsilon_k^\alpha = 1/{f_k^\alpha}^2$$



(a) Original method



(b) 1xCV, standard objective function



(c) 1xCV, relative objective function

Conclusions and future work:

- Single Sweep is a promising method to reconstruct free energy landscapes of rather complex systems

- Results point to the “Non-local” hydrogen vacancy diffusion as the mobile species that appears during the first dissociation reaction of sodium alanates

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