Full representation:

$$\boldsymbol{\phi}'(t) = \boldsymbol{S}(\boldsymbol{\phi}(t))$$

$$\boldsymbol{\phi}(0) = \boldsymbol{\phi}^0 \in R^n$$

$$\boldsymbol{\phi}(\tau) = \boldsymbol{R}(\boldsymbol{\phi}^0, \tau)$$

$$J(\boldsymbol{\phi}) = D_{\boldsymbol{\phi}} \boldsymbol{S}(\boldsymbol{\phi})$$

$$A(\boldsymbol{\phi}^0, t) = D_{\boldsymbol{\phi}^0} \boldsymbol{R}(\boldsymbol{\phi}^0, t)$$

will also use $A(\boldsymbol{\phi}^0)$ or $A(t)$ when the other argument is fixed

Sensitivity matrix:

$$A(\boldsymbol{\phi}^0, t) = D_{\boldsymbol{\phi}^0} \boldsymbol{R}(\boldsymbol{\phi}^0, t)$$

will also use $A(\boldsymbol{\phi}^0)$ or $A(t)$ when the other argument is fixed

$$A(0) = I; \qquad A'(t) = J(\boldsymbol{\phi}(t))A(t)$$

$$\text{also,} \quad \boldsymbol{S}(\boldsymbol{\phi}(t)) = A(\boldsymbol{\phi}^0, t)\boldsymbol{S}(\boldsymbol{\phi}^0)$$

$$A = U\Sigma V^T$$

$\tilde{V} =$ last $(n-k)$ columns of V $=$ the most compressive directions for $\boldsymbol{\phi}^0$

$\tilde{U} =$ last $(n-k)$ columns of U $=$ the most compressed directions for $\boldsymbol{R}(\boldsymbol{\phi}^0, \tau)$

Reduced representation & reconstruction

B is an orthogonal $(n \times k)$ matrix with columns spanning the reduced space.

The reduced representation: $\boldsymbol{r}(t) = B^T \boldsymbol{\phi}(t) \in R^k$

Fix $\tau > 0$ and suppose $\boldsymbol{r} \in R^k$ is given.

Wanted: $\boldsymbol{\phi}^0 \in R^n$ such that

1.
$$B^T \boldsymbol{\phi}(\tau) = \boldsymbol{r} \ = B^T \boldsymbol{R}(\boldsymbol{\phi}^0, \tau) \qquad (k \text{ conditions})$$

2.
$$\tilde{U}^T \boldsymbol{S}(\boldsymbol{R}(\boldsymbol{\phi}^0, \tau)) = 0 \ = \tilde{V}^T \boldsymbol{S}(\boldsymbol{\phi}^0) \qquad ((n-k) \text{ conditions})$$

Assumptions:

There exists a k-dimensional attracting manifold.
The span of columns of B is a good reduced space.
The chosen $\tau > 0$ is large enough.

Note: strictly speaking, $D_{\boldsymbol{\phi}^0} A$ is needed to use Newton's method.

Wanted: $\boldsymbol{G}(\boldsymbol{\phi}^0) = \begin{bmatrix} B^T \boldsymbol{R}(\boldsymbol{\phi}^0, \tau) - \boldsymbol{r} \\ \tilde{V}^T \boldsymbol{S}(\boldsymbol{\phi}^0) \end{bmatrix} = 0.$

$$\boldsymbol{\phi}^0_{i+1} = \boldsymbol{\phi}^0_i + \Delta\boldsymbol{\phi}^0_i; \qquad D_{\boldsymbol{\phi}^0} \boldsymbol{G}(\boldsymbol{\phi}^0_i) \Delta\boldsymbol{\phi}^0_i = -\boldsymbol{G}(\boldsymbol{\phi}^0_i).$$

In computing $D_{\boldsymbol{\phi}^0} \boldsymbol{G}(\boldsymbol{\phi}^0_i)$, pretend that $\tilde{V}$ is constant:

$$D_{\boldsymbol{\phi}^0} \boldsymbol{G}(\boldsymbol{\phi}^0_i) \approx \begin{bmatrix} B^T A(\boldsymbol{\phi}^0_i, \tau) \\ \tilde{V_i}^T J(\boldsymbol{\phi}^0_i) \end{bmatrix}.$$

Under the rug:

1. Conservation constraints on $\boldsymbol{\phi}^0$.
2. Feasability constraints on $\boldsymbol{\phi}^0$.
3. A reasonable first guess $\boldsymbol{\phi}^0_0$.
4. Conditions for convergence of the relaxed-Newton's method ?

“Conserved” representation:

(enthalpy, total number of atoms of each element)

$$E^T \boldsymbol{\phi}(t) = \boldsymbol{e} \in R^{(n-c)} \qquad \text{for all } t$$

Suppose K is an orthogonal $(n \times c)$ matrix, whose columns span $Ker(E^T)$ and $\boldsymbol{\mu}(t) \in R^c$ is such that

$$\boldsymbol{\phi}(t) = \hat{\boldsymbol{\phi}}_0 + K\boldsymbol{\mu}(t); \qquad \boldsymbol{\phi}^0 = \hat{\boldsymbol{\phi}}_0 + K\boldsymbol{\mu}^0.$$

$$\boldsymbol{\mu}(t) = K^T \boldsymbol{\phi}(t) = \boldsymbol{\mu}^0 + K^T(\boldsymbol{\phi}(t) - \boldsymbol{\phi}^0) = \tilde{\boldsymbol{R}}(\boldsymbol{\mu}^0, t);$$

$$\boldsymbol{\mu}'(t) = K^T \boldsymbol{S}(\hat{\boldsymbol{\phi}}_0 + K\boldsymbol{\mu}(t)) = \tilde{\boldsymbol{S}}(\boldsymbol{\mu});$$

$$\tilde{J}(\boldsymbol{\mu}) = D_{\boldsymbol{\mu}} \tilde{\boldsymbol{S}}(\boldsymbol{\mu}) = K^T J(\hat{\boldsymbol{\phi}}_0 + K\boldsymbol{\mu}(t))K;$$

$$\tilde{A}(\boldsymbol{\mu}^0, \tau) = K^T A(\hat{\boldsymbol{\phi}}_0 + K\boldsymbol{\mu}^0, \tau)K.$$

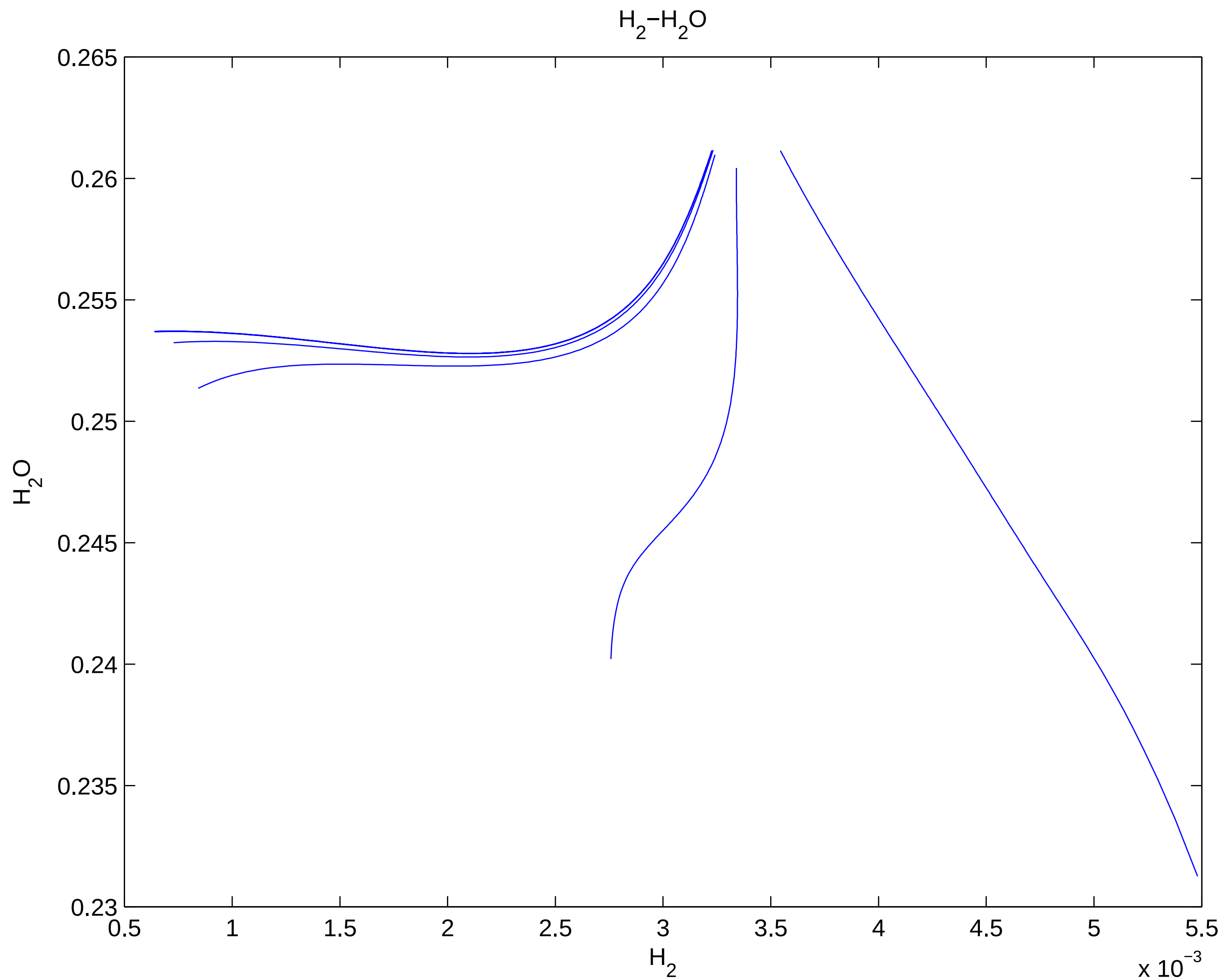
$\tilde{V} =$ last $(c-k)$ columns of V $=$ the most compressive directions for $\boldsymbol{\mu}^0$

Wanted: $\boldsymbol{G}(\boldsymbol{\mu}^0) = \left[\begin{array}{l} B^T(\hat{\boldsymbol{\phi}}_0 + K\tilde{\boldsymbol{R}}(\boldsymbol{\mu}_0, \tau)) - \boldsymbol{r} \\ \tilde{V}^T K^T \boldsymbol{S}(\hat{\boldsymbol{\phi}}_0 + K\boldsymbol{\mu}_0) \end{array} \right] = 0.$

$$\boldsymbol{\mu}^0_{i+1} = \boldsymbol{\mu}^0_i + \Delta\boldsymbol{\mu}^0_i; \qquad D_{\boldsymbol{\mu}^0}\boldsymbol{G}(\boldsymbol{\mu}^0_i)\Delta\boldsymbol{\mu}^0_i = -\boldsymbol{G}(\boldsymbol{\mu}^0_i).$$

In computing $D_{\boldsymbol{\mu}^0}\boldsymbol{G}(\boldsymbol{\mu}^0_i)$, pretend that $\tilde{V}$ is constant:

$$D_{\boldsymbol{\mu}^0}\boldsymbol{G}(\boldsymbol{\mu}^0_i) \approx \left[\begin{array}{c} B^T K \tilde{A}(\boldsymbol{\mu}^0_i, \tau) \\ \tilde{V}_i^{\,T} \tilde{J}(\boldsymbol{\mu}^0_i) \end{array} \right].$$



H2−H2O
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0.26
0.255
0.25
0.245
0.24
0.235
0.23
H2O
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
H2
x 10−3