Derivative-Free Optimization Methods for the Surface Structure Determination Problem

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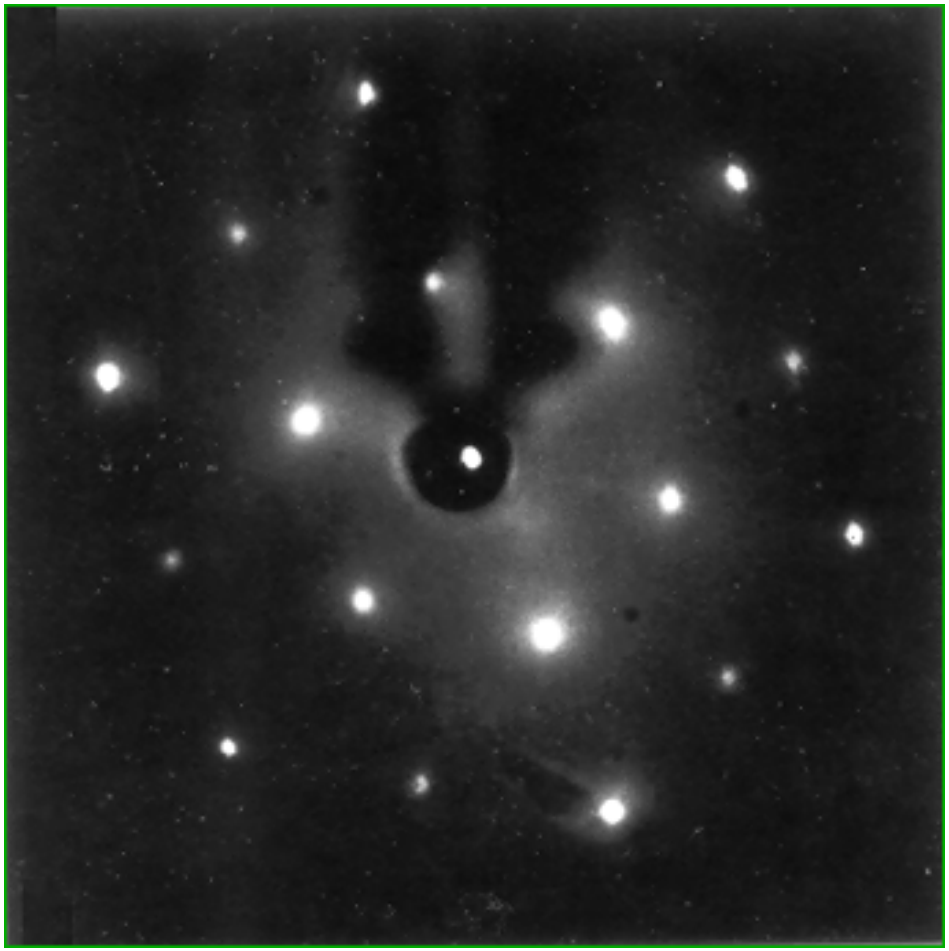
Surface structure determination

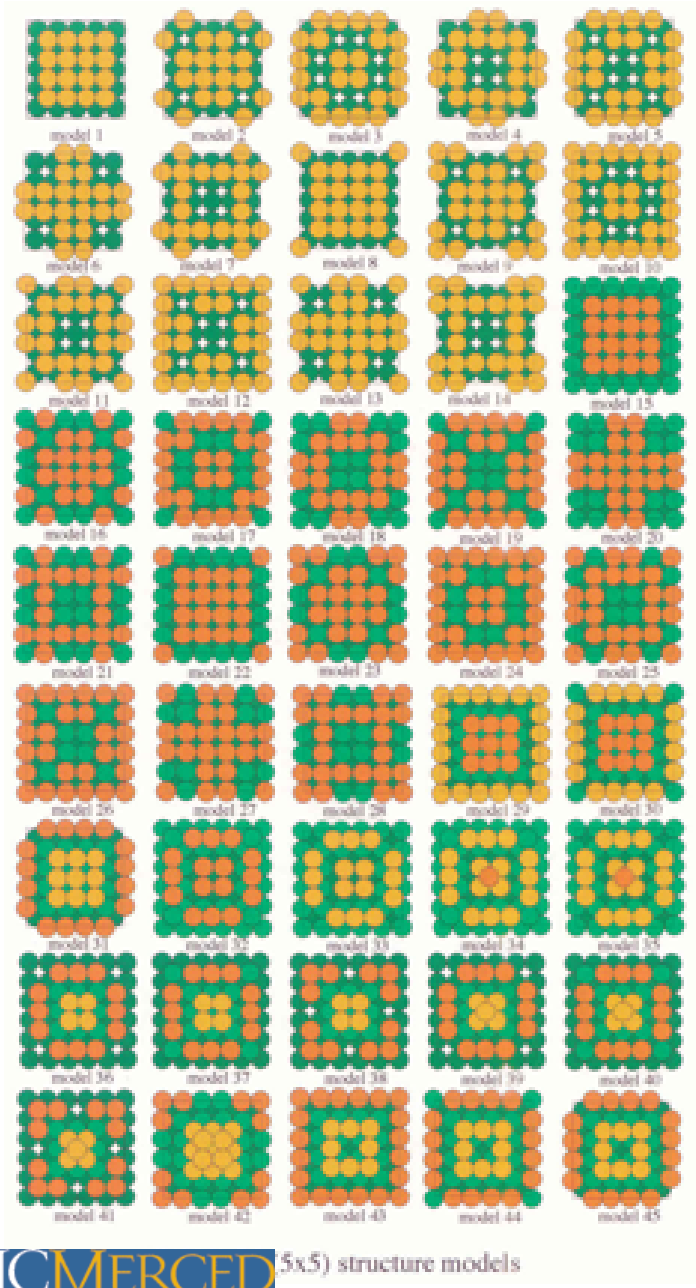
- Surface structure determines many important properties of materials.
- Possibility of electron diffraction first proposed by deBroglie (1924).
- Over 40 years before it became a tool in surface structure determination.
- Low-energy electrons are surface sensitive, requiring a well-ordered surface.
- Experimental data could not be quantitatively described by kinematic theory and necessitated the development of a theory of multiple scattering in the late 1960s.

Low-energy electron diffraction (LEED)

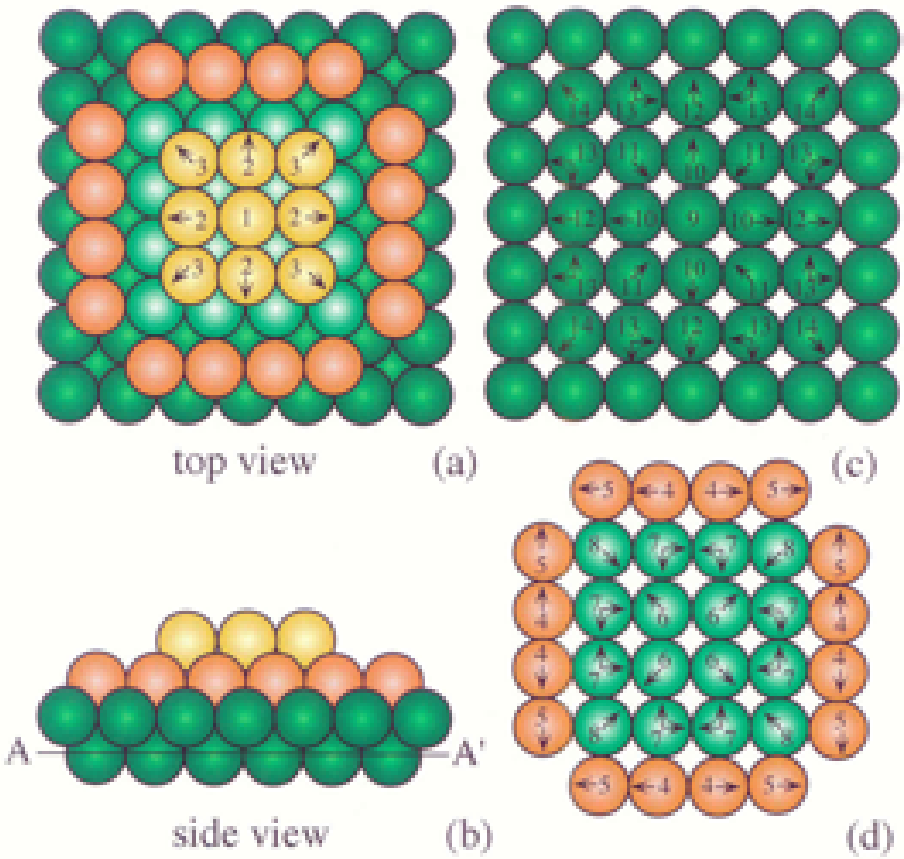


- Goal is to determine surface structure through low energy electron diffraction (LEED).
- Need to determine the coordinates and chemical identity of each atom: Li atoms on a Ni surface
- Non-structural parameters, i.e. inner potential, phase shift δ, thermal effects and damping.
- `www.answers.com/topic/low-energy-electron-diffraction`

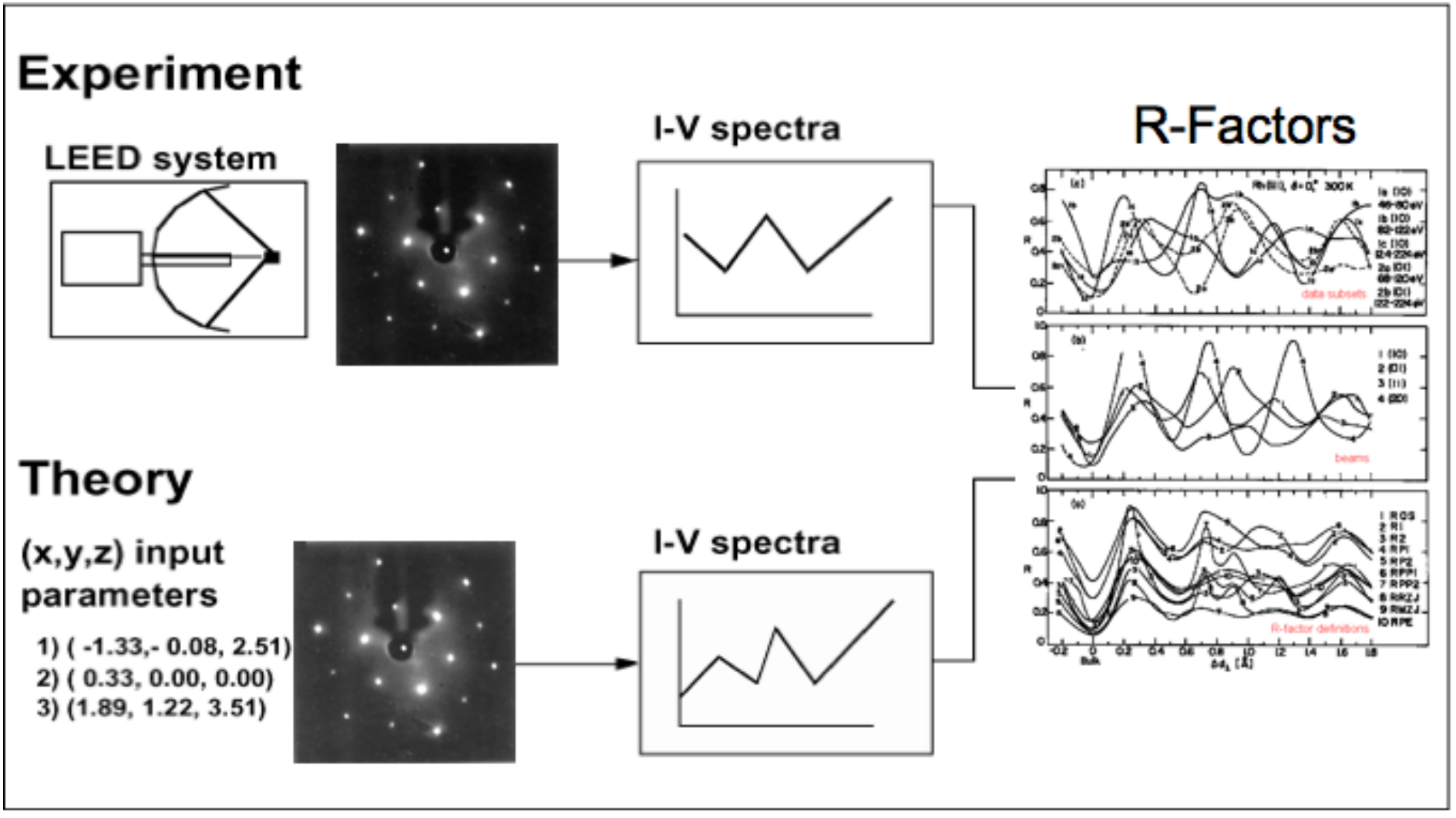
Surface structure determination using LEED



(5x5) structure models



LEED setup


Experiment
LEED system
I-V spectra
R-Factors
Theory
(x,y,z) input parameters
1) (-1.33,- 0.08, 2.51)
2) (0.33, 0.00, 0.00)
3) (1.89, 1.22, 3.51)
I-V spectra

Pendry R-factor

- Pendry R(eliability) -factor (1980) is defined by:

$$
\begin{aligned}
R &= \sum_{i,g}(Y_{gth} - Y_{gexp})^2 / \sum_{i,g}(Y_{gth}^2 + Y_{gexp}^2) \\
Y(E) &= L/(1 + L{V_{oi}}^2), \\
L(E) &= I'/I, \\
L &\approx \sum_j \frac{-2(E - E_j)}{(E - E_j)^2 + V_{oi}^2}
\end{aligned}
$$

- LEED curves consist for the main part of a series of Lorentzian peaks: $I \approx \sum a_j/(E - E_j)^2 + V_{oi}^2$
- Their widths are dictated by the imaginary part of the electron self-energy (optical potential): $\Delta E = 2|V_{oi}|$
- Pendry R-factor emphasizes positions of the maximum and minimum rather than the heights of the intensities
- Ideal agreement corresponds to $R = 0$; uncorrelated spectra yields $R = 1$.

Optimization formulation

- Inverse problem
  - minimize R-factor - defined as the misfit between theory and experiment
  - Several ways of computing the R-factor, we will use the Pendry R-factor.
- Combination of continuous and categorical variables
  - Atomic coordinates: x, y, z
  - Chemical identity: Ni, Li
- No derivatives available; function may also be discontinuous
- Invalid (unphysical) structures lead to function being undefined in certain regions and returning special values

Previous Work

- Early attempts used Hooke-Jeeves, nonlinear least squares, genetic algorithms[1−2],
- We have also used pattern search methods
- Effective, but expensive
  - Several 100 to 1000s of function calls typically needed
  - Each function call can take up to 2 minutes on a workstation class computer

1. Global Optimization in LEED Structure Determination Using Genetic Algorithms, R. Dll and M.A. Van Hove, Surf. Sci. 355, L393-8 (1996).
2. G. S. Stone, MS dissertation, Computer Science Dept., San Francisco State University, 1998.

General MVP algorithm

Initialization: Given values Δ_0, x_0, M_0, P_0,

1 For $k = 0, \ldots,$ maxit do
2 Search: Evaluate f on a finite subset of trial points on the mesh M_k.
3 Poll: Evaluate f on the frame P_k.
4 If (successful)
5 $x_{k+1} = x_k + \Delta_k d_k$
6 Update Δ_k
7 End

- Global Search phase can include user heuristics or surrogate functions
- Local Poll phase is more rigid, but needed to ensure convergence.

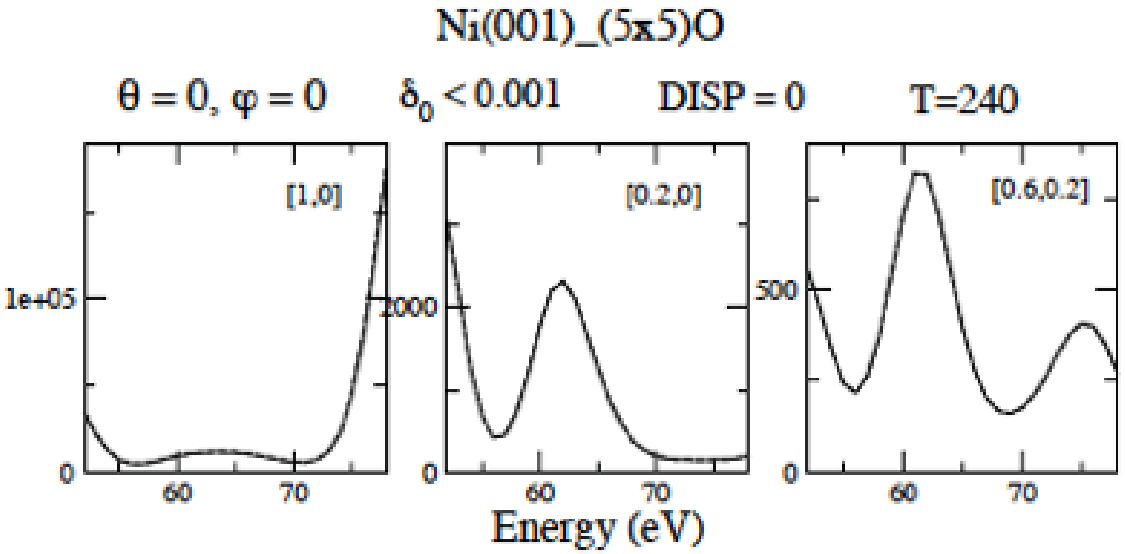
Variations on LEED

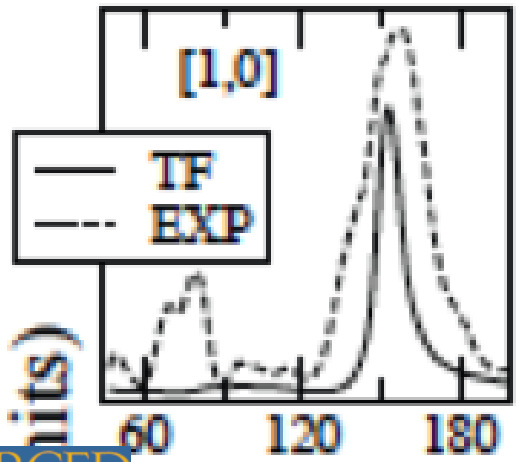
- LEED
  - Multiple scattering model
  - I-V spectra computed repeatedly until best-fit structure is found
  - Computation time is proportional to the number of parameters
- TLEED (Tensor LEED)
  - For a reference structure use multiple scattering
  - Perturbation method to calculate I-V for a structure close to a reference structure
  - Efficient for local modifications (i.e. no categorical variables) - otherwise computationally expensive

Kinematic LEED as a simplified physics surrogate (SPS)

- R-factor depends on:
  - Structural parameters, i.e. atomic positions, chemical identity
  - Non-structural parameters, i.e. inner potential, phase shift δ, thermal effects and damping.
- KLEED (Kinematic LEED)
  - Basic assumption is that electrons are only scattered once by the surface atoms.
  - Surface unit cell size and symmetry can be determined, but not the exact positions of atoms
  - I-V spectra from KLEED can be computed in a few seconds compared to multiple scattering which takes $\approx$ 2 minutes to compute

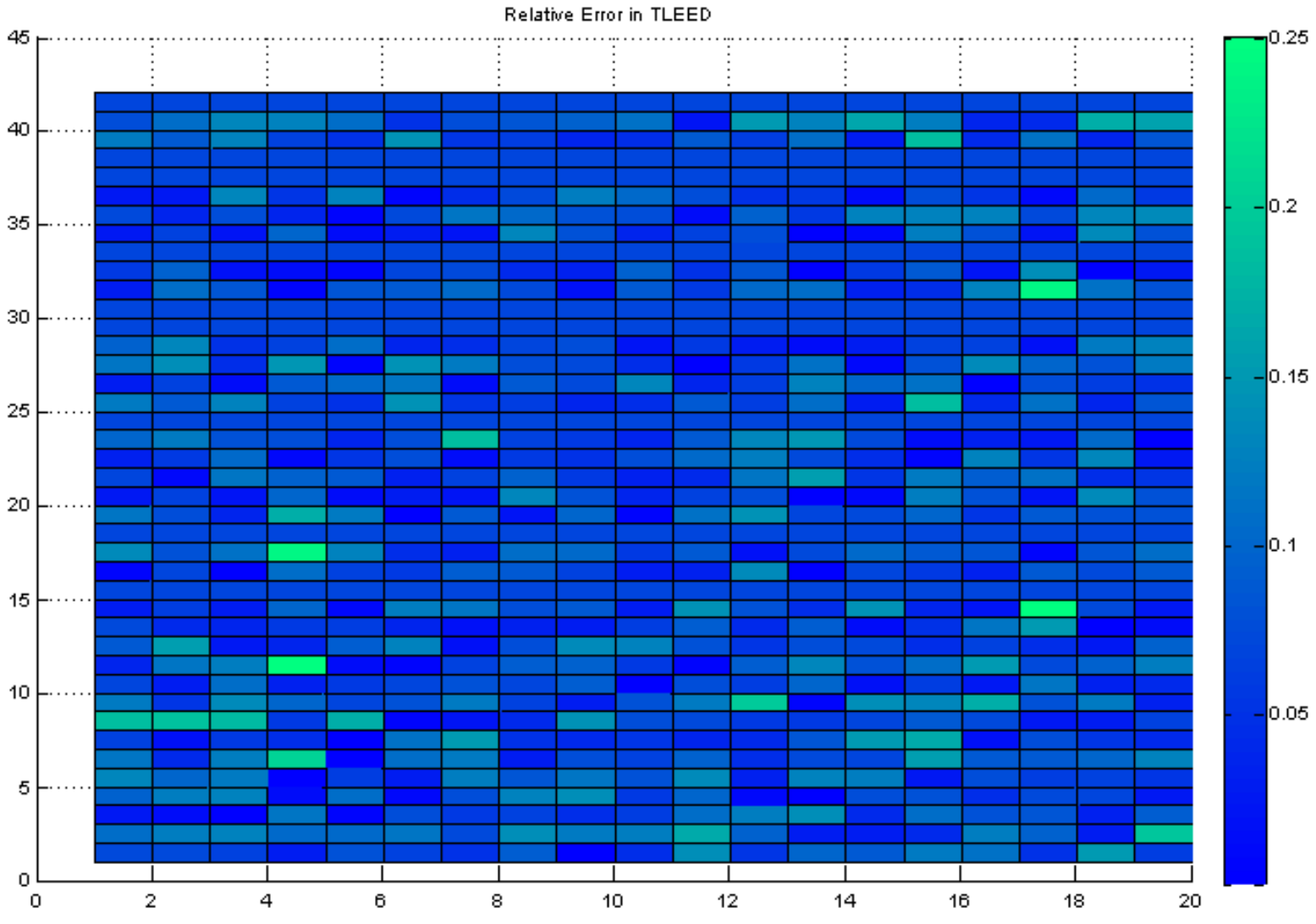
KLEED versus TLEED(multiple-scattering)





- KLEED agrees well with experimental data as long as the incident angle is close to perpendicular
- KLEED and multiple scattering agree well with small phase shift, i.e. as $\delta \rightarrow 0$.
- However for larger phase shift there is no guarantee of agreement

KLEED as a simplified physics surrogate



Simplified physics surrogate (SPS)

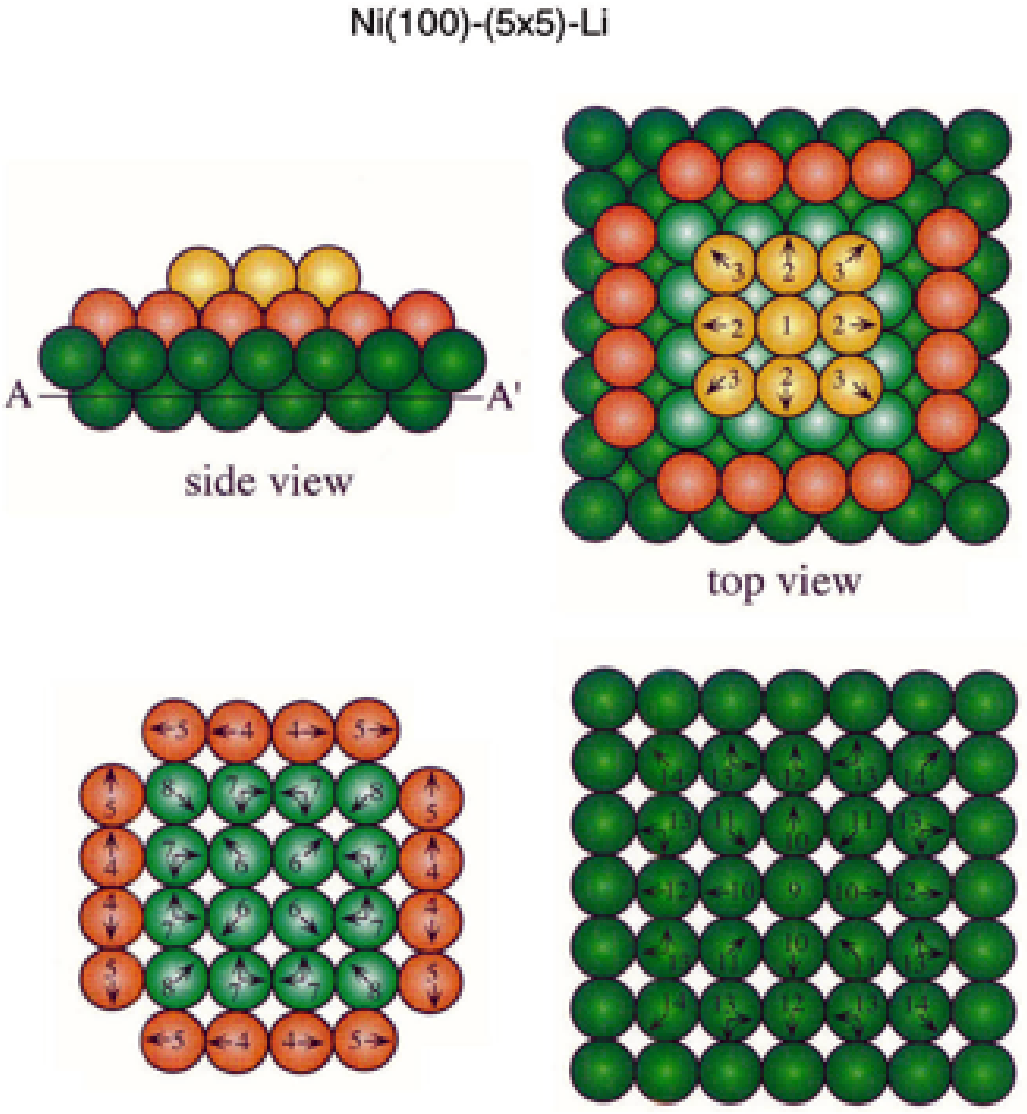
- Define $\phi_A(x) = \phi_S + \phi_I$, where

$$\begin{aligned} \phi_A &= \text{Additive surrogate,} \\ \phi_S &= \text{Simplified physics surrogate,} \\ \phi_I &= \text{Interpolatory surrogate} \end{aligned}$$

Search:

```
1    if (first search step) {
2        Initialize φ_I with Latin Hypercube sample.
3    else {
4        recalibrate φ_I with DACE model of φ_S − f.
5        }
6    Construct φ_A = φ_S + φ_I
7    Solve min φ_A
```

Test problem

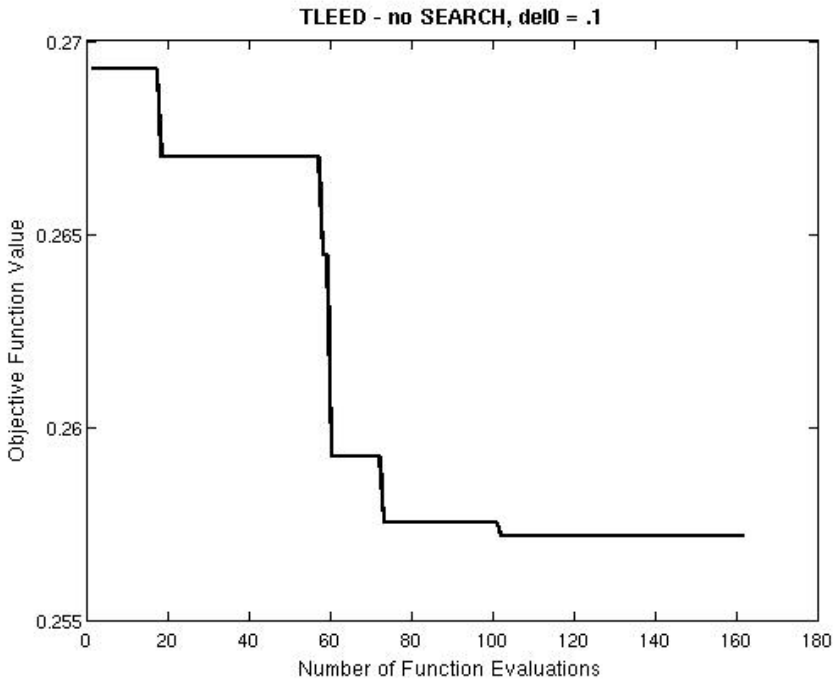


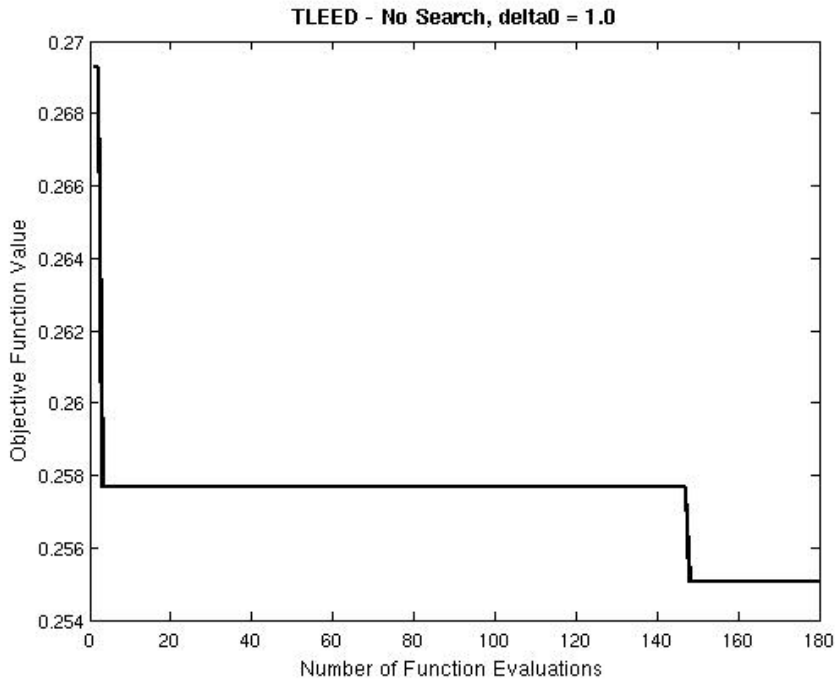
- Model 31 from set of model problem using three layers
  - 14 atoms
  - 14 categorical variables
  - 42 continuous variables
- Additional constraint added so that positions of atoms are constrained to lie within a box
- Used NOMADm, developed by M. Abramson

Test cases

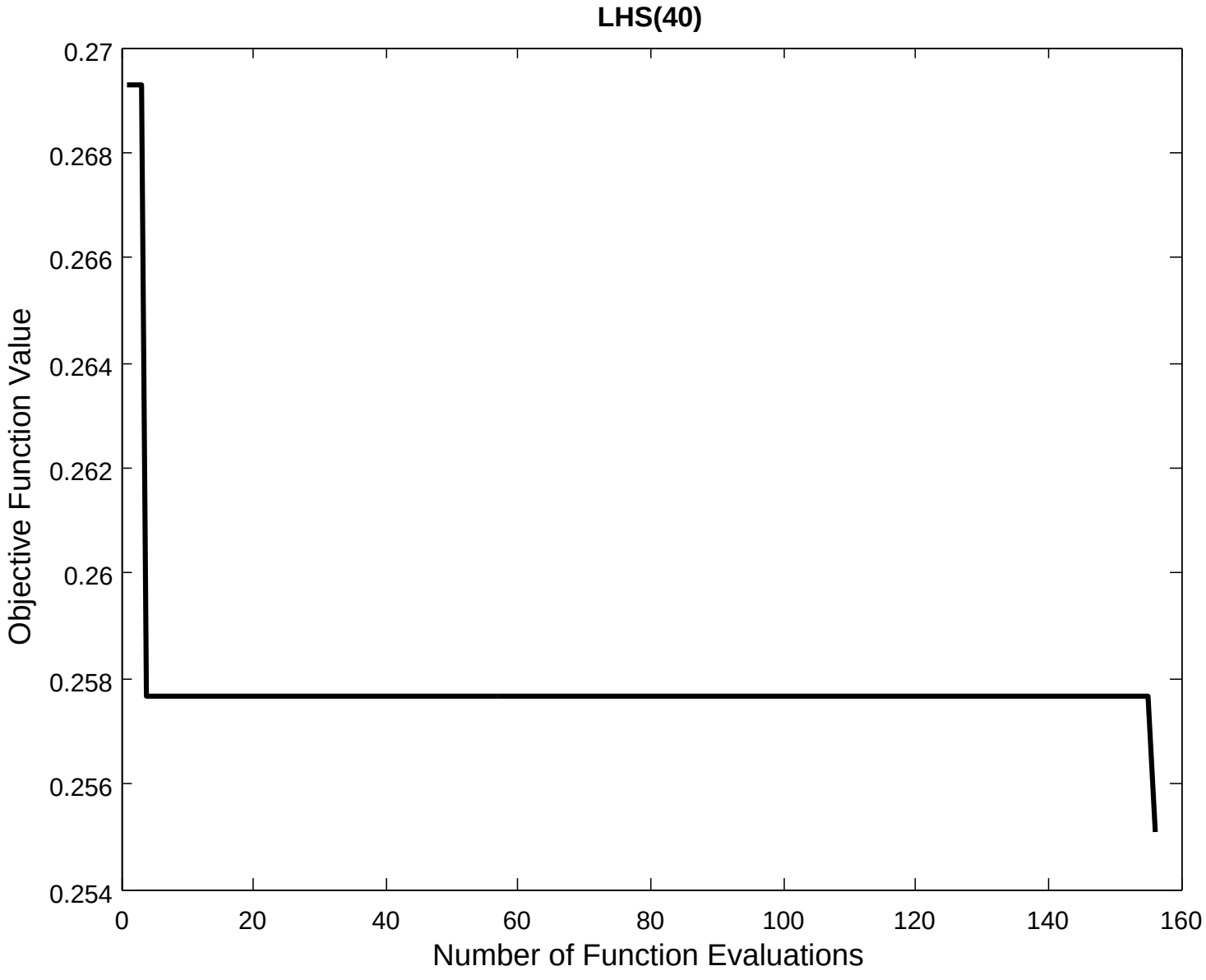
- Start with best known feasible point
- Three different approaches
  - No search step
  - LHS search
  - Simplified physics surrogate (DACE model)
    - LHS with 5 and 15 points
    - $\Delta = 1.0$
    - $\Delta = 0.1$

Optimization of continuous variables using no search phase

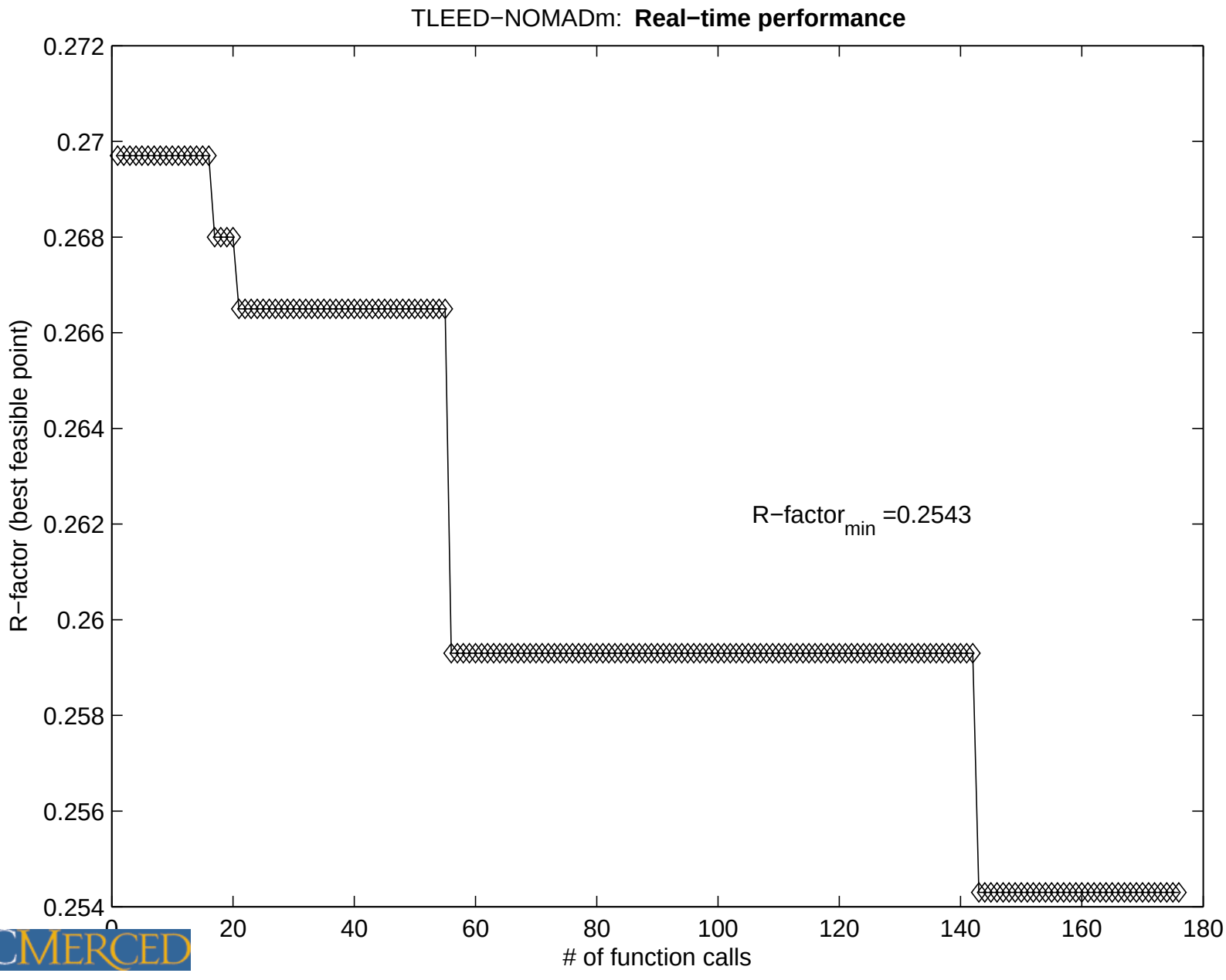




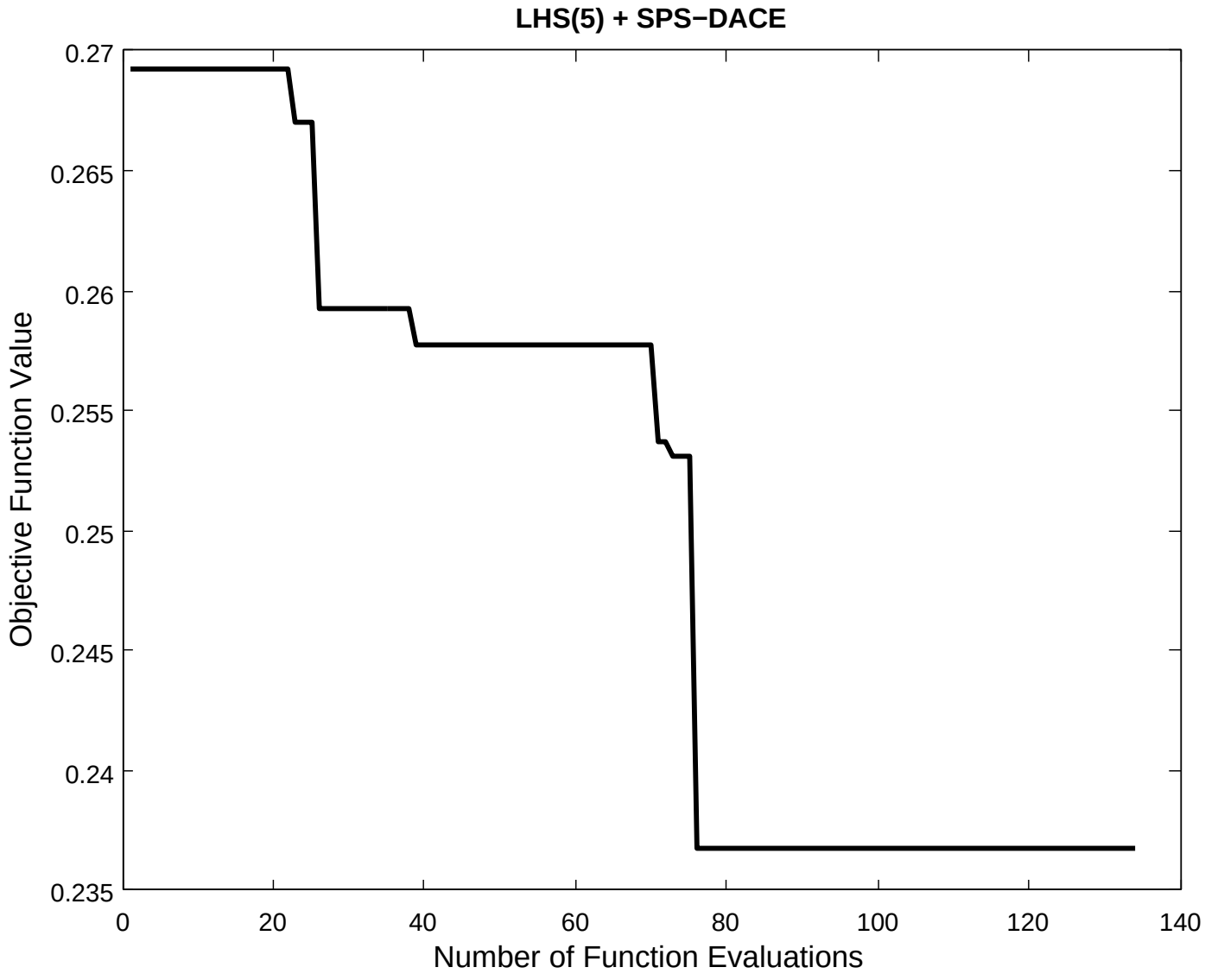
Optimization using LHS with 40 points



Optimization using additive surrogate, $\Delta_0 = 1.0$



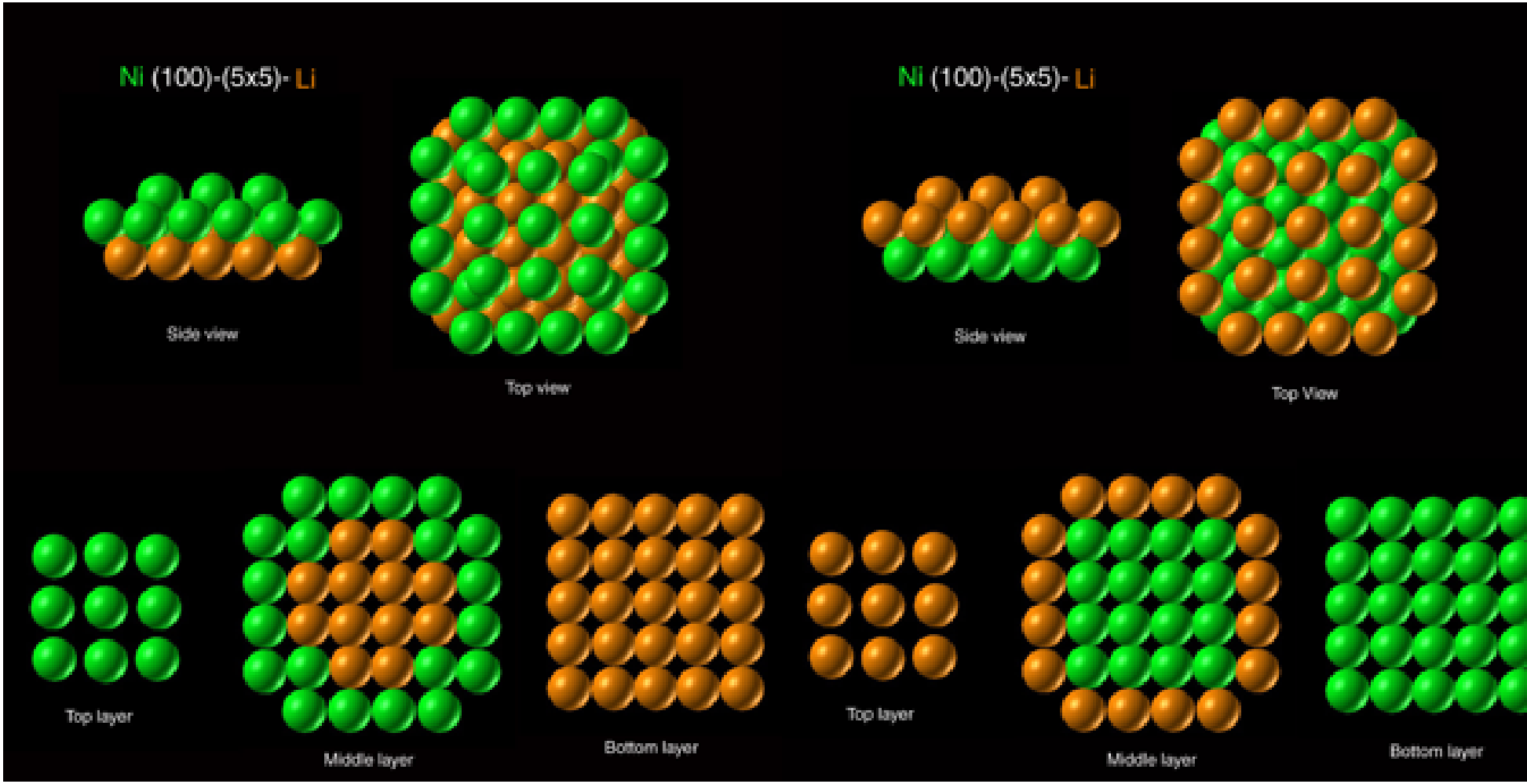
Optimization using additive surrogate, $\Delta_0 = 0.1$



Summary of numerical results

Method	LHS	$f(x^*)$	fevals
No search	0	0.2551	180
LHS	40	0.2551	160
SPS+DACE	15	0.2543	180
SPS+DACE	5	0.2354	135

LEED Chemical Identity Search: Ni (100)-(5x5)-Li



Summary

- Preliminary results indicate that performance can be enhanced by using an additive surrogate function in the search phase.
- Total number of function evaluations decreased by about 20%, which represents a reduction of $\approx$ 2 hours per model.
- Efficiency is (too) dependent on various algorithmic parameter.

Future Work

- Working on interfacing to new C++ version of Nomad
- Combine continuous with categorical variables
- Need to investigate alternatives to DACE model, e.g. Bayesian techniques

UC Merced is hiring