Surface Structure Determination of Nanostructures Using a Mesh Adaptive Optimization Method

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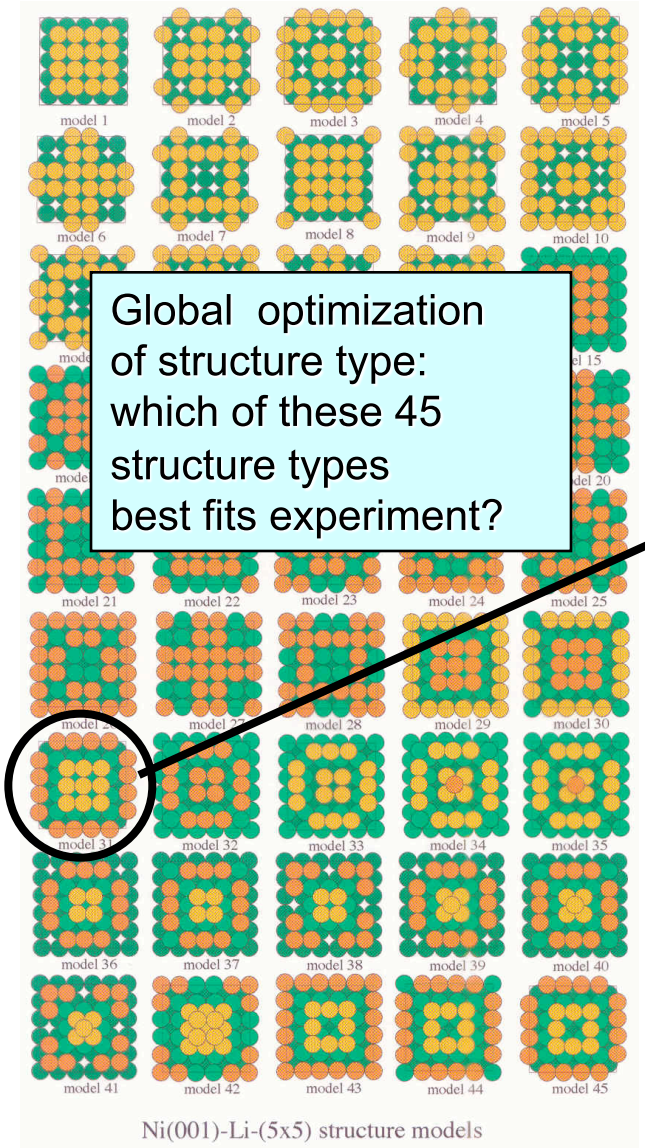
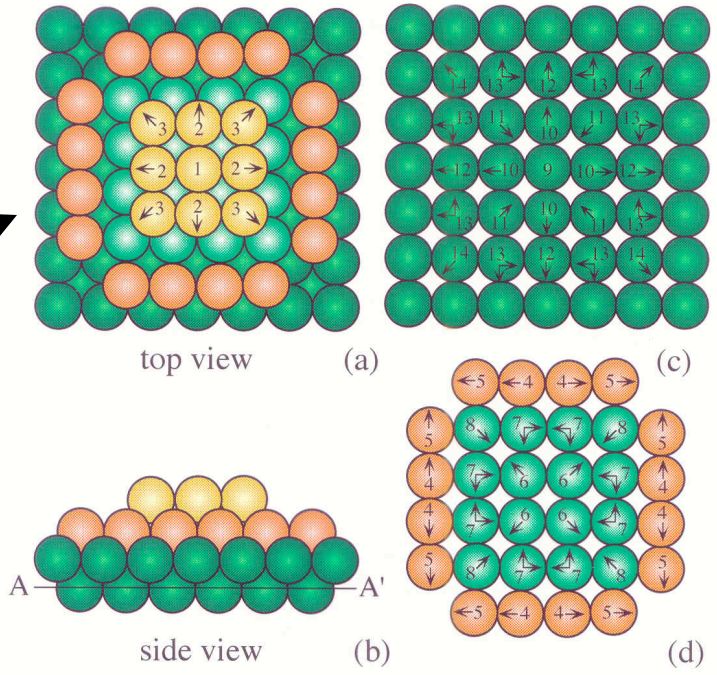
Surface structure determination from experiment



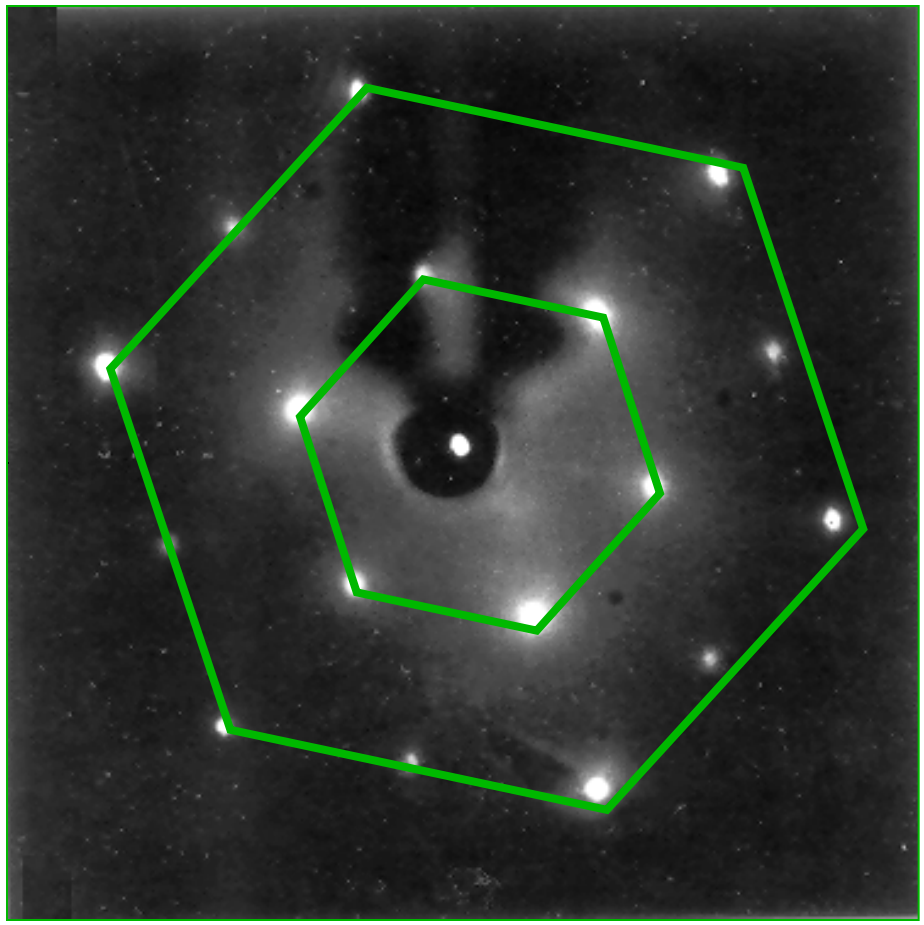
Global optimization of structure type: which of these 45 structure types best fits experiment?

- Electron diffraction determination of atomic positions in a surface:
  - Li atoms on a Ni surface



Local optimization of structure parameters: which are the best interatomic distances and angles?

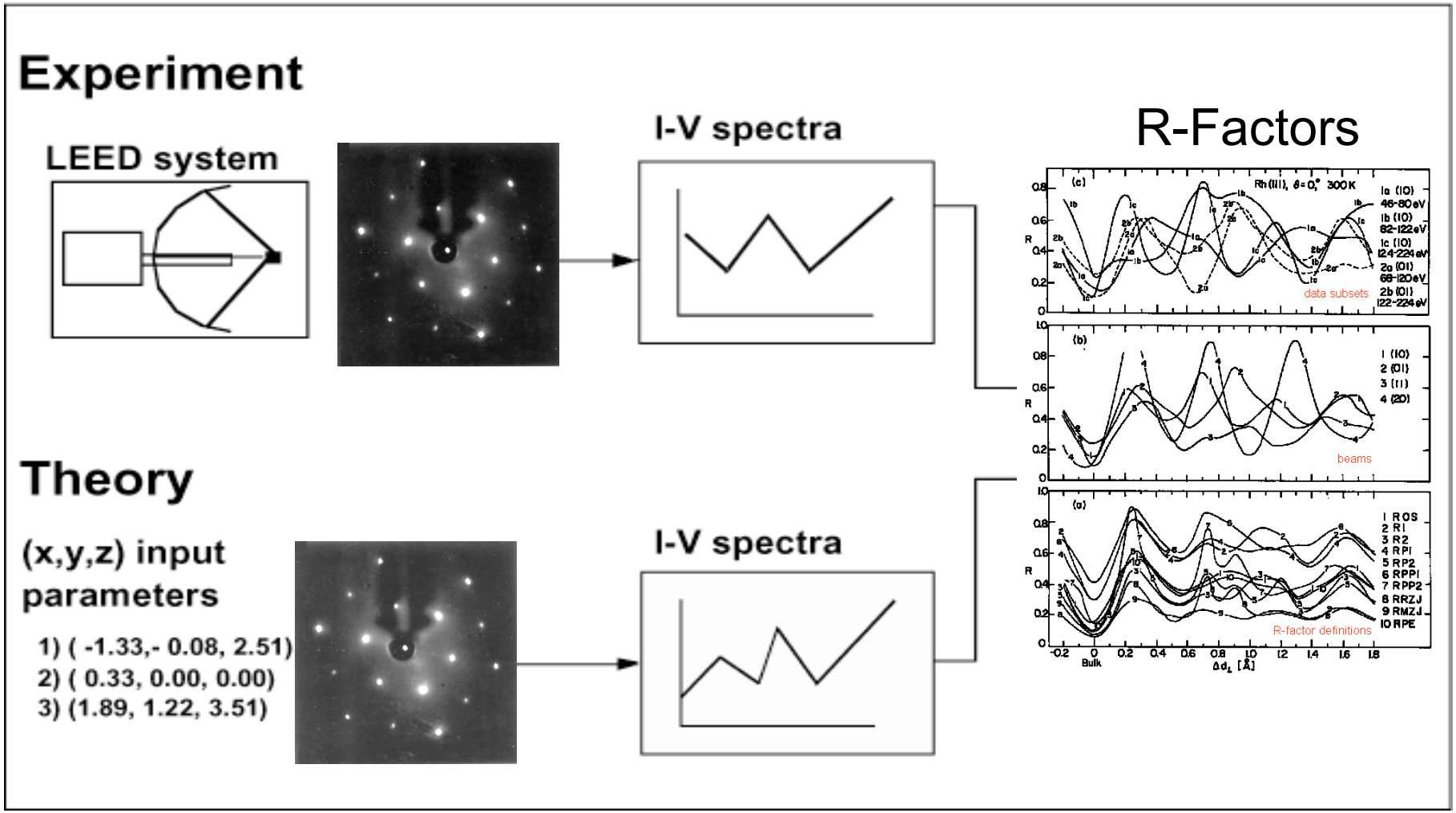
Low-energy electron diffraction (LEED)



Low-energy electron diffraction pattern due to monolayer of ethylidyne attached to a rhodium (111) surface

- Goal is to determine surface structure through low energy electron diffraction (LEED)
- Need to determine the coordinates and chemical identity of each atom
- Non-structural parameters, i.e. inner potential, phase shift δ, thermal effects and damping.

Low Energy Electron Diffraction



Pendry R-factor

$$R = \sum_g \int (Y_{gth} - Y_{gexp})^2 dE / \sum_g (Y_{gth}^2 - Y_{gexp}^2) dE$$

$$Y(E) = L^{-1} / (L^{-2} + V_{oi}^2),$$

$$L(E) = I' / I, \qquad L \approx \sum_j \frac{-2(E - E_j)}{(E - E_j)^2 + V_{oi}^2}$$

- LEED curves consist for the main part of a series of Lorentzian peaks:

$$I \approx \sum \frac{a_j}{(E - E_j^2) + V_{oi}^2}$$

- 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

Optimization formulation

- Inverse problem
  - minimize R-factor - defined as the misfit between theory an experiment
  - Several ways of computing the 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, …
- We've also used pattern search methods (NOMAD)
- Effective, but expensive
- Several hundred to 1000s of function calls typically needed
- Each function call can take up to 2 minutes on a workstation class computer

Global Optimization in LEED Structure Determination Using Genetic Algorithms, **R. Döll and M.A. Van Hove, Surf. Sci. 355, L393-8 (1996).**

G. S. Stone, MS dissertation, Computer Science Dept., San Francisco State University, 1998.

General MVP Algorithm

1. Initialization: Given Δ_0 , x_0 , M_0, P_0
2. For k = 0, 1, …
   1. SEARCH: Evaluate f on a finite subset of trial points on the mesh M_k
   2. POLL: Evaluate f on the frame P_k
3. Parameter Update: Update Δ_k
   - $x_{k+1} = x_k + \Delta_k d_k$
   - $\Delta_{k+1} = \Delta_k$

Global phase can include user heuristics or **surrogate** functions

Local phase more rigid, but needed to ensure convergence

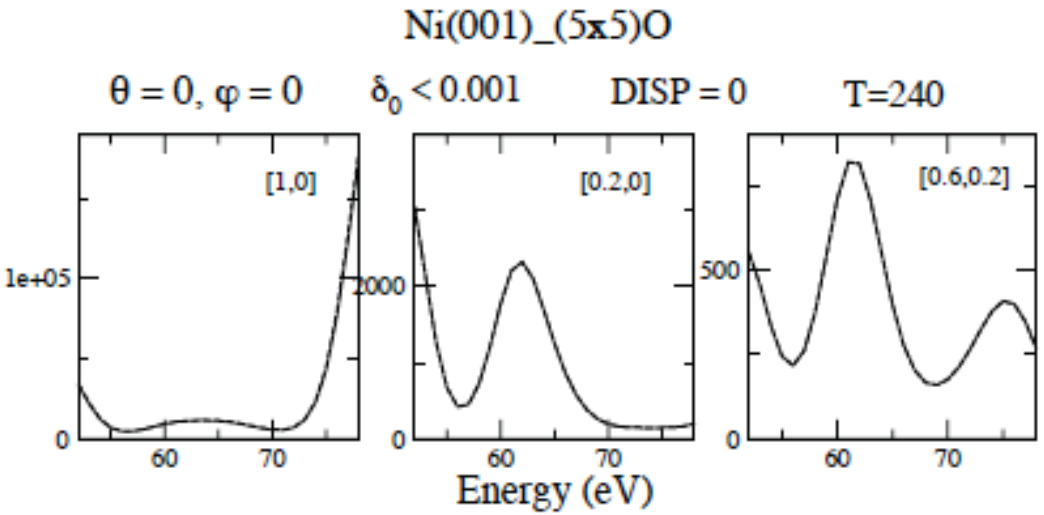
Variations on LEED

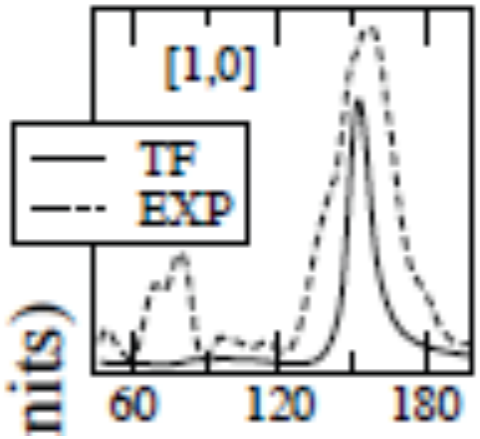
- LEED
  - Multiple scattering model
  - I-V spectra computed repeatedly until best-fit structure is found
  - Computation time is proportional to the number of parameters
- TLEED (Tensor LEED)
  - Perturbation method to calculate I-V for a structure close to a reference structure
  - For a reference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

Using 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
  - Single scattering model
  - I-V spectra computed in a few seconds
  - Compared to multiple scattering which takes ~ 2 minutes
- As $\delta \rightarrow 0$, KLEED agrees with multiple scattering

I-V curves for KLEED versus multiple-scattering





- Ni(001)-(5x5)Li structure
- KLEED and multiple scattering agree well with small phase shift
- KLEED agrees well with experimental data as long as the incident angle is close to perpendicular
- However for larger phase shift there is no guarantee of agreement

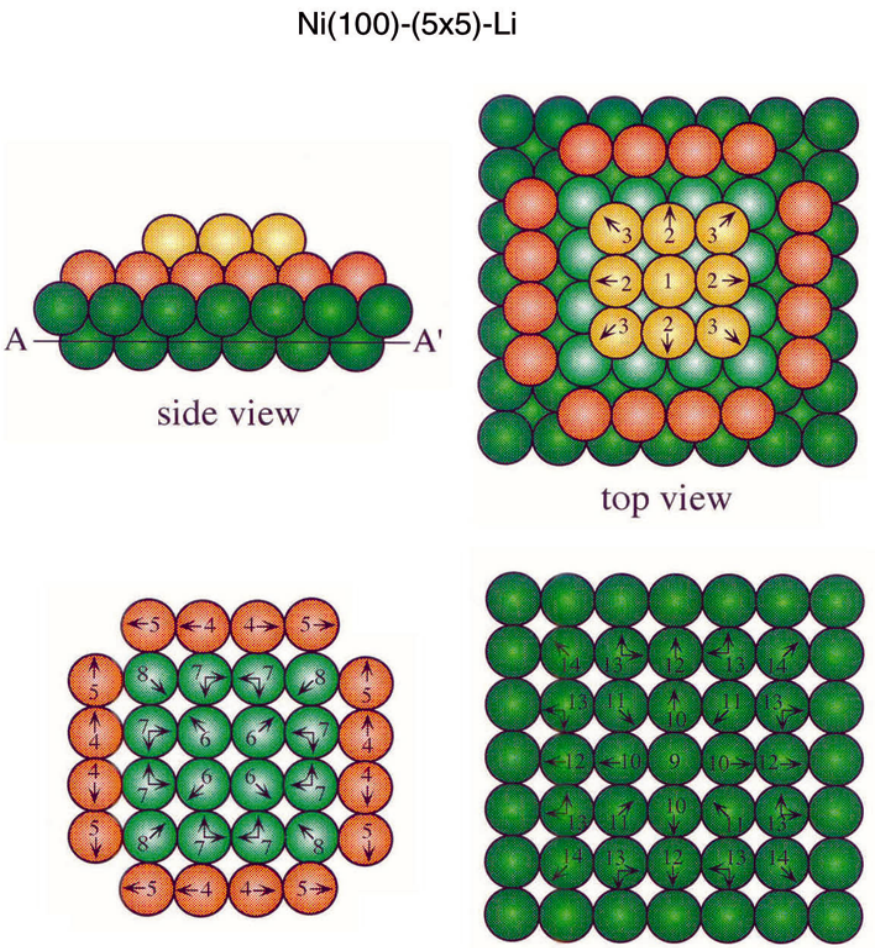
Additive Surrogate using a Simplified Physics Surrogate (SPS)

- Define $\phi_A(x) = \phi_S + \phi_I$
  - where $\phi_A = \text{Additive Surrogate},$
    $\phi_S = \text{Simplified Physics Surrogate},$
    $\phi_I = \text{Interpolatory Surrogate, e.g. DACE}$
- Search:
  - IF (first time)
    - THEN initialize ϕ_I with LHS
    - ELSE recalibrate ϕ_I with DACE
  - Construct Additive Surrogate
  - Solve $\min \phi_A = \phi_S + \phi_I$

KLEED

DACE model of difference between the SPS and Truth

Test problem

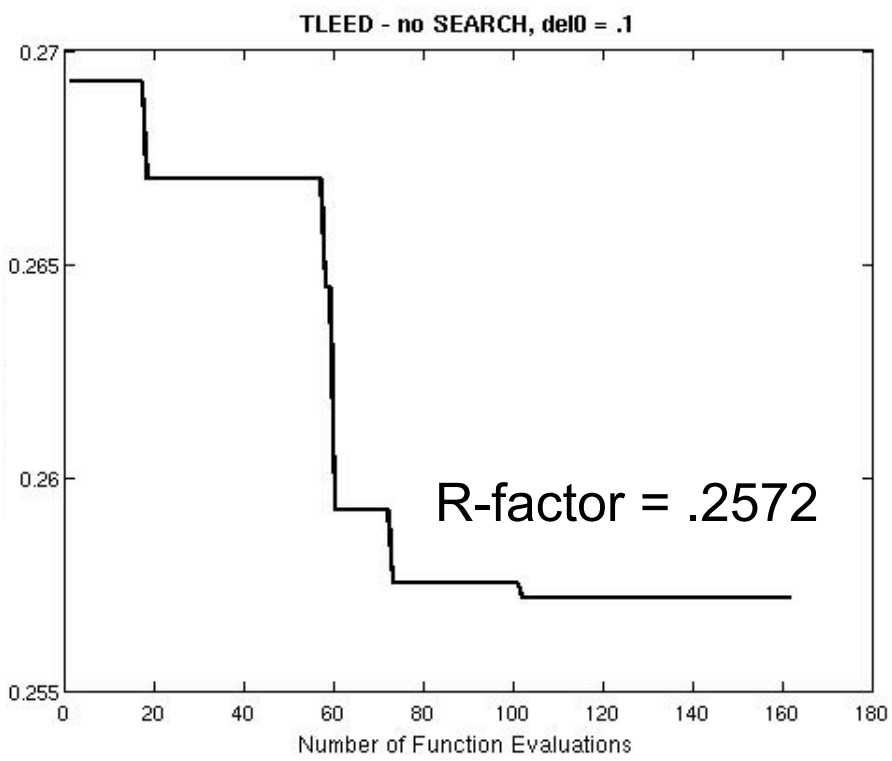


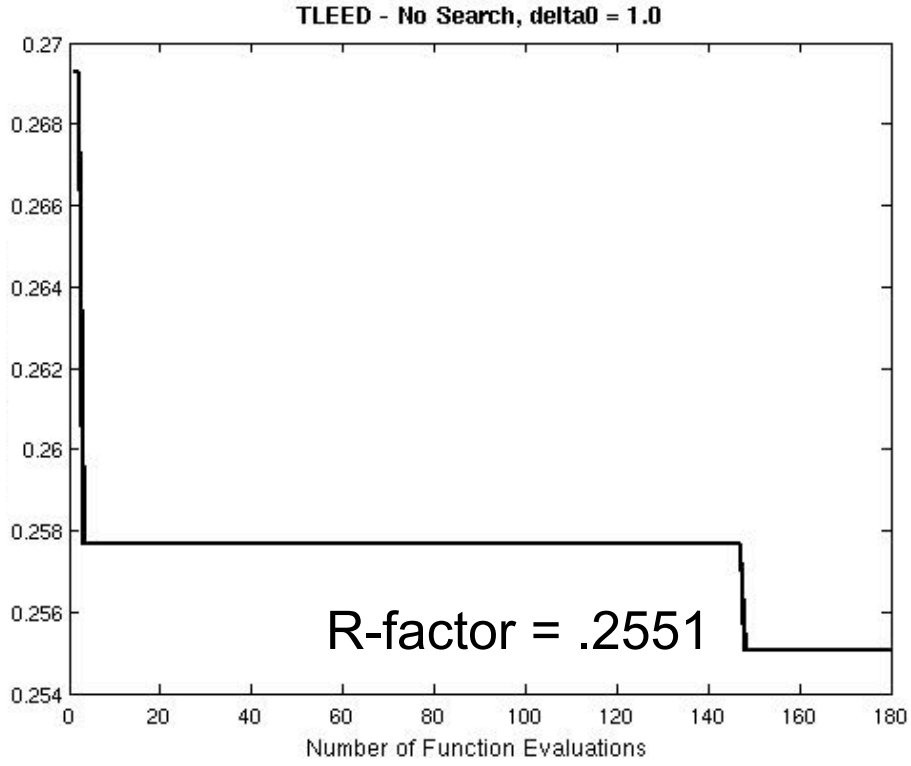
- Model 31 from set of model problems
- Three layers
- 14 atoms
  - 14 categorical variables
  - 42 continuous variables
- Positions of atoms constrained to lie within a box
- Used NOMADm: http://en.afit.edu/ENC/Faculty/MAbramson/NOMADm.html

Test cases

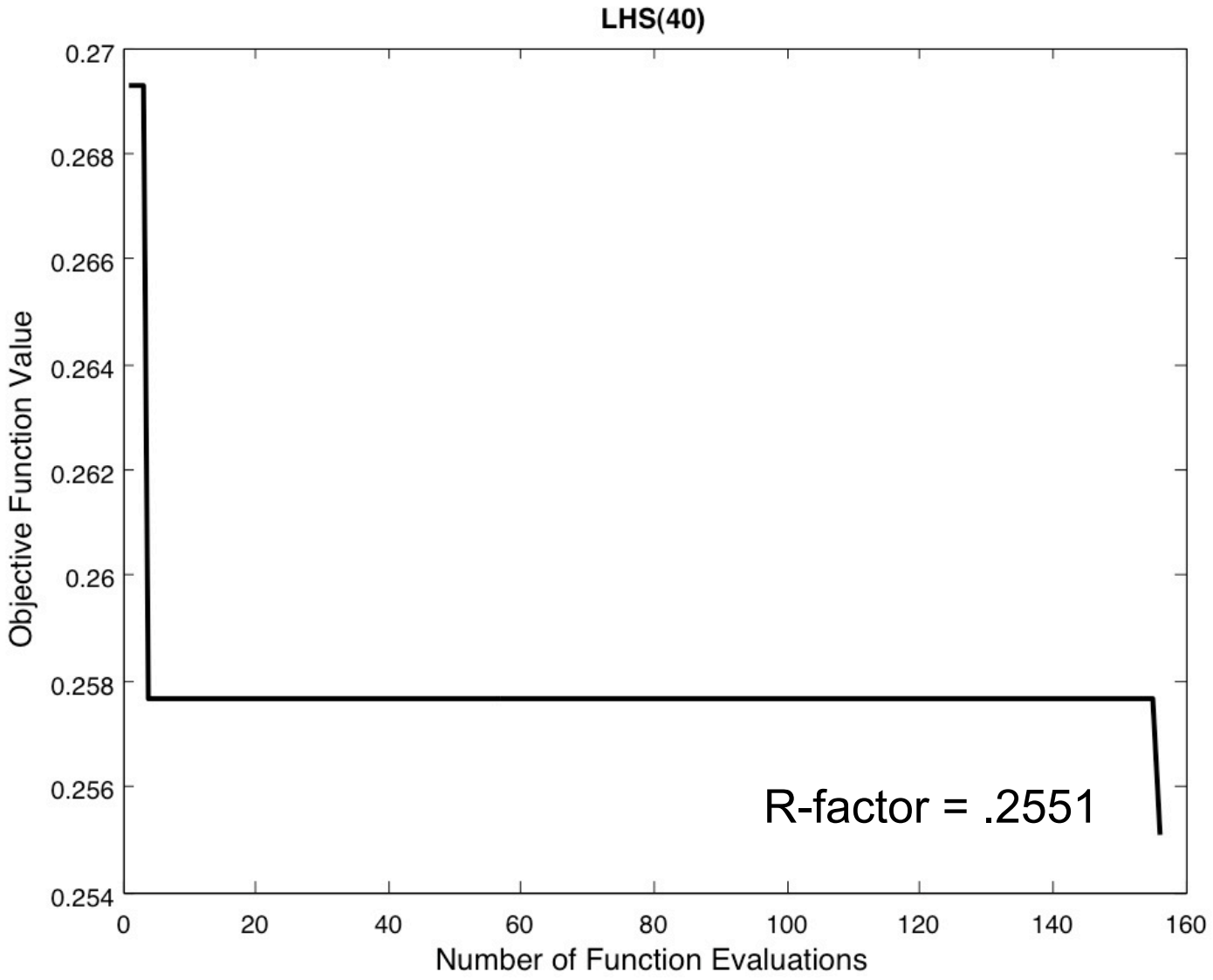
- Start with best known feasible point
- 3 different approaches
  - No Search Step
  - LHS Search
  - Simplified Physics Surrogate/DACE
    - LHS with 5 and 15 points
    - $\Delta = 1.0$
    - $\Delta = 0.1$

Relaxation of continuous variables using no search phase

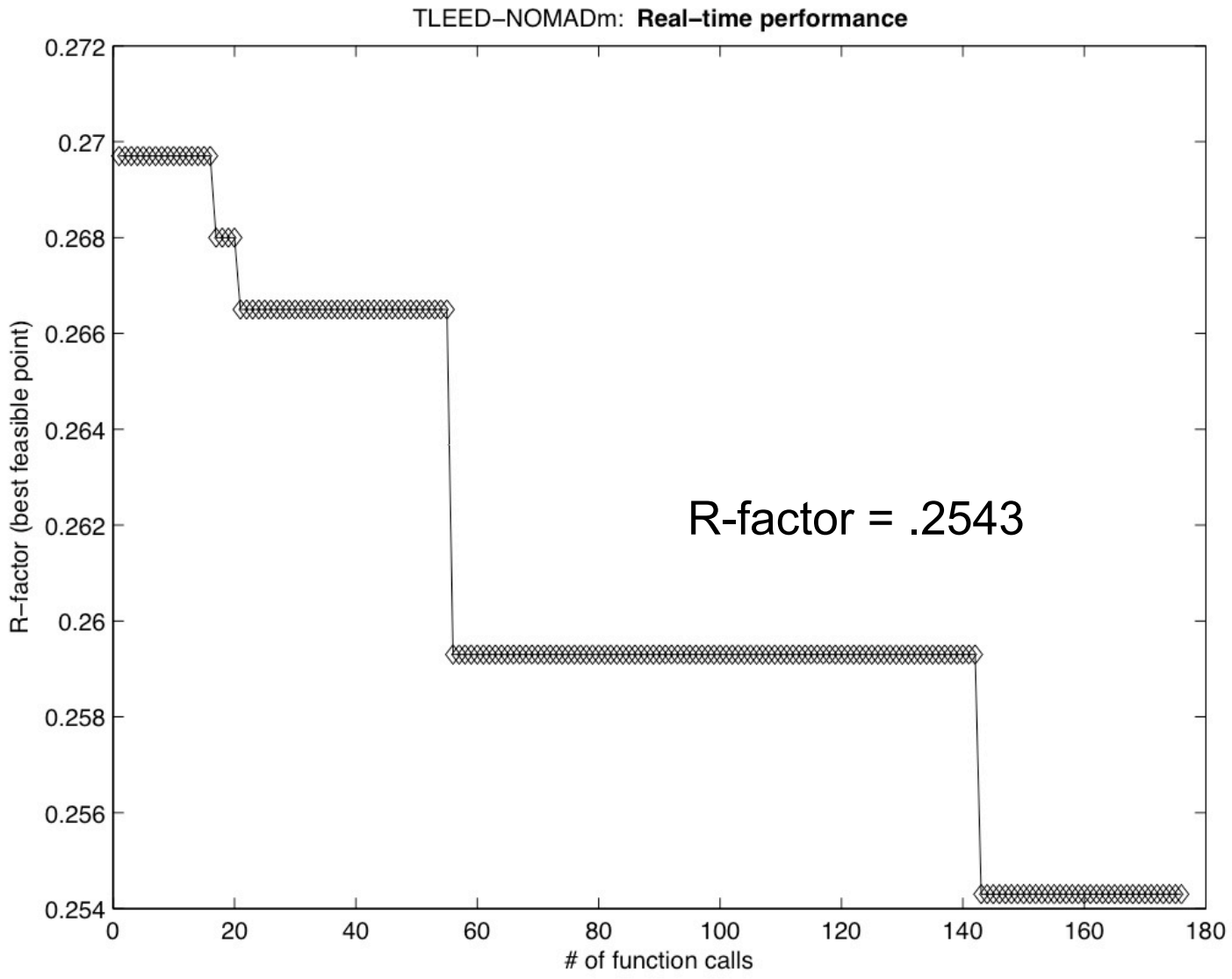




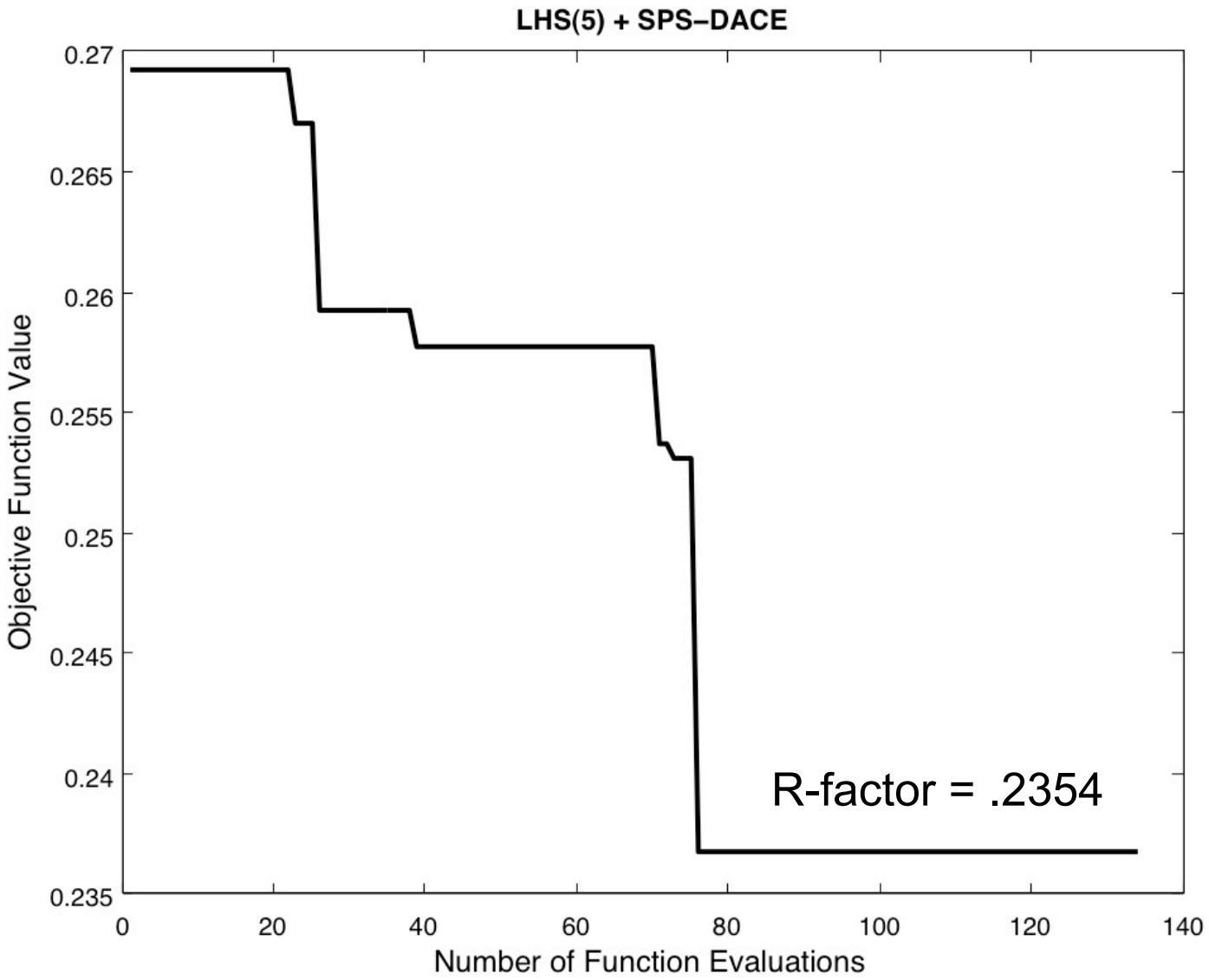
Relaxation of continuous variables using LHS with 40 points



Relaxation of continuous variables using Additive Surrogate, delta0 = 1.0

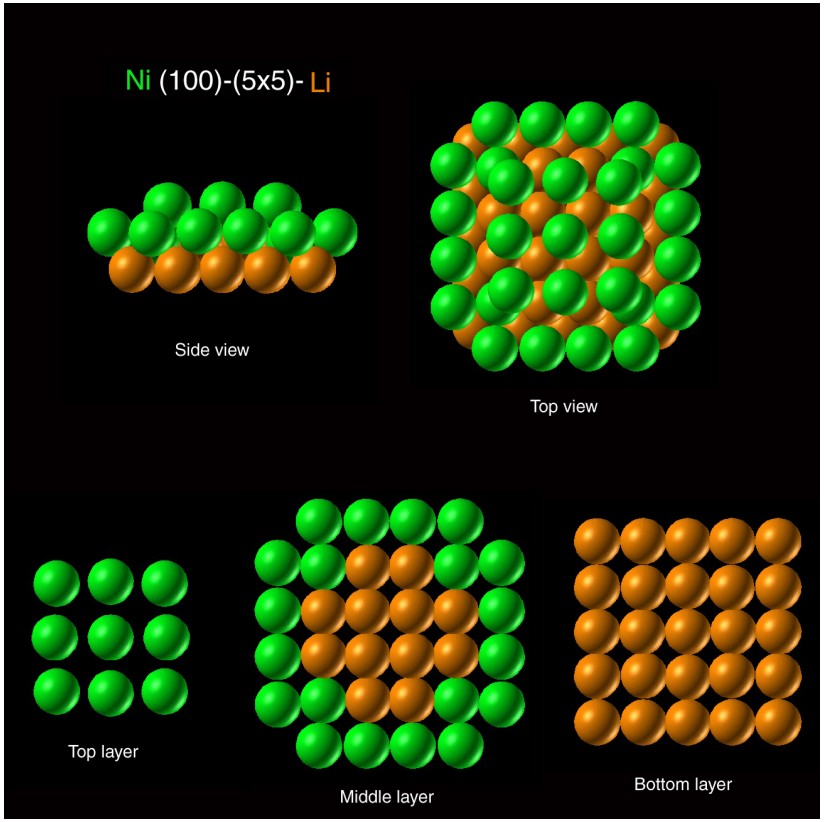


Relaxation of continuous variables using Additive Surrogate, delta0 = 0.1

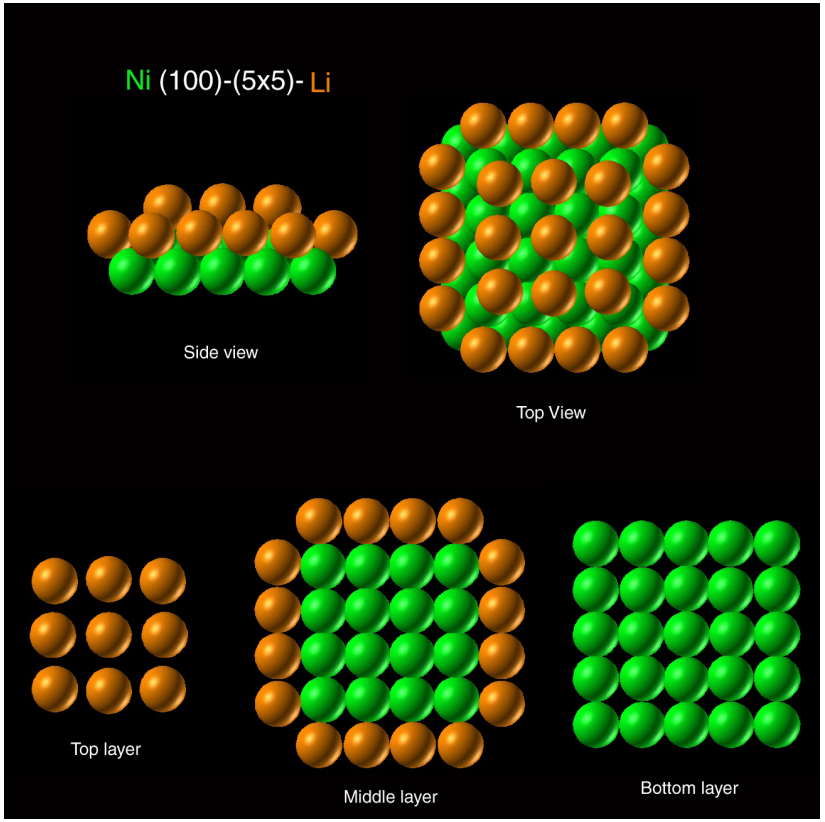


LEED Chemical Identity Search: Ni (100)-(5x5)-Li

New structure found (R = 0.1184)



Best known solution (R = 0.24)



Conclusions

- Preliminary results indicate that performance can be enhanced by using an additive surrogate function in the search phase
- Efficiency is highly dependent on various algorithmic parameters
- Several issues remain before we can declare victory

Future work

- Explore effect of initial delta, number of LHS points, minimum delta, …
- Explore different simplified physics surrogates
- Add capability for categorical variables

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