Global Optimization Methods
A **funnel** is a set of local minima with several low energy pathways which lead to the same lowest energy point.

It is significantly harder to find the global minimum of Potential Energy Surfaces with multiple funnels!
Issues with Basin Hopping

We could get stuck in the wrong funnel!
Modified Basin Hopping

• Next I will show you two methods which modify the original basin hopping algorithm to improve performance and deal with multiple funnels
• I am not including every method exist and I would encourage you to think of new ways to improve performance of these methods
Basin Hoping with Occasional Jumping

If number of visits >= Threshold:

**Basin Hoping with Occasional Jumping**

If number of visits $\geq$ Threshold:
Jump!

Basin Hoping with Occasional Jumping

If number of visits >= Threshold:

Accept multiple trial moves, run high temperature MD,
Or other *global moves*

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Basin Hopping with History

Change the acceptance rejection criteria to incorporate history.
Generate a random number between 0 and 1 called RAND

- if $e^{-\frac{(V(R_{opt'})-V(R_{opt}))}{kT}} > \text{RAND}$:
  - Accept this configuration
- Else:
  - reject
Generate a random number between 0 and 1 called RAND

1. **if** $e^{-(V(R')-V(R))+w(h(R')-h(R))/kT > RAND}$:
   - Accept this configuration
2. Else:
   - reject

![Diagram showing the process of generating a random number and accepting or rejecting configurations based on energy and height differences.](image-url)
Generate a random number between 0 and 1 called RAND

- if $e^{-(V(R')-V(R))+w(h(R')-h(R))/kT} > \text{RAND}$:
  - Accept this configuration
- Else:
  - reject

This change would make accepting $R'$ more likely since we have visited $R$ more than $R'$!
Alternative Global Optimization Methods

• Other researchers also saw issues with basin hopping and developed their own methods to tackle its pitfalls.

• Stefan Goedecker created Minima Hopping, a global optimization algorithm which tries to visit as many low energy states as possible by
  – never revisiting the same state more than once
  – Using a trial move which is likely to go to low energy states
**Bell-Evans-Polanyi (BEP) Principle**: Crossing low barriers is correlated with going to low energy states or local minima.
Bell-Evans-Polanyi Principle

The data below was generated from 130,000 saddle points (or energy barriers) in a 55 atom LJ cluster. The y-axis is the free energy difference between the initial and final state.

https://doi.org/10.1103/PhysRevE.77.056707
Minima Hopping Trial Moves

The strategy minima hopping takes is to run molecular dynamics at as low of a temperature as possible...

Because we are more likely to cross low energy barriers and find low energy states. Minima Hopping raises the temperature when we can’t escape the current minima or if we continue to sample the same state.
Minima Hopping Algorithm

• Next I will introduce the minima hopping algorithm.

• This algorithm is split into two parts:
  – A *trial move* where we run dynamics to find a new unvisited state
  – An *acceptance criteria* where we accept or reject states based on the minima hopping criteria
To start the Minima Hopping algorithm, pick the following initial conditions:

- $M_{\text{current}}$
- Kinetic energy ($E_{\text{kinetic}}$)
Minima Hopping: Trial Move

- Start a NVE MD trajectory with kinetic energy $E_{\text{kinetic}}$
- Once you pass a minimum $m_{\text{dmin}} = 2$ stop the trajectory
Minima Hopping: Trial Move

- Start a NVE MD trajectory with kinetic energy $E_{\text{kinetic}}$
- Once you pass a minimum $\text{mdmin} = 2$ stop the trajectory
- Optimize your structure to obtain a $M_{\text{new}}$
Minima Hopping: Trial Move

If \( M_{\text{new}} = M_{\text{current}} \):

Increase \( E_{\text{kinetic}} \rightarrow E_{\text{kinetic}} = E_{\text{kinetic}} \times \beta_1 \) where \( \beta_1 > 1 \)
Minima Hopping: Trial Move

- Start a NVE MD trajectory with kinetic energy $E_{\text{kinetic}}$
- Once you pass a minimum $md_{\text{min}} = 2$ stop the trajectory and optimize your structure to obtain a $M_{\text{new}}$
Minima Hopping: Trial Move

If \( M_{\text{new}} == M_{\text{current}} \):
Increase \( E_{\text{kinetic}} \) \( \rightarrow \) \( E_{\text{kinetic}} = E_{\text{kinetic}} \times \beta_1 \) where \( \beta_1 > 1 \)
Minima Hopping: Trial Move

If \( M_{\text{new}} == M_{\text{current}} \):

Increase \( E_{\text{kinetic}} \rightarrow E_{\text{kinetic}}=E_{\text{kinetic}} \times \beta_1 \) where \( \beta_1 > 1 \); reject state

Elif we have visited the state previously:

Increase \( E_{\text{kinetic}} \rightarrow E_{\text{kinetic}}=E_{\text{kinetic}} \times \beta_2 \) where \( \beta_2 > 1 \); reject state

Else:

Decrease \( E_{\text{kinetic}} \rightarrow E_{\text{kinetic}}=E_{\text{kinetic}} \times \beta_3 \) where \( \beta_3 < 1 \)

Move on to acceptance criteria
Minima Hopping: Acceptance Criteria

IF $V(M_{\text{new}}) < V(M_{\text{current}}) + \text{Ediff}$:
Accept this state! Add $M_{\text{current}}$ to history
Decrease Ediff $\Rightarrow$ Ediff = Ediff * alpha1 where alpha1 < 1

Else:
Reject this state
Increase Ediff $\Rightarrow$ Ediff = Ediff * alpha2 where alpha2 > 1
If $M_{\text{new}} = M_{\text{current}}$:
Increase $E_{\text{kinetic}} \rightarrow E_{\text{kinetic}} = E_{\text{kinetic}} \times \beta_1$ where $\beta_1 > 1$; reject state

Elif we have visited the state previously:
Increase $E_{\text{kinetic}} \rightarrow E_{\text{kinetic}} = E_{\text{kinetic}} \times \beta_2$ where $\beta_2 > 1$; reject state

Else:
Decrease $E_{\text{kinetic}} \rightarrow E_{\text{kinetic}} = E_{\text{kinetic}} \times \beta_3$ where $\beta_3 < 1$
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Move on to acceptance criteria
If $M_{\text{new}} == M_{\text{current}}$:

- Increase $E_{\text{kinetic}} \rightarrow E_{\text{kinetic}} = E_{\text{kinetic}} \times \beta_1$ where $\beta_1 > 1$; reject state

Elseif we have visited the state previously:

- Increase $E_{\text{kinetic}} \rightarrow E_{\text{kinetic}} = E_{\text{kinetic}} \times \beta_2$ where $\beta_2 > 1$; reject state

Else:

- Decrease $E_{\text{kinetic}} \rightarrow E_{\text{kinetic}} = E_{\text{kinetic}} \times \beta_3$ where $\beta_3 < 1$

Move on to acceptance criteria
Minima Hopping: Acceptance Criteria

If $V(M_{\text{new}}) < E_{\text{diff}} + V(M_{\text{current}})$:
    Accept new minimum; $M_{\text{current}} = M_{\text{new}}$
Else:
    Reject this minimum and increase $E_{\text{diff}}$
    $E_{\text{diff}} = E_{\text{diff}} \times \alpha_2$ where $\alpha_2 > 1$
initialize a current minimum ‘Mcurrent’

MDstart

ESCAPE TRIAL PART

start a MD trajectory with kinetic energy Ekinetic from current minimum ‘Mcurrent’. Once the potential reaches the mth minimum along the trajectory stop MD and optimize geometry to find the closest local minimum ‘M’

if (‘M’ equals ‘Mcurrent’) then

    Ekinetic=Ekinetic*beta1 (beta1>1)

    goto MDstart

else if (‘M’ equals a minimum visited previously) then

    Ekinetic=Ekinetic*beta2 (beta2>1)

    goto MDstart

else if (‘M’ equals a new minimum) then

    Ekinetic=Ekinetic*beta3 (beta3<1)

endif

DOWNWARD PREFERENCE PART

if (energy(‘M’)–energy(‘Mcurrent’)<Ediff) then

    accept new minimum: ‘Mcurrent’=‘M’

    add ‘Mcurrent’ to history list

    Ediff=Ediff*alpha1 (alpha1<1)

else if rejected

    Ediff=Ediff*alpha2 (alpha2>1)

endif

goto MDstart

# Comparison of Minima and Basin Hopping

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<th>Method</th>
<th>Trial Move</th>
<th>Acceptance Criteria</th>
<th>History</th>
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<td>Random displacement</td>
<td>Metropolis Monte Carlo</td>
<td>$e^{\frac{-(V(R')-V(R)+w(H(R)-H(R'))}{k_bT}}$</td>
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<tr>
<td>Minima Hopping</td>
<td>Molecular Dynamics</td>
<td>$(V(M_{\text{new}}) - V(M_{\text{current}})) &lt; \text{Ediff}$</td>
<td>Reject a states visited previously and increase kinetic energy of MD</td>
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References
