

# Location of transition states in complex systems; methods and problems

Andrew Walkingshaw  
Department of Earth Sciences  
University of Cambridge

July 6, 2004

## *Chemical transition states*

- the “midpoint” between reactants and products
- sufficient to reconstruct an entire reaction coordinate
- permits calculation of activation energy - thermodynamics and kinetics of a process

## *Transition states, mathematically*

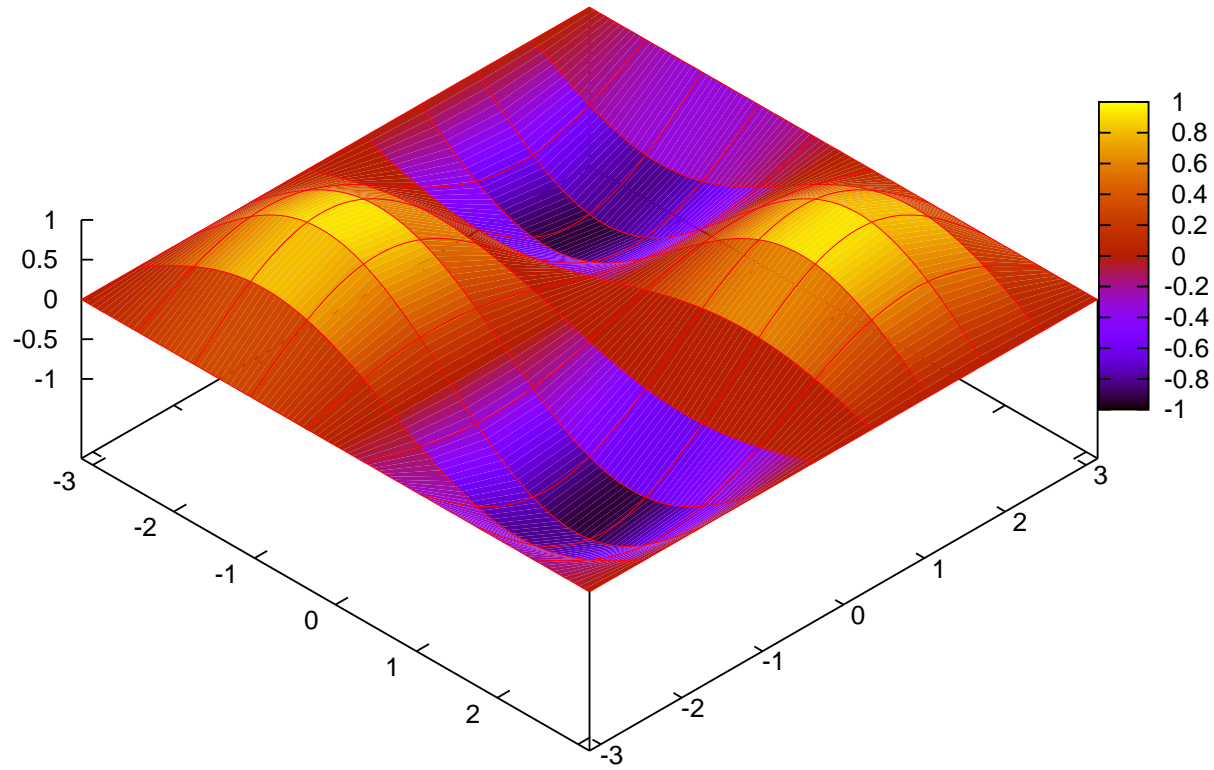
Given some configuration of atoms,  $\bar{x}$ , and a Hamiltonian  $H(\bar{x})$  which evaluates their energy, one can obtain the matrix known as the Hessian:

$$\frac{\delta^2 H}{\delta x_i \delta x_j} \quad (1)$$

At a transition state, the eigenvalues of this matrix (except one) are all real and positive.

The remaining eigenvalue will be real and *negative* - transition states are first-order saddle points on the potential energy surface.

*A saddle point...*



## *A strategy for finding transition states*

One strategy (ART Nouveau, after Mousseau et al.) is:

- excite the system to a point in configuration space where one of the eigenvalues of the Hessian becomes negative.
- then travel uphill along the most negative (smallest) eigenvalue,  $\lambda$  (with corresponding unit vector  $\bar{v}$ ) while minimizing energy in the subspace defined by:

$$F(x') = F(x) - (F(x) \cdot \bar{v})\bar{v} \quad (2)$$

## *Variational methods*

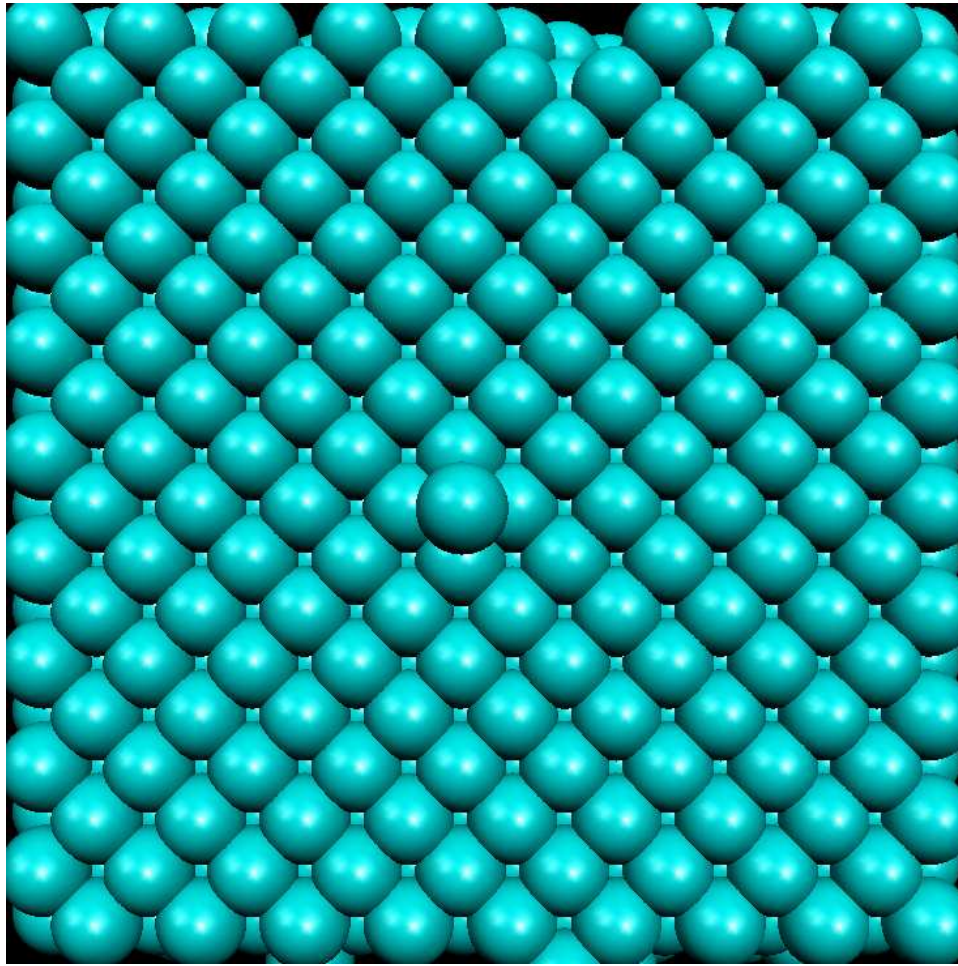
It is possible to find the minimum eigenvalue (and corresponding eigenvector) of the Hessian variationally. This was first demonstrated by Munro and Wales.

$$\lambda(y) = \frac{\langle \mathbf{y} | \mathbf{H} | \mathbf{y}^T \rangle}{\langle \mathbf{y} | \mathbf{y}^T \rangle} \quad (3)$$

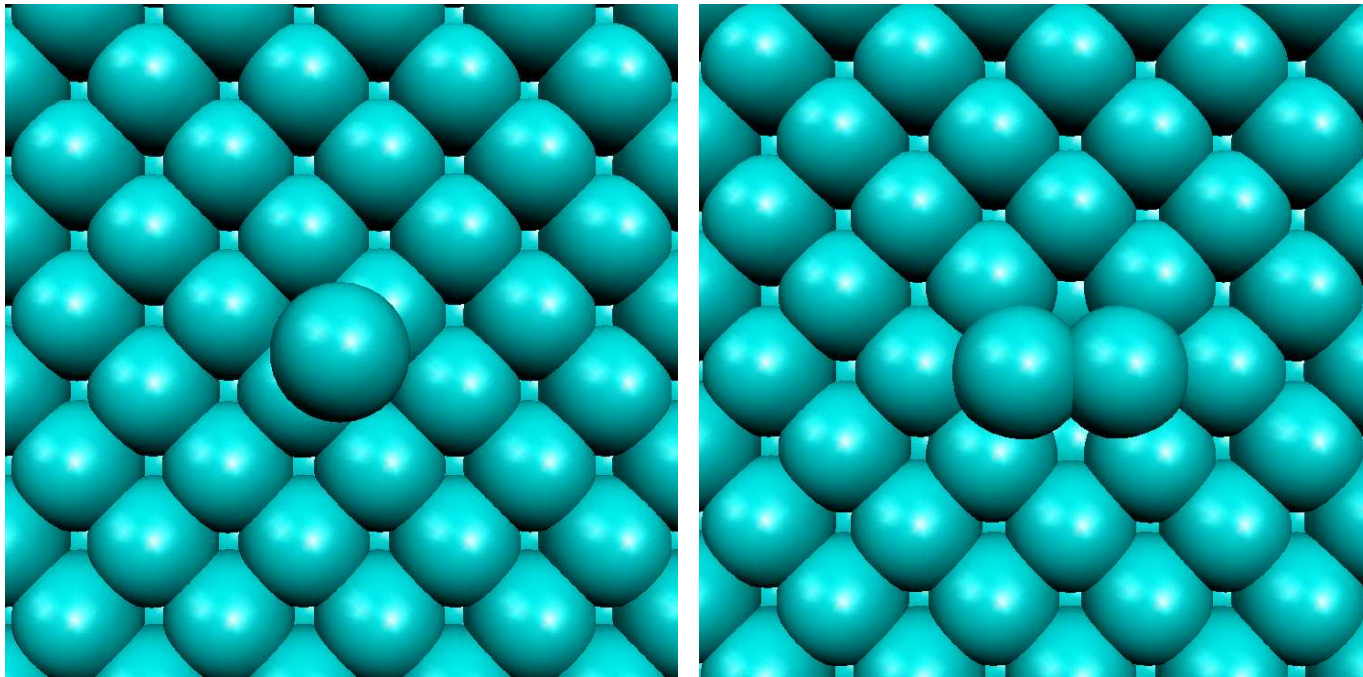
Take a numerical approximation to the second derivative of energy along a specific vector,  $\mathbf{y}$ , as:

$$\lambda(\mathbf{y}) = \frac{E(\mathbf{x} + \mu\mathbf{y}) + E(\mathbf{x} - \mu\mathbf{y}) - 2E(\mathbf{x})}{(\mu\mathbf{y})^2} \quad (4)$$

*A model system: Pt [100] self-diffusion with an EMT potential*



*Two accessible transition states...*



These have activation energies of 0.66eV and 0.91eV respectively.



## *Caveats*

So...

- It is possible to capture non-trivial multiple atom transition states using this technique.
- these results don't chime with experimental results for diffusion on a Pt [001] surface: the two transition states are misordered. This is probably a weakness of the underlying simulation.
- Most runs take between 400 and 900 force evaluations to converge; good but not great.

## *Problems*

- To get chemically accurate energies and reaction pathways, highly converged electronic structure calculations are necessary. These are slow.
- This suggests a hybrid approach - preliminary search with an empirical potential, then switch to DFT - might be fruitful.
- The eggbox effect in Siesta is a problem; this is under investigation to fully quantify, but looks like a real issue.

## *The eggbox syndrome*

- The eggbox force breaks the translational invariance of space
- Means that: the three expected zero-frequency modes (translations) have non-zero frequency
- Breaks variational minimization...

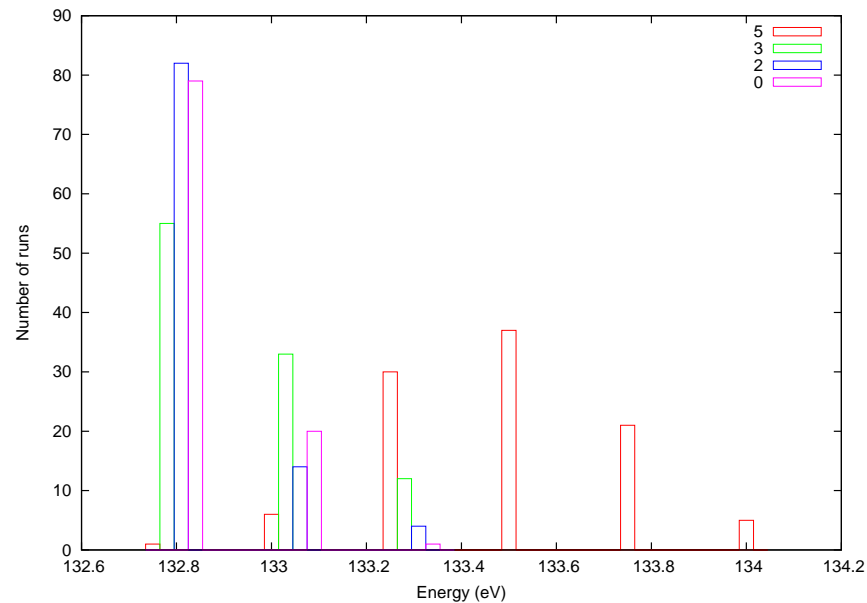
## *Avoiding Hessian evaluation entirely*

- Idea comes from the maximization process in ART.
- Instead of iteratively making a step, minimizing in the tangent space, and evaluating  $\lambda_{min}$ , why not maximize the energy of our system along a given eigenvector whilst minimizing in the tangent space?
- This has been tested and found effective in the ART Nouveau context, using (effectively) Brent's minimization algorithm.

## *Back to eigenvectors*

- Try maximizing along one direction whilst minimizing along the others...
- ... which gives you a point with one negative-curvature direction and all the others positive-curvature: a transition state!
- Pick a vector from the subspace around an “active” atom - e.g. the surface atom in our EMT test system, at random, and maximize along it.

*Testing the theory...*



Assuming our trial vector contains the true minimum eigenvector (as any vector in the space is a linear combination of the eigenvectors of the hessian), motion should tend towards that direction.

## *Resultant states*

- When the maximization is restricted to atoms near the surface adatom, we obtain states close to the two transition states shown earlier.
- Therefore important to choose subspace to maximize in carefully: this is what variational minimization does!
- Is it possible to deduce the active subspace from other considerations?