Location of transition states in complex systems; methods and problems

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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:

$$\frac{\delta^2 H}{\delta x_i \delta x_j}$$

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:

\[
F(x') = F(x) - (F(x) . \bar{v}) \bar{v}
\]  

(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.

\[ \lambda(y) = \frac{\langle y | H | y^T \rangle}{\langle y | y^T \rangle} \]  

(3)

Take a numerical approximation to the second derivative of energy along a specific vector, \( y \), as:

\[ \lambda(y) = \frac{E(x + \mu y) + E(x - \mu y) - 2E(x)}{(\mu y)^2} \]  

(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?