Implementation of Nudged Elastic Band in CRYSTAL

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Abstract

Locating transition states and energies is a very important problem in many areas of chemistry. The rate of chemical reactions and diffusion events are, in part, determined by the energy barrier between the reactants and the products. The Nudged Elastic Band algorithm locates transition states using knowledge of the end states (the reactants and products) along with the energy and its first derivatives. A parallel version of this algorithm has been implemented in CRYSTAL. The method has been rigorously tested to ensure that it performs effectively and does not interfere with any other functionality within CRYSTAL.

Key words: NUDGED ELASTIC BAND, TRANSITION STATE SEARCH

1 Introduction

The CRYSTAL program computes the electronic structure of periodic systems within Hartree Fock, density functional or various hybrid approximations. The code may be used to perform studies of the physical, electronic and magnetic structure of molecules, polymers, surfaces and crystalline solids. The program is jointly developed by the Theoretical Chemistry Group at the University of Torino and the Computational Materials Science group in CCLRC [1]. New functionalities are continually being developed and implemented into CRYSTAL. Recent developments to the code include analytical first derivatives, a Broyden-Fletcher-Goldfarb-Shannon

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(BFGS) optimiser and the ability to calculate quasi harmonic phonon modes. This paper concerns the implementation of a transition state finder in CRYSTAL.

Determining a transition state is a very important problem. The rate of chemical reactions and diffusion events are all, in part, determined by the energy barrier between the reactants and the products. The transition state is a saddle point on the potential energy surface. Locating saddle points on a high dimensional surface is not a straight forward task. Several methods have been developed to accomplish this task. There are algorithms that require second derivative information, and others that only require first derivatives to be calculated. CRYSTAL does not have the ability to calculate analytical second derivatives. Thus we are limited to methods that only require first derivatives. Methods that have been developed include Conjugate Peak Refinement, Drag, Nudged Elastic Band and Ridge. These methods have been reviewed and it was found that the Nudged Elastic Band (NEB) method was the most efficient and reliable [2], hence this method has been chosen for inclusion in CRYSTAL.

The NEB algorithm requires that the structure of both the reactants and the products are known. The algorithm attempts to locate a minimum energy path (MEP) for a given chemical reaction or absorption event. The NEB algorithm initially makes an estimate of the MEP. A number of images are constructed along this path. A spring interaction between adjacent images is added to encourage the images to remain equally spaced. Optimising all the images along the band by minimising the total force converges the band to a MEP. The algorithm is described in detail in section 2.

The NEB algorithm can be parallelised very efficiently, allowing a given calculation to be run on a large number of processors. The majority of the CPU time is spent on calculating the energy and first derivatives of each image. These calculations are each independent of the other images, hence they are ideal candidates for task farming parallelisation. The implementation of the NEB method in crystal, including parallelisation of the method is described in section 3.

The NEB algorithm has been rigorously tested in CRYSTAL. Several simple molecular reactions have been run and results compared to published values. The efficiency of the parallelisation has been tested and benchmarked. The results of these tests are presented in section 4.

It is intended that the NEB algorithm will be included in the next release of CRYSTAL which is scheduled for 2006.

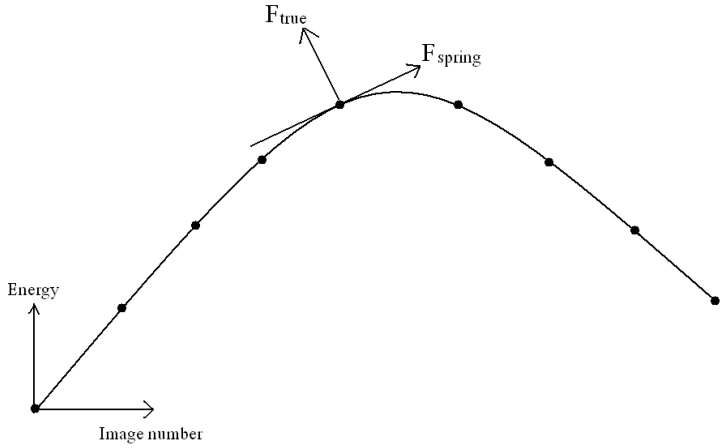

Fig. 1. Diagram showing how the true force and the spring force are projected out perpendicularly and parallel to the band of images.

2 The Nudged Elastic Band Method

The NEB algorithm takes an initial estimate of the MEP and iterates towards a local MEP. If the local MEP is the MEP of the system then the highest point along the MEP is, by definition, the transition state.

Several images are constructed along the initial estimate of the MEP (this is usually obtained from linear interpolation between the two minima). This forms a band of N+1 images (typically 3-10 images are used). These images can be denoted by [$\mathbf{R}_0$, $\mathbf{R}_1$, $\mathbf{R}_2$,... $\mathbf{R}_N$] where $\mathbf{R}_i$ defines the co-ordinates of image *i*. $\mathbf{R}_0$ and $\mathbf{R}_N$ are the end points and remain fixed throughout the calculation. Spring forces between adjacent images are added to encourage continuity and equal spacing of the images along the band. The minimisation of the total forces acting on the images results in convergence to a local MEP. The main distinguishing feature of this method to other band methods is its use of force projections to eliminate interferences between the spring forces and the true forces. The tangent of the band at each image point is estimated. The spring force is projected out parallel to the tangent while the true force is projected out perpendicular to the tangent as shown in figure 1. The total force acting on each image is

$$\mathbf{F}_i = \mathbf{F}_i^{\mathrm{spr}} \mid_{\parallel} -\nabla E(\mathbf{R}_i) \mid_{\perp} \tag{1}$$

where $\mathbf{F}_i^{\mathrm{spr}}$ is the force due to the spring interactions and E($\mathbf{R}_i$) is the energy of the image at position $\mathbf{R}_i$.

The tangent estimation used is the one proposed by Henkelman and Jónsson [3]

$$\boldsymbol{\tau}_i = \begin{cases} \boldsymbol{\tau}_i^+ & \text{if} \quad E_{i+1} > E_i > E_{i-1} \\ \boldsymbol{\tau}_i^- & \text{if} \quad E_{i+1} < E_i < E_{i-1} \end{cases} \tag{2}$$

where

$$\boldsymbol{\tau}_i^+ = \mathbf{R}_{i+1} - \mathbf{R}_i \text{ and } \boldsymbol{\tau}_i^- = \mathbf{R}_i - \mathbf{R}_{i-1} \tag{3}$$

If image *i* is at an extrema then the tangent estimate becomes

$$\boldsymbol{\tau}_i = \begin{cases} \boldsymbol{\tau}_i^+ \Delta E_i^{\max} + \boldsymbol{\tau}_i^- \Delta E_i^{\min} & \text{if} \quad E_{i+1} > E_{i-1} \\ \boldsymbol{\tau}_i^+ \Delta E_i^{\min} + \boldsymbol{\tau}_i^- \Delta E_i^{\max} & \text{if} \quad E_{i+1} < E_{i-1} \end{cases} \tag{4}$$

where $\boldsymbol{\tau}^+$ and $\boldsymbol{\tau}^-$ are defined by equation 3,

$$\Delta E_i^{\max} = \max(|E_{i+1} - E_i|, |E_{i+1} - E_i|) \tag{5}$$

and

$$\Delta E_i^{\min} = \min(|E_{i+1} - E_i|, |E_{i+1} - E_i|) \tag{6}$$

The tangent must then be normalised.

The spring force is defined as

$$\mathbf{F}_i^{\text{spr}}|_{\|} = k(|\mathbf{R}_{i+1} - \mathbf{R}_i| - |\mathbf{R}_i - \mathbf{R}_{i-1}|)\hat{\boldsymbol{\tau}}_i \tag{7}$$

This ensures equal spacing of the images when the same spring constant, *k*, is used for all the springs. Often it is preferable to have higher resolution of the MEP close to the saddle point. This can be achieved by the use of stronger springs close to the saddle point. A variable spring constant scheme has been implemented in CRYSTAL; the spring constant depends linearly on the energy of the images, such that images with higher energies are connected via stronger spring constants.

$$k_i = \begin{cases} k_{\max} - \Delta k \left(\frac{E_{\max} - E_i}{E_{\max} - E_{\text{ref}}} \right) & \text{if} \quad E_i > E_{\text{ref}} \\ k_{\max} - \Delta k & \text{if} \quad E_i < E_{\text{ref}} \end{cases} \tag{8}$$

where

$$E_i = \max(E_i, E_{i-1}) \tag{9}$$

E_{max} is the maximum value of E_i over the whole band and E_{ref} is a reference value for the energy, it is set to the larger energy of the two end points. $k_{\max}$ and Δk are constants that can be set by the user to ensure the desired spacings of the images along the band.

Once all the forces have been calculated the images are all instantaneously moved along the force vectors using a velocity Verlet algorithm.

$$\mathbf{R}(t+\delta t) = \mathbf{R}(t) + \boldsymbol{\nu}(t)\delta t + \frac{1}{2}\mathbf{a}(t)\delta t^2 \tag{10}$$

$$\boldsymbol{\nu}(t+\frac{\delta t}{2}) = \boldsymbol{\nu}(t) + \frac{1}{2}\mathbf{a}(t)\delta t \tag{11}$$

$$\boldsymbol{\nu}(t+\delta t) = \boldsymbol{\nu}(t+\frac{\delta t}{2}) + \frac{1}{2}\mathbf{a}(t+\delta t)\delta t \tag{12}$$

where $\mathbf{a}(t) = -\frac{1}{m}E(t)$ is the acceleration at time *t*. $\boldsymbol{\nu}(t)$ is the velocity at time *t* and m is the mass of a given atom. The timestep is a constant. If this is set too small the convergence to an MEP will be very slow, if it is set too large then the system may oscillate or become unstable. The velocity is initially zero and is allowed to increase after each timestep in the direction of the current force. To obtain a minimisation using this method, it is necessary to damp the kinetic energy, this is achieved by keeping only the velocity component which is parallel to the force at the current step. It has been suggested that the most efficient place to quench the velocities is after equation 11 [4].

$$\boldsymbol{\nu}(t+\frac{\delta t}{2}) = \boldsymbol{\nu}(t+\frac{\delta t}{2})\frac{\boldsymbol{\nu}(t+\frac{\delta t}{2})\cdot a(t)}{|a(t)|} \tag{13}$$

2.1 Modifications to the NEB algorithm

In this implementation of NEB a common problem is that a large number of images are required to get a good estimate of the transition state. A solution to this problem is to use the Climbing Image (CI) NEB algorithm. This method allows the image that is highest in energy to move along the MEP to the highest point [5].

This is achieved by modifying the calculation of the force acting on the image with the highest energy. The spring force acting on this image is ignored and instead the parallel component of the force is calculated as the inverse of the true parallel force.

$$\mathbf{F}_{i_{max}} = -\nabla E(\mathbf{R}_{i_{max}}) + 2\nabla E(\mathbf{R}_{i_{max}})\mid_{\|} \tag{14}$$

This modified force is normally implemented after several iterations of the standard NEB algorithm.

An adapted NEB algorithm has also been implemented [6]. This modification to the original algorithm always uses just three images. After these images have converged to a given tolerance the images adjacent to the highest energy image become the new end points. An additional two images are then inserted between the new end points and the highest energy image. This method of adapting the images is subsequently repeated once the new images have converged to a given tolerance. The advantage of this method is that it allows high resolution of the MEP around the area close to the transition state while using only three images.

3 Implementation into CRYSTAL

The NEB method has been implemented in the CRYSTAL code as a separate module that interacts with the main code via calls to functions in CRYSTAL to calculate the energy and first derivatives. This modular implementation allows the NEB code and CRYSTAL to be developed independently and minimises the complexity due to interdependancy.

The method has been implemented to allow it to be run in parallel across the images. For any given NEB calculation almost all of the CPU time is spent in the calculation of the energy and forces for each of the images. The calculation for each image is completely independent of any of the other images, hence this part of the calculation can be run in parallel very efficiently. This makes the NEB algorithm a perfect candidate for running on large parallel machines. Figure 2 shows the basic structure of the parallelisation of the algorithm.

3.1 Running the NEB Code in CRYSTAL

Use of the NEB algorithm in CRYSTAL requires the keyword NEB to be inserted into the SCF section of a standard CRYSTAL input deck. A further two sections are also required at the end of a standard input deck to provide CRYSTAL with the appropriate input information for a NEB calculation.

Although there are default values for all of the parameters used by the NEB algorithm it is often necessary to specify them explicitly. For example, by default CRYSTAL will use five images but the user may wish to change this. Other parameters that can be modified include when to switch from NEB to CI-NEB, the convergence criteria and the velocity Verlet time step. The energy of each of the end points must also be input if available else CRYSTAL will recalculate these values.

There are also many additional functionalities that can be turned on using commands from the input deck. The adaptive version of NEB, as described in section

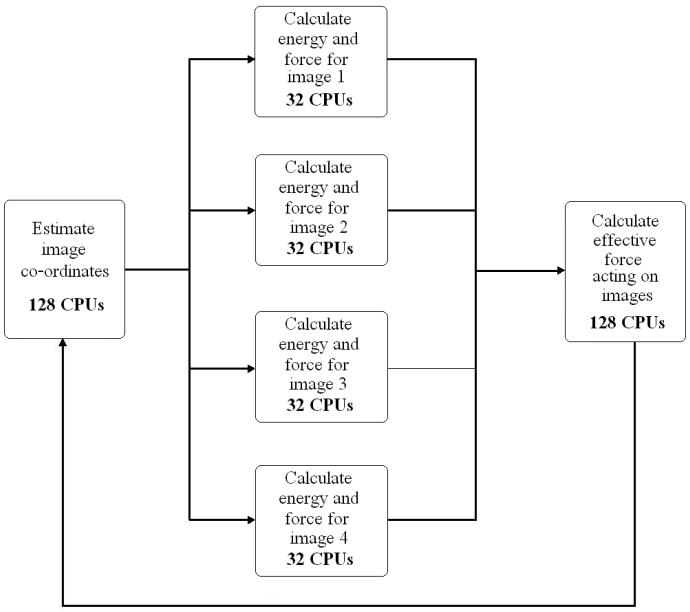

Fig. 2. Parallelisation of the NEB algorithm.

2.1 can be selected. The atom positions after each iteration can be written to a text file to form a Daresbury Laboratory Visualisation (DLV) sequence file [8]. This can be loaded in DLV to produce a movie showing the current reaction pathway. After each iteration over the images a restart file is written, this can then be used to restart a partially converged calculation. There are several other useful functionalities that can be used to aid a calculation. Please refer to the NEB section of the CRYSTAL user manual for more details [7].

4 Testing and Validation

The code has been rigorously tested on several small molecular systems. A sample of the test cases that have been studied are summarised in Table 1. The transition energies obtained using this code have been compared to those from the National Institute for Standards and Technology (NIST) website [9]. The energies are relative to the initial products. Hartree Fock theory and 3-21G basis sets have been used to obtain the results. Figure 3 shows the resultant MEP for the reaction $CH_3CH_2Cl \rightarrow C_2H_4$ + HCl. Several of the images along the MEP are shown diagrammatically.

It is important to be aware that NEB will not necessarily find the lowest transition state for a given reaction. For instance, in the reaction shown in figure 3 there are two possible reaction mechanisms, as shown in figure 4. The energy barrier along the MEP for mechanism A is 261 KJmol^{-1} compared with 638 KJ^{-1} for mechanism B. The MEP found for mechanism B is only a local MEP.

	Transition Energy (KJ/mol)	
Reaction	CRYSTAL-NEB	NIST
H_2+H $\rightarrow H + H_2$	69.6	71.1
H_2O+H $\rightarrow OH + H_2$	73.9	78.0
$CH_3CH_2Cl \rightarrow C_2H_4$ + HCl	260.8	264.6

Table 1
Comparison of transition state energies obtained by NEB in CRYSTAL to those available from the NIST website [9].

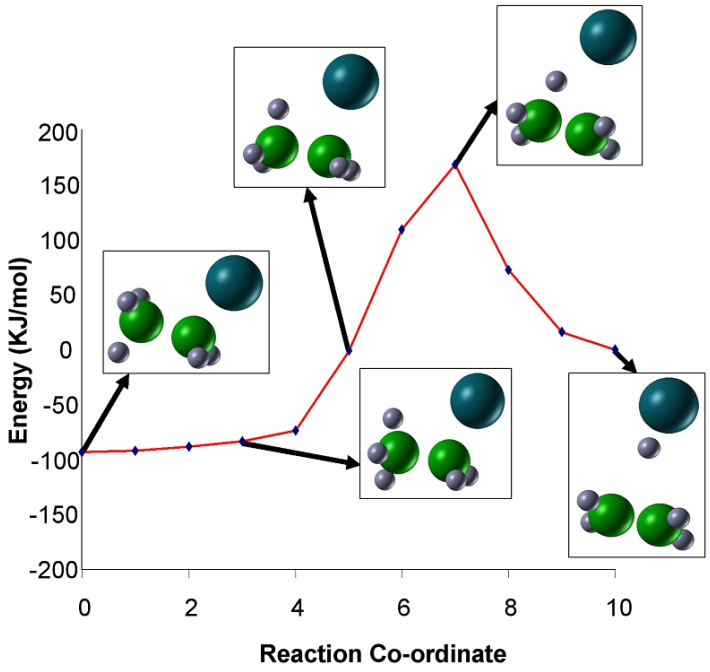

Fig. 3. The reaction pathway for $CH_3CH_2Cl \rightarrow C_2H_4$ + HCl

4.1 Testing the Parallelisation

The parallel version of CRYSTAL enables a given energy and derivatives calculation to be efficiently run in parallel. The NEB code allows for an additional parallelisation across the images in the band. For example, a calculation could involve 16 processors on each of eight images, hence a total of 128 processors. Alternatively it is possible to run such a calculation on 64 processors, still with 16 processors per image but calculating two images on each set of processors. It is also possible to set a calculation up on 80 processors, still using 16 processors per calculation. In this case three processor groups will calculate two images each and the other two will calculate one each. This obviously is not a good use of resources, as it leads to poor load balancing, also on some machines this may result in the idle CPUs timing out.

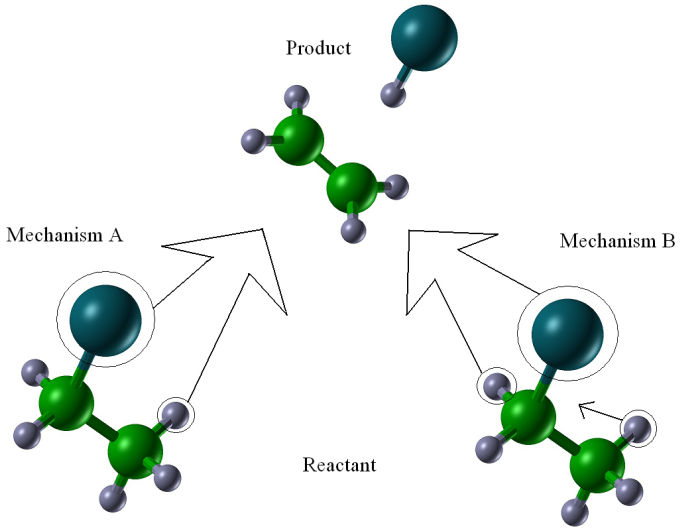

Fig. 4. Two alternate mechanisms for the reaction $CH_3CH_2Cl \rightarrow C_2H_4$ + HCl

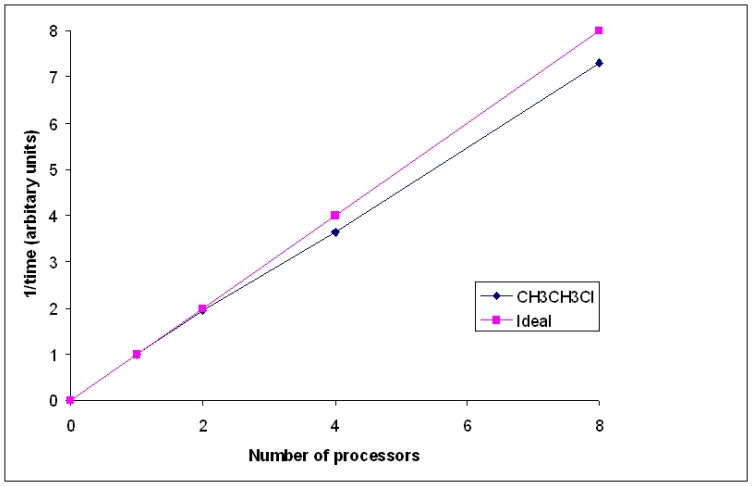

Fig. 5. Parallelisation across images

The parallel scalability of the $CH_3CH_2Cl \rightarrow C_2H_4$ + HCl test case is shown in Figure 5. Eight images where used in this calculation. It was run on 1,2,4 and 8 processors. It can be seen that the scaling of the method is very good. Problems with scaling will occur however when one image takes significantly more time to converge than other images.

4.2 Continuation of Testing

The NEB algorithm is currently being used on some larger, scientifically significant problems. The absorption of oxygen on MgO has been investigated. There are four different positions on the (100) surface of MgO for an oxygen to be absorbed. The

transition barriers for an oxygen moving between these different sites are being calculated using the NEB code.

Calculations are also being run to look at the the reaction of CO with a ZnO surface. CO is absorbed onto the ZnO surface, it can then react with an oxygen on the ZnO surface to form CO_2. There are two different types of oxygen the CO can combine with on the surface along with two possible mechanisms that can lead to these reaction events. The NEB code in CRYSTAL is currently being used to determine transition barriers for these reactions and to determine which is the energetically favourable reaction pathway.

5 Future Development

As the NEB algorithm is tested on a larger range of systems, methods to improve it may become apparent. There are alternate methods to the damped velocity

Verlet algorithm that can be used to move the images towards the MEP. For example, an Adapted Basis Newton Raphson method has been implemented in CHARMM [10] and a BFGS optimiser has also been implemented in the VASP code [4] for use with the NEB algorithm. Another area for improvement may be in the definition of the spring forces. Using the current constant spring force method, if the value for the spring force is too small then the images will begin to fall downhill, conversely if they are too large then this can lead to instabilities in the convergence. An alternate method would be to iteratively move each image along their tangents until the images are all equally spaced to within a given tolerance.

6 Code Availability

The current release of CRYSTAL is CRYTAL03 This version does not include the NEB algorithm, it will be available in the next release which is planned for release in 2006.

7 Conclusion

The CI-NEB algorithm has been successfully integrated into CRYSTAL. This allows CRYSTAL to be used to calculate transition states and MEPs for chemical reactions and diffusion events. The code can be used in parallel across the images in a NEB calculation, this allows efficient scaling to a large number of processors. The code has been rigorously tested on several small molecular test cases.

8 Acknowledgements

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