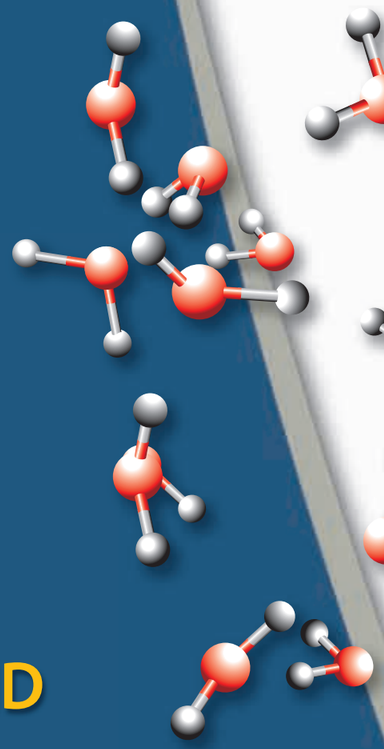
DL-FIND is a geometry optimisation library for use with atomistic simulation codes [1]. It offers a variety of optimisation algorithms for common tasks, such as finding minimum energy structures or identifying transition states on a reaction path.

Excited State and Parallel Geometry Optimisation with DL-FIND



The energies and gradients for a given geometry are provided by an external program through a well-defined interface. Currently interfaces exist to ChemShell, GAMESS-UK and CRYSTAL. In a previous article in Frontiers [2], the common features of DL-FIND were outlined (such as the coordinate systems available) and the nudged elastic band and dimer methods for optimising transition states were covered in detail. In this article we describe two further strengths of DL-FIND: conical intersection optimisation in excited state systems and parallel stochastic search methods for global and local minimisation.

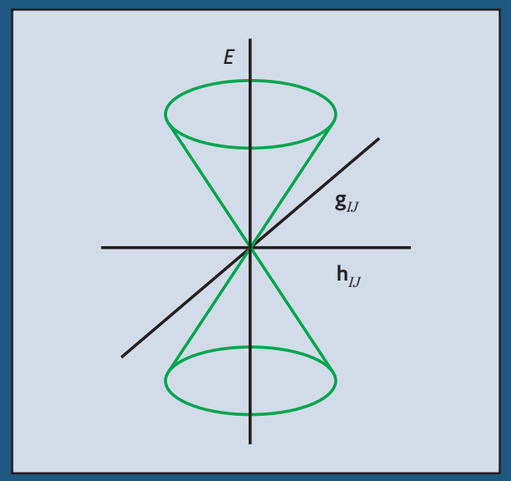


Figure 1: A point of conical intersection between two electronic states. The conical shape results from plotting the energy of the states against the gradient difference vector and the interstate coupling gradient vector.

Conical Intersection Optimisation

For many photochemical processes an understanding of the regions in which two electronic states have the same energy (the intersection space) is vital, as when reached a radiationless transition between the states can take place with 100% probability.

In a polyatomic system with N vibrational degrees of freedom, the intersection space is a seam with $(N-2)$ dimensions. The conical shape of any given point on this seam can be observed if the energy surfaces are plotted against the special coordinates $\mathbf{g}_{IJ}$ and $\mathbf{h}_{IJ}$, where $\mathbf{g}_{IJ}$ is the difference of the gradients of the two states I and J and $\mathbf{h}_{IJ}$ is the gradient of the coupling between the two states (Figure 1). Together these coordinates describe the 'branching space' in which the degeneracy is broken.

The intersection space can be characterised by finding the minimum energy crossing point (MECP) on the seam. The search for the MECP is an example of a constrained optimisation problem, where the energies of the states are minimised under the constraint that the energy difference between the two states is zero.

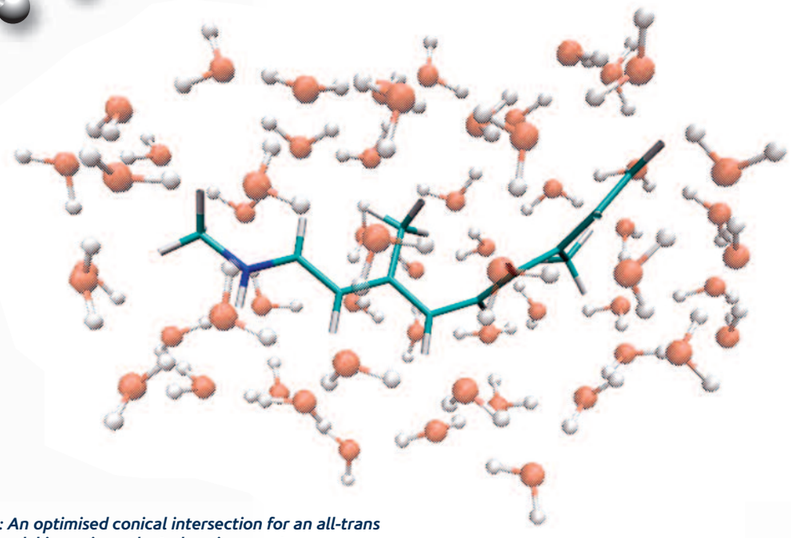


Figure 2: An optimised conical intersection for an all-trans retinal model in a microsolvated environment.

We have implemented three algorithms in DL-FIND for performing the MECP optimisation. The most efficient is a Lagrange-Newton algorithm, where the constraint is enforced by Lagrange multipliers. This requires the values of both $\mathbf{g}_{IJ}$ and $\mathbf{h}_{IJ}$ from the external program. The gradient projection algorithm works by minimising the energy difference in the branching space while minimising the upper state energy in the intersection space. Again $\mathbf{g}_{IJ}$ and $\mathbf{h}_{IJ}$ information is required. The third algorithm associates a penalty function with the energy difference between the states. It does not require knowledge of $\mathbf{h}_{IJ}$ and can therefore be used with a wider range of quantum mechanical methods. However, it is much less efficient than the other two algorithms.

DL-FIND can be combined with the ChemShell computational chemistry environment, which provides facilities for combined quantum mechanical /molecular mechanical (QM/MM) calculations. We demonstrated the validity of the implementation using an all-trans model of retinal in a microsolvated environment.

The photoisomerisation of retinal is the basis of vision in animals, and is thought to occur by an ultrafast process involving a conical intersection. In the validation study the retinal model was treated at the QM level of theory and the water molecules at the MM level. Figure 2 shows an optimised MECP between the ground state and first excited state of the model system due to a C_{11}-C_{12} torsion.

Parallel Optimisation

Many techniques for locating a minimum-energy configuration from a given starting point, including those implemented in DL-FIND, operate in an inherently serial fashion by propagating an ordered sequence of structures. For example, the steepest descent approach finds a local minimum by following the gradient vector "downhill" on the potential energy surface to geometries of progressively lower energy. For an individual geometry optimisation employing such methods, an advantage can often be gained by using a parallel computer and

Excited State and Parallel Geometry Optimisation with DL-FIND continued

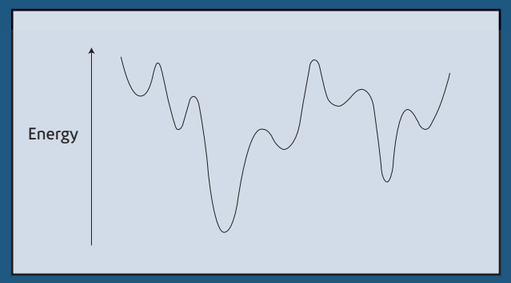


Figure 3: A one-dimensional potential energy function that exhibits multiple local minima.

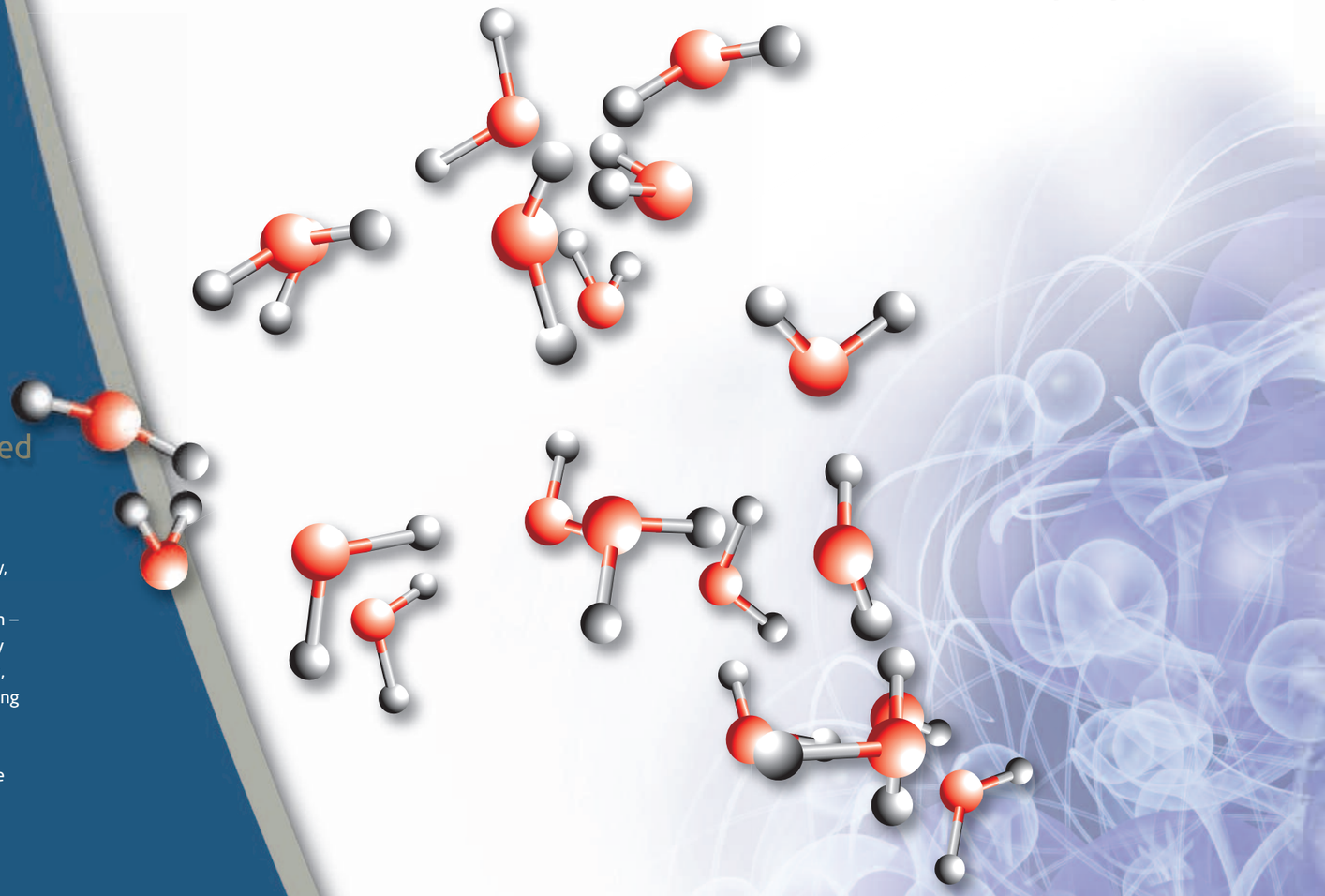
distributing components of each energy and gradient evaluation over the processors. However, such parallelism generally does not scale to more than around 1000 processors.

In order to exploit massively-parallel computers in situations where the time to solution is more important than the total CPU time used, a number of geometry optimisation algorithms that are amenable to an additional level of parallelism have recently been implemented in DL-FIND. The approaches chosen, which incorporate a stochastic element and are therefore non-deterministic, maintain a "population" of independent structures at each iteration. Consequently, a straightforward and efficient coarse-grained parallelism is possible: the energy and any required derivatives for each member of the current population may be evaluated simultaneously on separate subsets of the processors. The communications requirements are low, as the energy evaluations do not interact. A further advantage of these parallel stochastic techniques is that, by choosing the search method and the control parameters appropriately, they can be used for either local or global minimisation. The ability to identify candidates for the global minimum – the configuration of lowest energy on a potential energy surface - will prove highly valuable in many applications, including structure prediction in biology and the modelling of functional materials.

A genetic algorithm and various techniques based on the "creeping random" method have been implemented in DL-FIND. Genetic algorithms are biologically-inspired global optimization methods in which populations of structures ("individuals") evolve by genetic operations and natural selection according to a fitness function, which in this case is the potential energy. The genetic operations include breeding, mutation and catastrophe. In the creeping random method, a new population at each "generation", or iteration, is derived from the known individual of lowest energy via random coordinate perturbations within an allowed range. With each generation the allowed range decreases, thus enabling the algorithm to explore a wider region of configuration space in its initial phase, but to subsequently zoom in on low-energy structures. The coordinate perturbations may be uniformly distributed, or can depend on the gradient vector for the lowest-energy geometry. The latter class of search strategy, in combination with an appropriate choice of control parameters for the algorithm, provides a method for local rather than global minimisation.

Availability

The DL-FIND library is distributed under the open-source GNU LGPL licence. It can be downloaded at http://ccpforge.cse.rl.ac.uk/projects/dl-find.



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References:

[1] J Kästner, JM Carr, TW Keal, W Thiel, A Wander, P Sherwood, J Phys Chem A, doi: 10.1021/jp9028968.

[2] J Kästner, P Sherwood, T Keal, Finding Minima, Transition States, and Conical Intersections: the Development of a Geometry Optimiser for Atomistic Simulation, Frontiers 2007.