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Geometry Optimization

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Overview of lecture

- Background Theory
  - Hellman-Feynman theorem
  - BFGS and other algorithms
- CASTEP details
  - Useful keywords for geometry optimization
  - Variable cell – additional considerations

Background Theory

QM Forces

- Classically we have the force **F** at position **R** is determined from the potential energy as

$$\mathbf{F} = -\frac{\partial U(\mathbf{R})}{\partial \mathbf{R}}$$

- Quantum mechanically we therefore have

$$\mathbf{F} = -\frac{\partial \langle E \rangle}{\partial \mathbf{R}} = -\frac{\partial}{\partial \mathbf{R}} \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

- For a position-independent basis set

$$\mathbf{F} = -\frac{\partial \langle E \rangle}{\partial \mathbf{R}} = -\langle \Psi | \frac{\partial H}{\partial \mathbf{R}} | \Psi \rangle$$

Density Functional Theory (I)

- In DFT we have the Kohn-Sham Hamiltonian:

$$\hat{H}(\mathbf{r},\mathbf{R}) = -\frac{1}{2}\nabla^2_{\mathbf{r}} + V_{e-e}(\mathbf{r}) + V_{ion-e}(\mathbf{r},\mathbf{R}) + V_{XC}(\mathbf{r}) + V_{ion-ion}(\mathbf{R})$$

- Therefore we only get contributions to the forces from the electron-ion (pseudo)potential and the ion-ion Coulomb interaction (the Ewald sum).
- As we do not have a complete basis, the wavefunction will not be exact even within DFT.
- Need to test for convergence carefully wrt cut-off energy and k-points etc.

Density Functional Theory (II)

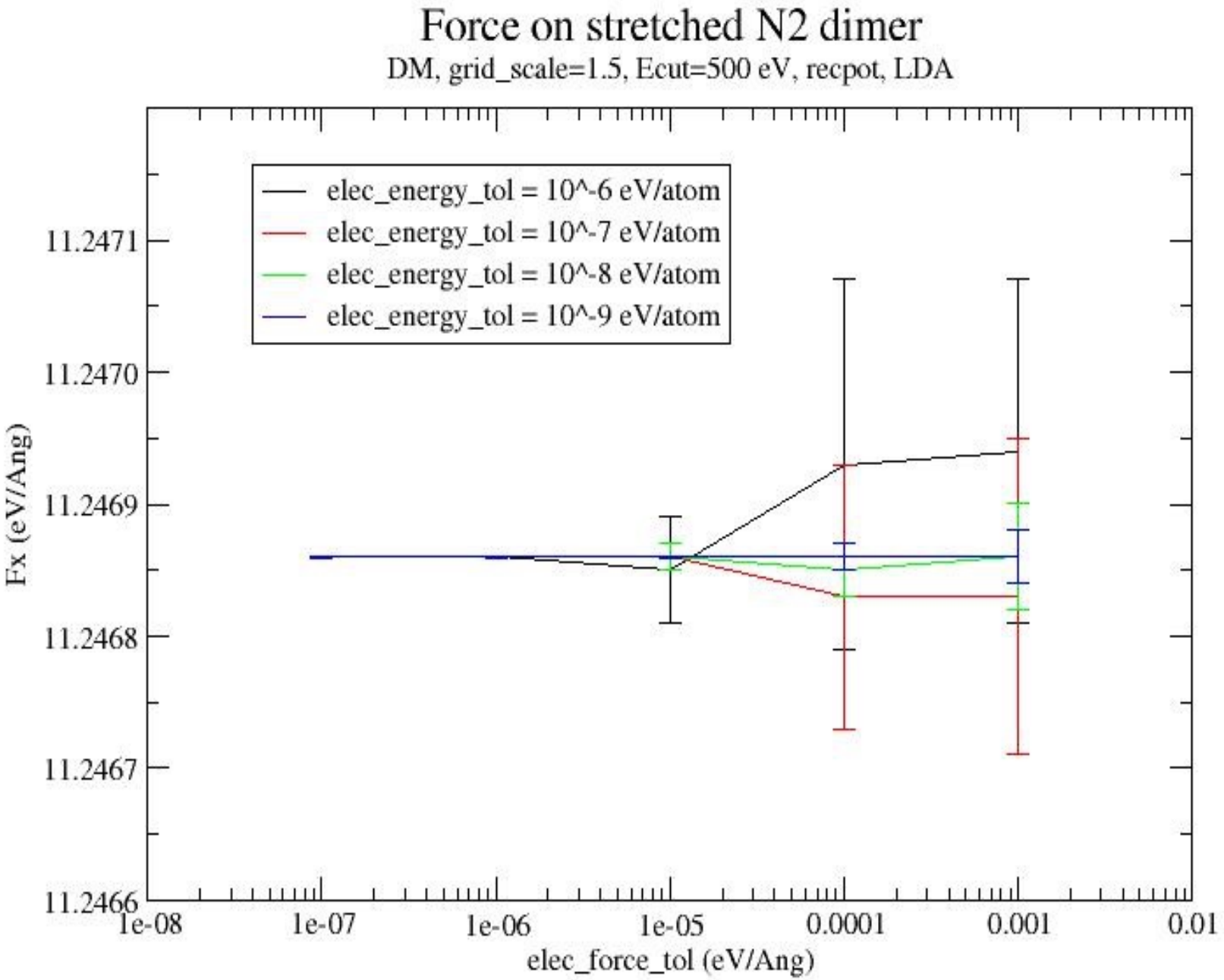
- With a variational minimization of the total energy, the energy and wavefunction will be correct to second order errors.
  - Forces are given by energy differences and hence get some error cancellation
- With a non-variational minimization technique, such as *density mixing*, then no upper-bound guaranteed on true E_0
  - So need good convergence if using non-variational forces and stresses

Quality of Forces/Stresses

- Can only find a good structure if have reliable forces/stresses
- Stresses converge more slowly than energies as increase number of plane waves
  - CONVERGENCE!
- Should also check degree of SCF convergence

  elec_energy_tol (fine quality ≤ 10^{-6} eV/atom)
  can also set **elec_force_tol** – useful with DM

  Stresses converge slower than forces!

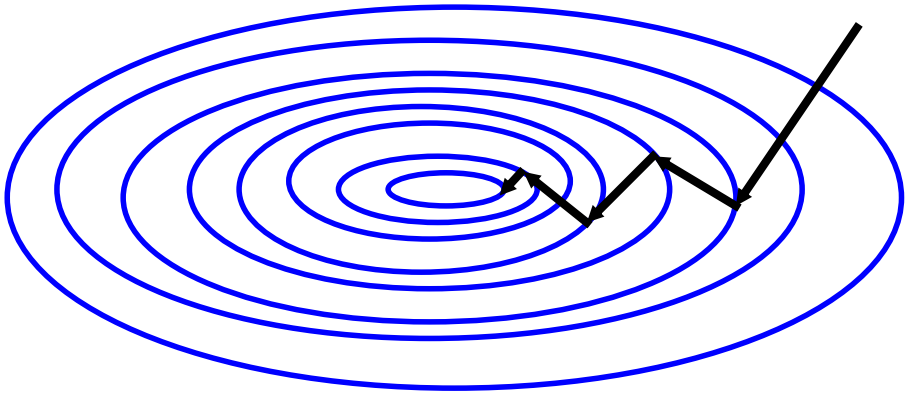

Force on stretched N2 dimer
DM, grid_scale=1.5, Ecut=500 eV, recpot, LDA
elec_energy_tol = 10^-6 eV/atom
elec_energy_tol = 10^-7 eV/atom
elec_energy_tol = 10^-8 eV/atom
elec_energy_tol = 10^-9 eV/atom
11.2471
11.2470
11.2469
11.2468
11.2467
11.2466
Fx (eV/Ang)
1e-08
1e-07
1e-06
1e-05
0.0001
0.001
0.01
elec_force_tol (eV/Ang)

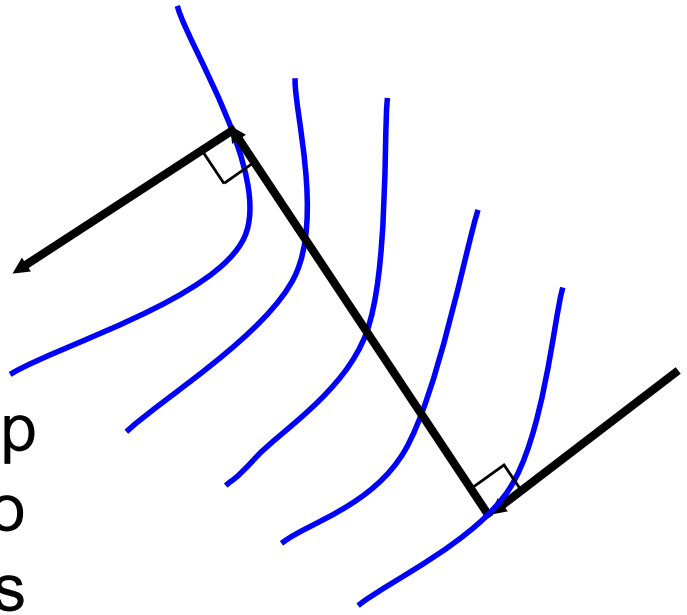
How Does Geom Opt Work?

- Electrons adjust instantly to position of ions
  - Multi-dimensional potential energy surface and want to find global minimum
- Treat as an optimisation problem
  - Simplest approach is steepest descents
  - More physical approach is damped MD
  - More sophisticated approaches are conjugate gradients or BFGS
  - All of these can get stuck in local minima
  - Hence recent research in how best to find global minimum

Steepest Descents

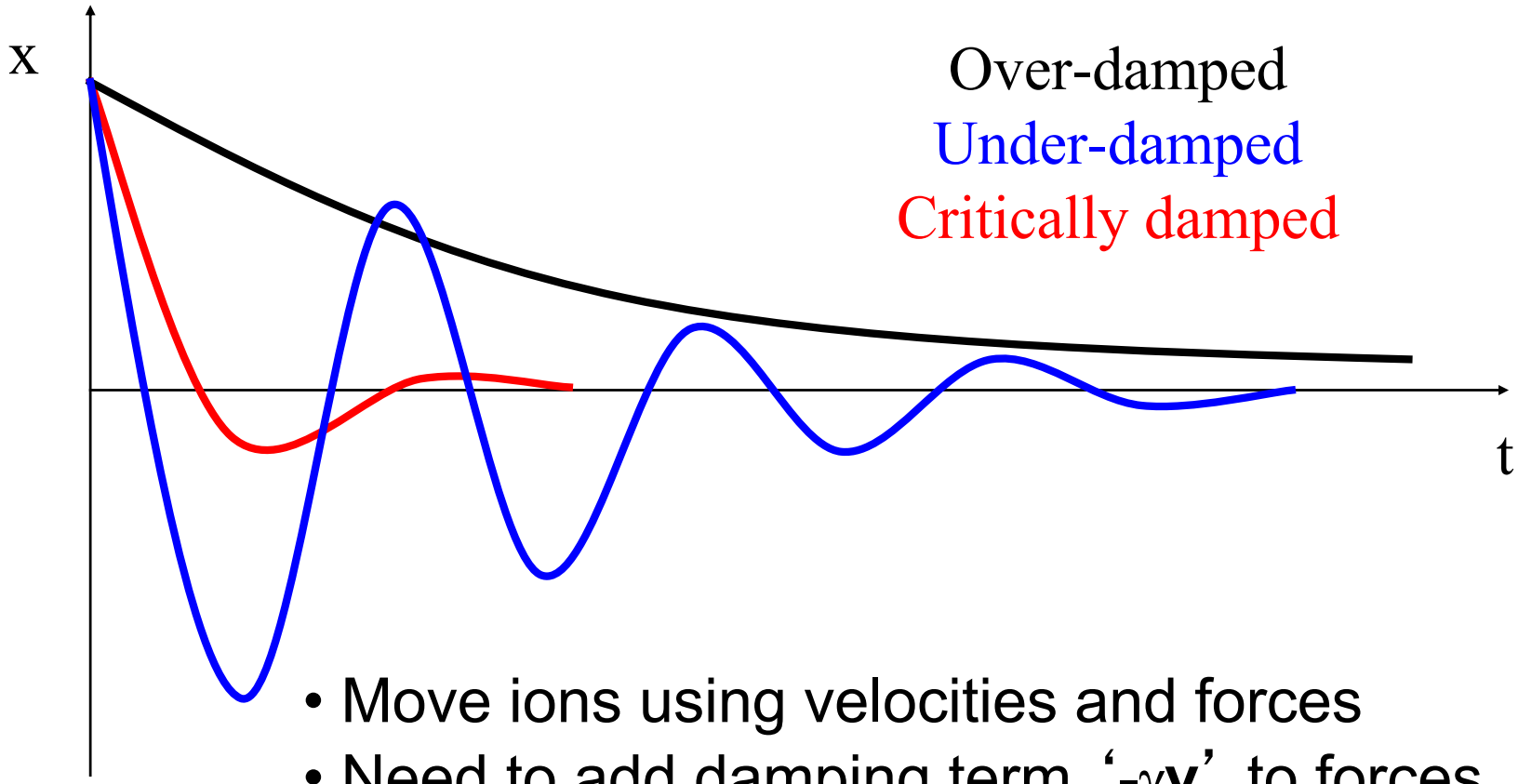
Traversing a long, narrow valley





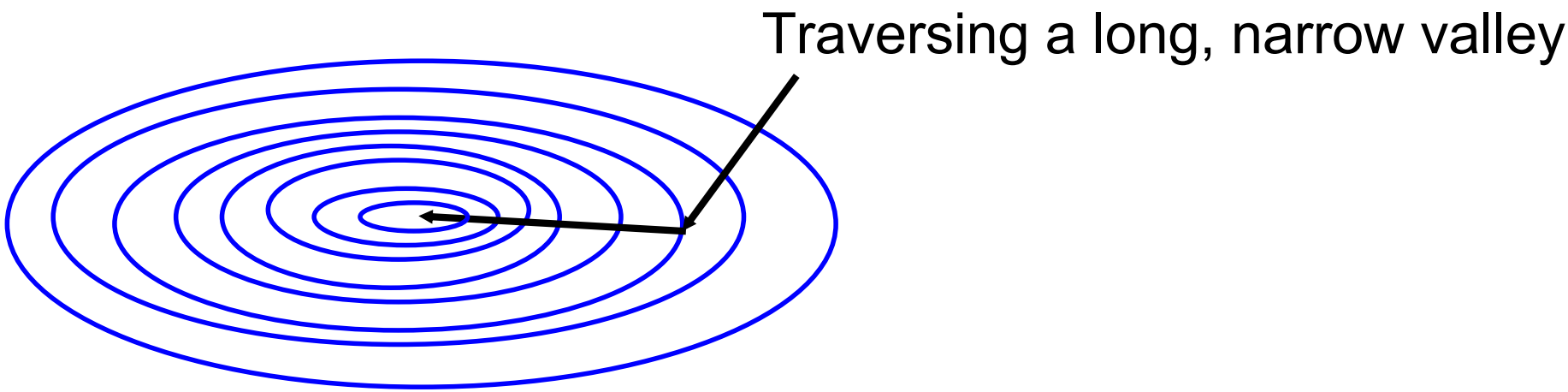
Enlargement of a single step showing the line minimisation in action – the step continues until the local energy starts to rise again whereupon a new direction is selected which is orthogonal to the previous one

Damped MD



- Move ions using velocities and forces
- Need to add damping term '$-\gamma\mathbf{v}$' to forces
- Algorithm to set 'optimal damping' factor
- Can also adjust δt for max. convergence
- More efficient than Steepest Descents

Conjugate Gradients



- The initial search direction is given by steepest descents.
- Subsequent search directions are constructed to be orthogonal to the previous *and* all prior search directions.
- No explicit Hessian required or generated.

BFGS (I)

- Basic idea:
  - Energy surface around a minima is quadratic in small displacements and so is totally determined by the Hessian matrix **A** (the matrix of second derivatives of the energy):

$$\mathbf{A} = \begin{pmatrix} \partial^2 E / \partial x_1 \partial x_1 & \cdots & \partial^2 E / \partial x_1 \partial x_N \\ \vdots & \ddots & \\ \partial^2 E / \partial x_N \partial x_1 & & \partial^2 E / \partial x_N \partial x_N \end{pmatrix}$$

$$\delta E = \frac{1}{2}\left(\mathbf{X} - \mathbf{X}_{\min}\right)^T \bullet \mathbf{A} \bullet \left(\mathbf{X} - \mathbf{X}_{\min}\right)$$

  - so if we knew **A** then could move from any nearby point to the minimum in 1 step!

BFGS (II)

- The Problem
  - We do not know **A** *a priori*
  - Therefore we build up a progressively improving approximation to **A** (or the inverse Hessian $\mathbf{H}=\mathbf{A}^{-1}$) as we move the ions according to the BFGS (Broyden-Fletcher-Goldfarb-Shanno) algorithm.
  - Also known as a *quasi-Newton* method.
- Positions updated according to: $\mathbf{X}_{i+1} = \mathbf{X}_i + \lambda \Delta \mathbf{X}_i$

$$\Delta \mathbf{X}_i = \mathbf{H}_i \mathbf{F}_i$$

CASTEP details

How to do it …

- Just put

```
task = Geometry Optimisation
```

in your `.param` file

- Is that all?
- What is going on behind the scenes?
- What might go wrong?
- What can you control?

Choice of Scheme

- **`geom_method = LBFGS`** (default)
  - variable ions and/or cell
  - uses fractional ionic coordinates and strains as basic variables
  - improved estimates based analysis of approx. **H** built up over convergence path printed at end
  - a “low memory” version of **`geom_method = BFGS`** as it only stores a limited number of updates and not full Hessian

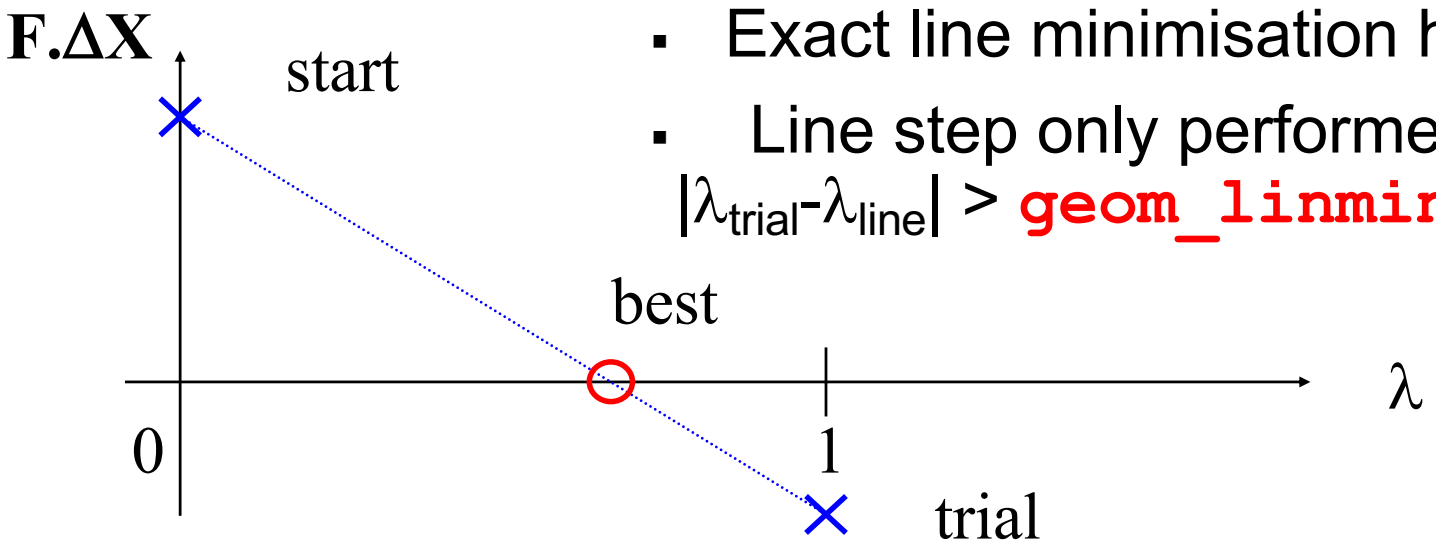
Choice of Scheme

- **`geom_method = TPSD`**
  - Very low memory requirements
  - No line search and no history
    - Ought to be a lot worse than (L)BFGS but we have a smart preconditioner & so not so bad
    - Much better than (L)BFGS with constraints
    - Much better if start a long way from the harmonic region
    - Can use **`geom_tpsd_iterchange`** to switch to BFGS after given number of TPSD steps
  - Can use **`geom_tpsd_init_stepsize`** to control size of initial step

(L)BFGS in CASTEP

$$\mathbf{X}_{i+1} = \mathbf{X}_i + \lambda \Delta \mathbf{X}_i$$

$$\Delta \mathbf{X}_i = \mathbf{H}_i \mathbf{F}_i$$



- Trial step performed (default) if **geom_use_linmin=true**
- A quadratic system has optimal λ=1
- Exact line minimisation has **F.ΔX**=0
- Line step only performed if predicted $|\lambda_{trial}-\lambda_{line}| >$ **geom_linmin_tol**

No restriction on the value of λ as long as does not cause too large an ionic displacement or change in lattice parameters – big advantage of doing a 'line step'

Geometry Convergence

- Will continue for **geom_max_iter** steps (default=30) unless converged:

  geom_energy_tol (default=$2*10^5$ eV/atom) for **geom_convergence_win** steps

  Changing ions:

  geom_force_tol (default =0.05 eV/Å)

  geom_disp_tol (default=0.001 Å)

  Changing cell:

  geom_stress_tol (default=0.1 GPa)

Variable cell calculations

Variable cell calculations

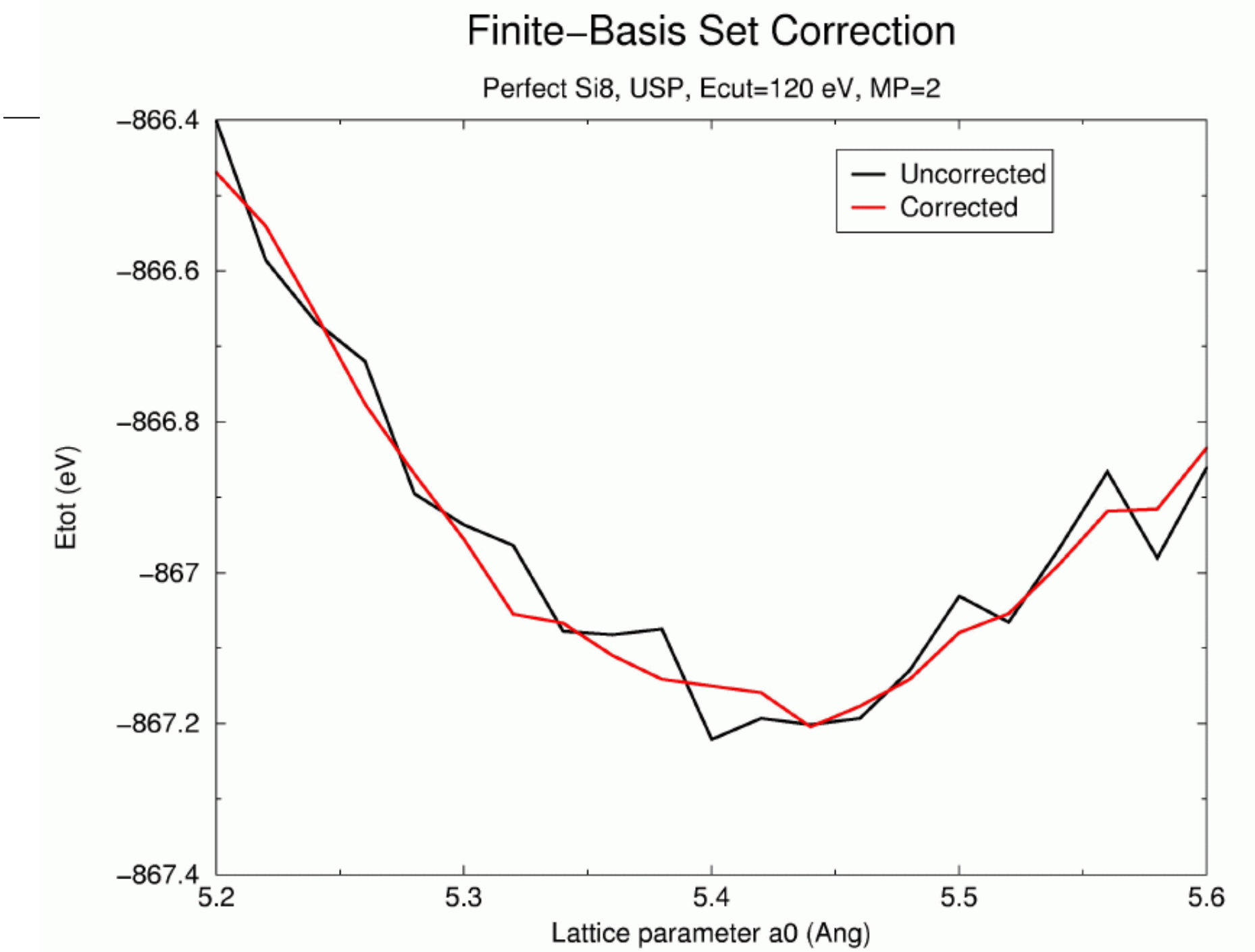
- If can calculate internal stress then can use this to adjust the cell parameters
- Convention: $\mathbf{P}_{ext} + \sigma = 0$ at equilibrium
  - i.e. P>0 = compression, $P_{int}=1/3\ Tr(\sigma)$
  - Look for a state of minimum enthalpy
    - $H=E+P_{ext}V$
  - With BFGS we use an augmented Hessian
    - Work in space of “fractional positions and strains” with “fractional forces and stresses”
    - Then possible to mix cell & ion terms

Changing Cell and Plane Waves

- Plane wave basis is independent of ionic positions but NOT of the unit cell size/shape
- **`fix_NPW=true`**
  - the number of plane waves is fixed
  - hence the variational principle applies and we can search for the minimum of enthalpy as cell changes
  - but the effective cut-off energy varies!
- **`fix_NPW=false`**
  - number of plane waves varies to keep Ecut constant
  - breaks variational principle
  - search for zero force & stress not minimum enthalpy
  - but physically more reasonable

Finite Basis Set Correction

- Change unit cell at constant **cut_off_energy** :
  - changes number of plane-waves
  - change in total energy due to variational principle
  - hence difficult to compare results at different cell sizes.
- Use the Finite Basis Set Correction
  - **finite_basis_corr = automatic/manual/none**
  - calculates the total energy **finite_basis_npoints** times with **finite_basis_spacing** change to **cut_off_energy** at fixed cell
  - hence calculates and prints **basis_de_dloge**
  - CASTEP can then use this to correct the total energy and stress at nearby cell sizes


Finite–Basis Set Correction
Perfect Si8, USP, Ecut=120 eV, MP=2
Uncorrected
Corrected
–866.4
–866.6
–866.8
–867
–867.2
–867.4
Etot (eV)
5.2
5.3
5.4
5.5
5.6
Lattice parameter a0 (Ang)

.cell file keywords

fix_all_ions (default = false)

fix_all_cell (default = false)

fix_com (default = NOT `fix_all_ions`)

symmetry_generate

snap_to_symmetry

```
%block external_pressure
   [units]
   Pxx  Pxy  Pxz
        Pyy  Pyz
             Pzz
%endblock external_pressure
```

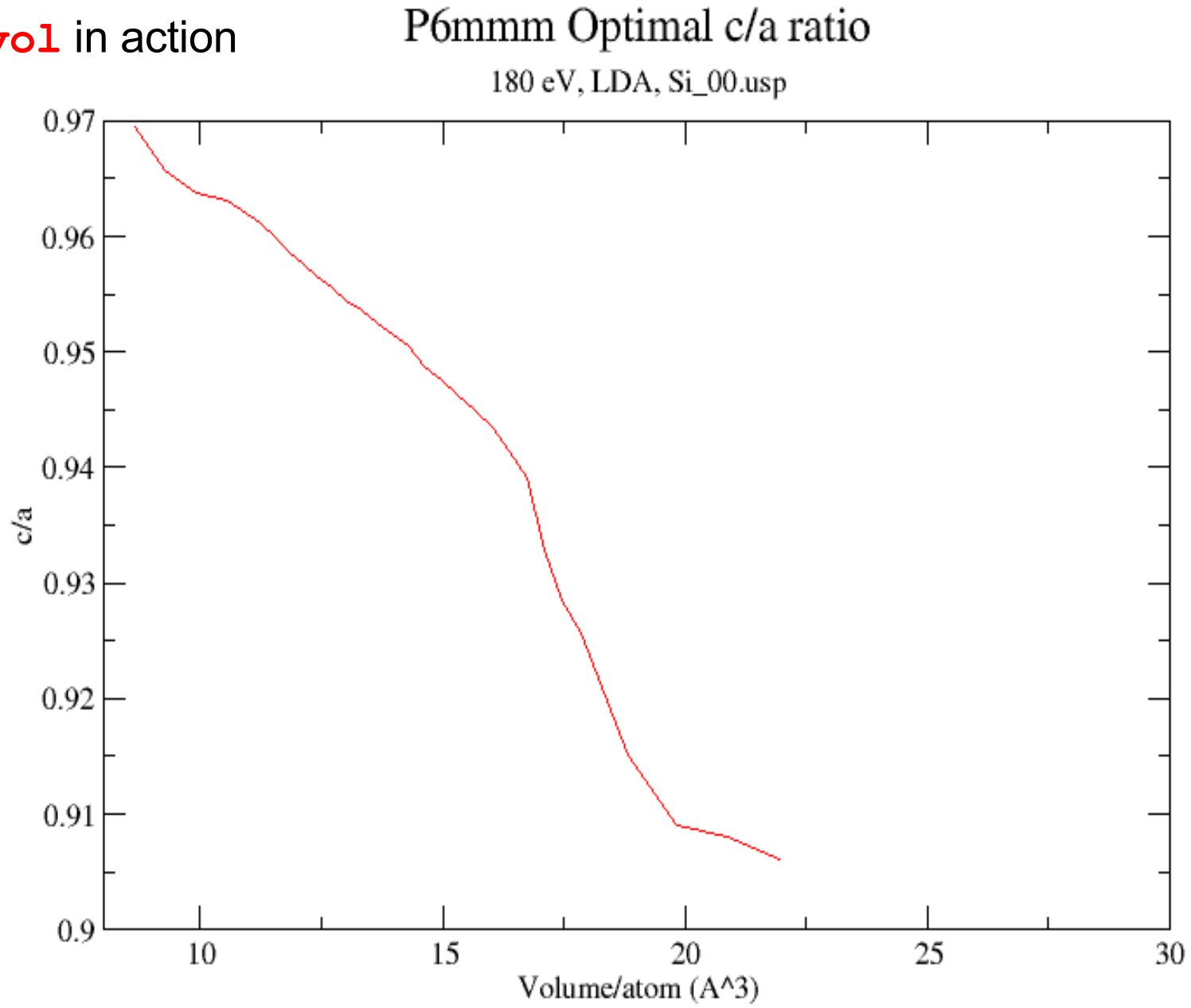
Hence hydrostatic P is $P_{xx}=P_{yy}=P_{zz}=P$ and $P_{xy}=P_{xz}=P_{yz}=0$

Cell Constraints

```
%block cell_constraints
|a| |b| |c|
 α   β   γ
%endblock cell_constraints
```

- Any length (angle) can be held constant (=0), or tied to one or both of the others (=same)
  - e.g. cell optimisation of 2D structures or keeping subset of symmetry etc
  - also `fix_vol` (= false by default)

fix_vol in action



The .geom file

- Records the final configuration after each step:

```
      10
    -7.93316351E+000 -7.85316331E+000                  <-- E
     0.00000000E+000  5.13126785E+000  5.13126785E+000 <-- h
     5.13126785E+000  0.00000000E+000  5.13126785E+000 <-- h
     5.13126785E+000  5.13126785E+000  0.00000000E+000 <-- h
    -3.56997760E-003  0.00000000E+000 -3.33783917E-013 <-- S
     0.00000000E+000 -3.56997760E-003  8.32597229E-013 <-- S
    -3.33783917E-013  8.32597229E-013  5.93008591E-004 <-- S
Si 1  0.00000000E+000  0.00000000E+000  0.00000000E+000 <-- R
Si 2  7.56877069E+000  2.52292356E+000  7.56877069E+000 <-- R
Si 1 -5.22300739E-003  6.43530285E-003 -1.71774942E-003 <-- F
Si 2  5.22300739E-003 -6.43530285E-003  1.71774942E-003 <-- F
```

  - Uses Cartesian coordinates and atomic units throughout
  - Designed for other analysis programs, visualisation tools, etc.

Visualization

- Final geom “trajectory” can be visualized using jmol – just drag & drop `.geom` file
- Or can add **`write_cell_structure=true`** or **`write_cif_structure=true`** to output final structure in cell/cif format
- Or can use utilities such as geom2xyz to convert `.geom` file to `.xyz` format for visualization by many packages

Ionic Constraints

- Can specify any arbitrary number of *linear constraints* on the atomic coordinates, up to the number of degrees of freedom.
  - E.g. fixing an atom, constraining an atom to move in a line or plane, fixing the relative positions of pairs of atoms, fixing the centre of mass of the system, etc.
- Non-linear constraints
  - Much more difficult to apply and specify in general, e.g. fixing a bond length
  - Only supported by Delocalised Internals

General Specification

```
%block ionic_constraints
con spec atom Ax Ay Az
. . .
%endblock ionic_constraints
```

where each constraint fixes 1 degree of freedom

- `con` is the number of the constraint (can have multiple atoms/constraint) and multiple constraints/calculation
- `spec` is the species label, `atom` is the number of the atom for this species
- `Ax,Ay,Az` specify the constraint coefficient such that $\sum \mathbf{A}.\mathbf{r} = const$

Example Linear Constraints

General format:

```
%block ionic_constraints
1 Si 1   0 0 1
%endblock ionic_constraints
```

fixes the z-coordinate of the 1st Si atom

Shortcut for fixing 1 or more atoms:

```
%block ionic_constraints
fix: Si 1
%endblock ionic_constraints
```

Can also do things like `fix: all unfix: H`
to fix all atoms except H etc.

Summary

Summary

- Need accurate forces and stresses
- Pre-requisite for many property calculations
  - e.g. phonons, NMR, etc.
- Can do optimisation of ions and/or cell
  - (L)BFGS or TPSD with Cartesian coords
- Can also for fixed cell use
  - BFGS with Cartesian or delocalised internal coordinates, or
  - damped MD or FIRE with Cartesians

Useful References

- SJ Clark, MD Segall, CJ Pickard, PJ Hasnip, MIJ Probert, K Refson and MC Payne, *"First principles methods using CASTEP",* Zeitschrift für Kristallographie **220**, 567 (2005)
- BG Pfrommer, M Cote, SG Louie and ML Cohen "*Relaxation of crystals with the quasi-Newton method",* J.Comput. Phys. **131**, 233 (1997)
- MIJ Probert, "*Improved algorithm for geometry optimisation using damped molecular dynamics*", J. Comput. Phys. **191**, 130 (2003)
- E Bitzek, P Koskinen, F Gahler, M Moseler and P Gumbsch, "*Structural relaxation made simple*" Phys. Rev. Lett. **97** 17021 (2006)
- J Andzelm, RD King-Smith, and G Fitzgerald, "*Geometry optimization of solids using delocalized internal coordinates*", Chem. Phys. Lett. **335** 321 (2001)