Practical calculations using first-principles QM
Convergence, convergence, convergence

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September 13, 2006

Results of First-Principles Simulations

First-principles methods may be used for subtle, elegant and accurate computer experiments and insight into the structure and behaviour of matter.

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First principles results may be worthless nonsense

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Further reading: *Designing meaningful density functional theory calculation in materials science - a primer* Anne E Mattson *et al. Model. Sim. Mater. Sci Eng.* **13** R1-R31 (2005).

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- Fortunately well converged *properties* may frequently be computed using an incomplete basis.

Error Cancellation

- Consider energetics of simple chemical reaction
  $\mathrm{Mg\,O_{(s)}} + \mathrm{H_2O_{(g)}} \rightarrow \mathrm{Mg(OH)_{2,(s)}}$
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  MgO -0.021eV $\mathrm{H_2O}$ -0.566eV $\mathrm{Mg(OH)_2}$ -0.562eV
  Convergence error in ΔE -0.030eV
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- **Always use same cutoff for all reactants and products**.

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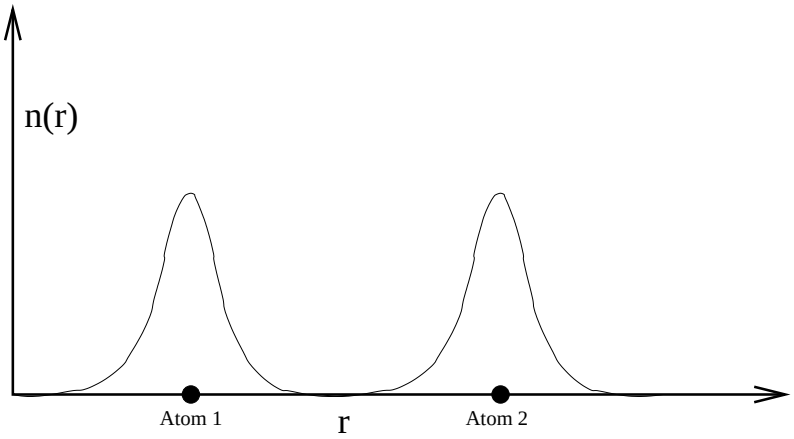

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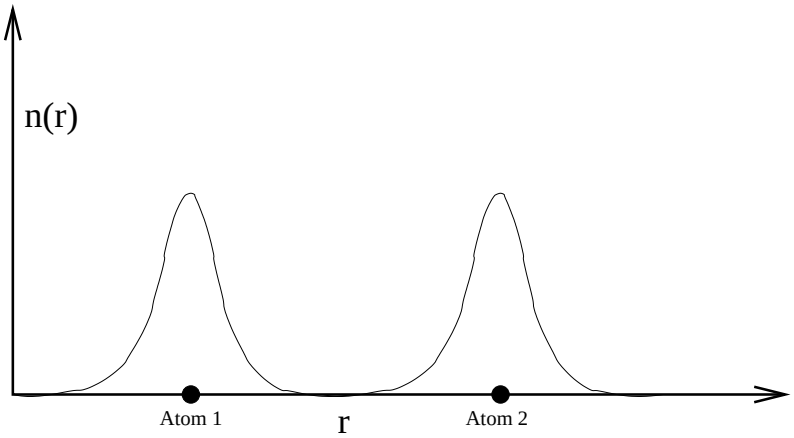
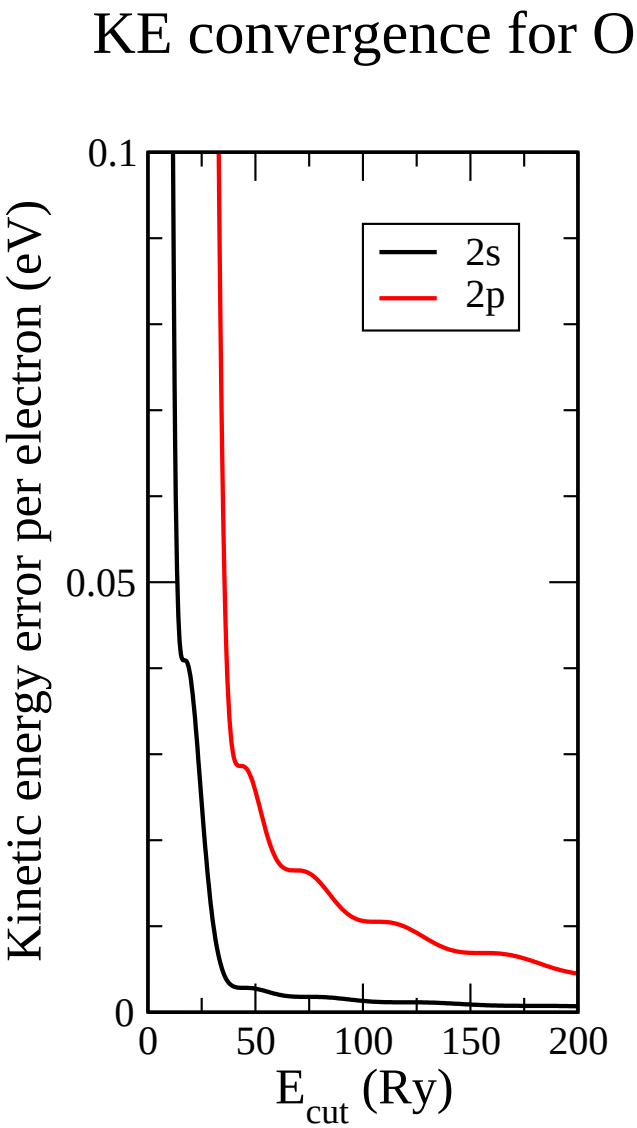


- E_{cut} (and G_{max}) depend only on *types* of atoms, not numbers.
- Simulation cutoff is maximum over pseudopotentials used.
- Required cutoff is *system-independent* but not *property-independent*.

Pseudopotentials and cutoff behaviour

- When performing cutoff test you can not always assume completely smooth approach to convergence.
- Can get plateaus or other non-asymptotic behaviour
- Sometimes cause is over-optimization of the pseudopotential too low a desired cutoff.
- In cases with this behaviour can choose criterion for convergence energy to be plateau values.
- Absolute energy convergence is rarely desirable. *Force and stress convergence is much more useful criterion.*
- (Example is *not* a pseudpotential from the CASTEP database)



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- GGA XC functionals give density with higher fourier components, and need $1.75G_{\mathrm{MAX}}$ - $2G_{\mathrm{MAX}}$
- Finer grid may be needed to represent USP augmentation charges or core-charge densities.
- CASTEP incorporates a second, finer grid for charge density to accommodate core/augmentation charges while using G_{MAX} for orbitals.

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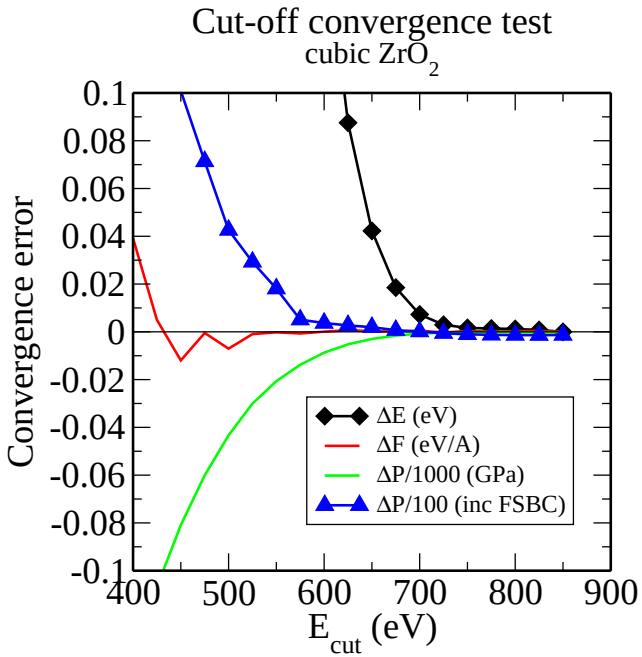

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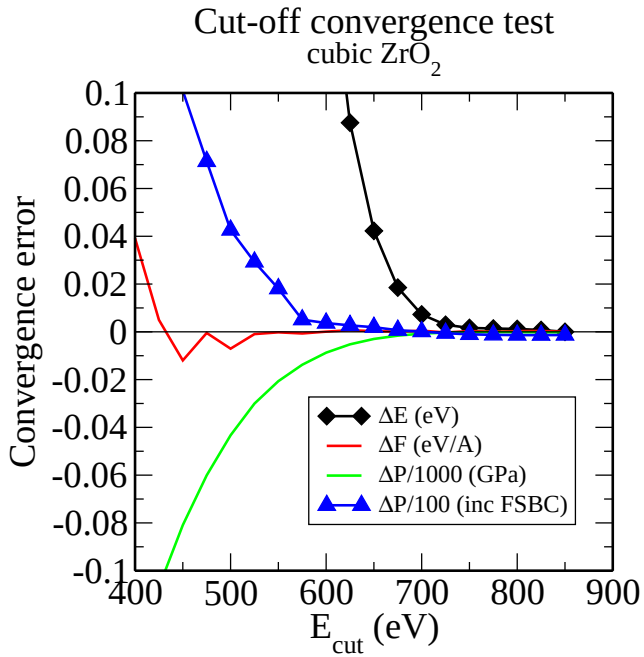

- different physical quantities converge at different rates.
- Always test convergence specifically of **quantities of importance to your planned calculation**

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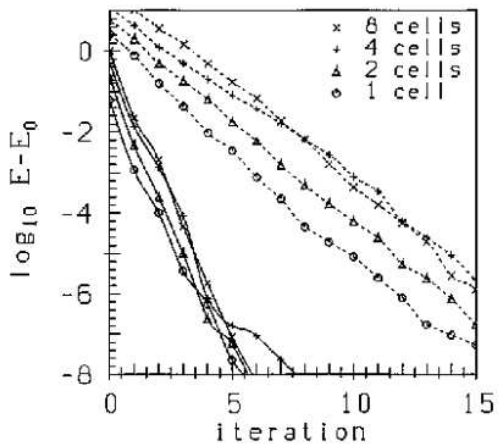

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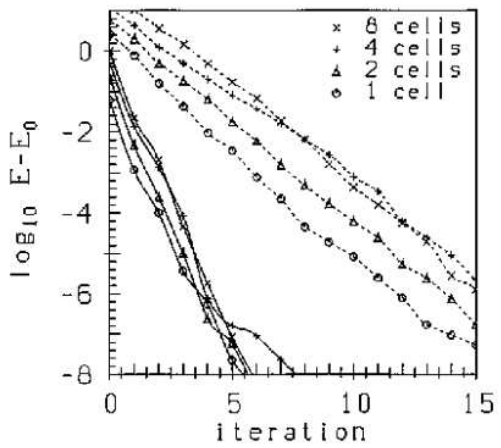

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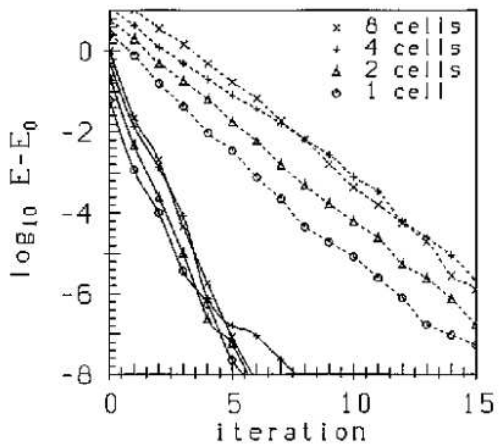

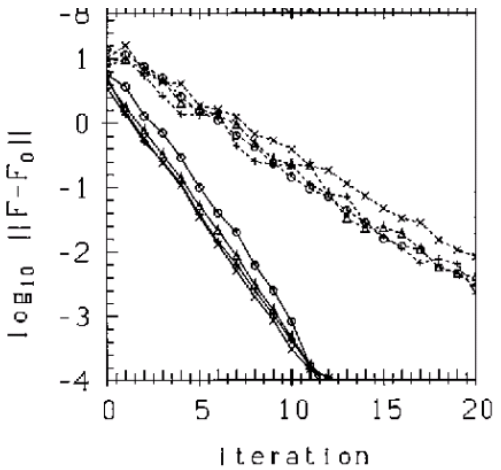

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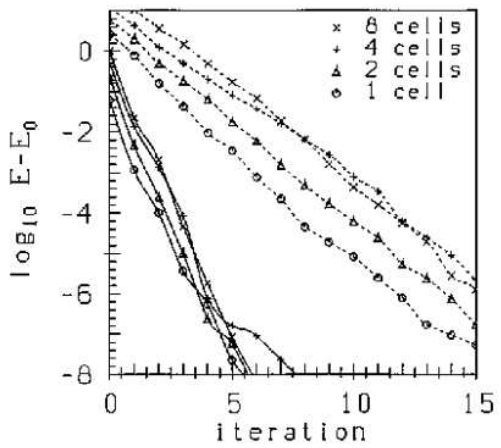

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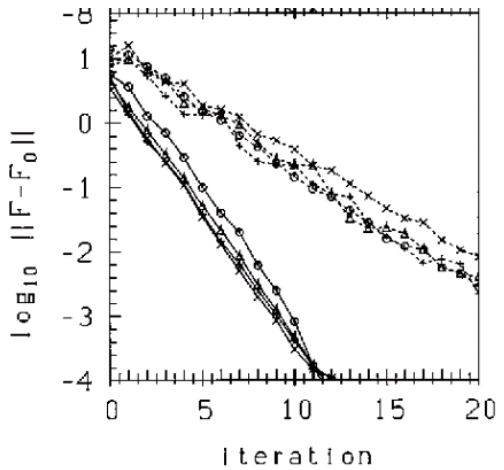

- Inaccurate forces are common cause of geometry optimization failure.

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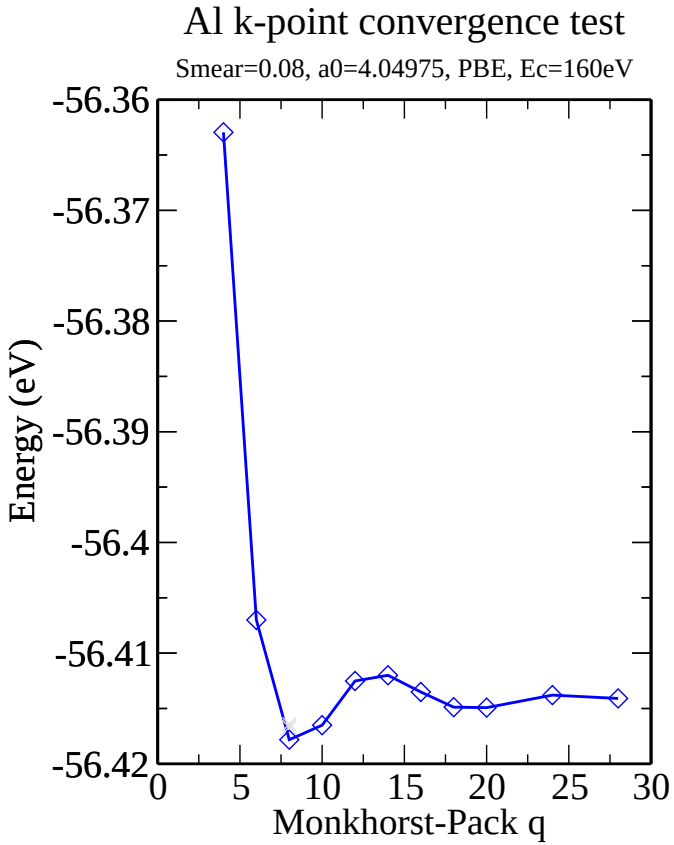

Structural Calculations

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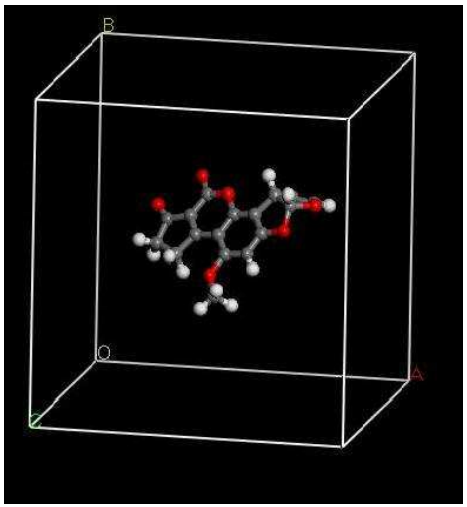

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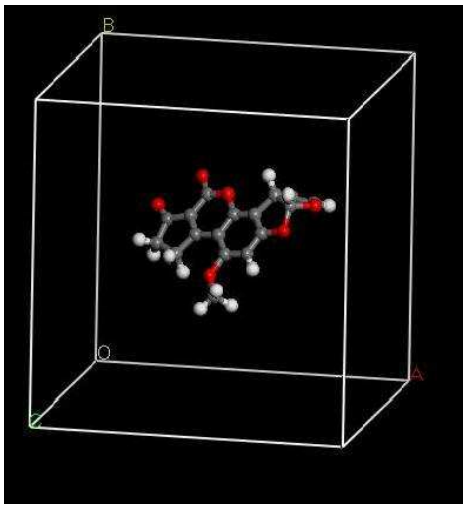

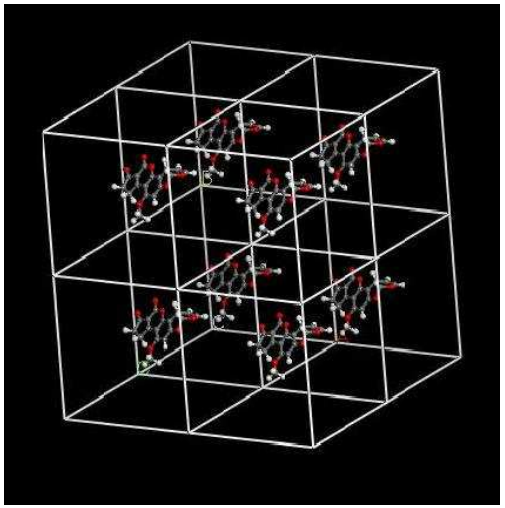

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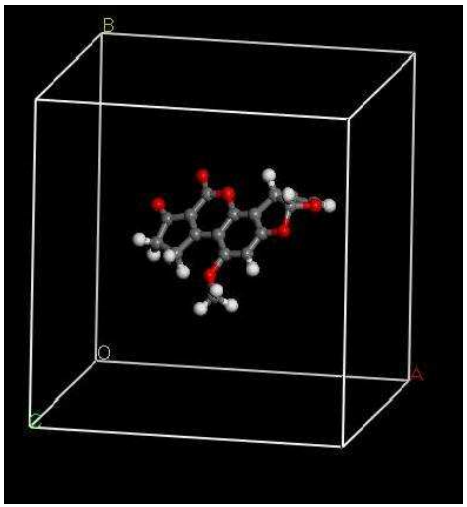
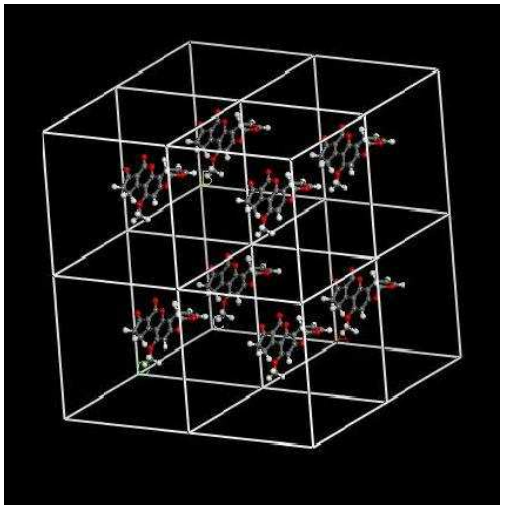
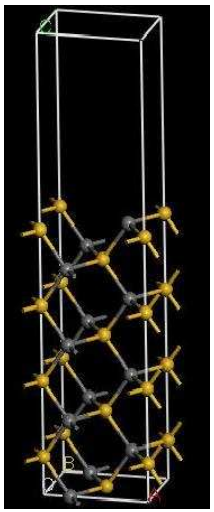
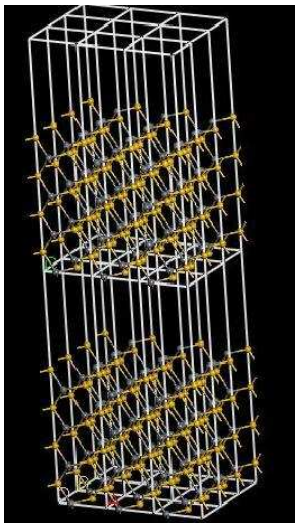

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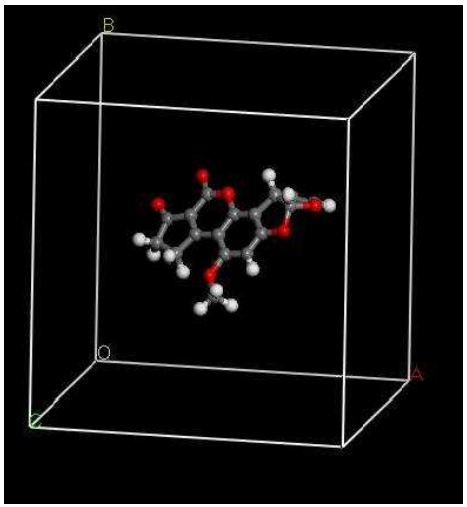
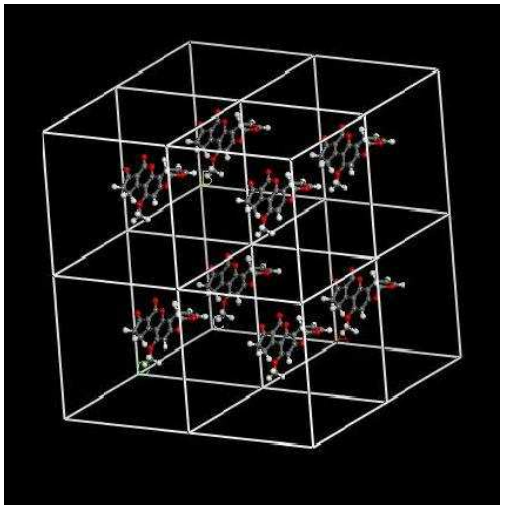
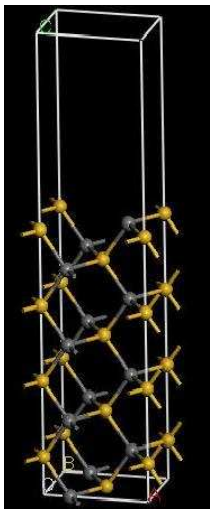
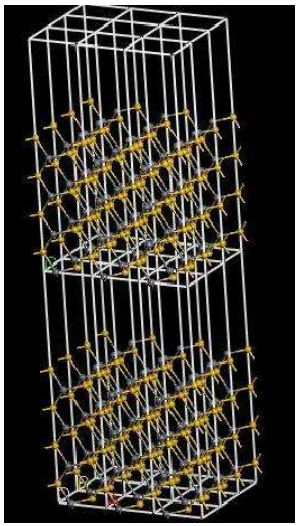

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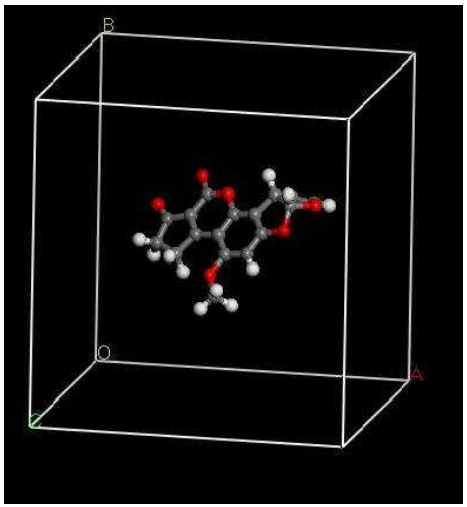
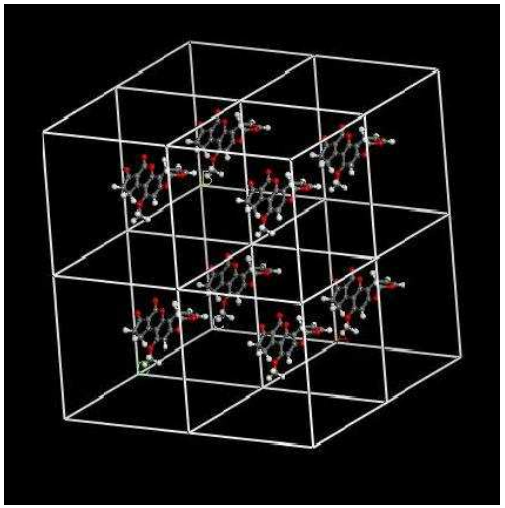
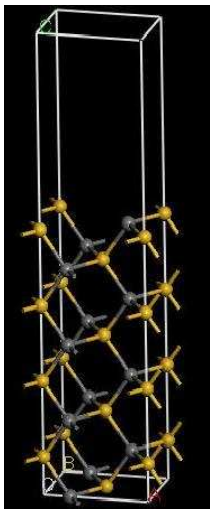
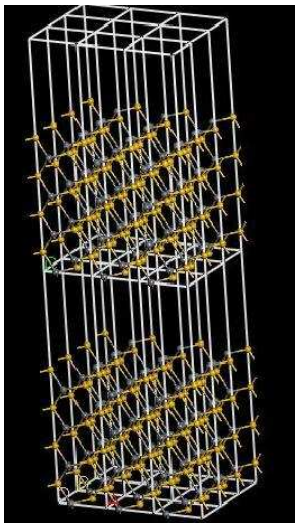

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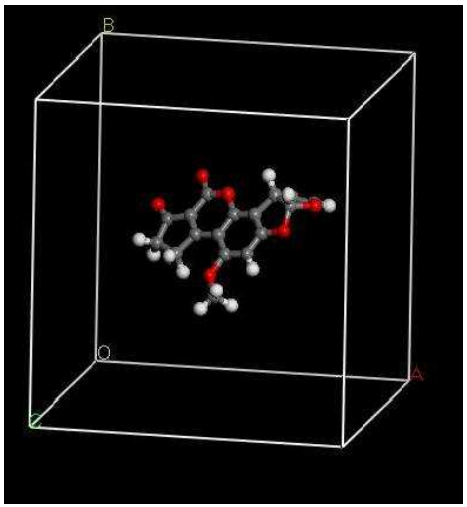
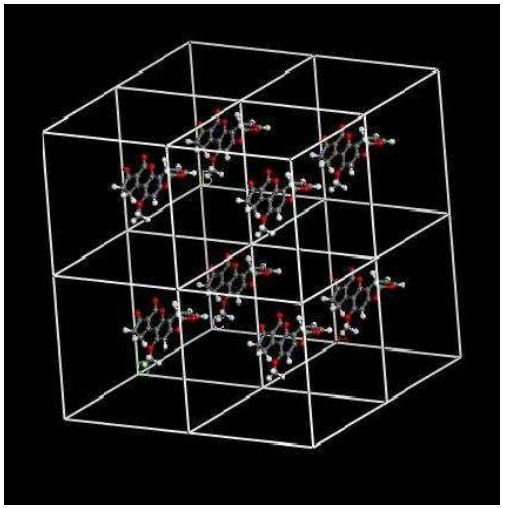
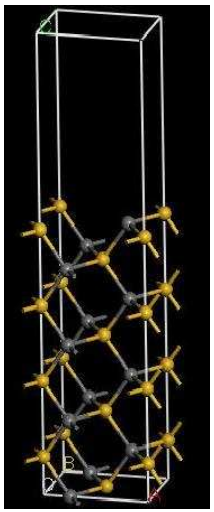
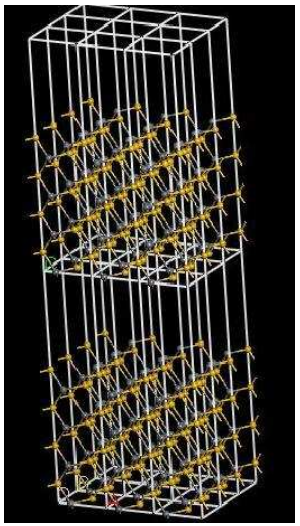

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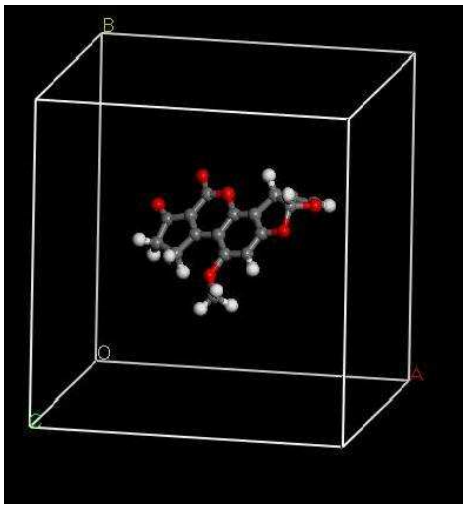
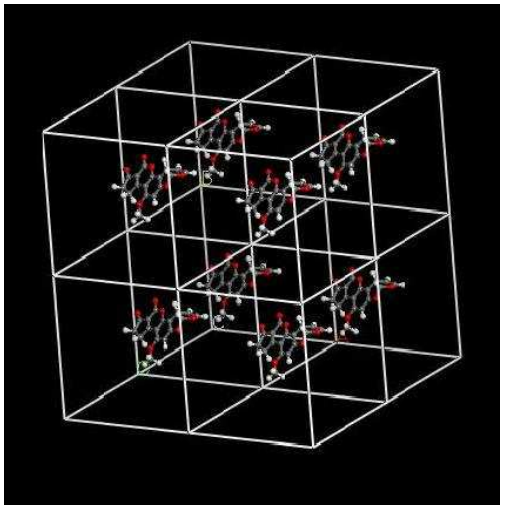
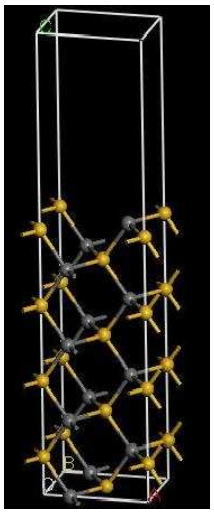
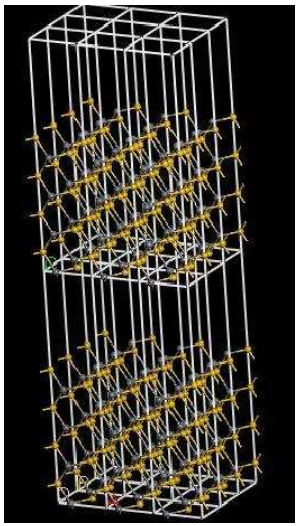

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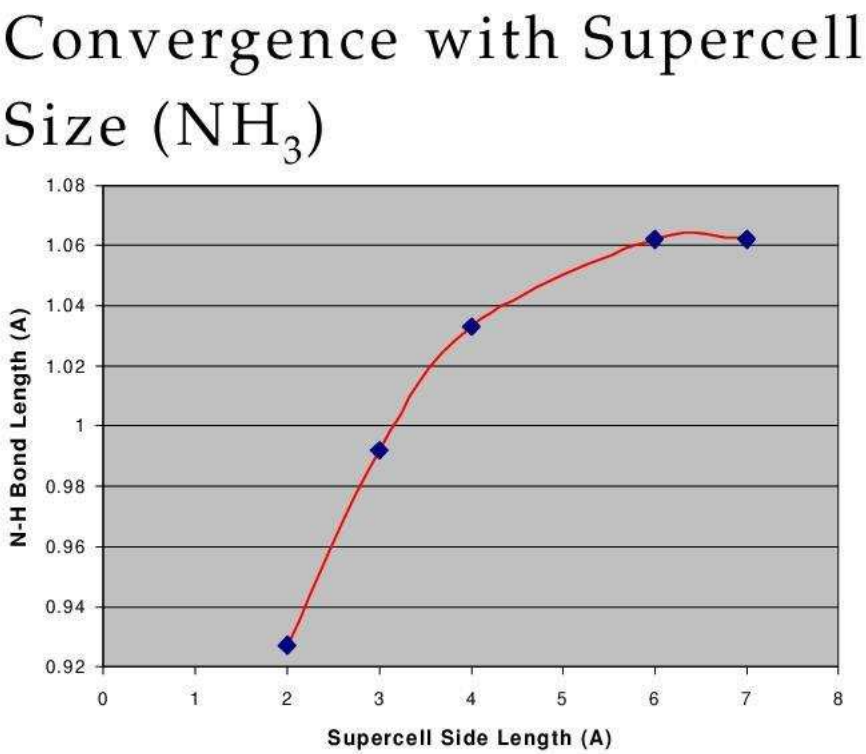

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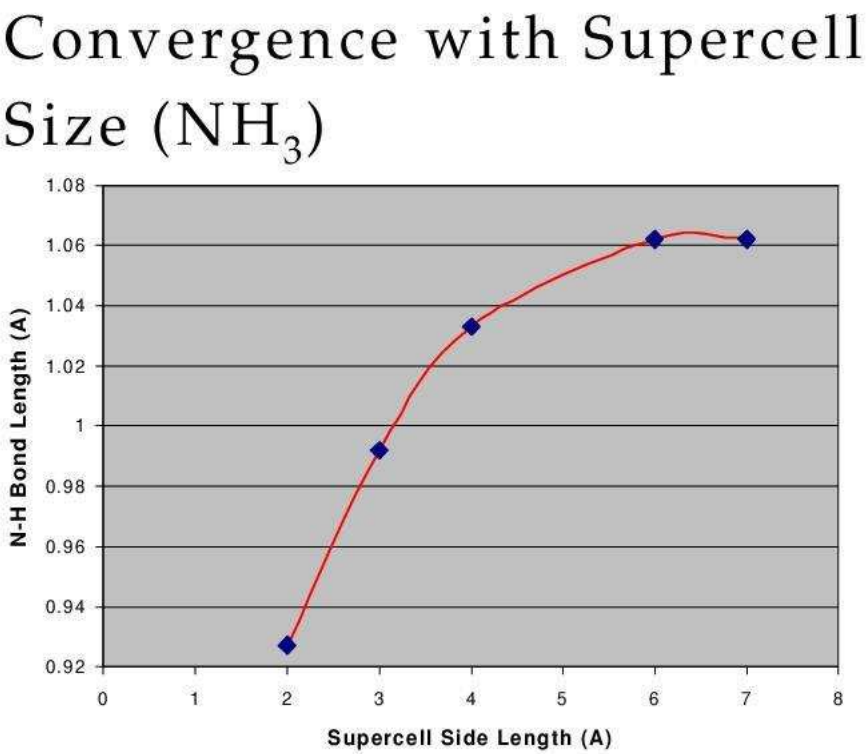

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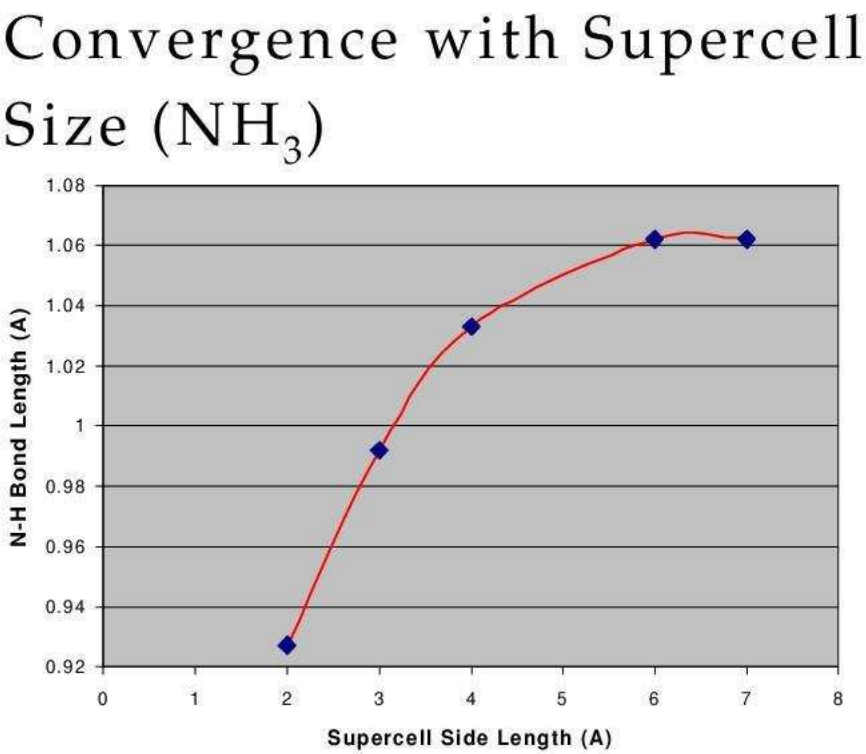

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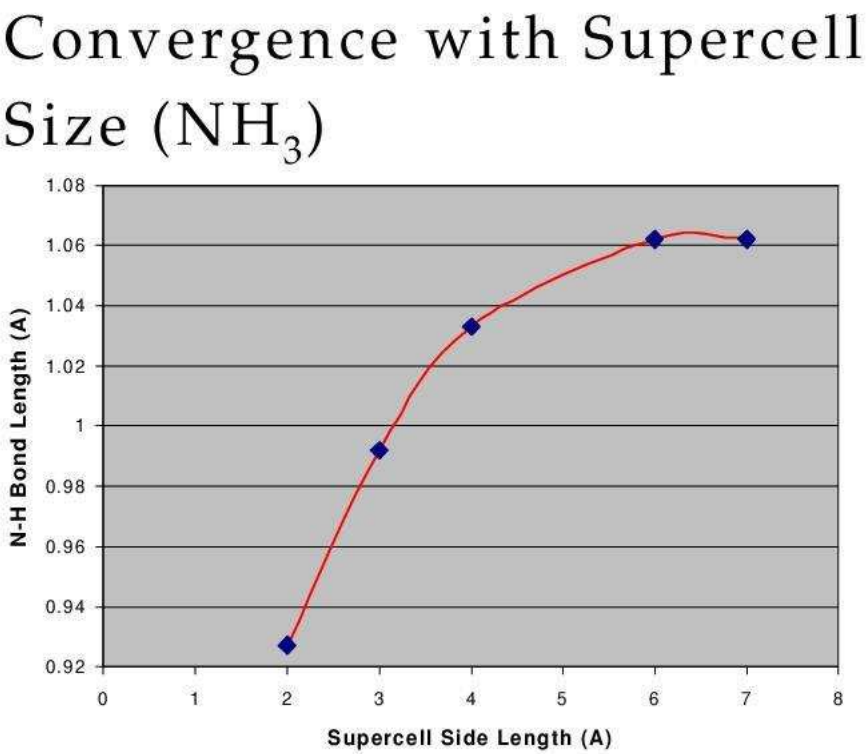

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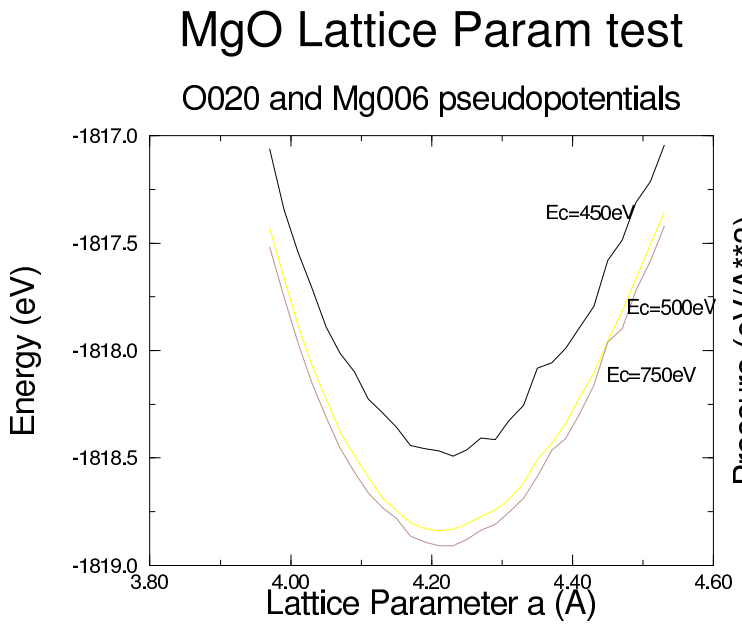

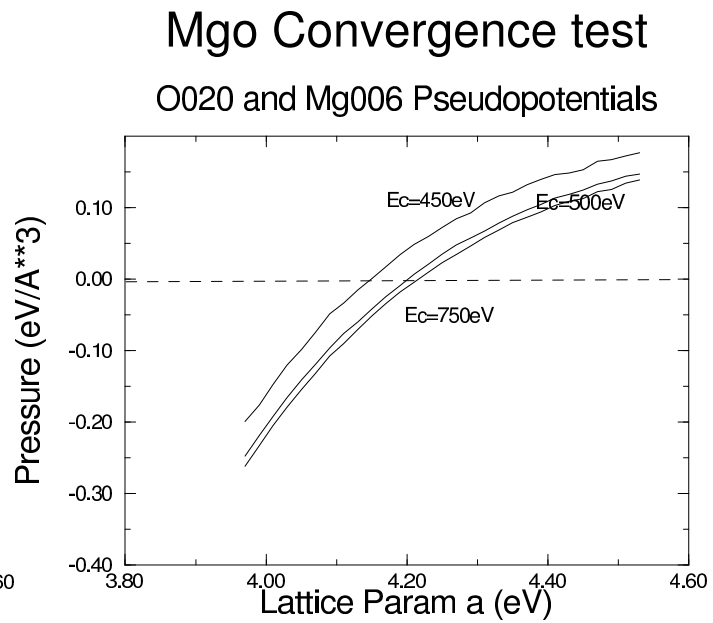

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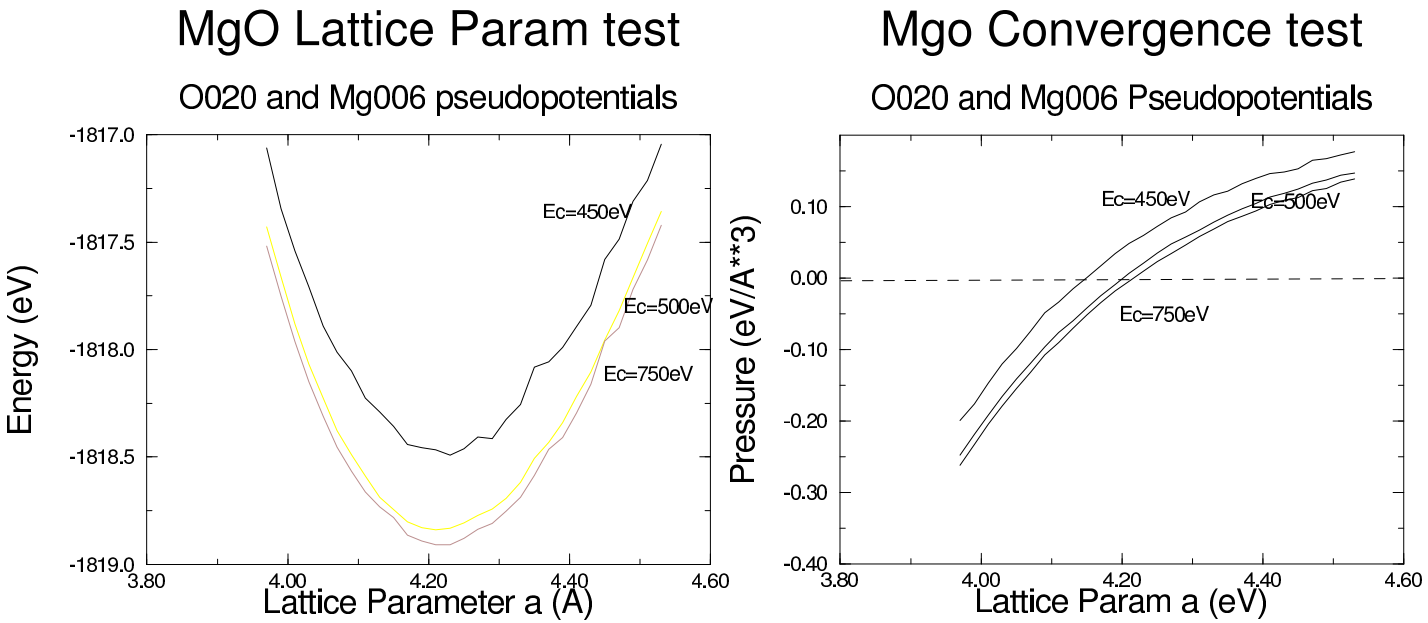

- Incomplete basis error in stress approximated by **Pulay stress** correction.
- "Jagged" E vs V curve due to discreteness of N_{PW}. Can be corrected using Francis-Payne method (J. Phys. Conden. Matt **2**, 4395 (1990))
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- *fixed cutoff* calculations reset basis for each volume, changing N_{PW} but keeping G_{max} and E_c fixed.
- This is almost always the correct method to use.

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