Some Correlation Problems – and One Partial Solution

A partially solved problem

He scattering from MgO(100)

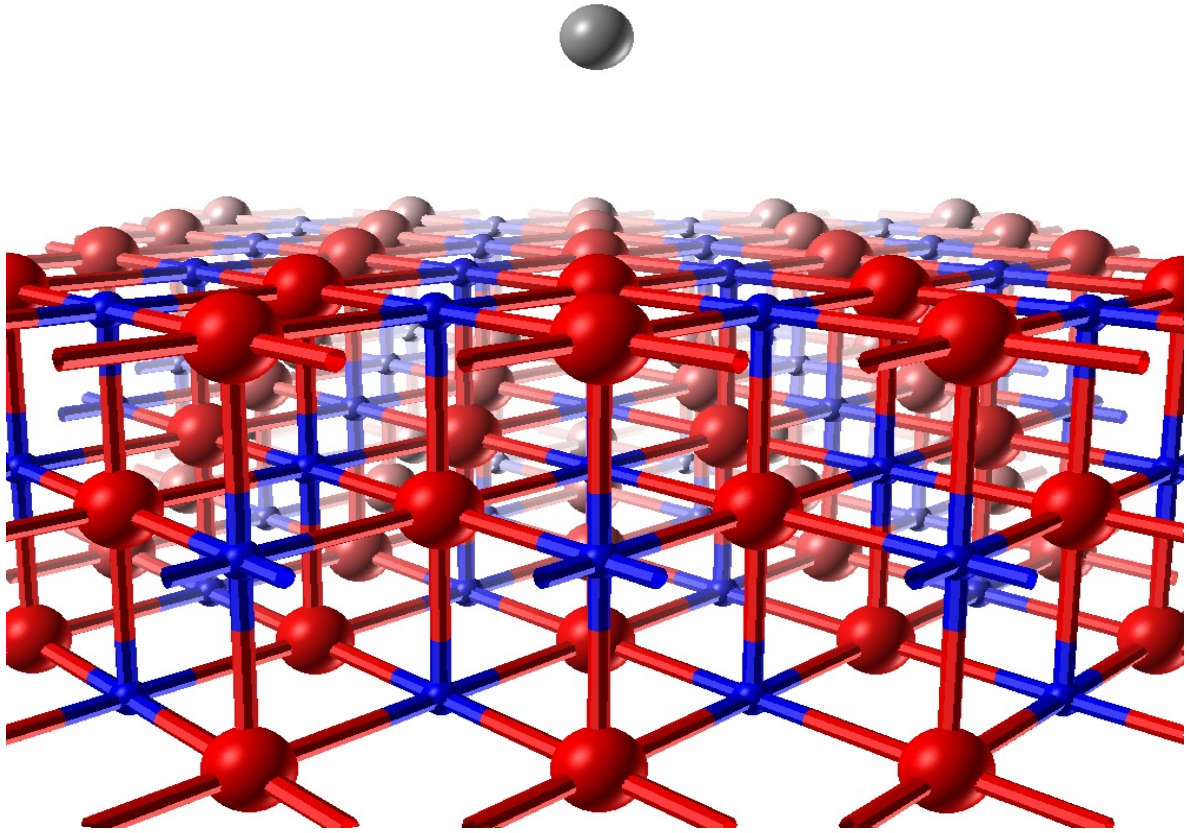
An interesting problem

Polyacetylene (again)

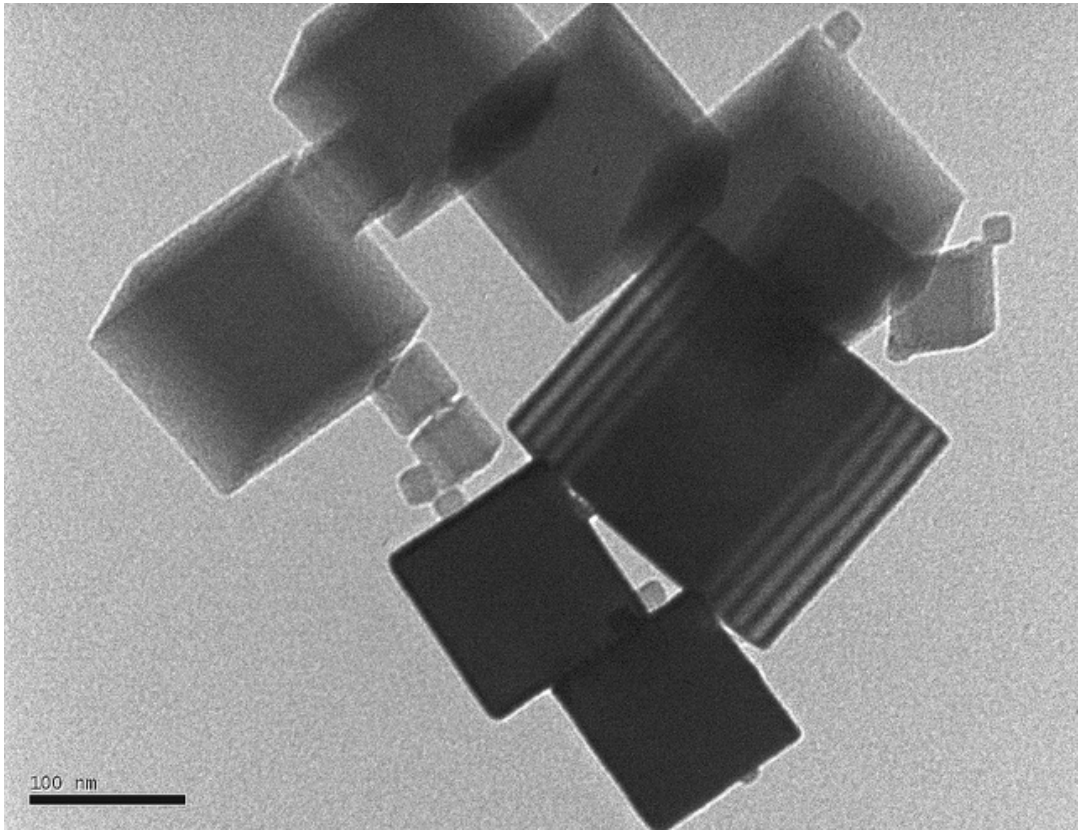
The ultimate problem (unsolved, obviously)

Magnetocaloric cooling of systems like (Ca,La)MnO_3

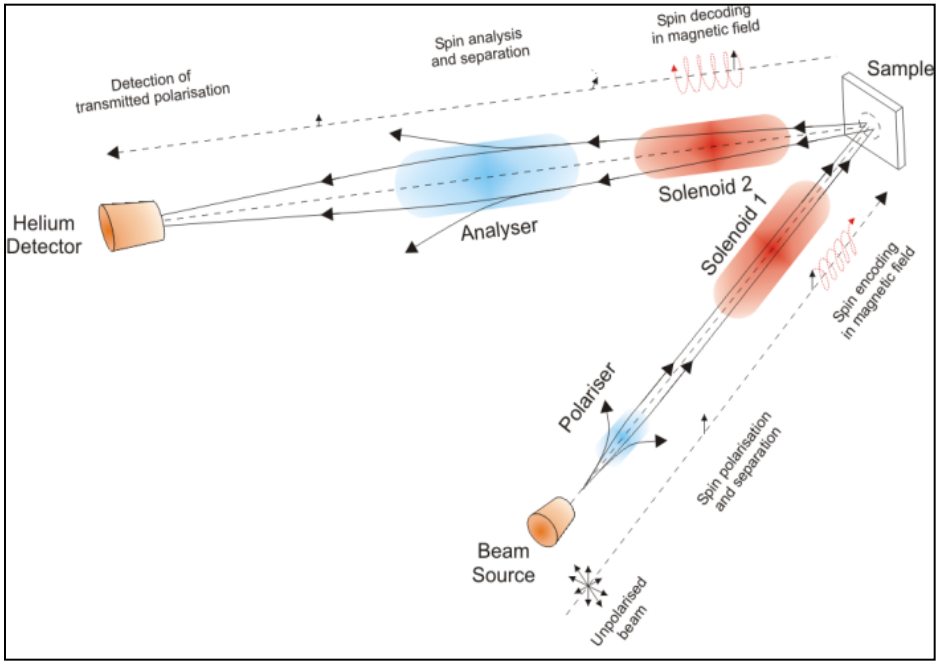
1. He Scattering From MgO(100)

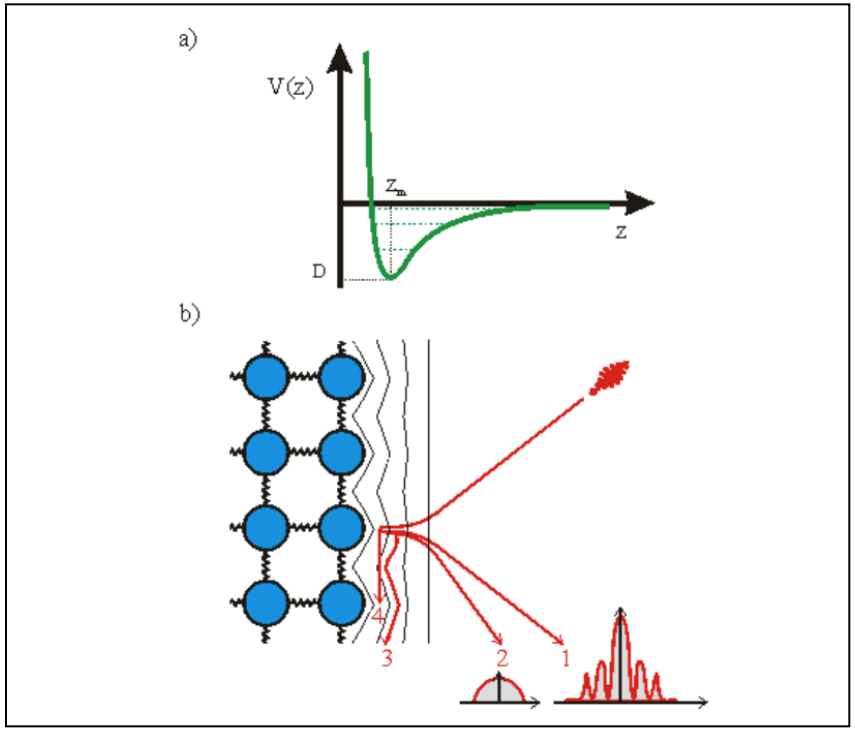


A Well Defined Problem (for an oxide surface)



The Experiment



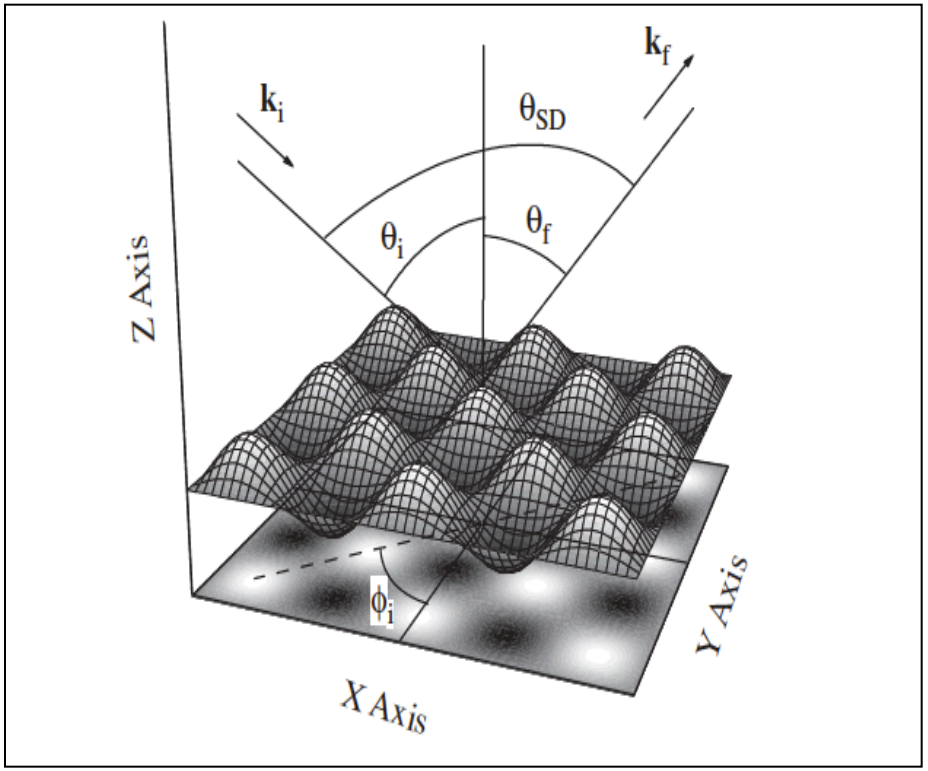


Peter Toennies, Göttingen

Bill Allison, Cambridge

1. **Elastic Diffraction**
2. **Inelastic energy loss**
3. **Resonance in traps**
4. **Trapping**

The Problem – Compute the Potential



Weak interaction – London dispersion at long range

Methodology

CRYSTAL14 – local Gaussian orbitals

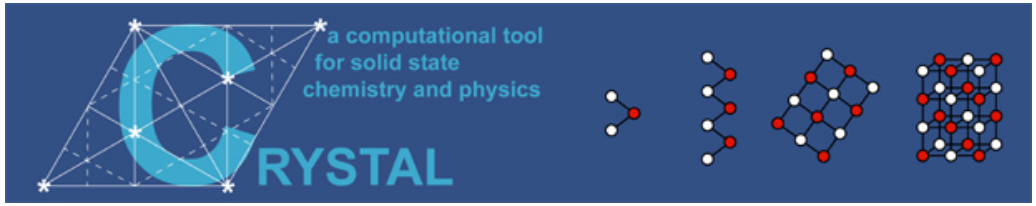
Truncated summation of analytic integrals on the periodic lattice => exact exchange calculated efficiently

Hybrid exchange: B3LYP functional (20% Fock exchange)

(Reliablity established now in some 100+ periodic systems)

Triple / Quadruple + polarisation valence basis sets

http://www.crystal.unito.it



Who did the hard work – CRYSTAL / CRYSCOR

Torino

Cesare Pisani
Silvia Casassa
Lorenzo Maschio
Migen Halo
Alessandro Erba

Regensburg

Martin Schütz
Denis Usvyat
Marco Lorenz

…with fundamental contributions by:

Roberto Dovesi
Fred Manby
Claudio Zicovich-Wilson

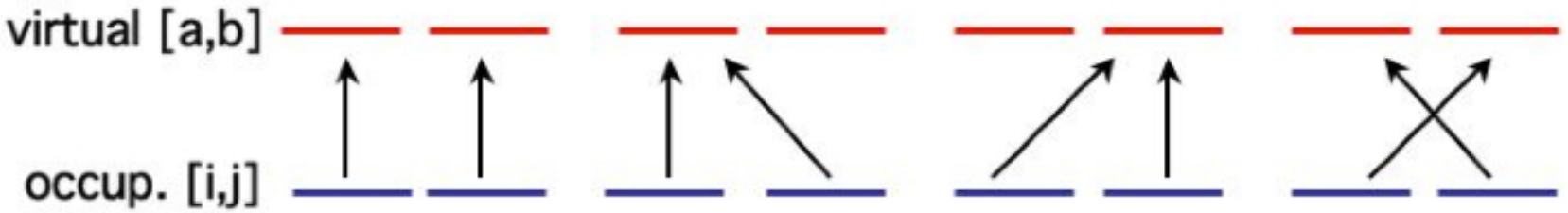
A reliable and efficient code for periodic MP2 theory

EPSRC

Imperial College London

Science & Technology Facilities Council

Local MP2



Local functions describing the occupied manifold

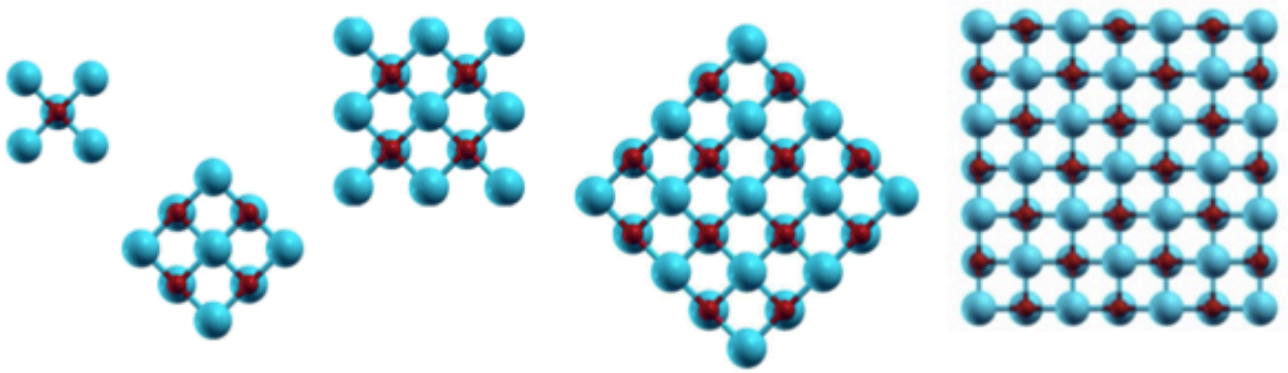
Local functions describing the virtual manifold

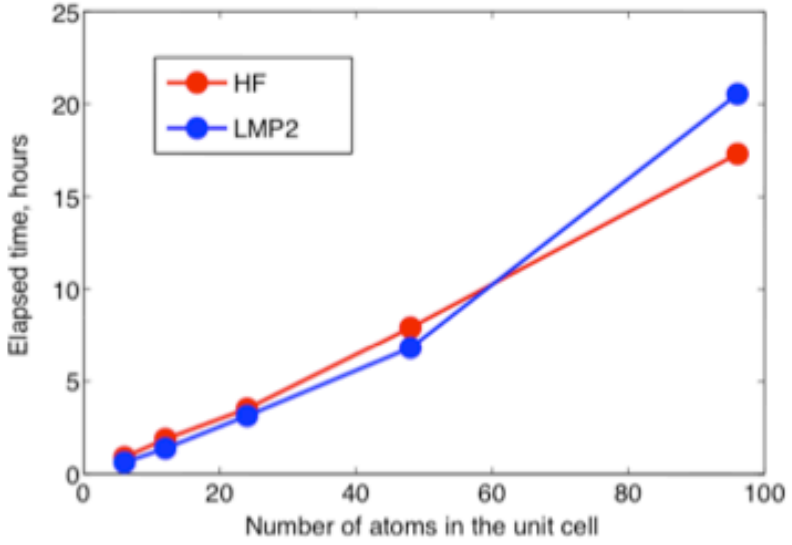
Truncation of the occupied space: Wannier-Wannier pairs

Reduction of the virtual space: PAOs & W-W pair domains

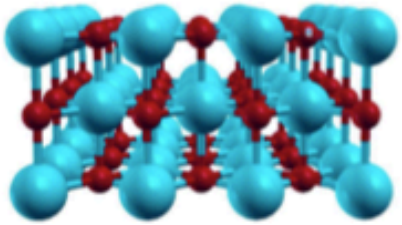
Scaling with system size

Single processor AMD Opteron 2.2 GHz



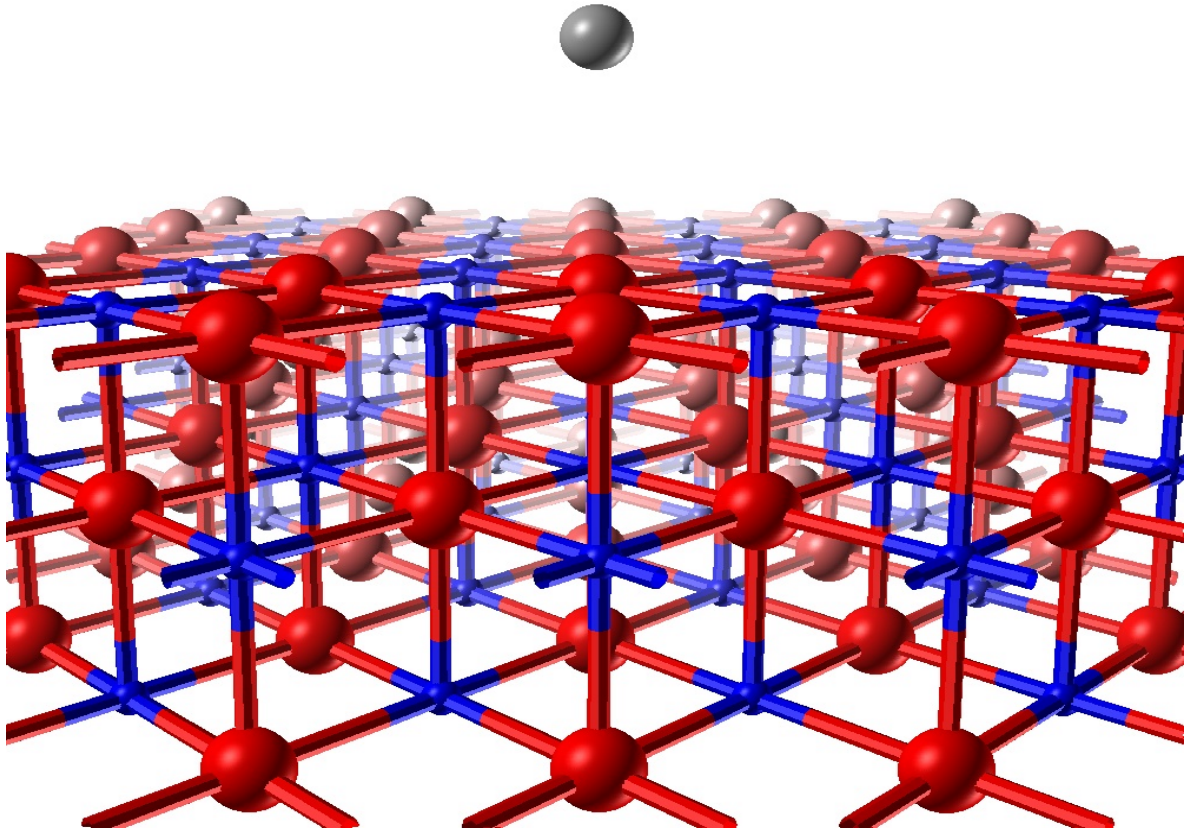


Basis set: [4s3p2d1f]
Number of Atoms: 96
Number of AOs: 2880
Number of WFs: 192

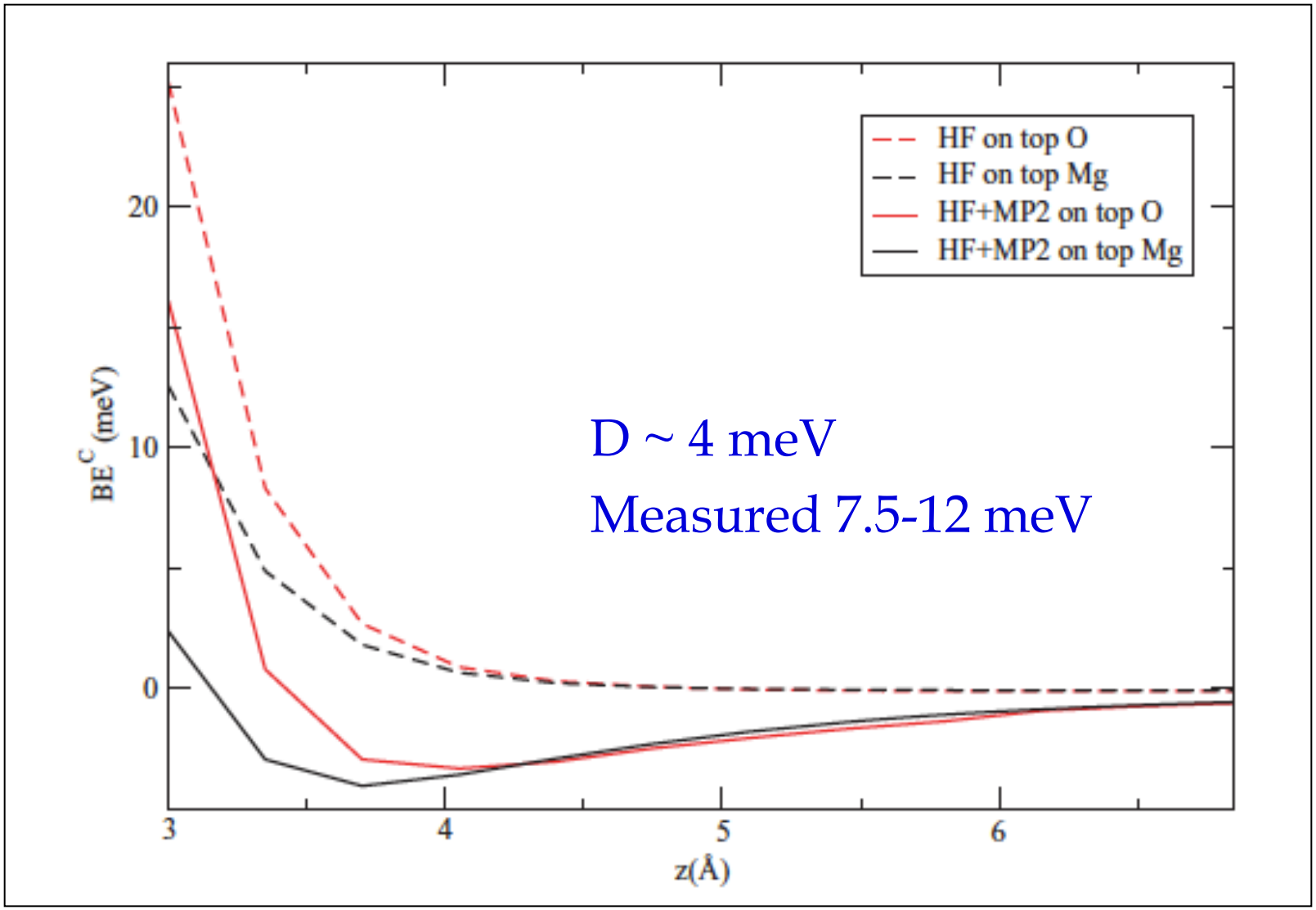


MgO(100)-He

2x2 supercell (negligable lateral interactions)
5 layer slab + extrapolation to infinite slab



HF + LMP2 Binding



Diffraction Data for a range of He KE (27 – 60 meV)

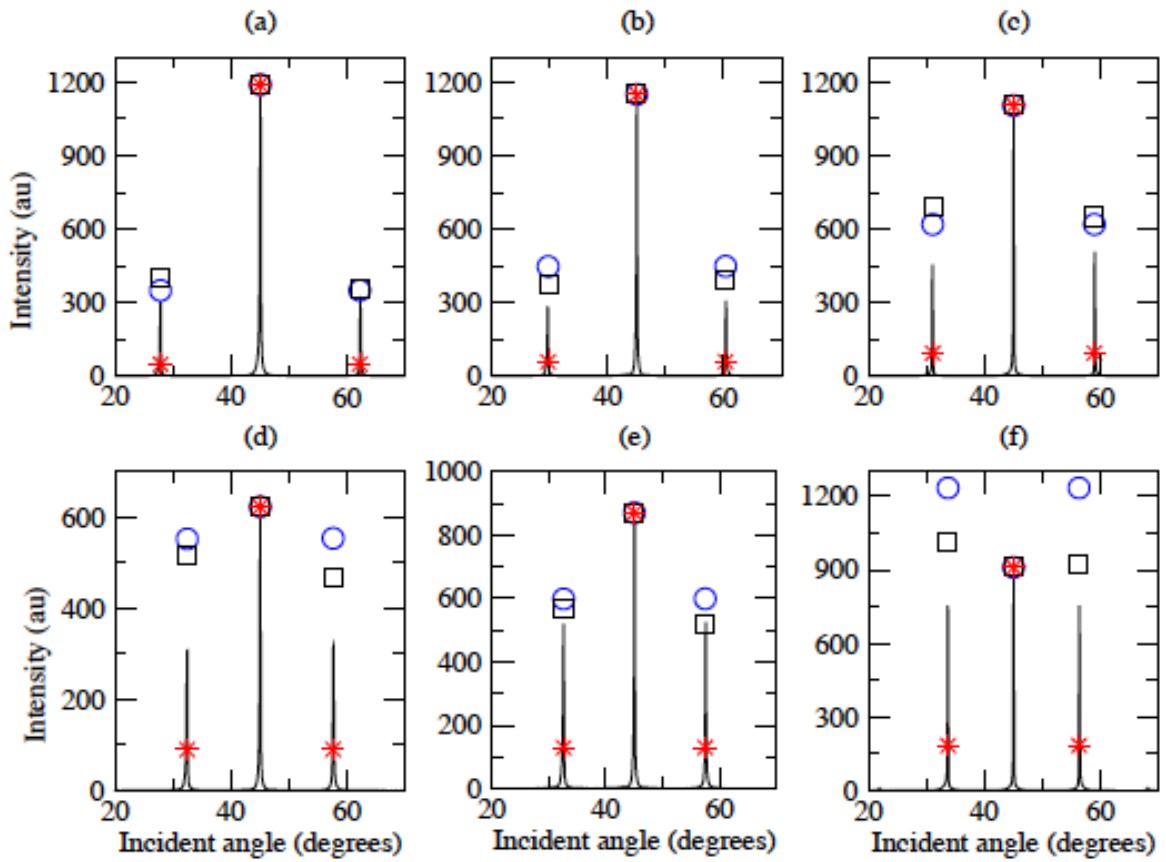


FIG. 4: Comparison of the CC intensities for case 1 (red stars) and case 2 (blue circles) with the experimental spectra (black lines) and the peak areas (black squares). Diffraction peaks are given in counts/s; peak areas and CC intensities have been normalized in a way that the specular (central) peak appears at the maximum of the experimental peak. The considered incident energy are the following: (a) $E_i = 26.62$ meV, (b) $E_i = 33.30$ meV , (c) $E_i = 40.02$ meV, (d) $E_i = 48.96$ meV, (e) $E_i = 50.20$ meV and (f) $E_i = 60.47$ meV.

■ **Expt.**

★ **MP2**

Pragmatic Approaches….. (Fiddling)

Scaling the MP2 contribution by comparison to CCSD(T) in model systems:

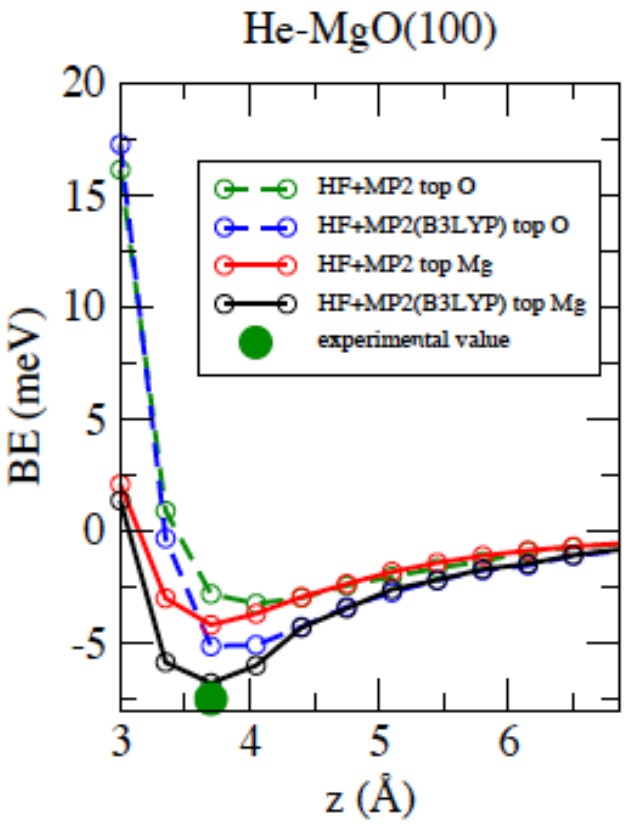
$$E = HF + 1.65 * MP2$$

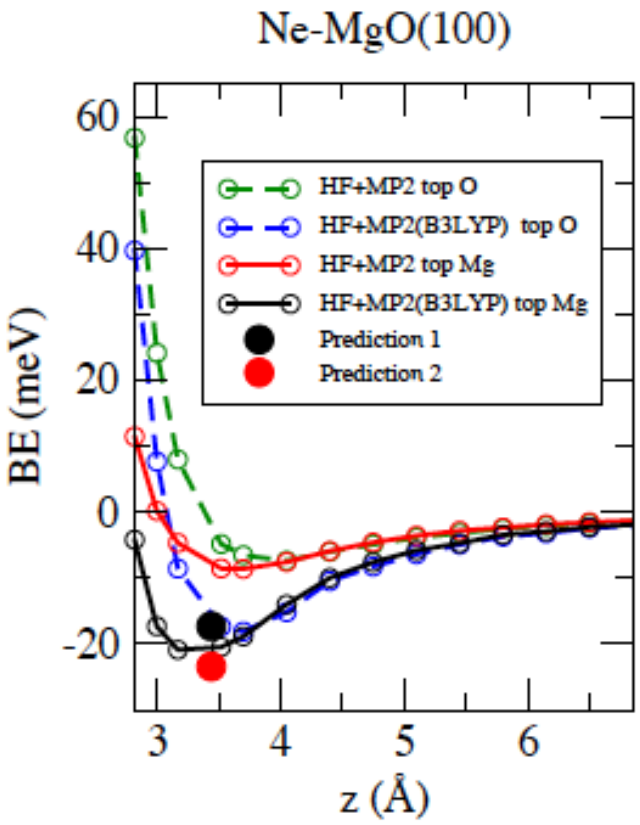
Close the single particle gap and the MP2 contribution increases suggesting:

$$E = B3LYP + MP2(B3LYP)$$

Both give similar energy surfaces with a deeper minimum…

Computed Binding Energy : He-MgO(100)



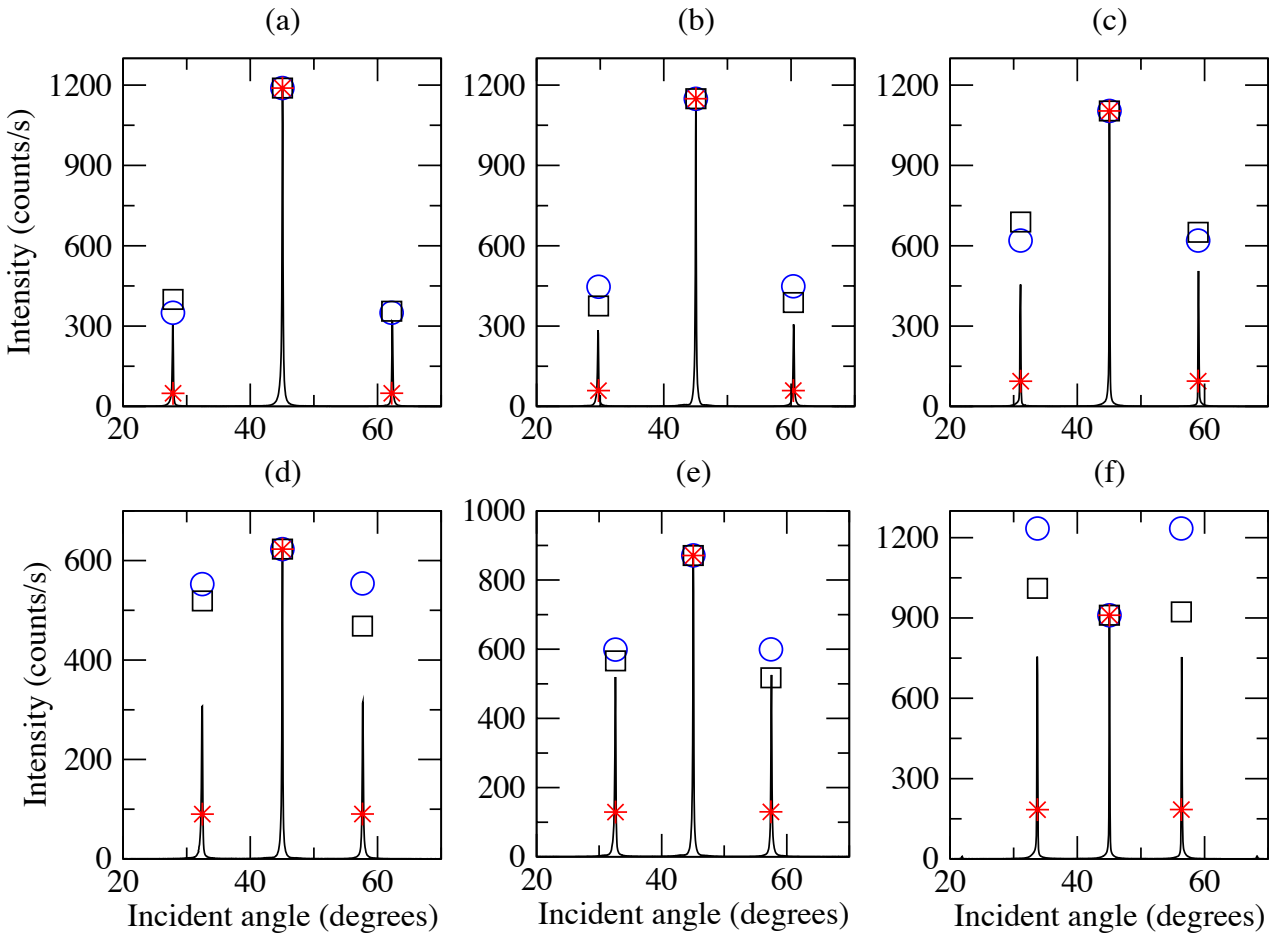


Well depth measured 7.0 - 12.5 meV

MP2 [4meV]

MP2(B3LYP) [6.7 meV]

Comparison with Measured He Scattering



□ - expt

★ - MP2

O - MP2(B3LYP)

Incident Energies (meV)

a. 26.62

b.33.30

c.40.02

d.48.96

e.50.20

f.60.47

Bound States

	Exp.1 (meV)	Exp.2 (meV)
E_0	---	-10.2
E_1	-5.5	-5.3
E_2	-2.6	-2.4
E_3	-1.2	-0.9
E_4	-0.5	-0.6
E_5	-0.3	-0.2

Exp.1- M. Mahgefteh and D.R. Jung and D.R. Frankl, Phys. Rev. B 39, 3900 (1989)

Exp.2 - G. Benedek and G. Brusdeylins and V. Senz and J. G. Skofronick and J. P. Toennies and F. Traeger and R. Vollmer, Phys. Rev. B 64, 125421 (2001)

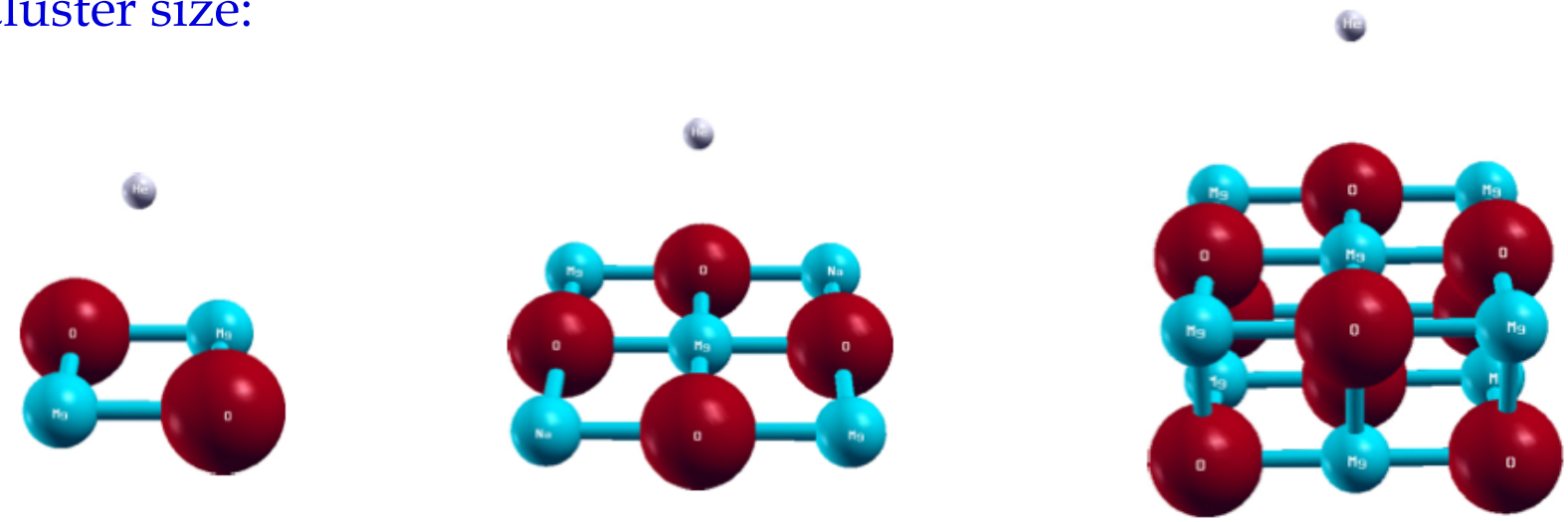
Approaching the Exact Energy Surface

Calculate the difference between the MP2 energy and the exact energy using a finite cluster

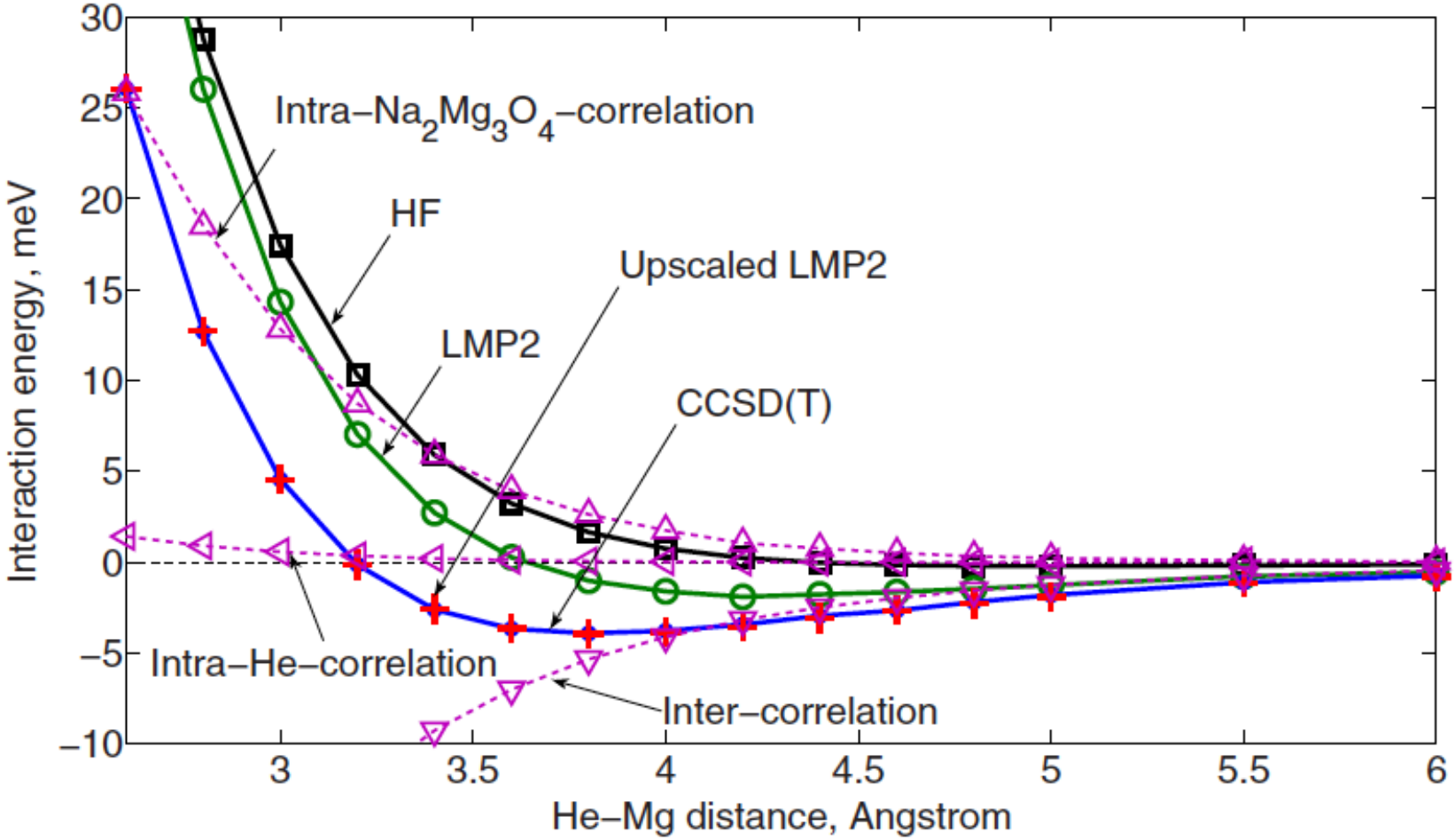
Systematically improve:

$$\sum_z \left(\Delta E^{\mathrm{CCSD(T)}} - \Delta E^{\mathrm{LMP2}}_{\text{intra-He}} - f_{\text{intra-Mg}_3\mathrm{Na}_2\mathrm{O}_4} \Delta E^{\mathrm{LMP2}}_{\text{intra-Mg}_3\mathrm{Na}_2\mathrm{O}_4} - f_{\text{inter}} \Delta E^{\mathrm{LMP2}}_{\text{inter}} \right)^2$$

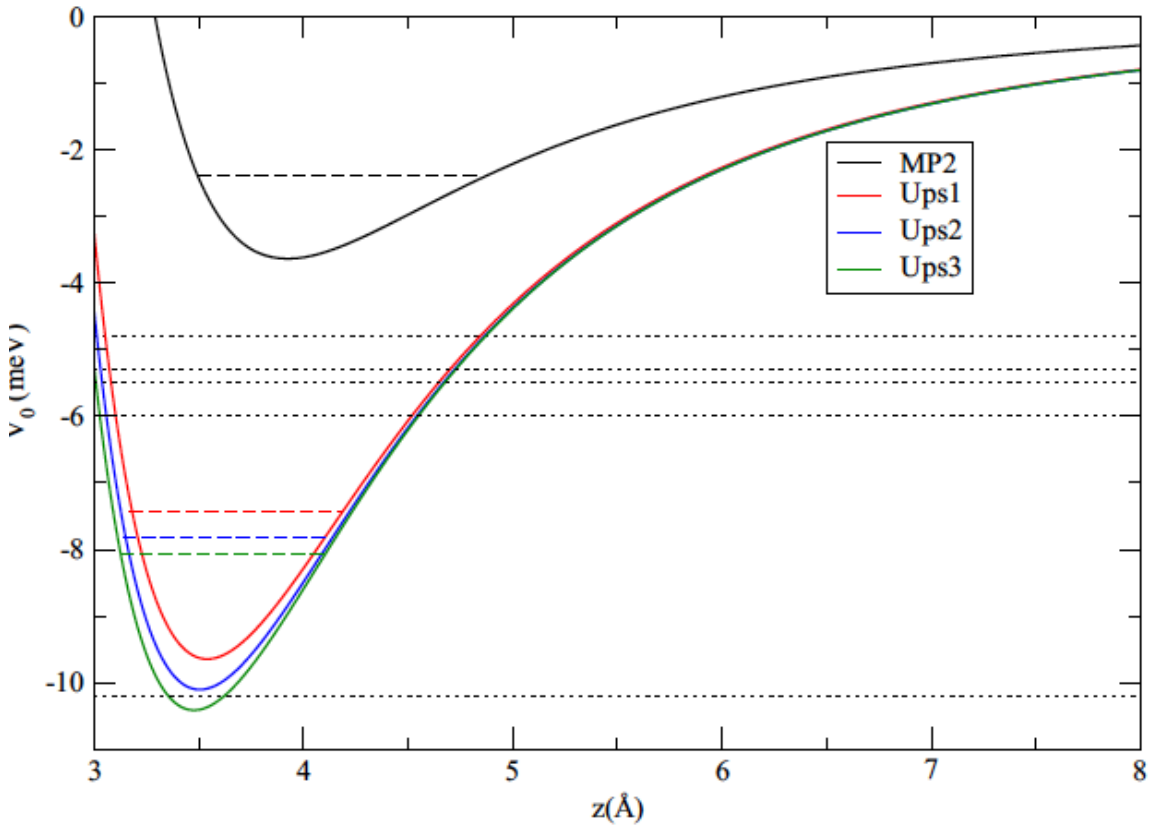
1. Theory: MP2 – CCSD – CCSD(T) – CCSDT(Q)
2. Basis Set: aug-cc-VDZ – VTZ – VQZ
3. Cluster size:



For $Na_2Mg_3O_4$ Cluster Scaled MP2 Energy



Approaching the Exact Answer (Lateral Average)



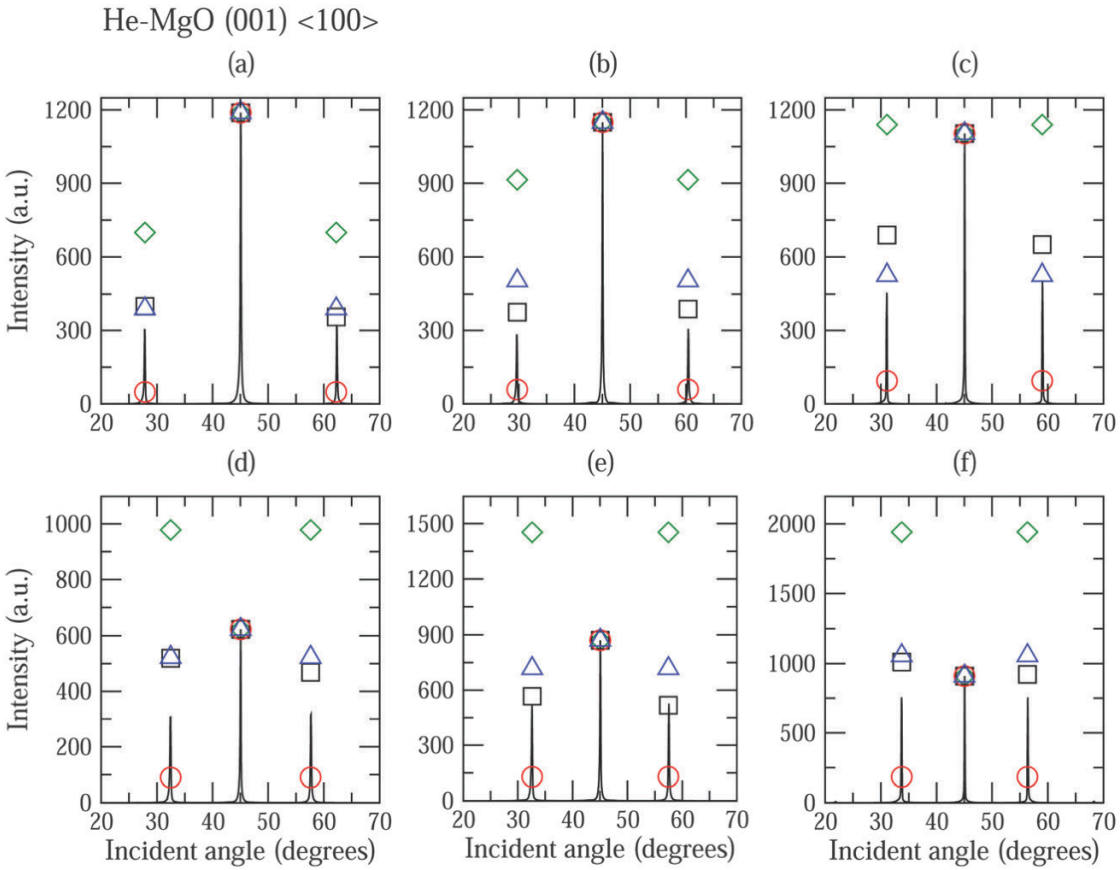
	Exp.1	Exp.2	Calc (UPS3)
E_0	---	-10.2	-8.1
E_1	-5.5	-5.3	-4.5
E_2	-2.6	-2.4	-2.2
E_3	-1.2	-0.9	-0.9
E_4	-0.5	-0.6	-0.3
E_5	-0.3	-0.2	---

A deeper bound state in the potential… but error analysis suggests that 10.2eV is not present

Reasonable agreement with the diffraction intensities

Diffraction Intensities

	Exp.1	Exp.2	Calc.
E_0	---	-10.2	-8.1
E_1	-5.5	-5.3	-4.5
E_2	-2.6	-2.4	-2.2
E_3	-1.2	-0.9	-0.9
E_4	-0.5	-0.6	-0.3
E_5	-0.3	-0.2	---



A deeper bound state in the potential… but error analysis suggests that 10.2eV is not present

Reasonable agreement with the diffraction intensities

He-Scattering MgO(100)

A powerful method for surface analysis if the potential is known.

It seems that it is possible to get close to the exact potential in a systematic way but only with some effort.

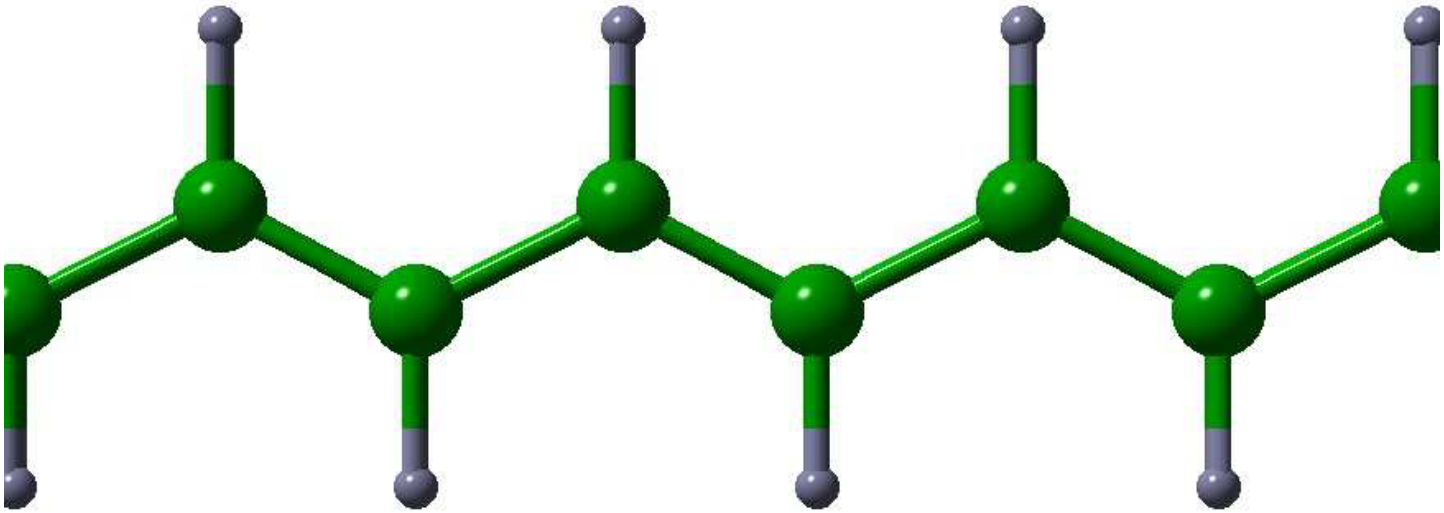
He Scattering the Structural Probe….

High quality data for LiF (etc), TiO_2 ….

Solving for a structure requires a simple potential model.

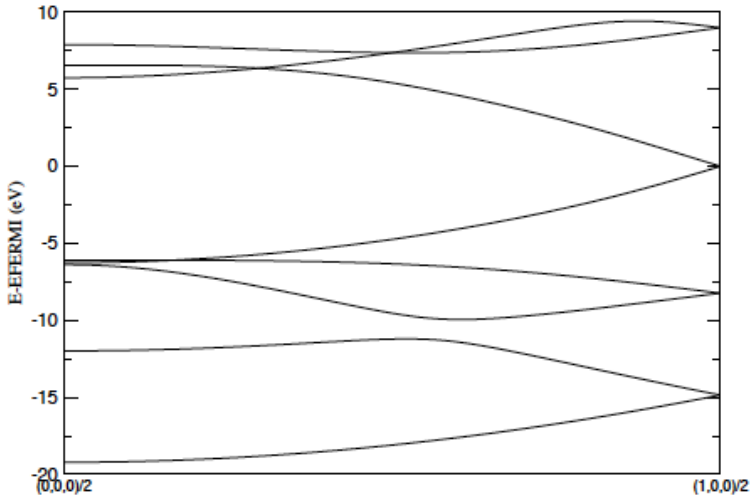
1. Develop a pairwise O^{2-}-He interaction potential (none of the obvious functional forms fit well) and test transferability
2. A much faster method with ~1meV accuracy

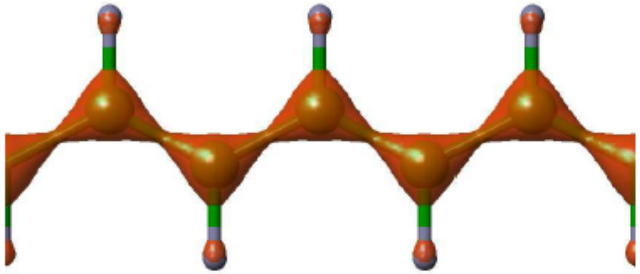
2. Polyacetylene



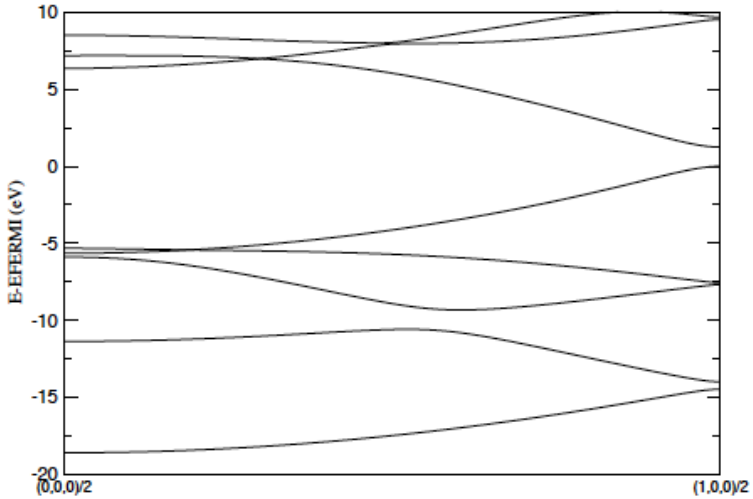
Peierls Distortion

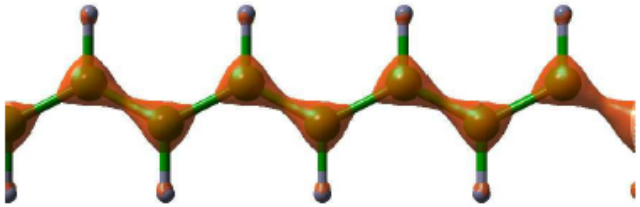
B3LYP nospin - equal CC distances





B3LYP nospin dimerised

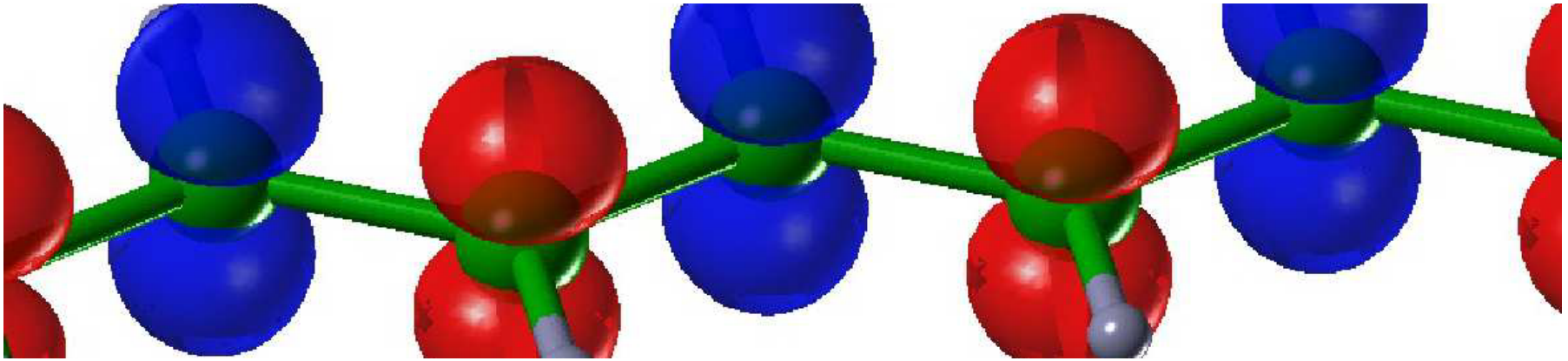




Energy Gap and Bond Length Alternation

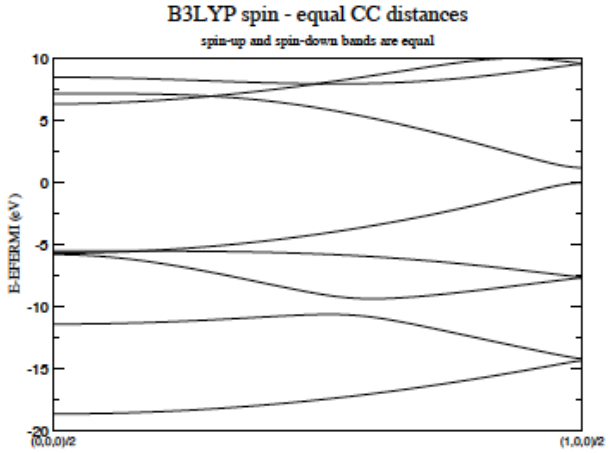
Method	a(Å)	C-C (Å)	BLA (Å)	x_C	E_g (eV)	ΔE (eV)
EXP	2.46	1.36, 1.44	0.08	-	1.4-1.9	-
B3LYP	2.467	1.363,1.424	0.061	0.514	1.246	0.015
LDA	2.450	1.379,1.391	0.012	0.503	0.102	0.000
HF	2.460	1.328,1.455	0.126	0.529	7.270	0.146

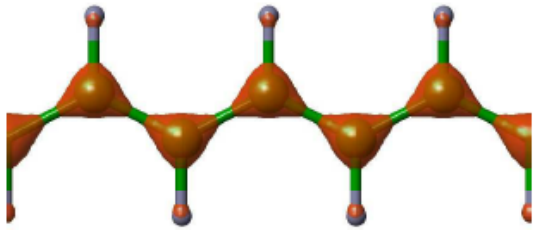
Spin Polarisation – Symmetric Geometry

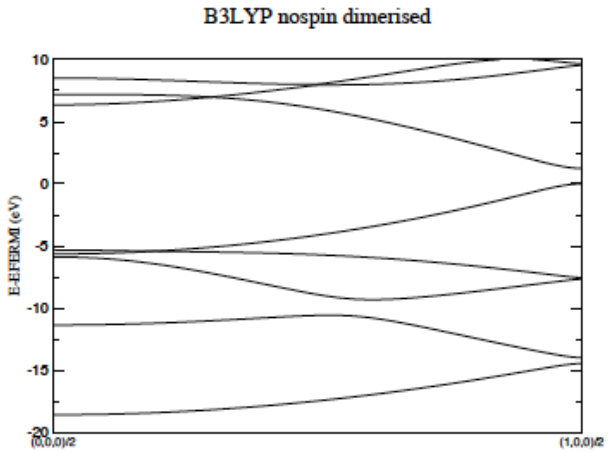


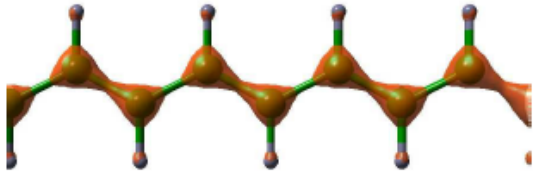
spin moment (μ_B)	B3LYP	LDA	HF
$\lvert S \rvert_C$	0.22	0.01	0.86
$\lvert S \rvert_H$	0.01	0.00	0.05

Spin Polarisation vs Dimerisation



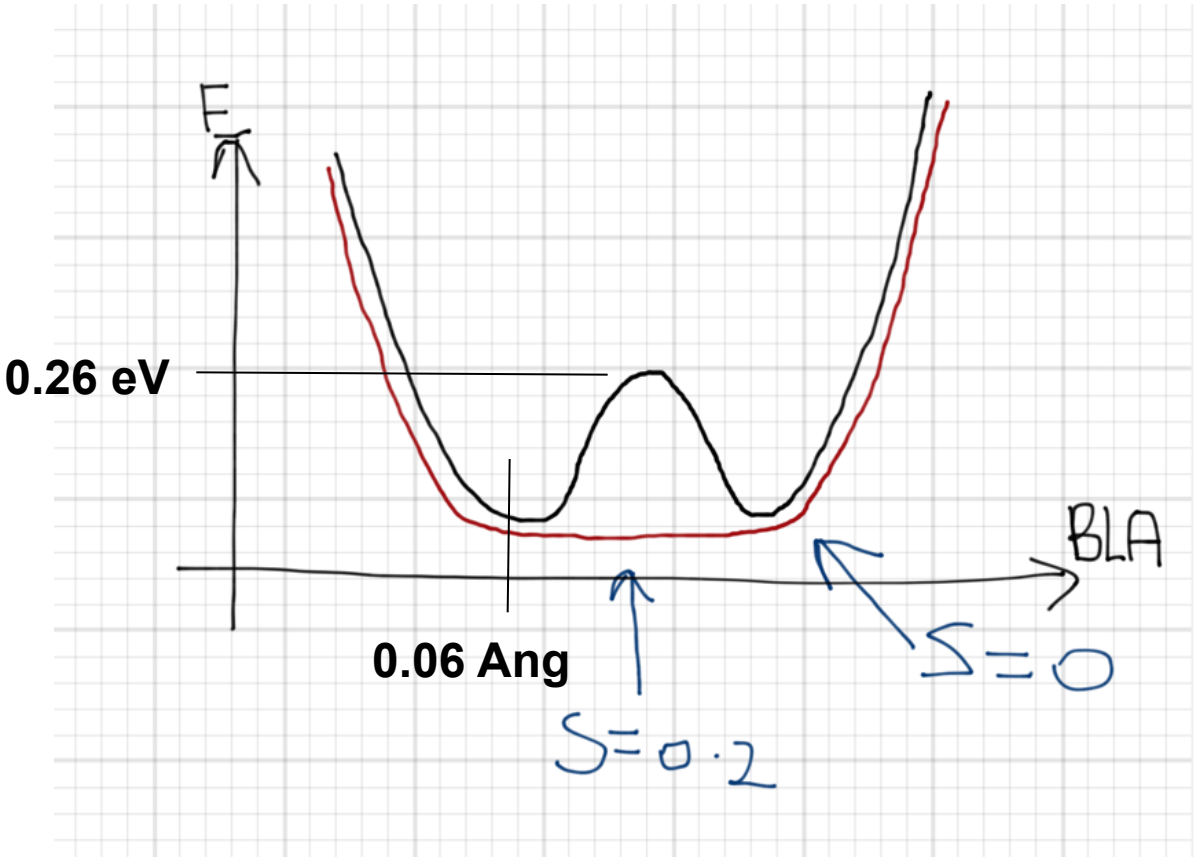






Same energy (~0.3 meV) in B3LYP

Summarising…. (B3LYP)



Band gap after spin or spatial (or both) symmetry breaking always ~1eV

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