

# NMR PARAMETER PREDICTION AT THE LIMITS OF DENSITY FUNCTIONAL THEORY

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*“First-principles calculation of the  $^{17}\text{O}$  NMR parameters in Ca oxide and Ca aluminosilicates: the partially covalent nature of the Ca-O bond, a challenge for density functional theory”*

*JACS, 2004 (to appear)*

# OUTLINE

- Why bother with the theory of NMR?
- The curious case of calcium aluminosilicates
  - motivation
  - problems with the calculations
  - an attempted solution
  - final results
  - theoretical discussion

# WHY BOTHER WITH A THEORY OF NMR?

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## WHAT IS NMR?

- An excellent probe of local atomic and electronic structure
- A ubiquitous experimental technique
- Used in both standard analytical mode, and in state-of-the-art experiments

# MOTIVATION 1

## TO HELP EXPERIMENTALISTS

- A useful theory predicts the NMR parameters (chemical shifts, quadrupolar coupling constants) for a given atomic configuration
- The allows the assignment of spectra, testing of hypotheses, and design of experiments
- We have the GIPAW method: applies to solid state too

# MOTIVATION 2

## TO TEST OUR THEORIES

- Comparing with accurate, repeatable experimental results is an unforgiving test of a theory
- Given the common use of NMR, there is a wealth of data
- Experiments can be lead by theory

# CALCIUM ALUMINOSILICATES

- Aluminosilicates: a large class of natural and technological materials
  - minerals, zeolites, ceramics, concretes, glasses and melts
- Can contain (in addition to Al, Si, O)  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$
- $^{29}\text{Si}$  and  $^{27}\text{Al}$  common, but enrichment allows  $^{17}\text{O}$

# FIRST RESULTS

- We have previously had very good results for the silicates and the sodium silicates
- And for many other systems
- We were expecting something similar . . .

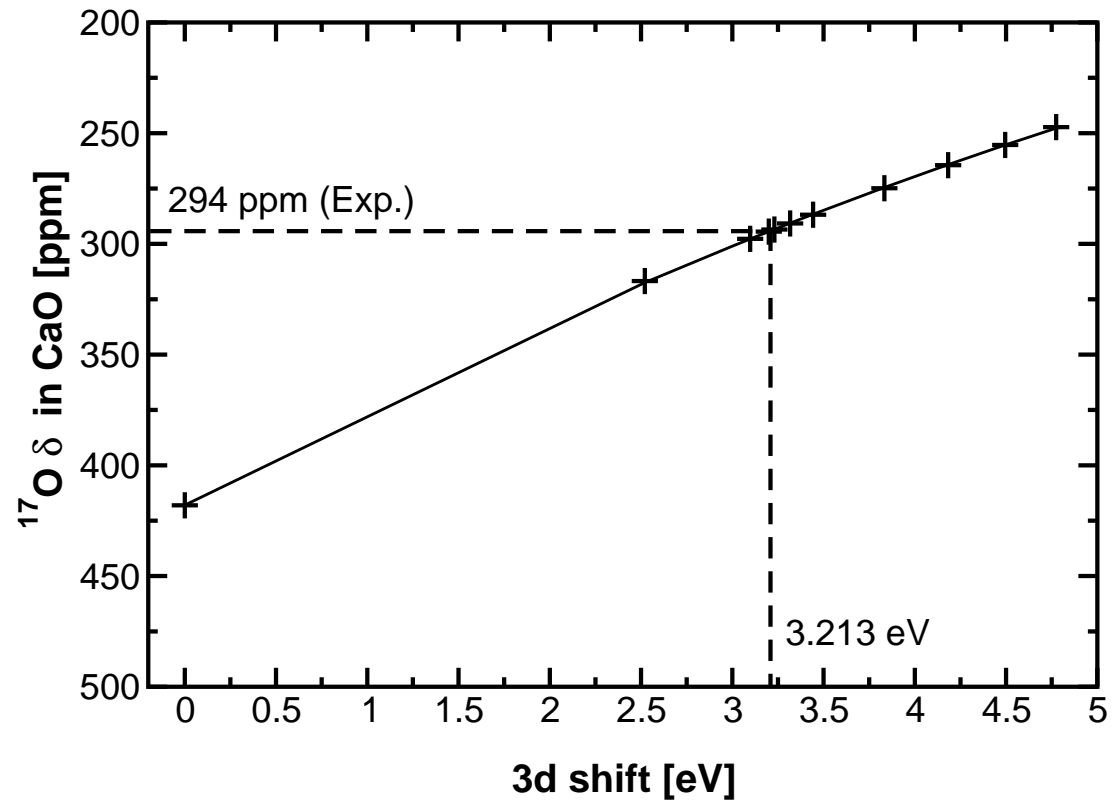


Compound	Experiment			PBE-DFT		
	$\delta$	$Cq$	$\eta$	$\delta$	$Cq$	$\eta$
MgO	47.0	0.0	0.0	58.8	0.0	0.0
CaO	294.0	0.0	0.0	418.05	0.0	0.0
grossite	71.6	1.9	0.7	91.82	2.13	0.67
	61.5	1.8	0.5	82.69	1.77	0.64
	56.8	2.1	0.5	72.34	1.84	0.43
	40.6	2.5	0.4	42.95	2.46	0.23
	$\delta$	$Pq$		$\delta$	$Pq$	$\eta$
Wollastonite	115	2.3		153.11	2.42	0.18
	114	2.6		146.43	2.31	0.10
	107	2.2		138.88	2.26	0.07
	97	2.0		133.11	2.34	0.37
	103	2.9		136.90	3.01	0.40
	88	2.6		118.89	2.74	0.07
	75	4.8		82.69	4.91	0.53
	75	4.8		81.82	5.02	0.51
	67	4.7		71.61	4.90	0.10

# MgO AND CaO

- MgO and CaO have the same structure
- But, Ca has unoccupied  $3d$  states near the occupied states
- Mg-O is purely ionic
- Ca-O is iono-covalent (the Ca  $3d$  can partially hybridise with the O  $2p$ )

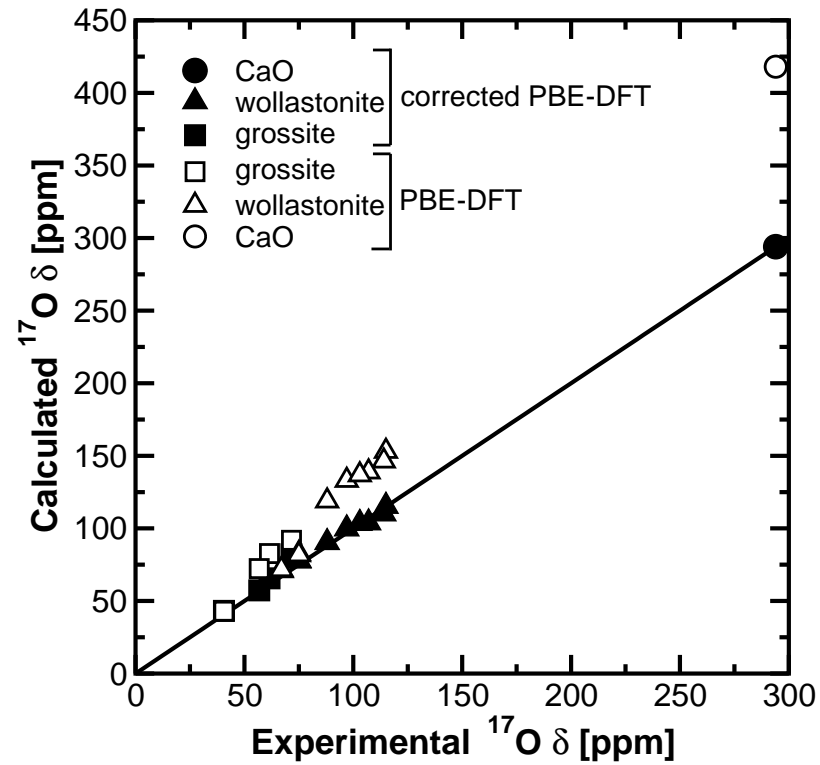
# A SPECIAL PSEUDOPOTENTIAL



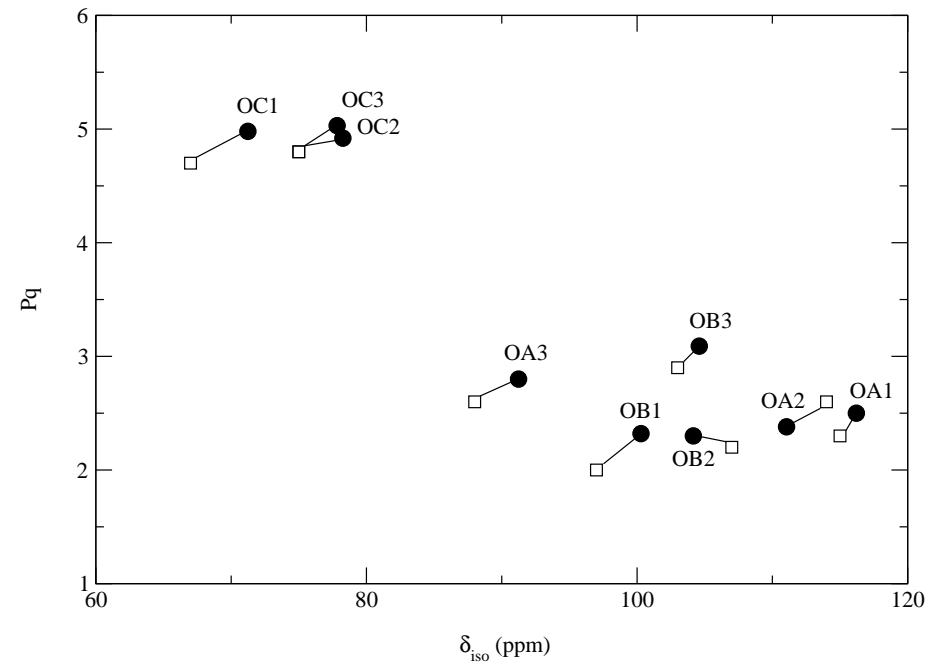
# A SPECIAL PSEUDOPOTENTIAL

- The Ca  $3d$  energy level shift is chosen to fix CaO  $^{17}\text{O}$  chemical shift
- It must be transferable to be useful
- Only the chemical shifts are changed: EFGs and forces stay the same

# BETTER RESULTS



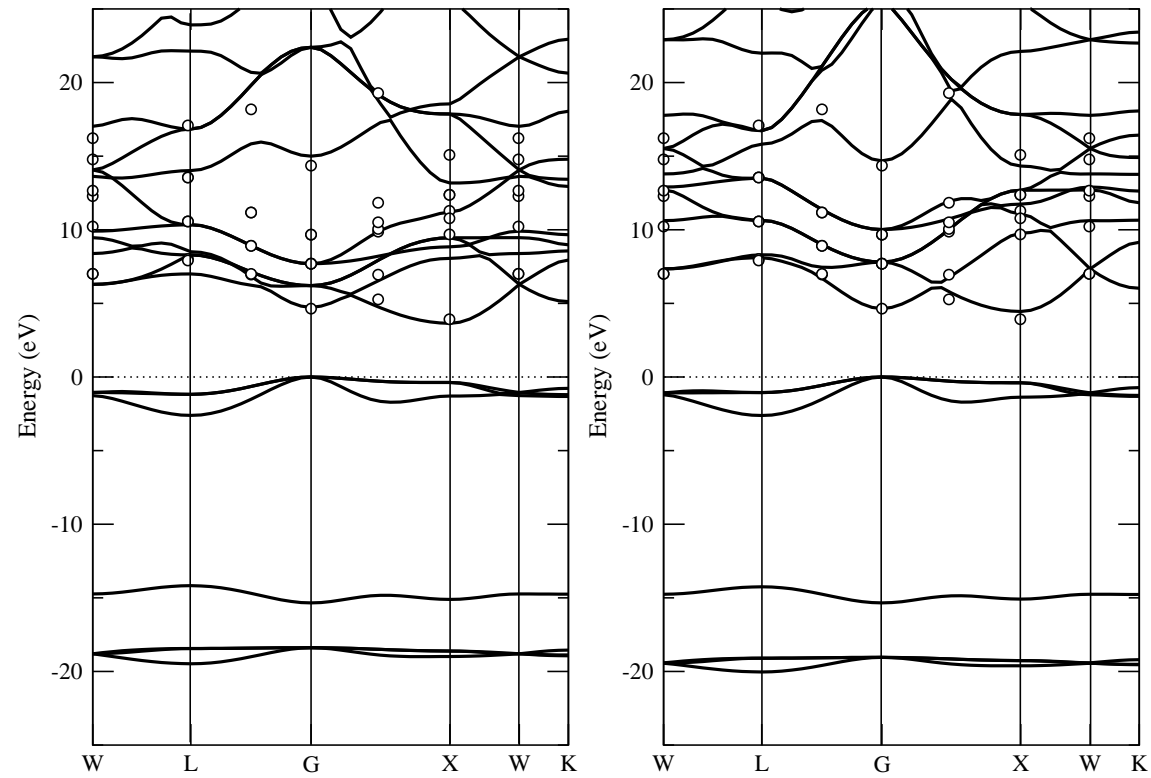
# THE ASSIGNMENT OF WOLLASTONITE



# THEORETICAL CONTEXT

- DFT-LDA/GGA does not give the correct excited state spectrum
- The “band-gap problem” exists for all insulators
- But chemical shifts are generally good
- It can be more complex: localised orbitals can shifted relatively
- This changes the degree of hybridisation, and hence response properties

# COMPARISON WITH GW RESULTS





# OUTLOOK

- Straightforward DFT (PBE) has its limits
- We have gained an insight as to what an improved theory must achieve
  - we need a self consistent approach like our level shifted PSP
  - what about SIC PSPs (Nicola Spaldin)