Center for Molecular Modeling

Department of Materials Science and Engineering

Computational Materials Physics

forces and point group symmetry

Stefaan.Cottenier@ugent.be
Technologiepark 903, Zwijnaarde

http://molmod.ugent.be
http://www.ugent.be/ea/dmse/en
my talks on Youtube: http://goo.gl/P2b1Hs

Quantum forces

The Born-Oppenheimer hamiltonian for our solid was:

$$H = \cancel{-\sum_i \frac{\nabla^2}{M_i}} - \sum_i \frac{\nabla^2}{m_i} - \sum_{i,j} \frac{(eZ_i)\ e}{|\vec{R}_i - \vec{r}_j|} + \frac{1}{2}\sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2}\sum_{i \neq j} \frac{(eZ_i)(eZ_j)}{|\vec{R}_i - \vec{R}_j|}$$

The position vectors $\mathbf{R}_i$ of the nuclei are consistent with a given space group and wyckoff positions.

Implications for forces ?

➔ If your DFT code imposes symmetry, then only atoms with freedom in their wyckoff positions can move (=can be subject to forces). Any other motion would alter the symmetry.

Quantum forces

Example for $P4_2/mnm$ (nr. 136):

Wyckoff Positions of Group 136 ($P4_2/mnm$)

Multiplicity	Wyckoff letter	Site symmetry	Coordinates
16	k	1	(x,y,z) (-x,-y,z) (-y+1/2,x+1/2,z+1/2) (y+1/2,-x+1/2,z+1/2) (-x+1/2,y+1/2,-z+1/2) (x+1/2,-y+1/2,-z+1/2) (y,x,-z) (-y,-x,-z) (-x,-y,-z) (x,y,-z) (y+1/2,-x+1/2,-z+1/2) (-y+1/2,x+1/2,-z+1/2) (x+1/2,-y+1/2,z+1/2) (-x+1/2,y+1/2,z+1/2) (-y,-x,z) (y,x,z)
8	j	.m	(x,x,z) (-x,-x,z) (-x+1/2,x+1/2,z+1/2) (x+1/2,-x+1/2,z+1/2) (-x+1/2,x+1/2,-z+1/2) (x+1/2,-x+1/2,-z+1/2) (x,x,-z) (-x,-x,-z)
8	i	m.	(x,y,0) (-x,-y,0) (-y+1/2,x+1/2,1/2) (y+1/2,-x+1/2,1/2) (-x+1/2,y+1/2,1/2) (x+1/2,-y+1/2,1/2) (y,x,0) (-y,-x,0)
8	h	2.	(0,1/2,z) (0,1/2,z+1/2) (1/2,0,-z+1/2) (1/2,0,-z) (0,1/2,-z) (0,1/2,-z+1/2) (1/2,0,z+1/2) (1/2,0,z)
4	g	m 2 m	(x,-x,0) (-x,x,0) (x+1/2,x+1/2,1/2) (-x+1/2,-x+1/2,1/2)
4	f	m 2 m	(x,x,0) (-x,-x,0) (-x+1/2,x+1/2,1/2) (x+1/2,-x+1/2,1/2)
4	e	2 m m	(0,0,z) (1/2,1/2,z+1/2) (1/2,1/2,-z+1/2) (0,0,-z)
4	d	-4.	(0,1/2,1/4) (0,1/2,3/4) (1/2,0,1/4) (1/2,0,3/4)
4	c	2/m.	(0,1/2,0) (0,1/2,1/2) (1/2,0,1/2) (1/2,0,0)
2	b	m.m m	(0,0,1/2) (1/2,1/2,0)
2	a	m.m m	(0,0,0) (1/2,1/2,1/2)

Quantum forces

Example for $P4_2/mnm$ (nr. 136):

Take Hg_2Na_3 and TiO_2 , which both have this space group :

- Search their cif in COD
- Look into WYCKPOS (Bilbao) [see previous slide] and identify wyckoff positions
- Visualize it with vesta/jmol/xcrysden
- Inspect the wyckoff positions: fixed by symmetry or not ?

Quantum forces

TiO_2 :

Ti	2	a	m.m m	(0,0,0) (1/2,1/2,1/2)
O	4	f	m.2 m	(x,x,0) (-x,-x,0) (-x+1/2,x+1/2,1/2) (x+1/2,-x+1/2,1/2)

Hg_2Na_3 :

Hg	8	j	..m	(x,x,z) (-x,-x,z) (-x+1/2,x+1/2,z+1/2) (x+1/2,-x+1/2,z+1/2) (-x+1/2,x+1/2,-z+1/2) (x+1/2,-x+1/2,-z+1/2) (x,x,-z) (-x,-x,-z)
Na-1	4	c	2/m..	(0,1/2,0) (0,1/2,1/2) (1/2,0,1/2) (1/2,0,0)
Na-2	4	f	m.2 m	(x,x,0) (-x,-x,0) (-x+1/2,x+1/2,1/2) (x+1/2,-x+1/2,1/2)
Na-3	4	g	m.2 m	(x,-x,0) (-x,x,0) (x+1/2,x+1/2,1/2) (-x+1/2,-x+1/2,1/2)