Modelling Clusters of Lone-Pair Cation Containing Compounds by Embedded Localised Atomic Orbital Approach

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On today's talk

- **How to model sp-lone pair cations?**

  research motivation

  modelling idea: the effective valence state of lone pair cations
- **Development of the lone pair model**

  localised atomic orbital approach and it's integration to a traditional interatomic potential method

  model-adapted algorithms, details of energy and derivatives
- **Model application results**

  a single Sn(II) cation in BaO nanocluster as a defect

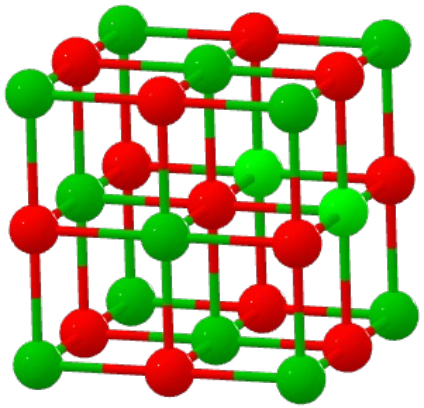
  characterisation of nanoclusters, PbO and PbF_2

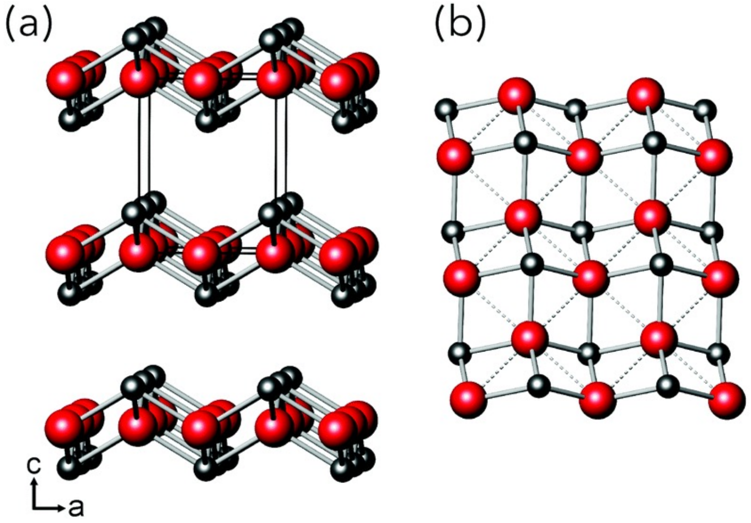
Structural distortions caused by stereo-actice lone pairs

What makes the structures of materials including lone pair cations different?

Sn(II), Pb(II), Bi(III) etcs. with electronic configuration of **d^{10}** **s^2p^0**

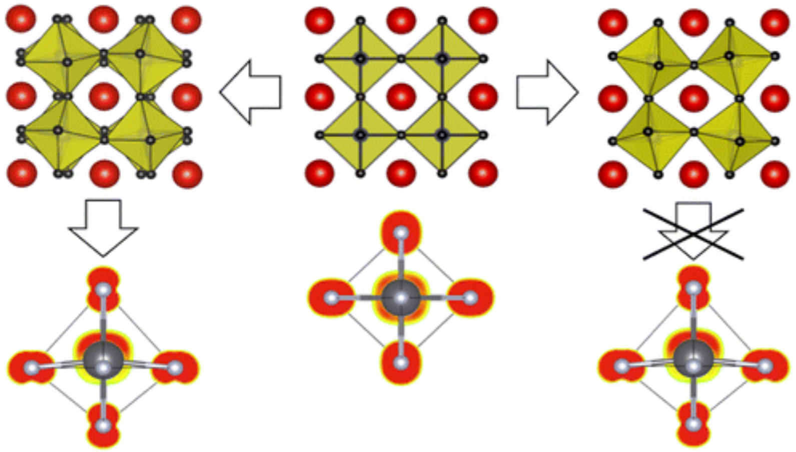
Hybridisation of s and p results in stereo-active lone pair lobes (valence state)





Structure of binary oxides: SnO and PbO [1]
Ball-and-stick model (black Sr/Pb and red O)

Crystal structures of alkali earth metal oxides:
SrO and BaO
c.f. ionic radii of
Sr(II) 132pm < Pb(II) 133pm < Ba(II) 149pm



lone pair induced distortions in halide perovskites [2]

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[1] Miller et. Al; J. Mater. Chem. C., 2017, 5. 10.1039
[2] E. H. Smith et. al; *Inorg. Chem*., 2015, 54, 8536–8543

Traditional Interatomic potential method

Modelling sp-lone pair cations using interatomic potential methods?

$$E_{\text{spherical}} = \sum_{i,j} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + A_{ij}\exp(-r_{ij}/\rho_{ij}) - \frac{C_{ij}}{r_{ij}^6}$$

Eq 1. Coulomb + Buckingham potential

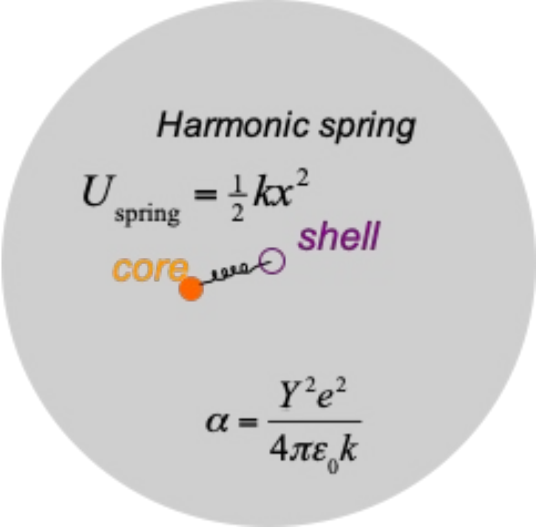
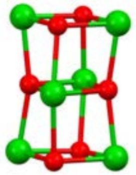

Harmonic spring
$U_{\text{spring}} = \frac{1}{2}kx^2$
shell
core
$\alpha = \frac{Y^2e^2}{4\pi\varepsilon_0 k}$

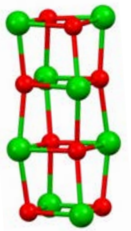
Fig 1. schematic diagram of an ion represented by the shell model

Typically, consists of:

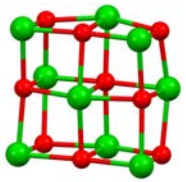
- Coulombic interaction between points charges (*q*)
- Buckingham / Born-Mayer potential (size of ions)
- **Shell model (two points charges per atom; polarisability of ions)**



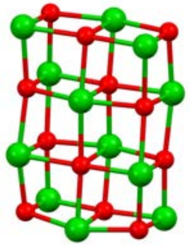
$(BaO)_6$



$(BaO)_8$



$(BaO)_9$



$(BaO)_{12}$

Possible limitations

- Polarisability of an ion shows only a linear responses and fitted for ions within to perfect bulk phase
- Struggles to model materials composed of ions those non-spherical shape depends on its environment [1]

New lone pair model

- should give a better physical description than the shell model.
  In particular, lone pair cations, highly polarisable.
- be computationally more affordable than the full electronic structure methods.

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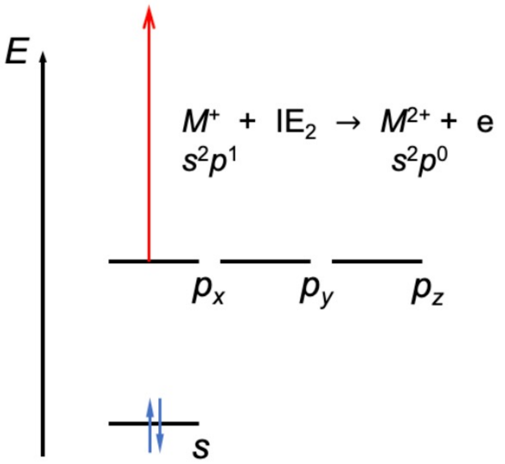
[1] *J. Phys. Chem. B* 2001, *105,* 6824-6830

Modelling sp-lone pair cations: embedding atomic orbtials

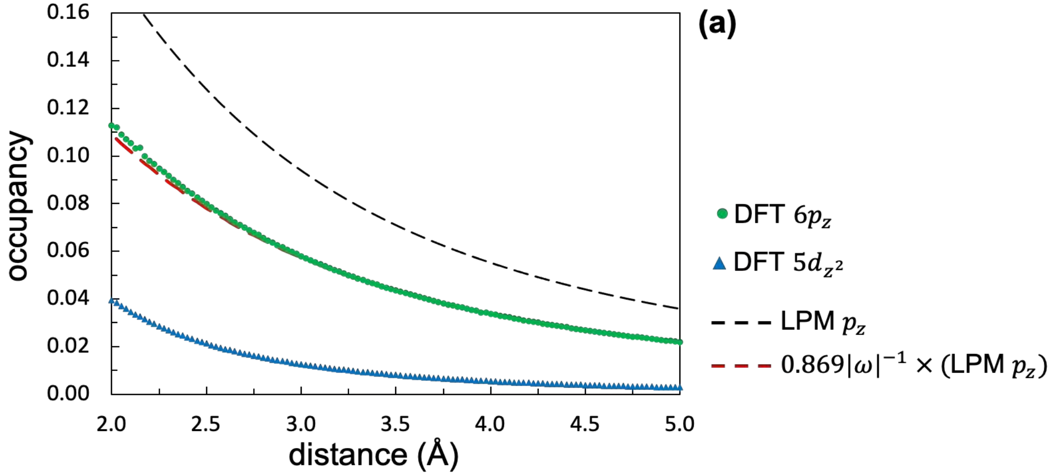
Sn(II), Pb(II), Bi(III) etcs. with electronic configuration of d^{10} **s^2p^0**
Modelling the **effective valence state** with **localised atomic orbital approach**

$$|\psi\rangle = c_1|s\rangle + c_2|p_x\rangle + c_3|p_y\rangle + c_4|p_z\rangle$$



(a) The second ionisation and the ground state of M^{2+}

Two-level system



Effective valence state of a lone pair cation
orbital occupancy of Pb(II) cation interacting with a point charge(e) as a function of their separation distance; calculated by DFT and LPM (lone pair model).

Modelling sp-lone pair cations : embedding atomic orbtials

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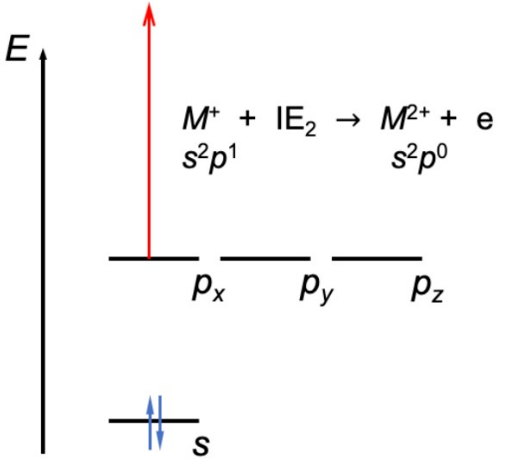


(a) The second ionisation and the ground state of M^{2+}

Two-level system

Energy of a lone pair:

$$E_{\mathrm{LP}} = \langle\psi|\widehat{\mathrm{H}}|\psi\rangle$$

$$E_{\mathrm{LP}} = \sum_{\mu,\nu} c_\mu c_\nu \langle\mu|\widehat{\mathrm{H}}|\nu\rangle = \sum_{\mu,\nu} c_\mu c_\nu H_{\mu\nu}$$

where $\widehat{\mathrm{H}} = \widehat{\mathrm{H}}^0 + \widehat{\mathrm{H}}^1$.

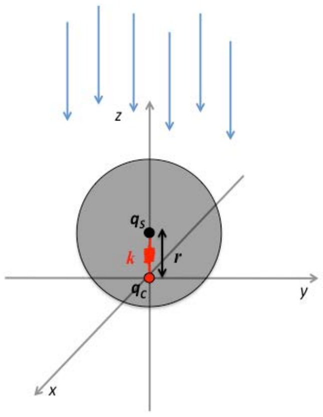
Fitting parameter, **λ**

$$H^0_{\mu\nu} \equiv \langle\mu|\widehat{\mathrm{H}}^0|\nu\rangle = \begin{cases} \lambda, & \text{if } \mu = \nu = p_x, p_y \text{ and } p_z \\ 0, & \text{otherwise.} \end{cases}$$

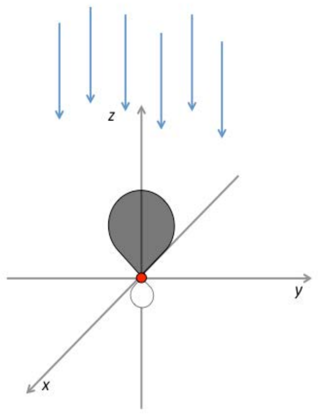
Modelling sp-lone pair cations: lone pair polarisabilities

Comparison with the classical shell model

$\widehat{\mathrm{H}}^1 \rightarrow$ const. Electric field (*F*)



SM



LPM

Energy

$$E(F) = \frac{1}{2}\left(\lambda - \sqrt{\lambda^2 + 4u^2F^2\omega^2}\right)$$

Dipole

$$\mu(F) = -\frac{\partial E}{\partial F} = \frac{2u^2\omega^2F}{(\lambda^2 + 4u^2F^2\omega^2)^{1/2}}$$

Dipole-polarisability

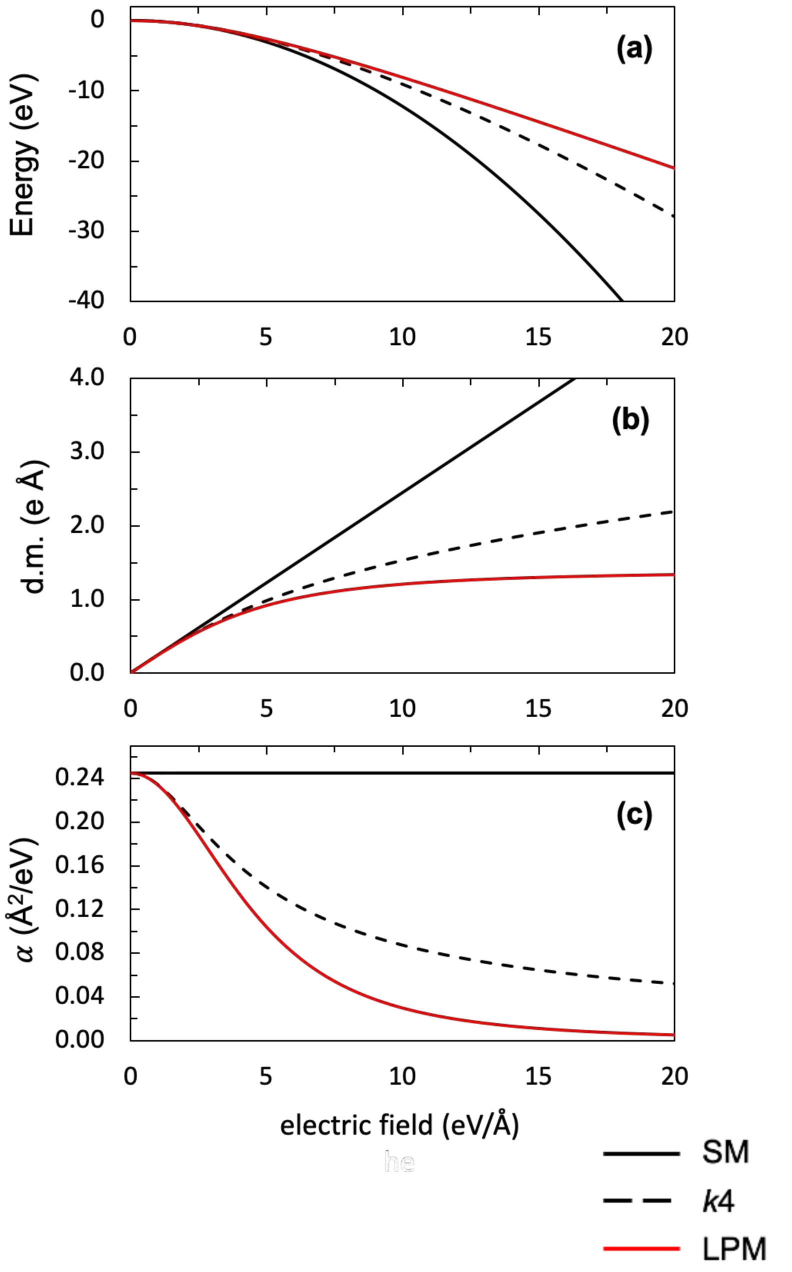
$$\alpha(F) = \frac{\partial \mu}{\partial F} = \frac{2u^2\lambda^2\omega^2}{(\lambda^2 + 4u^2F^2\omega^2)^{3/2}}$$

Hyper polarisability

$$\beta(F) = \frac{\partial \alpha}{\partial F} = -\frac{24u^4\lambda^2\omega^4F}{(\lambda^2 + 4u^2F^2\omega^2)^{5/2}}$$

Second hyper polarisability

$$\gamma(F) = \frac{\partial \beta}{\partial F} = -\frac{24\lambda^2(u^4\lambda^2\omega^4 - 16u^6F^2\omega^4)}{(\lambda^2 + 4u^2F^2\omega^2)^{7/2}}$$



Non-linear dipole-polarisability

Potentially useful, application in environments where electric fields are in-homogenous (e.g., as a defect – a single dilute dopant, surface etc.).

LPM response to constant electric field (*F*)

Including various higher-order effects

Modelling sp-lone pair cations: energy of lone pairs

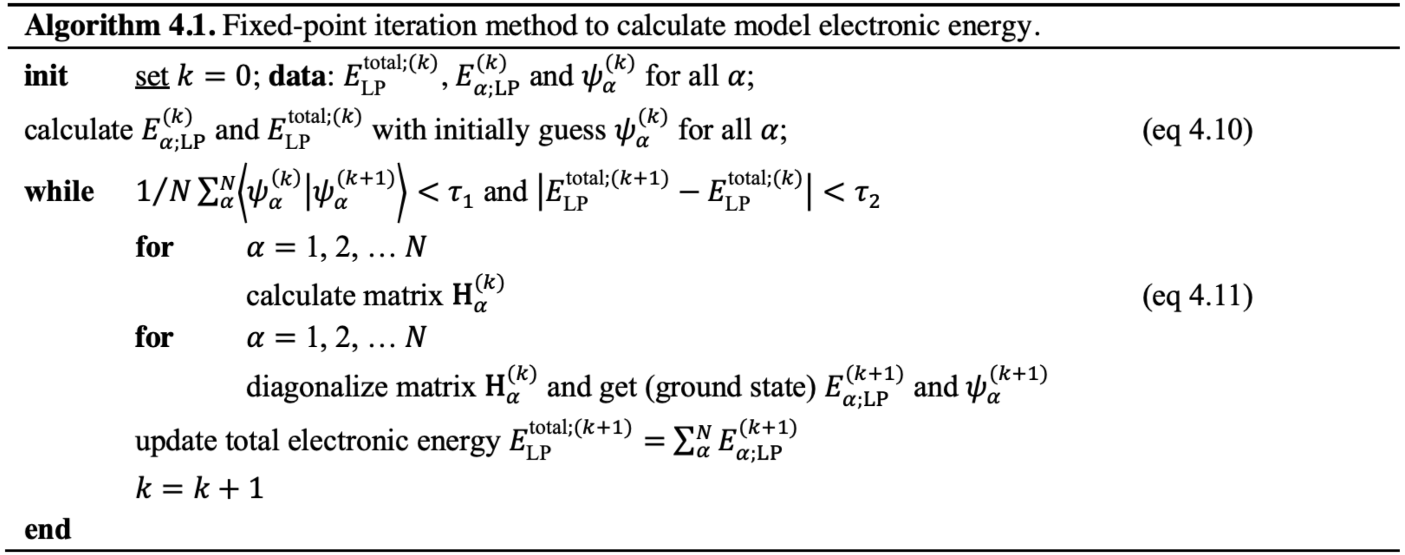
System including lone pair cations and other species

Total energy contribution by lone pairs

Energy of a lone pair

$$E_{\mathrm{LP}}^{\mathrm{total}} = \sum_{\alpha} E_{\alpha;\mathrm{LP}} = \sum_{\alpha} \langle \psi_\alpha | \widehat{\mathrm{H}}_\alpha | \psi_\alpha \rangle$$

Energy Calculation Algorithm – Self Consistent Field method

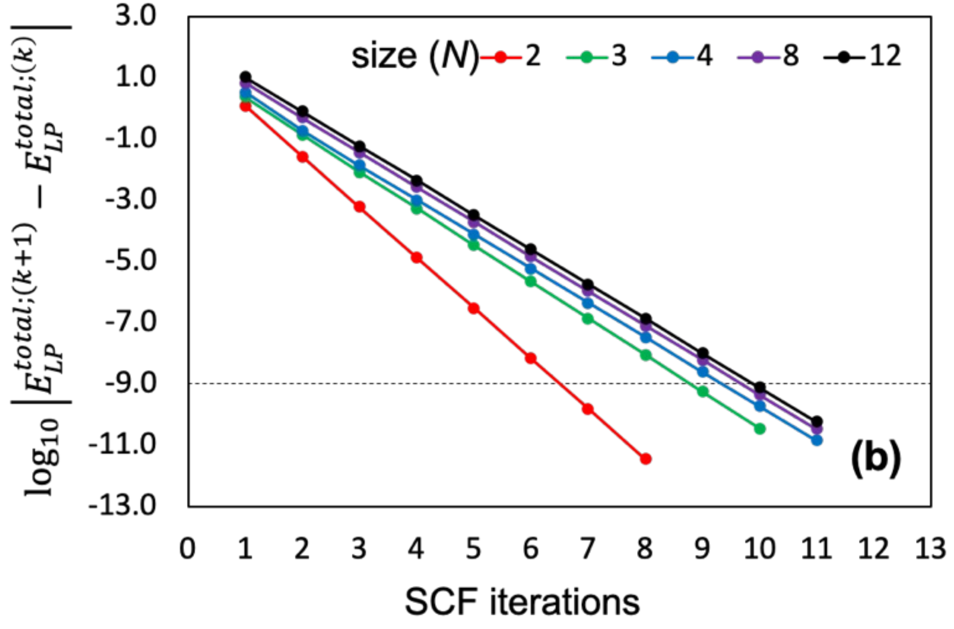


Algorithm 4.1. Fixed-point iteration method to calculate model electronic energy.

```
init    set $k = 0$; data: $E_{\mathrm{LP}}^{\mathrm{total};(k)}$, $E_{\alpha;\mathrm{LP}}^{(k)}$ and $\psi_\alpha^{(k)}$ for all $\alpha$;
calculate $E_{\alpha;\mathrm{LP}}^{(k)}$ and $E_{\mathrm{LP}}^{\mathrm{total};(k)}$ with initially guess $\psi_\alpha^{(k)}$ for all $\alpha$;        (eq 4.10)
while   $1/N \sum_\alpha^N \langle \psi_\alpha^{(k)} | \psi_\alpha^{(k+1)} \rangle < \tau_1$ and $|E_{\mathrm{LP}}^{\mathrm{total};(k+1)} - E_{\mathrm{LP}}^{\mathrm{total};(k)}| < \tau_2$
        for     $\alpha = 1, 2, \dots N$
                calculate matrix $\mathbf{H}_\alpha^{(k)}$        (eq 4.11)
        for     $\alpha = 1, 2, \dots N$
                diagonalize matrix $\mathbf{H}_\alpha^{(k)}$ and get (ground state) $E_{\alpha;\mathrm{LP}}^{(k+1)}$ and $\psi_\alpha^{(k+1)}$
        update total electronic energy $E_{\mathrm{LP}}^{\mathrm{total};(k+1)} = \sum_\alpha^N E_{\alpha;\mathrm{LP}}^{(k+1)}$
        $k = k + 1$
end
```

Generalised model for N number of lone pair cations

Model requires the Self-Consistent Field algorithm.



Numerical experiments of the SCF method
Linear profile on a logarithmic scale

Modelling sp-lone pair cations: derivatives of the energy of lone pairs

System including lone pair cations and other species

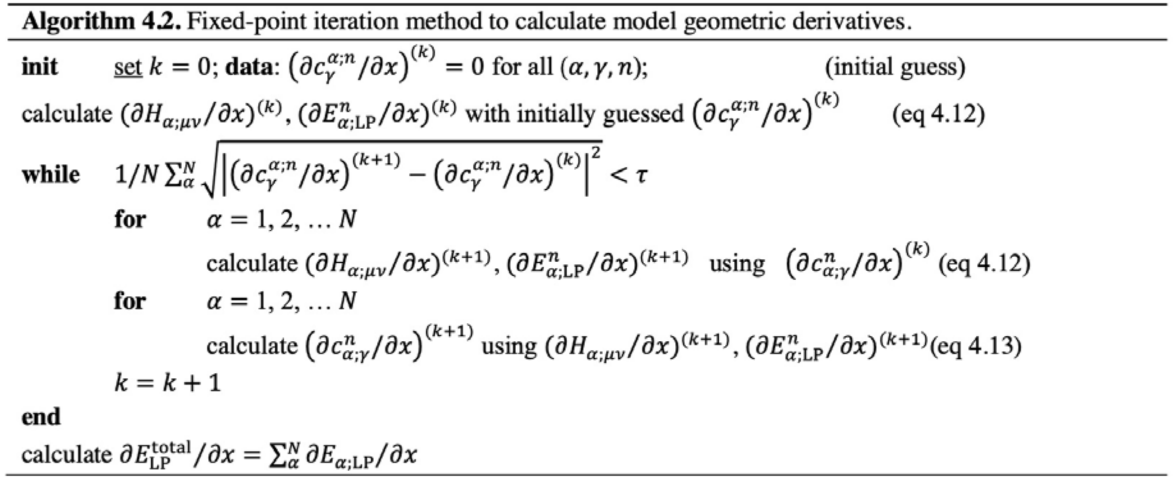
changes in molecular orbital

$$\frac{\partial E_{\mathrm{LP}}^{\mathrm{total}}}{\partial x} = \sum_{\alpha} \frac{\partial E_{\alpha;\mathrm{LP}}}{\partial x} = \sum_{\alpha} \sum_{\mu,\nu} c_{\mu}^{\alpha} c_{\nu}^{\alpha} \left[\sum_{A} \frac{\partial H_{\alpha A;\mu\nu}^{MM}}{\partial x} + \sum_{\beta \neq \alpha} \sum_{\lambda,\sigma} \left\{ \left(\frac{\partial c_{\lambda}^{\beta}}{\partial x} \right) c_{\sigma}^{\beta} \langle \mu_{\alpha} | \widetilde{\Phi}_{\alpha\beta;\lambda\sigma} | \nu_{\alpha} \rangle + \frac{1}{2} c_{\lambda}^{\beta} c_{\sigma}^{\beta} \left\langle \mu_{\alpha} \middle| \frac{\partial \widetilde{\Phi}_{\alpha\beta;\lambda\sigma}}{\partial x} \middle| \nu_{\alpha} \right\rangle \right\} \right]$$

Coupled perturbed Hartree-Fock equation

$$\frac{\partial c_{\gamma}^{\alpha;n}}{\partial x} = \sum_{m \neq n} \sum_{\mu,\nu} \frac{c_{\mu}^{\alpha;m} c_{\gamma}^{\alpha;m} c_{\nu}^{\alpha;n}}{E_{\alpha;\mathrm{LP}}^{m} - E_{\alpha;\mathrm{LP}}^{n}} \left(\frac{\partial E_{\alpha;\mathrm{LP}}^{n}}{\partial x} \delta_{\mu\nu} - \frac{\partial H_{\alpha;\mu\nu}}{\partial x} \right)$$

Force Calculation Algorithm



Algorithm 4.2. Fixed-point iteration method to calculate model geometric derivatives.

```
init      set $k = 0$; data: $(\partial c_{\gamma}^{\alpha;n}/\partial x)^{(k)} = 0$ for all $(\alpha, \gamma, n)$;          (initial guess)
calculate $(\partial H_{\alpha;\mu\nu}/\partial x)^{(k)}, (\partial E_{\alpha;\mathrm{LP}}^{n}/\partial x)^{(k)}$ with initially guessed $(\partial c_{\gamma}^{\alpha;n}/\partial x)^{(k)}$     (eq 4.12)
while     $1/N \sum_{\alpha}^{N} \sqrt{|(\partial c_{\gamma}^{\alpha;n}/\partial x)^{(k+1)} - (\partial c_{\gamma}^{\alpha;n}/\partial x)^{(k)}|^2} < \tau$
          for    $\alpha = 1, 2, \ldots N$
                 calculate $(\partial H_{\alpha;\mu\nu}/\partial x)^{(k+1)}, (\partial E_{\alpha;\mathrm{LP}}^{n}/\partial x)^{(k+1)}$ using $(\partial c_{\alpha;\gamma}^{n}/\partial x)^{(k)}$ (eq 4.12)
          for    $\alpha = 1, 2, \ldots N$
                 calculate $(\partial c_{\alpha;\gamma}^{n}/\partial x)^{(k+1)}$ using $(\partial H_{\alpha;\mu\nu}/\partial x)^{(k+1)}, (\partial E_{\alpha;\mathrm{LP}}^{n}/\partial x)^{(k+1)}$(eq 4.13)
          $k = k + 1$
end
calculate $\partial E_{\mathrm{LP}}^{\mathrm{total}}/\partial x = \sum_{\alpha}^{N} \partial E_{\alpha;\mathrm{LP}}/\partial x$
```

Once the energy and derivatives obtained
Its binding with local optimiser (BFGS, LS etc) is straightforward.

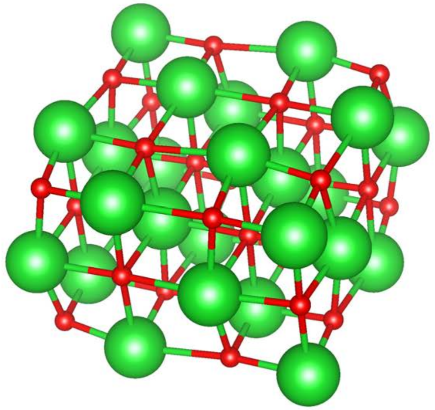
Simple iteration method

$$\mathbf{B}\,\mathbf{c}^{(k)} + \mathbf{d} = \mathbf{c}^{(\mathrm{k}+1)}$$

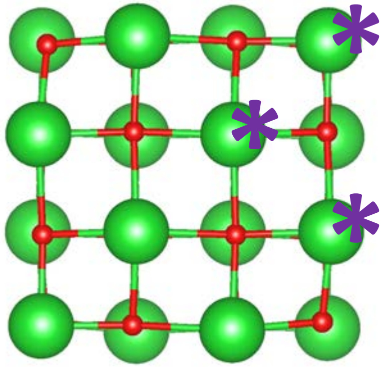
where the unknowns are in the vector **c**, and the iterative method generates a sequence of approximations, $\mathbf{c}^{(1)}$,$\mathbf{c}^{(2)}$, … with initially guessed $\mathbf{c}^{(0)}$ until the approximation meets the termination criteria.

Model application I.

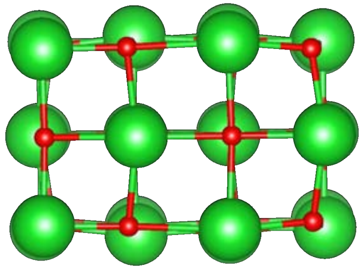
Creating a single Sn(II) defect on BaO nanoclusters



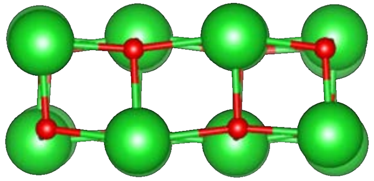
nanocluster structure of $(BaO)_{24}$[1]
Ball-and-stick model (green Ba / red O)
(4 x 4 x 3 slab)



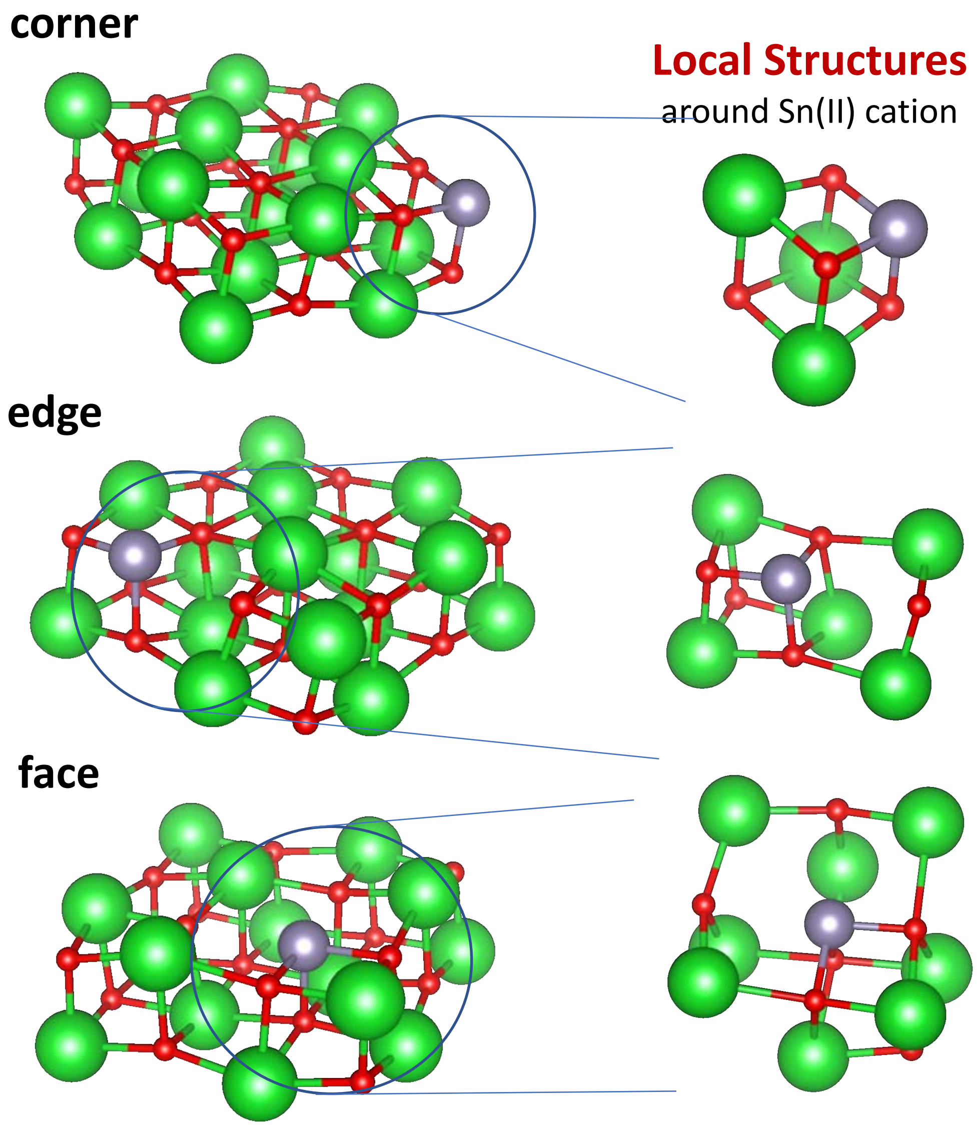
4 x 4 x 2 slab
top view



4 x 4 x 3 slab
side view



4 x 4 x 2 slab
side view



Local Structures

around Sn(II) cation

computational detail.
BaO IP parameters [2] + lone pair model Sn(II)

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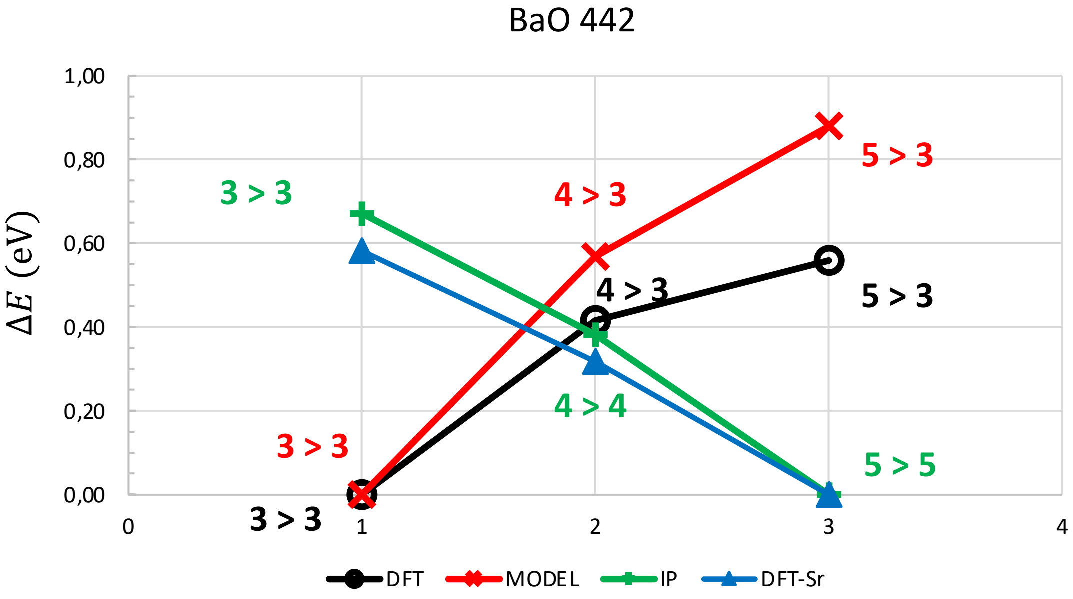
[1] S.G.E.T. Escher, T. Lazauskas, M.A. Zwijnenburg, S.M. Woodley, Comput. Theor. Chem 1107 (2017) 74–81
[2] Y. Z. Wang et. al,. *J. Phys. Chem. C* 2009, *113,* 20486–20492

Model application I.

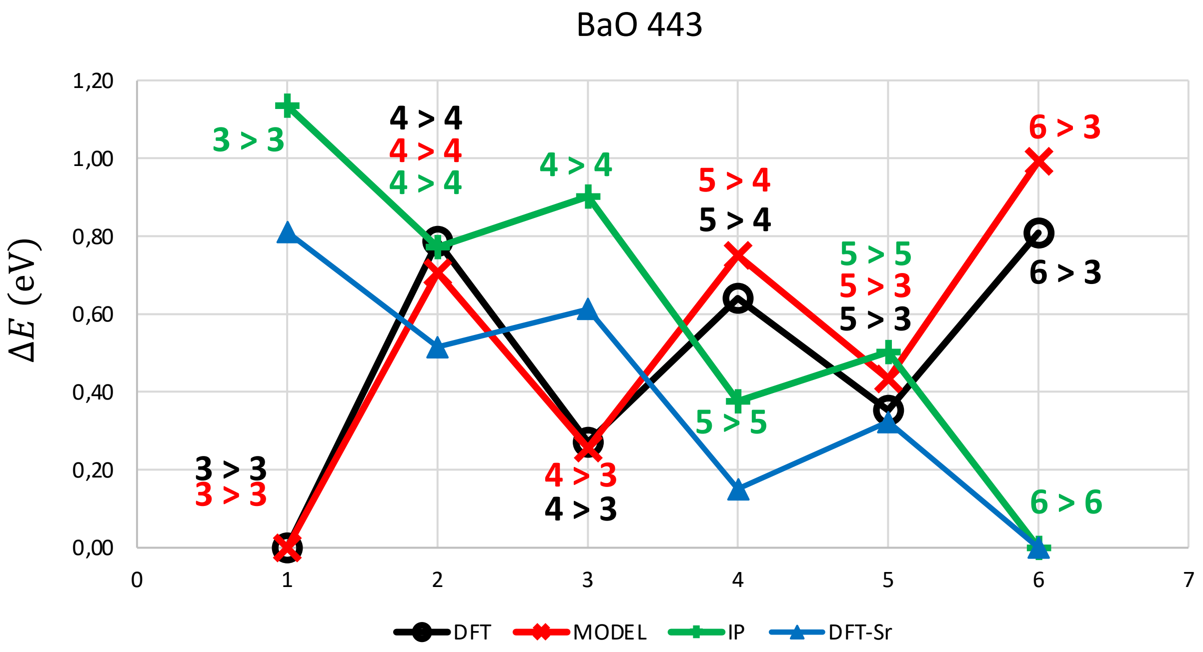
Creating a single Sn(II) defect on BaO nanoclusters

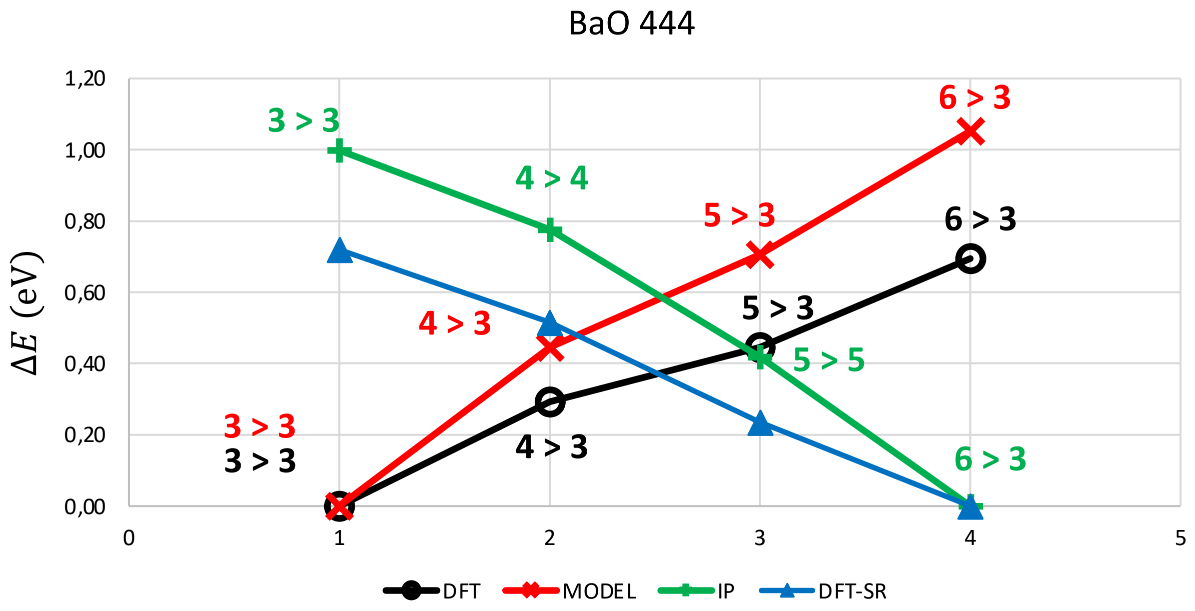


Example BaO 442 - 1: corner, 2: edge and 3: face

Coordination number Sn(II) or equivalent changes (*N* > *M*)

ΔE to create Sn(II) or Sr(II) defect – relative energy





computational detail.

DFT – FHIaims2018, intermediate basis, pbesol xc.

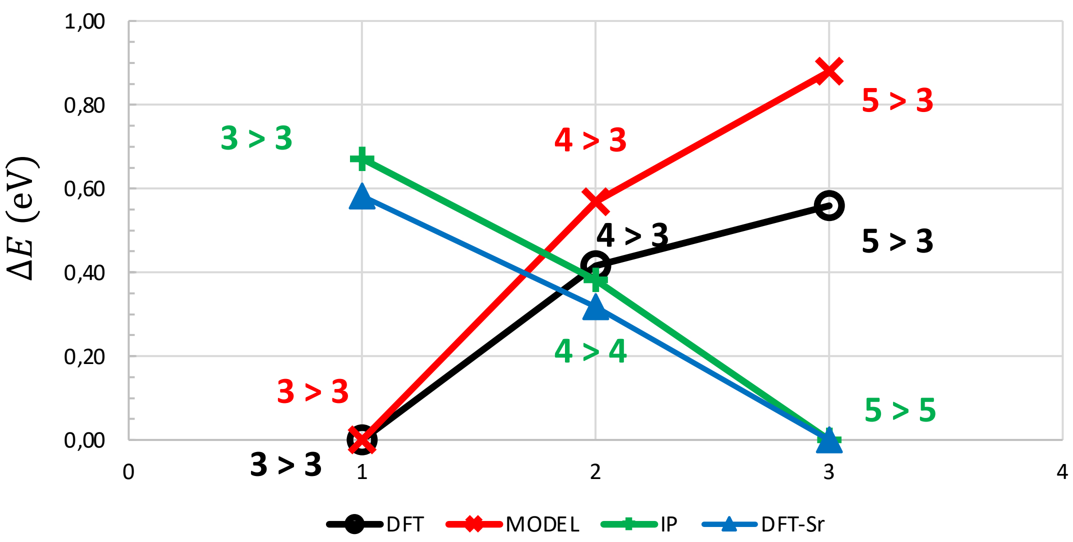
MODEL - BaO IP parameters [2] + lone pair model model Sn(II)

IP (shell model) - BaO IP paramters + SnO bulk IP parameters

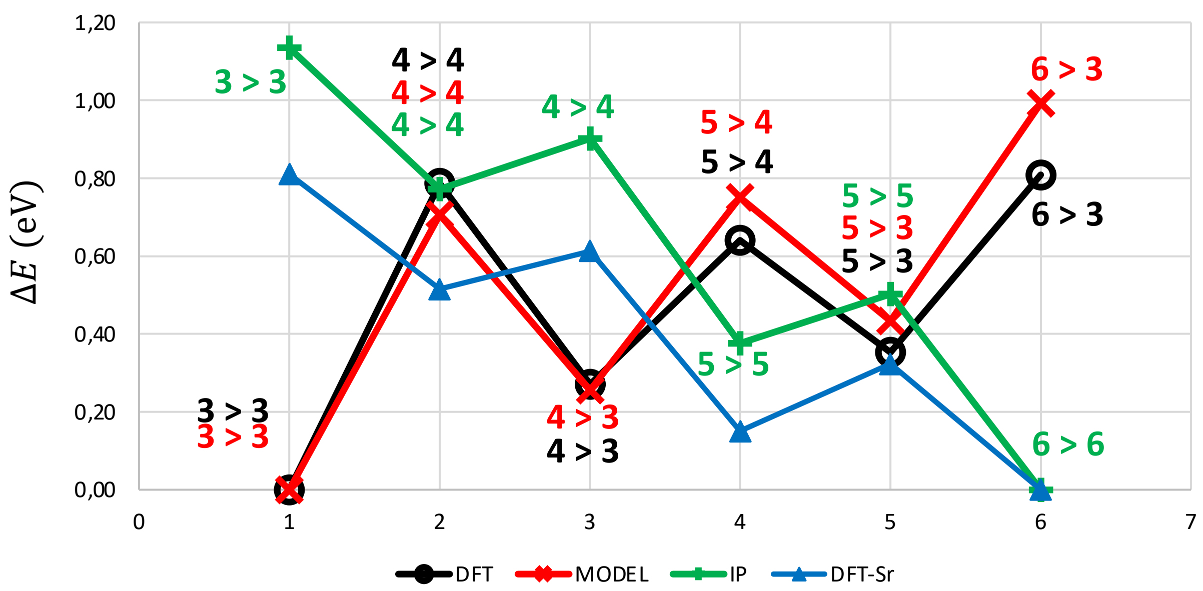
Model application I.

Creating a single Sn(II) defect on BaO nanoclusters

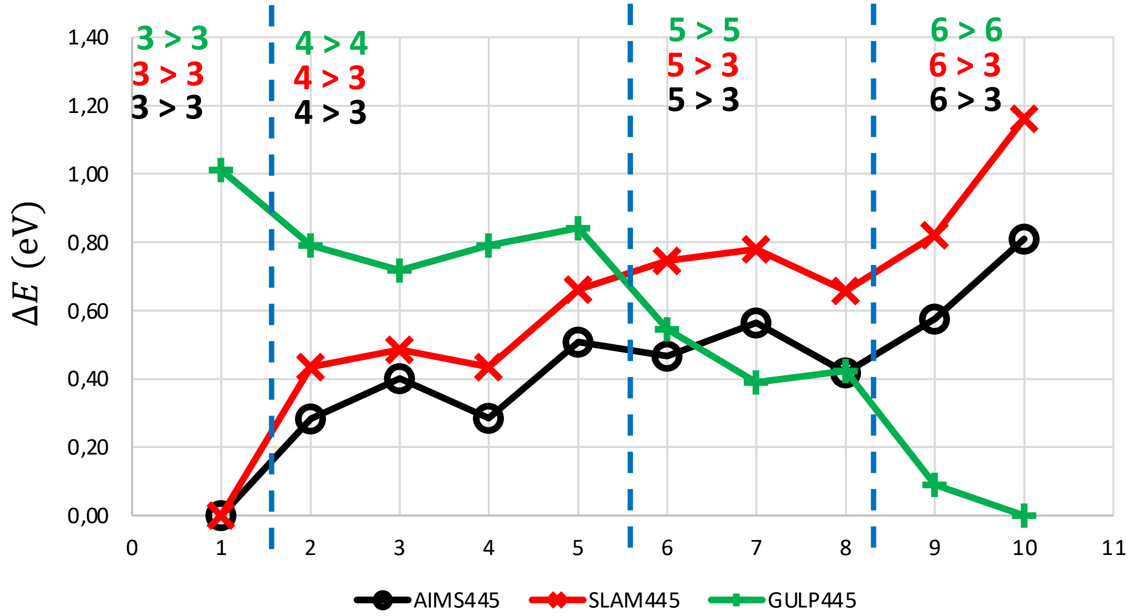
BaO 442



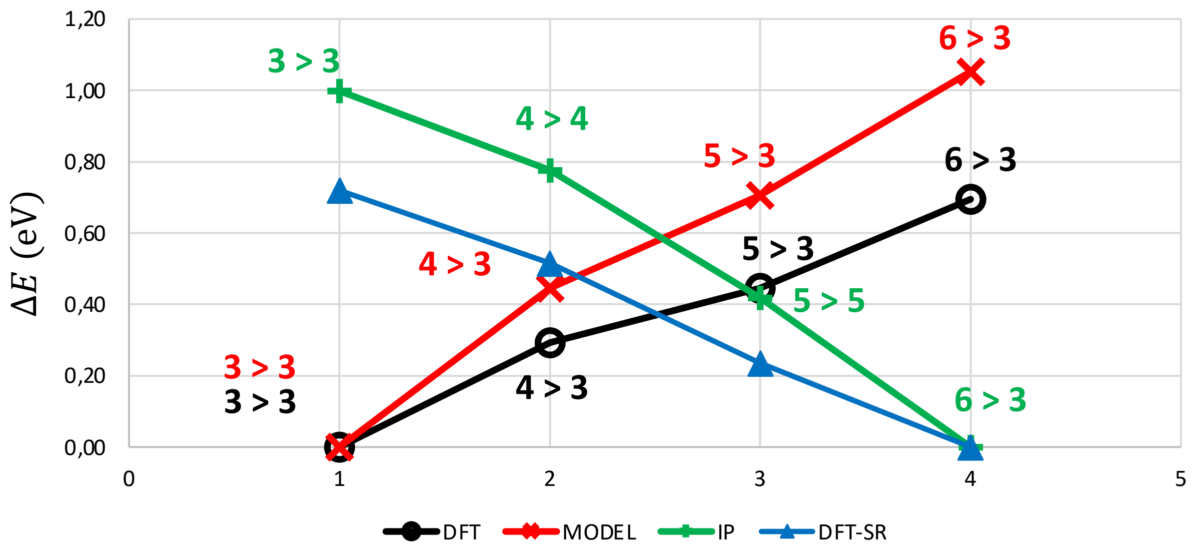
BaO 443



BaO 445



BaO 444



Model application I.

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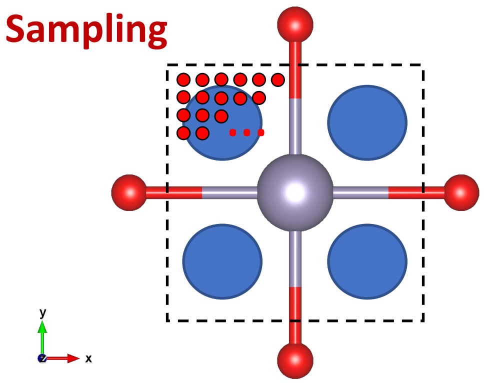
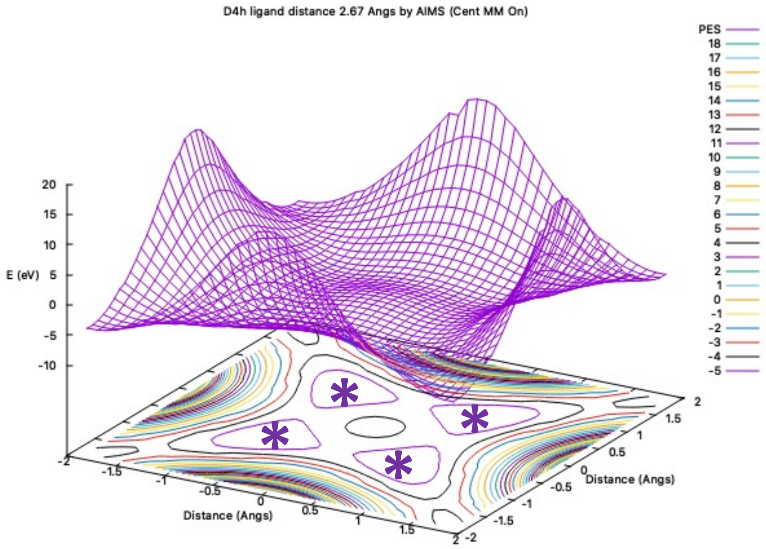


Sn(II) (grey ball) in surrounded by 4 O anions (red balls)

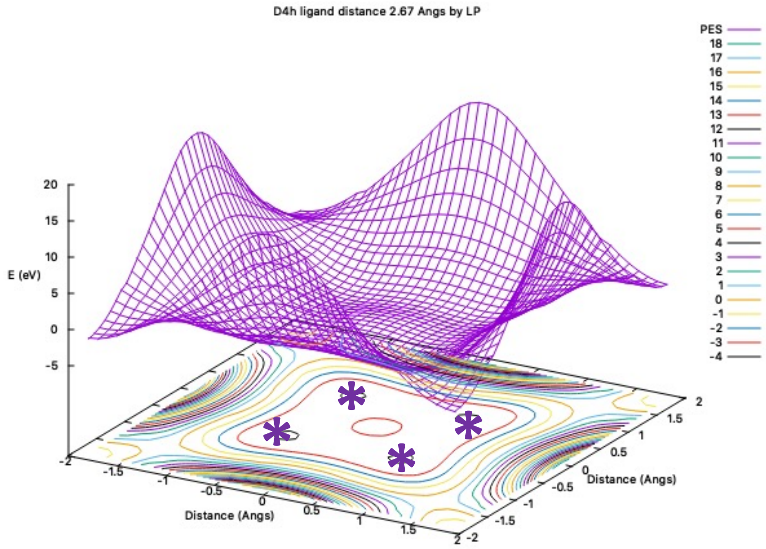
Investigating the effect of lone pair – energy landscape of a simple toy system. Bond distance Sn-O set to 2.67 Å (same with 6 x 6 x 4 BaO nanocluster).

Sn(II) cation is placed on various sample points (marked by red dots).

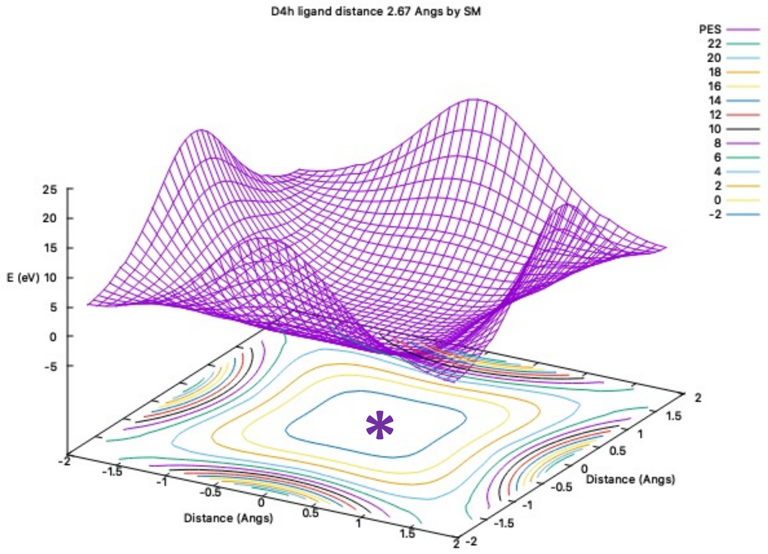
- **DFT** and **lone pair model** show four local minima around the vertices lone pair lobe occupies the centre area instead



DFT



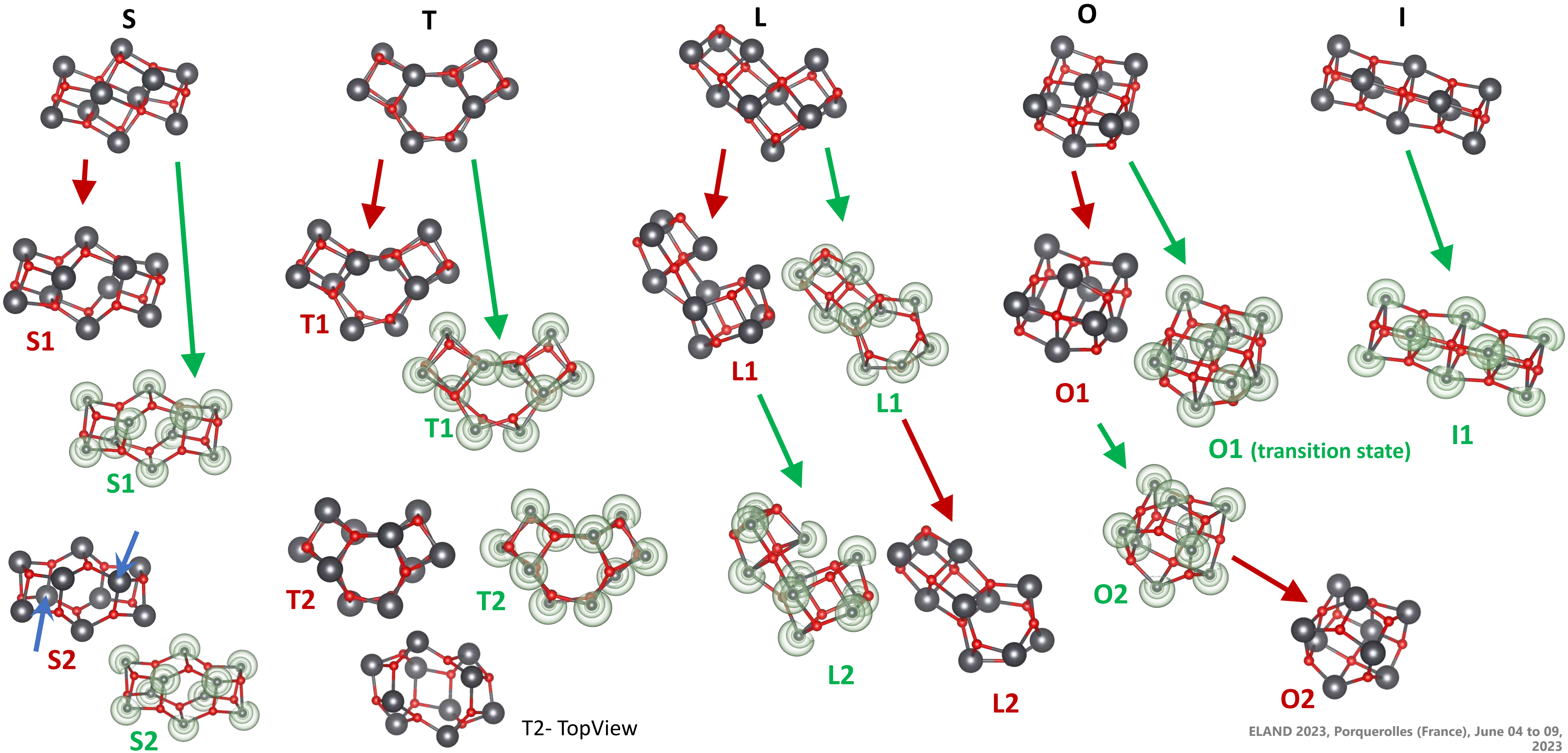
lone pair model



shell model

Model application II. Characterisation of nanoclusters PbO, ball-and-stick model (black Pb and red O)

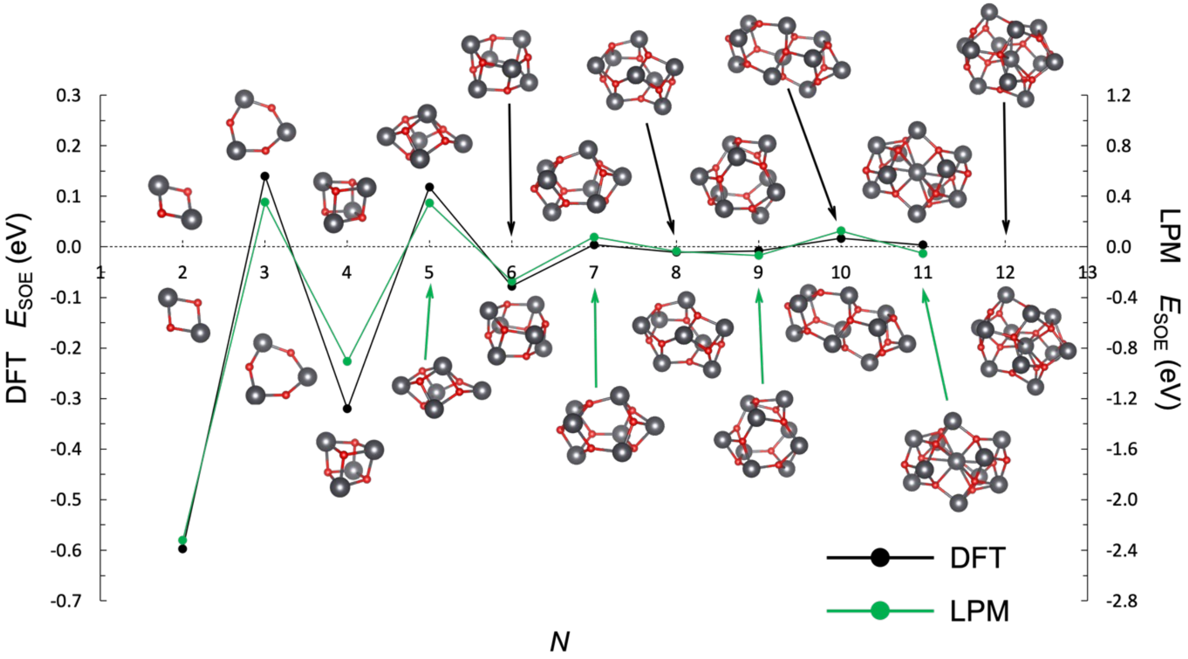
Optimising **tetromino structures** on energy landscapes of the **DFT** and the **Lone pair model**


S
T
L
O
I
S1
S1
T1
T1
L1
L1
O1
O1 (transition state)
I1
S2
S2
T2
T2
T2- TopView
L2
L2
O2
O2

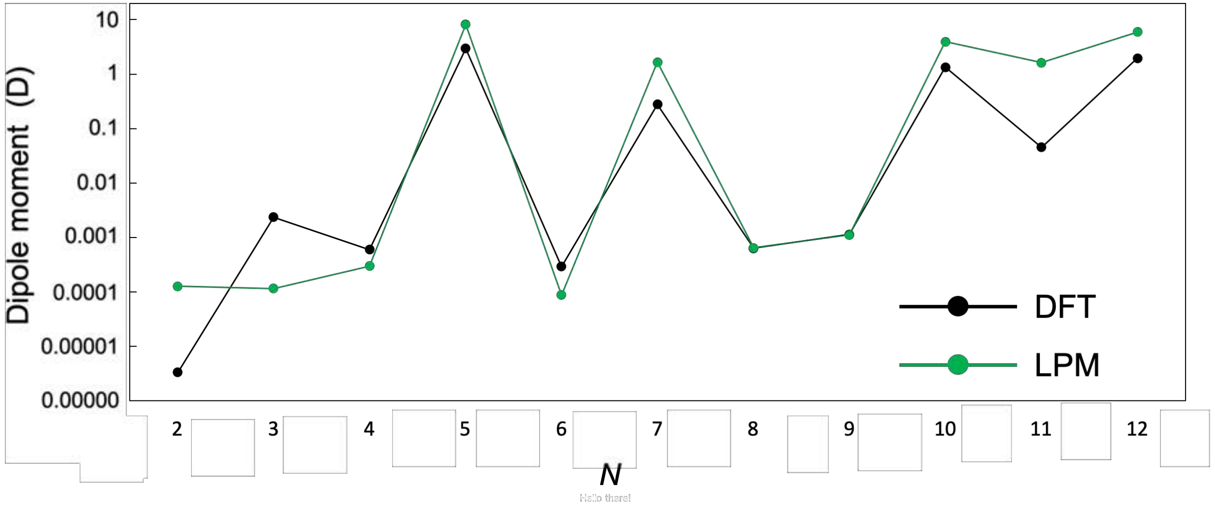
Model application II. Characterisation of nanoclusters PbO

Global optimisation results of the lone pair model

- Random quenching method used: (1) RIM population generation / (2) RIM→LPM refinement / (3) LPM→DFT refinement



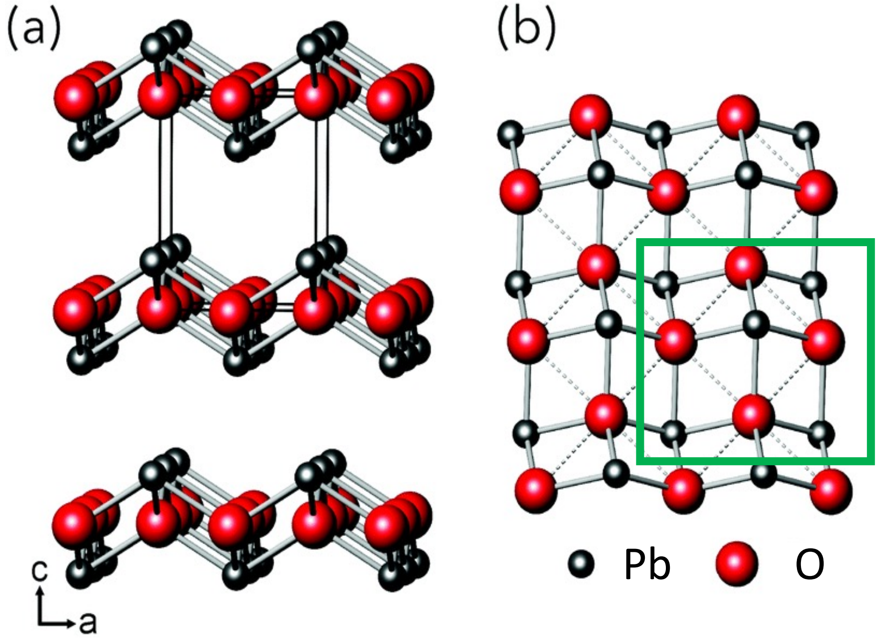
second-order energies of global minimum structures of $(PbO)_N$ nanoclusters characterised by the lone pair model (**LPM**), down, and **DFT**, up.



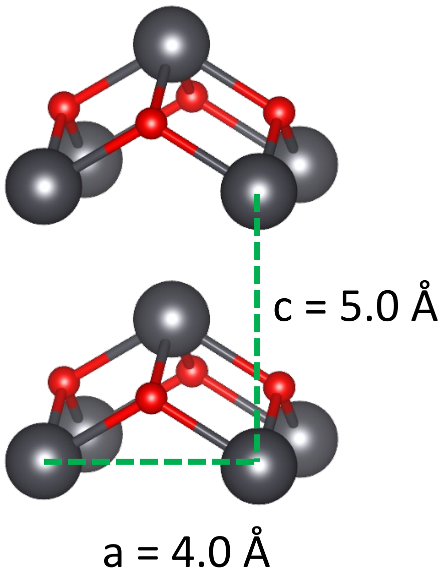
dipole moments of global minimum structures of $(PbO)_N$ calculated by the lone pair model (**LPM**), down, and **DFT**, up.

Model application II. Characterisation of nanoclusters PbO

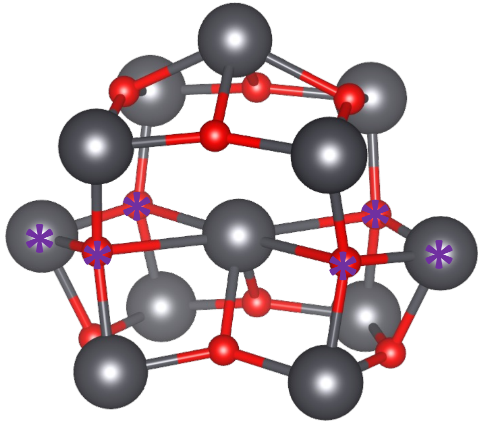
Possible building blocks of the crystal α-PbO structure ?



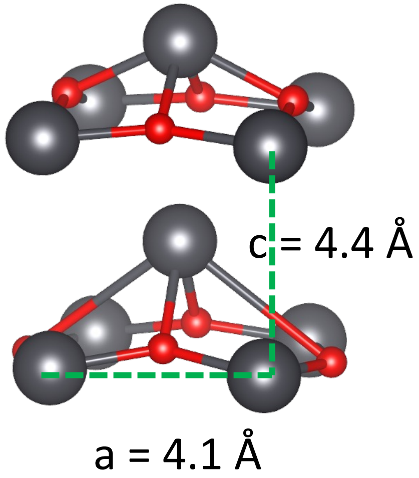
Structure α-PbO [1]
Ball-and-stick model (black Pb and red O)



double layer cut
$Pb_{10}O_8$
Not charge neutral !



3rd LM cluster of
$(PbO)_{12}$
$Pb_{10}O_8 + 2 \times (Pb_1O_2)$

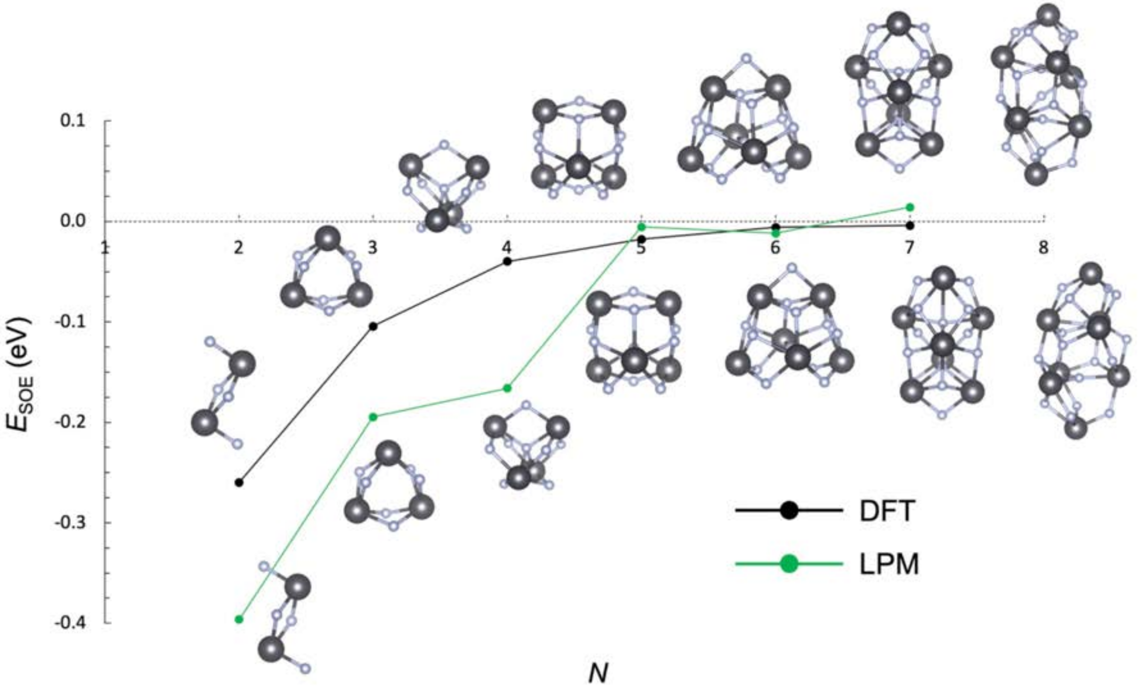


$Pb_{10}O_8$

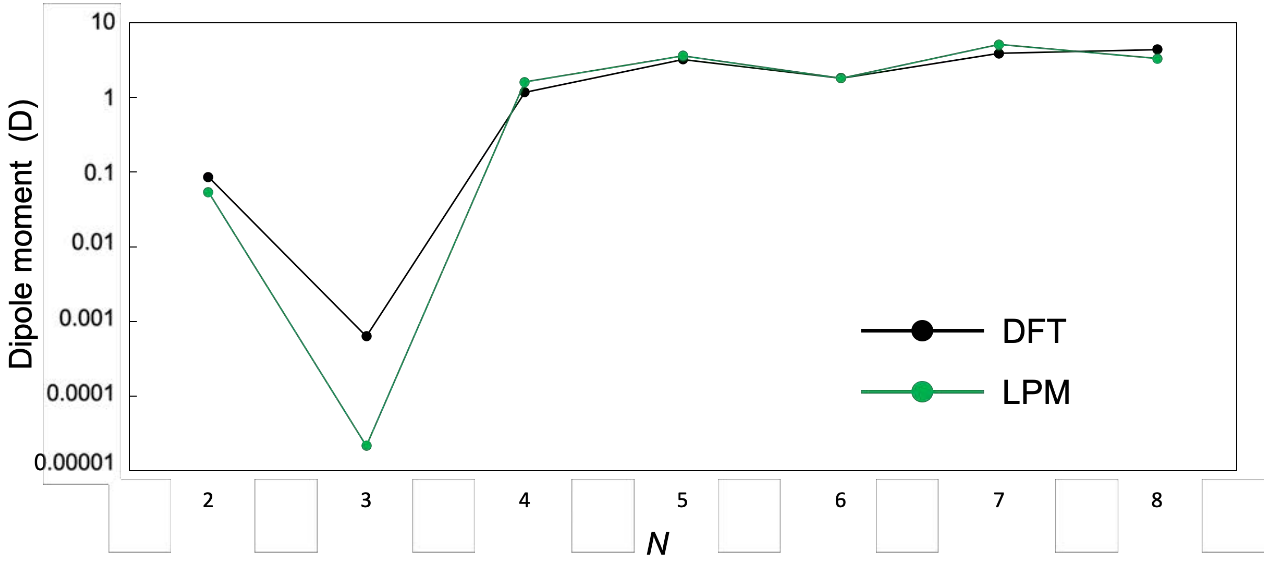
Model application II. Characterisation of nanoclusters PbF_2, (black Pb and grey F)

Global optimisation results of the lone pair model

- Random quenching method used: (1) RIM population generation / (2) RIM→LPM refinement / (3) LPM→DFT refinement



second-order energies of global minimum structures of $(PbF_2)_N$ nanoclusters characterised by the lone pair model (**LPM**), down, and **DFT**, up.

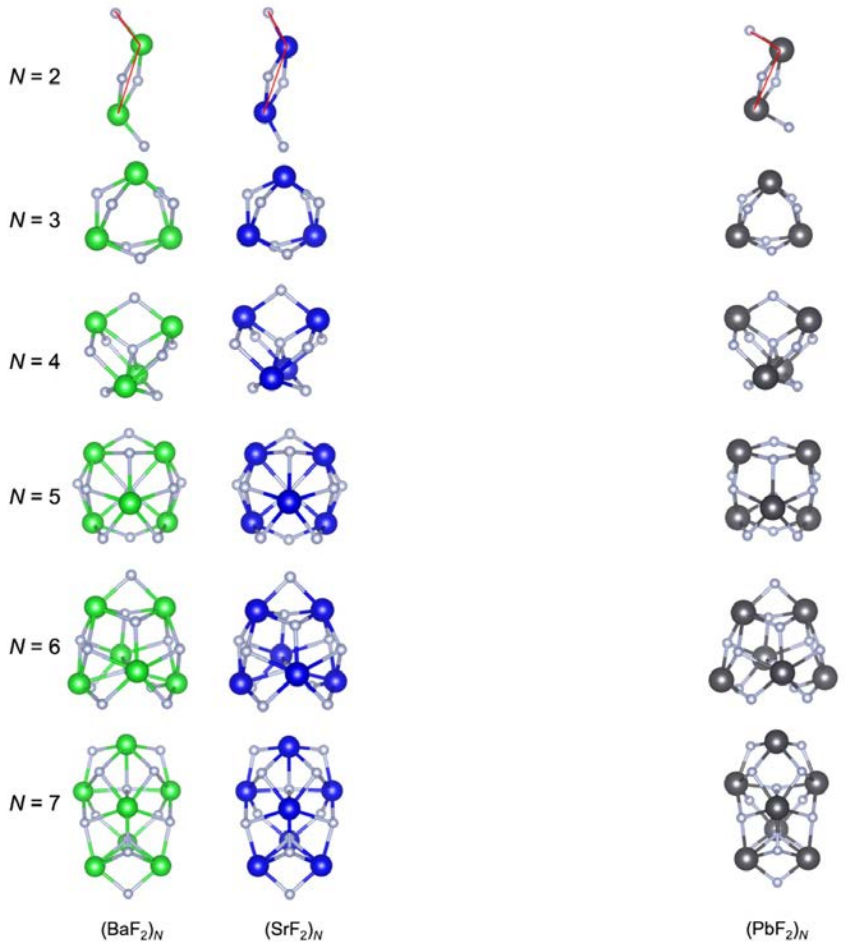


Hello there!

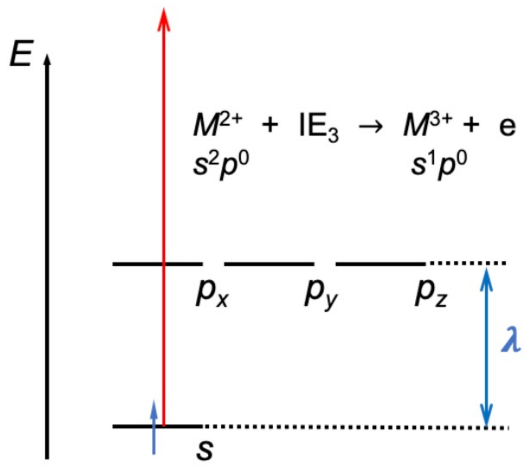
dipole moments of global minimum structures of $(PbO)_N$ calculated by the lone pair model (**LPM**), down, and **DFT**, up.

Model application II. Local lone pair effect on structures of nanoclusters (PbF_2)

Structure comparison with nanocluster structures lone pair free cations – SrF_2 and BaF_2 (by DFT-PBEsol calculations)



LPM reproduced BaF_2 and SrF_2 nanocluster structures, calculated by DFT, by **constraining the degree of model *sp*-hybridisation**



(b) The third ionisation and the ground state of M^{3+}

Energy of a lone pair:

$$E_{\mathrm{LP}} = \langle \psi | \hat{\mathrm{H}} | \psi \rangle$$

$$E_{\mathrm{LP}} = \sum_{\mu,\nu} c_\mu c_\nu \langle \mu | \hat{\mathrm{H}} | \nu \rangle = \sum_{\mu,\nu} c_\mu c_\nu H_{\mu\nu}$$

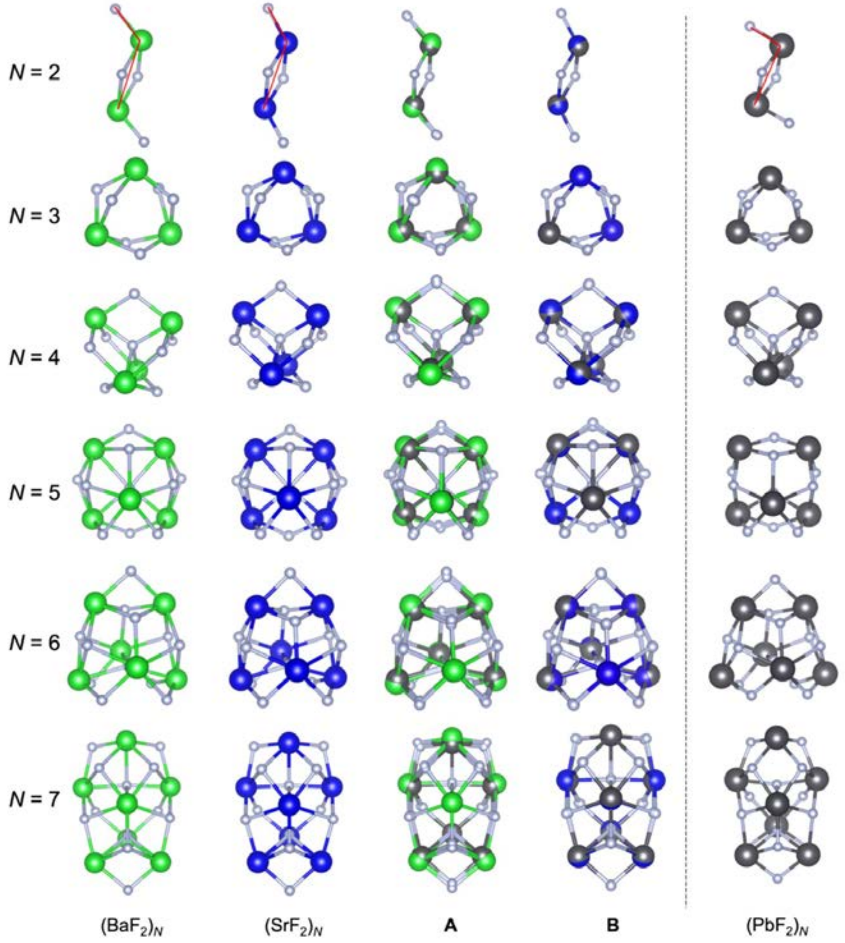
where $\hat{\mathrm{H}} = \hat{\mathrm{H}}^0 + \hat{\mathrm{H}}^1$.

Fitting parameter, **λ**

$$H^0_{\mu\nu} \equiv \langle \mu | \hat{\mathrm{H}}^0 | \nu \rangle = \begin{cases} \lambda, & \text{if } \mu = \nu = p_x, p_y \text{ and } p_z \\ 0, & \text{otherwise.} \end{cases}$$

Model application II. Local lone pair effect on structures of nanoclusters (PbF_2)

Structure comparison with nanocluster structures lone pair free cations – SrF_2 and BaF_2 (by DFT-PBEsol calculations)



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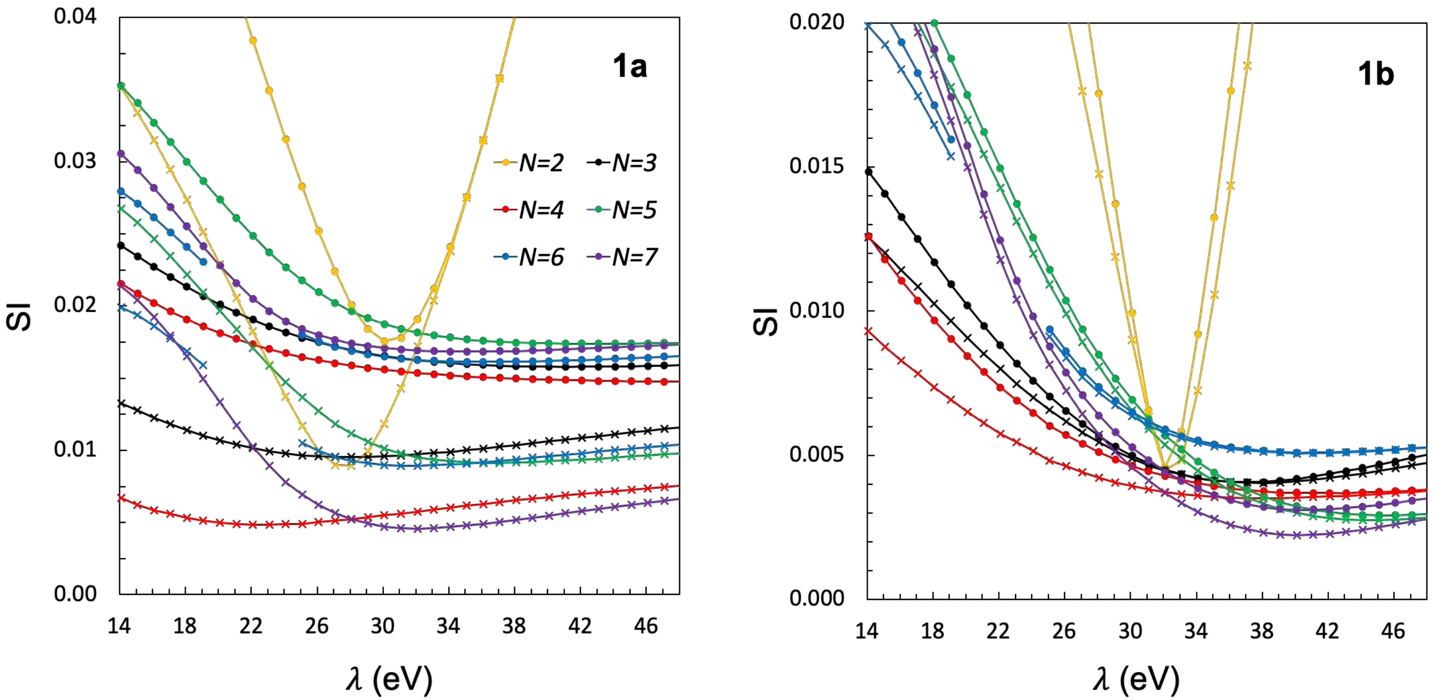
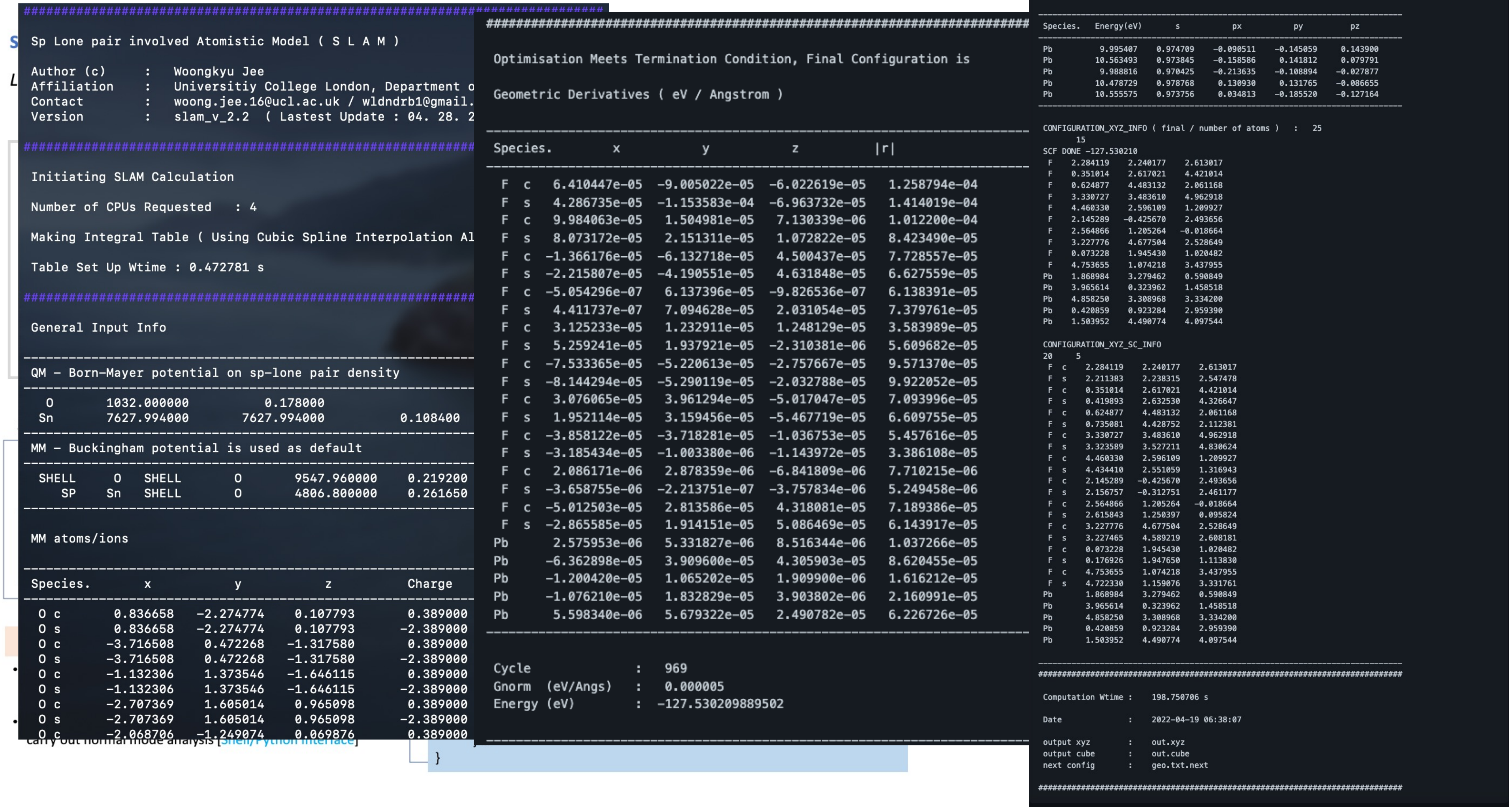


(**1a**) Similarity index (SI in Å unit) measures of $(BaF_2)_N$ and (**1b**) $(SrF_2)_N$ with respect to LPM calculated $(PbF_2)_N$ with various model parameters, λ. SI values were measured before (circle) and after (cross) applying uniform scaling, minimising the SI values.

Note. similarity index (SI) – RMSD measures of two nanocluster configurations (xyz) with modification applied: figures measured after translation (the centre of cluster) and rotations (using the principal moments of configurations).

Software Development



```
###############################################################################

 Sp Lone pair involved Atomistic Model ( S L A M )

 Author (c)     :   Woongkyu Jee
 Affiliation    :   Universitiy College London, Department o
 Contact        :   woong.jee.16@ucl.ac.uk / wldndrb1@gmail.
 Version        :   slam_v_2.2  ( Lastest Update : 04. 28. 2

###############################################################################

 Initiating SLAM Calculation

 Number of CPUs Requested   : 4

 Making Integral Table ( Using Cubic Spline Interpolation Al

 Table Set Up Wtime : 0.472781 s

###############################################################################

 General Input Info

-------------------------------------------------------------------------------
 QM - Born-Mayer potential on sp-lone pair density
-------------------------------------------------------------------------------
   O       1032.000000          0.178000
  Sn       7627.994000       7627.994000          0.108400
-------------------------------------------------------------------------------
 MM - Buckingham potential is used as default
-------------------------------------------------------------------------------
  SHELL      O   SHELL        O       9547.960000    0.219200
     SP     Sn   SHELL        O       4806.800000    0.261650
-------------------------------------------------------------------------------

 MM atoms/ions

-------------------------------------------------------------------------------
 Species.         x            y            z            Charge
-------------------------------------------------------------------------------
  O c        0.836658    -2.274774     0.107793        0.389000
  O s        0.836658    -2.274774     0.107793       -2.389000
  O c       -3.716508     0.472268    -1.317580        0.389000
  O s       -3.716508     0.472268    -1.317580       -2.389000
  O c       -1.132306     1.373546    -1.646115        0.389000
  O s       -1.132306     1.373546    -1.646115       -2.389000
  O c       -2.707369     1.605014     0.965098        0.389000
  O s       -2.707369     1.605014     0.965098       -2.389000
  O c       -2.068706    -1.249074     0.069876        0.389000
```

carry out normal mode analysis [Shell/Python interface]

}

```
###############################################################################

 Optimisation Meets Termination Condition, Final Configuration is

 Geometric Derivatives ( eV / Angstrom )

-------------------------------------------------------------------------------
 Species.         x             y             z             |r|
-------------------------------------------------------------------------------
  F  c    6.410447e-05  -9.005022e-05  -6.022619e-05   1.258794e-04
  F  s    4.286735e-05  -1.153583e-04  -6.963732e-05   1.414019e-04
  F  c    9.984063e-05   1.504981e-05   7.130339e-06   1.012200e-04
  F  s    8.073172e-05   2.151311e-05   1.072822e-05   8.423490e-05
  F  c   -1.366176e-05  -6.132718e-05   4.500437e-05   7.728557e-05
  F  s   -2.215807e-05  -4.190551e-05   4.631848e-05   6.627559e-05
  F  c   -5.054296e-07   6.137396e-05  -9.826536e-07   6.138391e-05
  F  s    4.411737e-07   7.094628e-05   2.031054e-05   7.379761e-05
  F  c    3.125233e-05   1.232911e-05   1.248129e-05   3.583989e-05
  F  s    5.259241e-05   1.937921e-05  -2.310381e-06   5.609682e-05
  F  c   -7.533365e-05  -5.220613e-05  -2.757667e-05   9.571370e-05
  F  s   -8.144294e-05  -5.290119e-05  -2.032788e-05   9.922052e-05
  F  c    3.076065e-05   3.961294e-05  -5.017047e-05   7.093996e-05
  F  s    1.952114e-05   3.159456e-05  -5.467719e-05   6.609755e-05
  F  c   -3.858122e-05  -3.718281e-05  -1.036753e-05   5.457616e-05
  F  s   -3.185434e-05  -1.003380e-06  -1.143972e-05   3.386108e-05
  F  c    2.086171e-06   2.878359e-06  -6.841809e-06   7.710215e-06
  F  s   -3.658755e-06  -2.213751e-07  -3.757834e-06   5.249458e-06
  F  c   -5.012503e-05   2.813586e-05   4.318081e-05   7.189386e-05
  F  s   -2.865585e-05   1.914151e-05   5.086469e-05   6.143917e-05
 Pb       2.575953e-06   5.331827e-06   8.516344e-06   1.037266e-05
 Pb      -6.362898e-05   3.909600e-05   4.305903e-05   8.620455e-05
 Pb      -1.200420e-05   1.065202e-05   1.909900e-06   1.616212e-05
 Pb      -1.076210e-05   1.832829e-05   3.903802e-06   2.160991e-05
 Pb       5.598340e-06   5.679322e-05   2.490782e-05   6.226726e-05
-------------------------------------------------------------------------------

 Cycle               :   969
 Gnorm  (eV/Angs)    :   0.000005
 Energy (eV)         :  -127.530209889502

-------------------------------------------------------------------------------
```

```
 Lone Pair Molecular Orbital ( Lowest Eigenvalue / EigenVector )

-------------------------------------------------------------------------------
 Species.   Energy(eV)       s            px           py           pz
-------------------------------------------------------------------------------
 Pb          9.995407    0.974709    -0.090511    -0.145059     0.143900
 Pb         10.563493    0.973845    -0.158586     0.141812     0.079791
 Pb          9.988816    0.970425    -0.213635    -0.108894    -0.027877
 Pb         10.478729    0.978768     0.130930     0.131765    -0.086655
 Pb         10.555575    0.973756     0.034813    -0.185520    -0.127164
-------------------------------------------------------------------------------

 CONFIGURATION_XYZ_INFO ( final / number of atoms )   :   25
        15
 SCF DONE -127.530210
  F    2.284119    2.240177    2.613017
  F    0.351014    2.617021    4.421014
  F    0.624877    4.483132    2.061168
  F    3.330727    3.483610    4.962918
  F    4.460330    2.596109    1.209927
  F    2.145289   -0.425670    2.493656
  F    2.564866    1.205264   -0.018664
  F    3.227776    4.677504    2.528649
  F    0.073228    1.945430    1.020482
  F    4.753655    1.074218    3.437955
 Pb    1.868984    3.279462    0.590849
 Pb    3.965614    0.323962    1.458518
 Pb    4.858250    3.308968    3.334200
 Pb    0.420859    0.923284    2.959390
 Pb    1.503952    4.490774    4.097544

 CONFIGURATION_XYZ_SC_INFO
 20      5
  F  c    2.284119    2.240177    2.613017
  F  s    2.211383    2.238315    2.547478
  F  c    0.351014    2.617021    4.421014
  F  s    0.419893    2.632530    4.326647
  F  c    0.624877    4.483132    2.061168
  F  s    0.735081    4.428752    2.112381
  F  c    3.330727    3.483610    4.962918
  F  s    3.323589    3.527211    4.830624
  F  c    4.460330    2.596109    1.209927
  F  s    4.434410    2.551059    1.316943
  F  c    2.145289   -0.425670    2.493656
  F  s    2.156757   -0.312751    2.461177
  F  c    2.564866    1.205264   -0.018664
  F  s    2.615843    1.250397    0.095824
  F  c    3.227776    4.677504    2.528649
  F  s    3.227465    4.589219    2.608181
  F  c    0.073228    1.945430    1.020482
  F  s    0.176926    1.947650    1.113830
  F  c    4.753655    1.074218    3.437955
  F  s    4.722330    1.159076    3.331761
 Pb         1.868984    3.279462    0.590849
 Pb         3.965614    0.323962    1.458518
 Pb         4.858250    3.308968    3.334200
 Pb         0.420859    0.923284    2.959390
 Pb         1.503952    4.490774    4.097544

-------------------------------------------------------------------------------
###############################################################################

 Computation Wtime :    198.750706 s

 Date              :    2022-04-19 06:38:07

 output xyz        :    out.xyz
 output cube       :    out.cube
 next config       :    geo.txt.next

###############################################################################
```

Lone pair model: summary of the results

Model feature/property

The minimum basis set approach of embedding atomic orbital has been validated

- With a few, s and p atomic orbitals, we could model the effective valence state of lone pair cations.
- LPM shows the capability of capturing the highly polarisable effect of lone pair cations

Model Application

By the model applications,

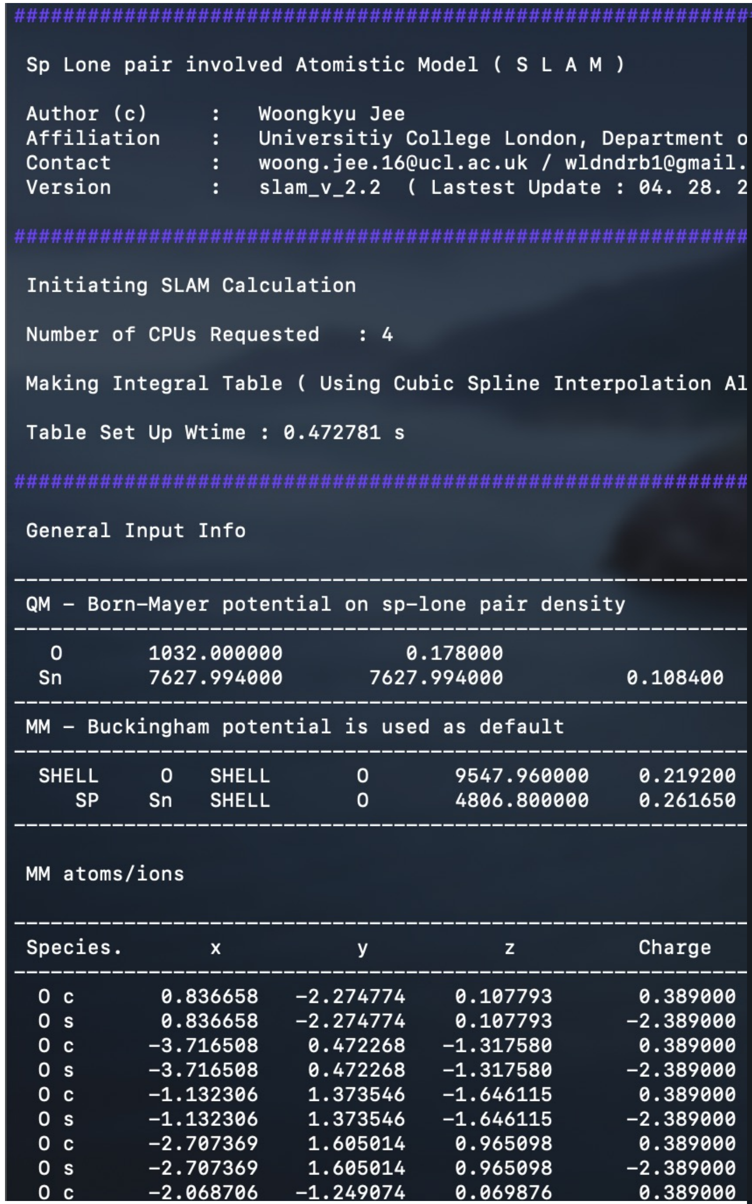
(1) A single Sn(II) cation defect created within BaO nanoclusters

(2) Global optimisation of PbO and PbF2 nanoclusters

- The LPM was effective to approximate the energy landscape of the DFT.
- In a cluster system, we demonstrated the local distortion effect of lone pair cations using the LPM.

Prof. Scott M. Woodley

Dr. Alexey A. Sokol



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##########################################################################

 Sp Lone pair involved Atomistic Model ( S L A M )

 Author (c)     :   Woongkyu Jee
 Affiliation    :   Universitiy College London, Department o
 Contact        :   woong.jee.16@ucl.ac.uk / wldndrb1@gmail.
 Version        :   slam_v_2.2  ( Lastest Update : 04. 28. 2

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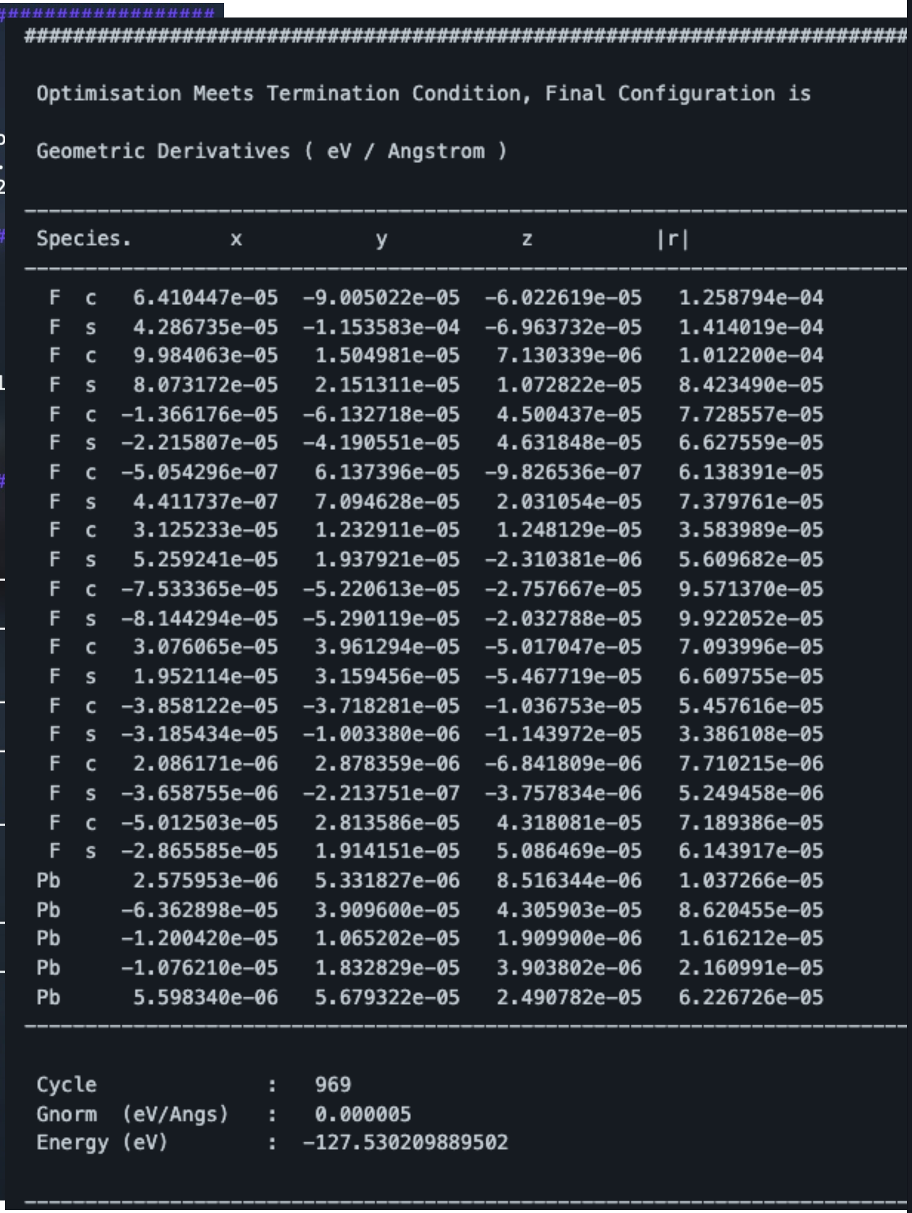
  O s      -2.707369    1.605014    0.965098       -2.389000
  O c      -2.068706   -1.249074    0.069876        0.389000
```



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##########################################################################

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  F  c   9.984063e-05  1.504981e-05  7.130339e-06  1.012200e-04
  F  s   8.073172e-05  2.151311e-05  1.072822e-05  8.423490e-05
  F  c  -1.366176e-05 -6.132718e-05  4.500437e-05  7.728557e-05
  F  s  -2.215807e-05 -4.190551e-05  4.631848e-05  6.627559e-05
  F  c  -5.054296e-07  6.137396e-05 -9.826536e-07  6.138391e-05
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  F  c  -3.858122e-05 -3.718281e-05 -1.036753e-05  5.457616e-05
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  F  c  -5.012503e-05  2.813586e-05  4.318081e-05  7.189386e-05
  F  s  -2.865585e-05  1.914151e-05  5.086469e-05  6.143917e-05
 Pb      2.575953e-06  5.331827e-06  8.516344e-06  1.037266e-05
 Pb     -6.362898e-05  3.909600e-05  4.305903e-05  8.620455e-05
 Pb     -1.200420e-05  1.065202e-05  1.909900e-06  1.616212e-05
 Pb     -1.076210e-05  1.832829e-05  3.903802e-06  2.160991e-05
 Pb      5.598340e-06  5.679322e-05  2.490782e-05  6.226726e-05
--------------------------------------------------------------------------

 Cycle              :   969
 Gnorm  (eV/Angs)   :   0.000005
 Energy (eV)        :  -127.530209889502

--------------------------------------------------------------------------
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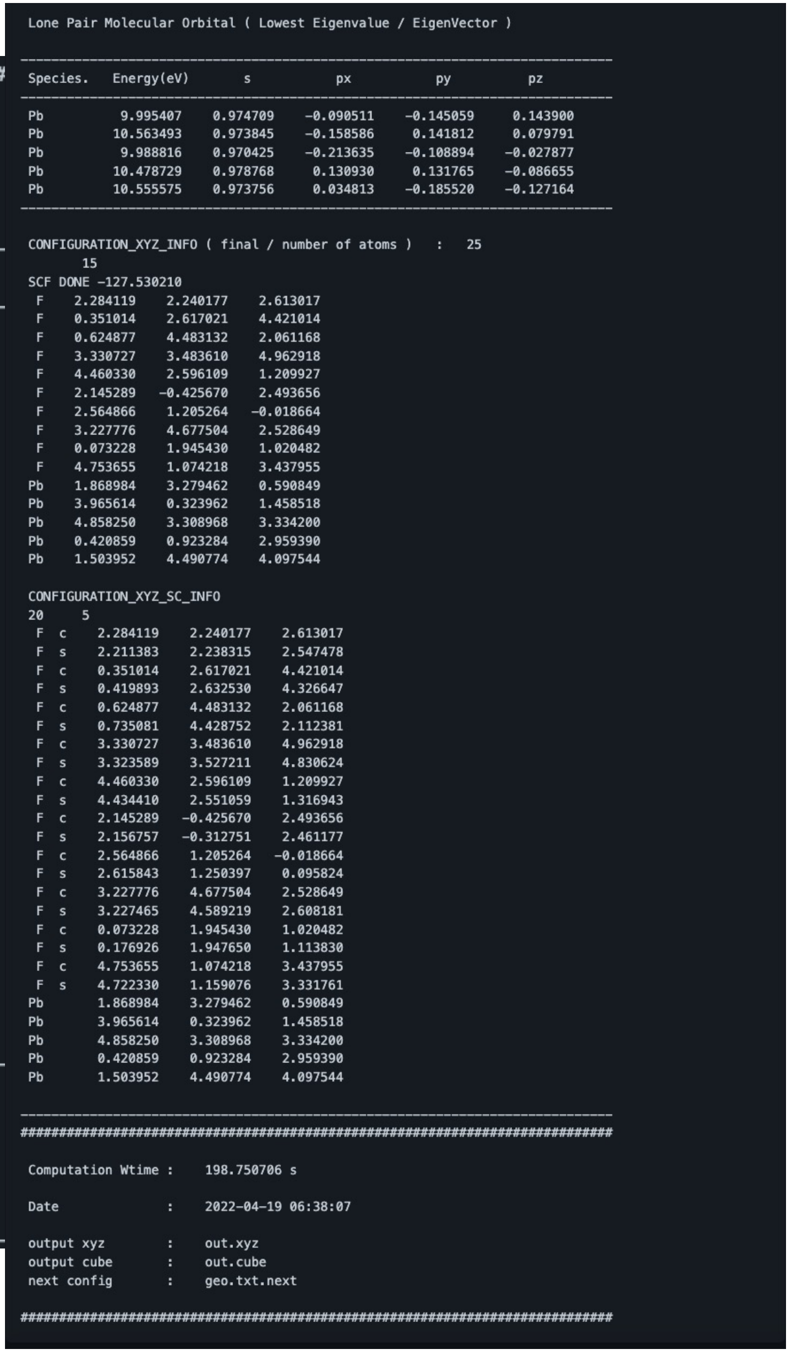

```
 Lone Pair Molecular Orbital ( Lowest Eigenvalue / EigenVector )

--------------------------------------------------------------------------
 Species.   Energy(eV)       s           px          py          pz
--------------------------------------------------------------------------
 Pb          9.995407    0.974709   -0.090511   -0.145059    0.143900
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 Pb          9.988816    0.970425   -0.213635   -0.108894   -0.027877
 Pb         10.478729    0.978768    0.130930    0.131765   -0.086655
 Pb         10.555575    0.973756    0.034813   -0.185520   -0.127164
--------------------------------------------------------------------------

 CONFIGURATION_XYZ_INFO ( final / number of atoms )   :   25
       15
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  F    0.351014    2.617021    4.421014
  F    0.624877    4.483132    2.061168
  F    3.330727    3.483610    4.962918
  F    4.460330    2.596109    1.209927
  F    2.145289   -0.425670    2.493656
  F    2.564866    1.205264   -0.018664
  F    3.227776    4.677504    2.528649
  F    0.073228    1.945430    1.020482
  F    4.753655    1.074218    3.437955
 Pb    1.868984    3.279462    0.590849
 Pb    3.965614    0.323962    1.458518
 Pb    4.858250    3.308968    3.334200
 Pb    0.420859    0.923284    2.959390
 Pb    1.503952    4.490774    4.097544

 CONFIGURATION_XYZ_SC_INFO
 20     5
  F  c    2.284119    2.240177    2.613017
  F  s    2.211383    2.238315    2.547478
  F  c    0.351014    2.617021    4.421014
  F  s    0.419893    2.632530    4.326647
  F  c    0.624877    4.483132    2.061168
  F  s    0.735081    4.428752    2.112381
  F  c    3.330727    3.483610    4.962918
  F  s    3.323589    3.527211    4.830624
  F  c    4.460330    2.596109    1.209927
  F  s    4.434410    2.551059    1.316943
  F  c    2.145289   -0.425670    2.493656
  F  s    2.156757   -0.312751    2.461177
  F  c    2.564866    1.205264   -0.018664
  F  s    2.615843    1.250397    0.095824
  F  c    3.227776    4.677504    2.528649
  F  s    3.227465    4.589219    2.608181
  F  c    0.073228    1.945430    1.020482
  F  s    0.176926    1.947650    1.113830
  F  c    4.753655    1.074218    3.437955
  F  s    4.722330    1.159076    3.331761
 Pb         1.868984    3.279462    0.590849
 Pb         3.965614    0.323962    1.458518
 Pb         4.858250    3.308968    3.334200
 Pb         0.420859    0.923284    2.959390
 Pb         1.503952    4.490774    4.097544

--------------------------------------------------------------------------
##########################################################################

 Computation Wtime :    198.750706 s

 Date              :    2022-04-19 06:38:07

 output xyz        :    out.xyz
 output cube       :    out.cube
 next config       :    geo.txt.next

##########################################################################
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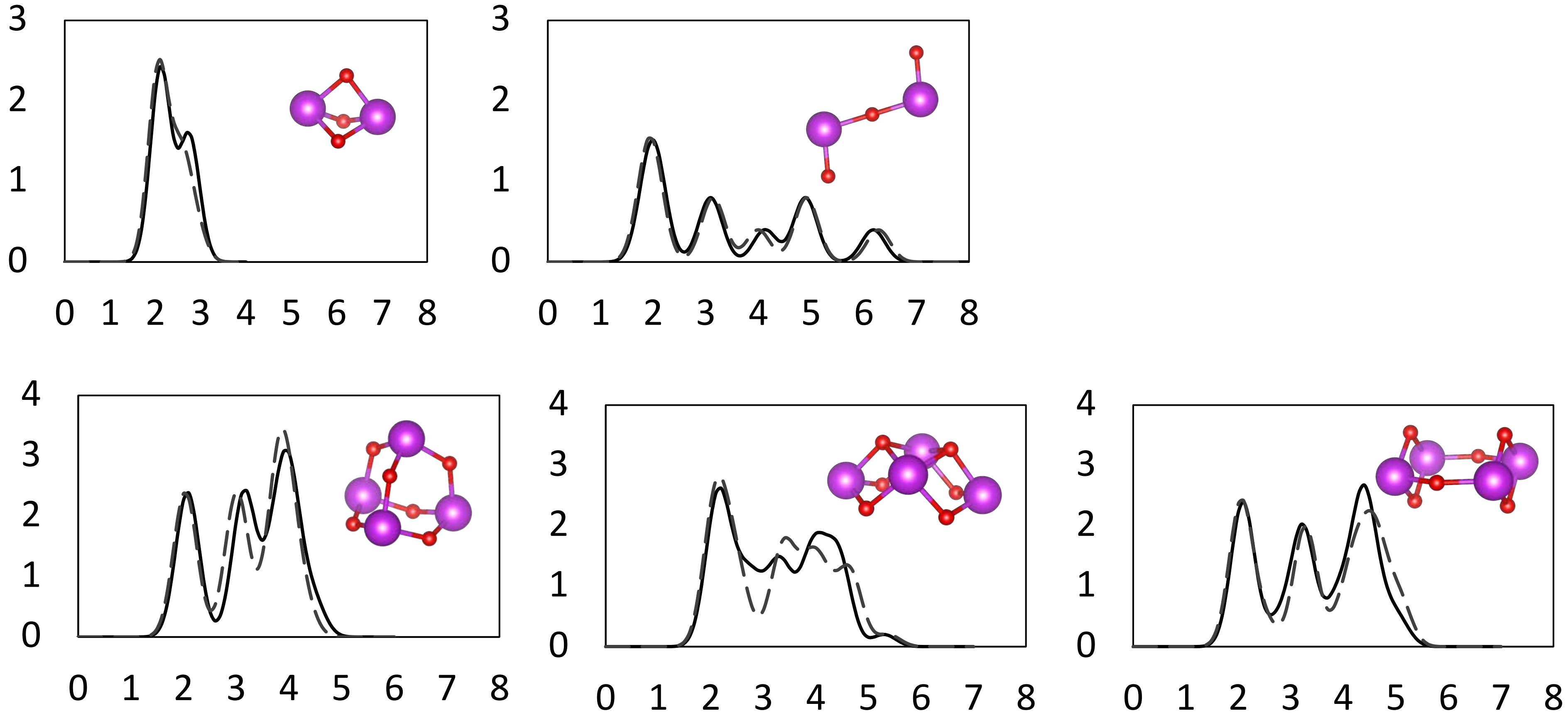
3
2
1
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0 1 2 3 4 5 6 7 8
3
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4
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4
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2
1
0
0 1 2 3 4 5 6 7 8
4
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2
1
0
0 1 2 3 4 5 6 7 8

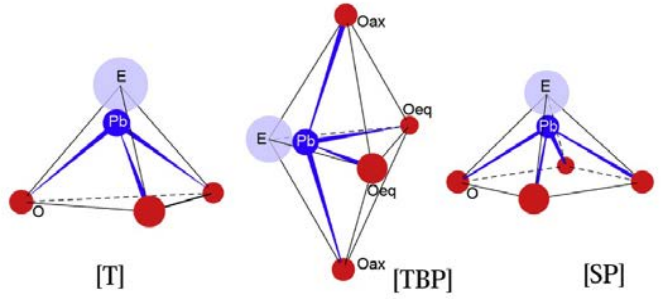
Model Application

3.1 LPM application results

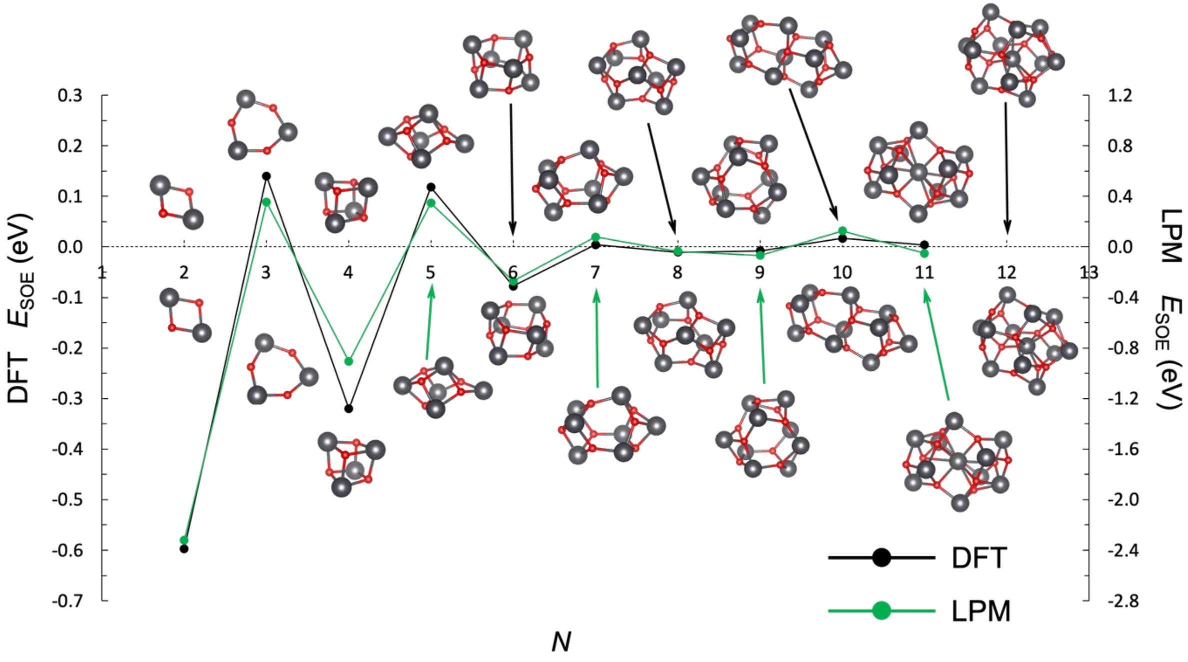
Nanocluster structure predictions for various lone pair compounds: PbO, PbF_2 etc.

Lone pair cations can take various polyhedral types due to the presence of LP density.

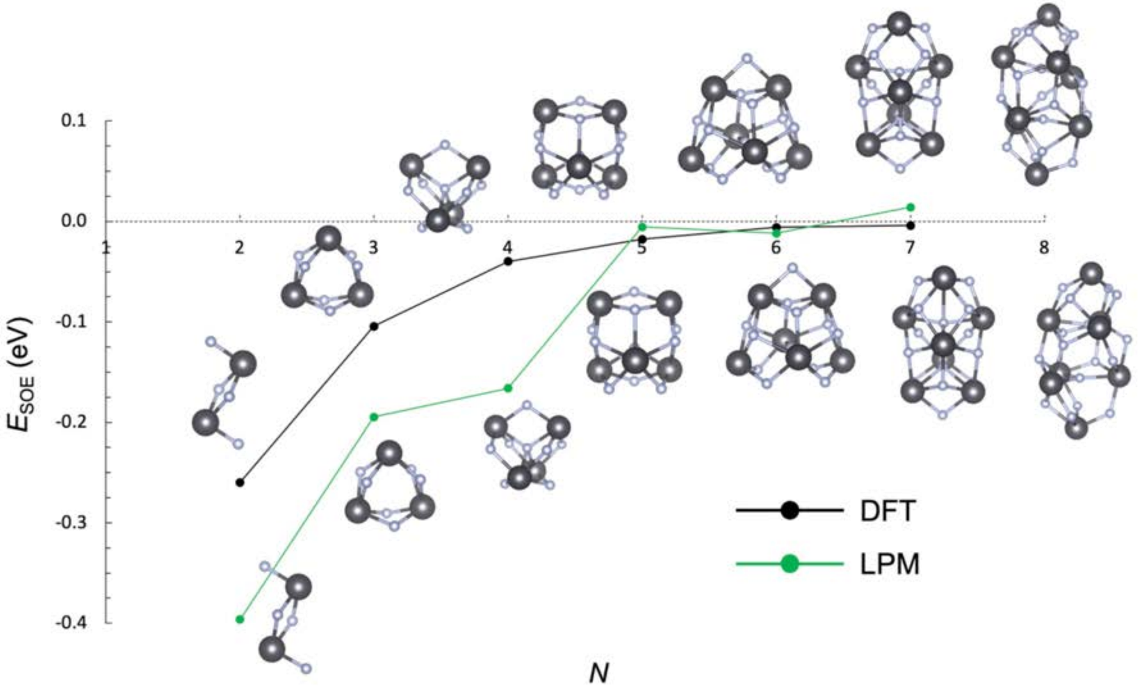
- Focusing on approximating the DFT energy landscape, i.e., *correct atomic configuration.*
- Global optimisation method.



Local coordination environment of lone pair cation



Global minima structures of $(PbO)_N$ nanoclusters characterised by LPM (below) an DFT (up)

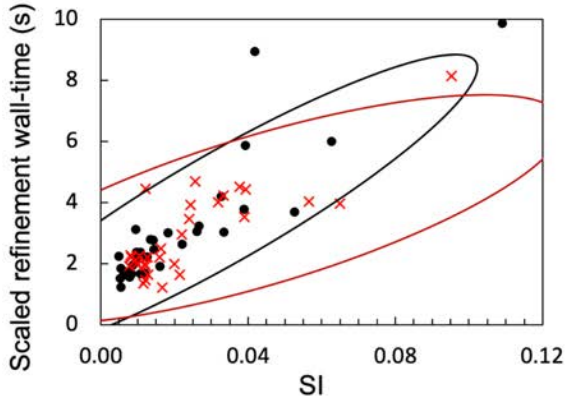


Global minima structures of $(PbF_2)_N$ nanoclusters characterised by LPM (below) an DFT (up)

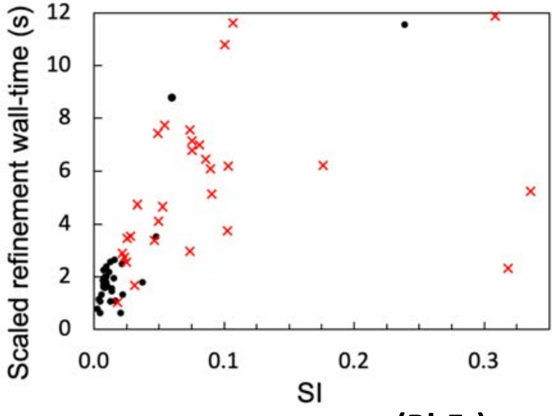
Model Application

3.2 Global optimisation comparison with the Shell Model

Statistical analysis : LPM/SM → DFT Refinement Wtime



$(PbO)_N$



$(PbF_2)_N$

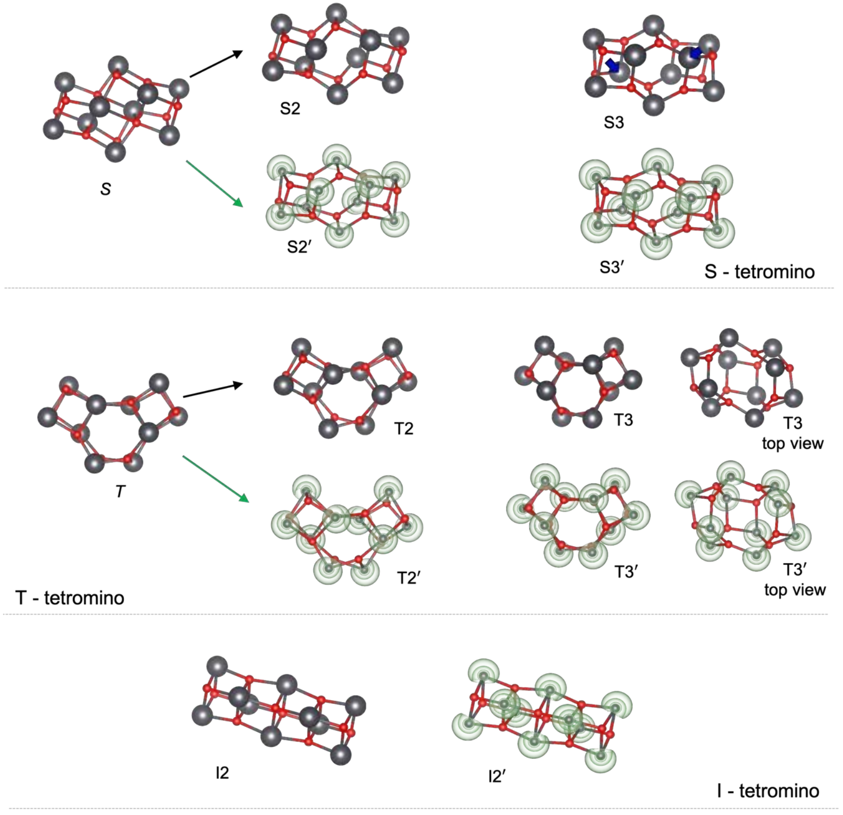
● LPM → DFT

× SM → DFT

SI (similarity index; quantified matching of the atomic configurations relaxed in different a

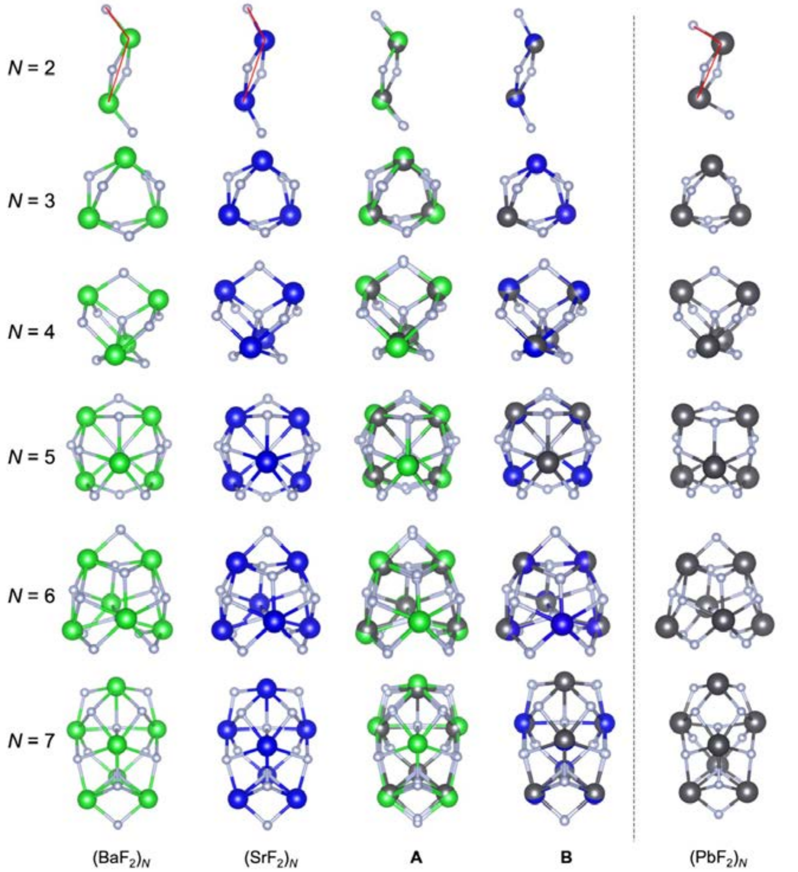
3.3 Lone pair induced structural distortions

Nanoclusters with lone pair free cations to lone pair distorted structures


S
S2
S2′
S3
S3′
S - tetromino
T
T2
T2′
T3
T3
top view
T3′
T3′
top view
T - tetromino
I2
I2′
I - tetromino

Lone pair induced structural distortions in cluster level

Comparison with DFT – LPM (with primes)


N = 2
N = 3
N = 4
N = 5
N = 6
N = 7
$(BaF_2)_N$
$(SrF_2)_N$
A
B
$(PbF_2)_N$

LPM reproduced BaF_2 and SrF_2 nanocluster structures, calculated by DFT, by constraining the *sp*-hybridisation effect

Lone pair model : summary of the results

- **Model feature/property**

  A. model minimal basis set approach with a single molecular orbital approach has been validated.

  B. capability of capturing the highly polarisable effect of lone pair cations.

  C. with respect to the shell model, LPM polarisability shows the forward compatibility.

- **Model Development/Implementation**

  A. calculating the total energy and atomic forces of an atomic configuration (cluster).

  B. perform local atomic relaxations to the LPM energy minimum.

  C. interfacing toolkits: calculating dipole moment and vibrational frequencies of clusters modelled by LPM.

  D. comparing two atomic cluster configurations (implementation of the similarity index that was designed as part of the thesis; for the comparison with DFT calculated cluster structures.

- **Model Application**

  A. investigation of PbO and PbF2 nanoclusters, using LPM and the results are compared with DFT.

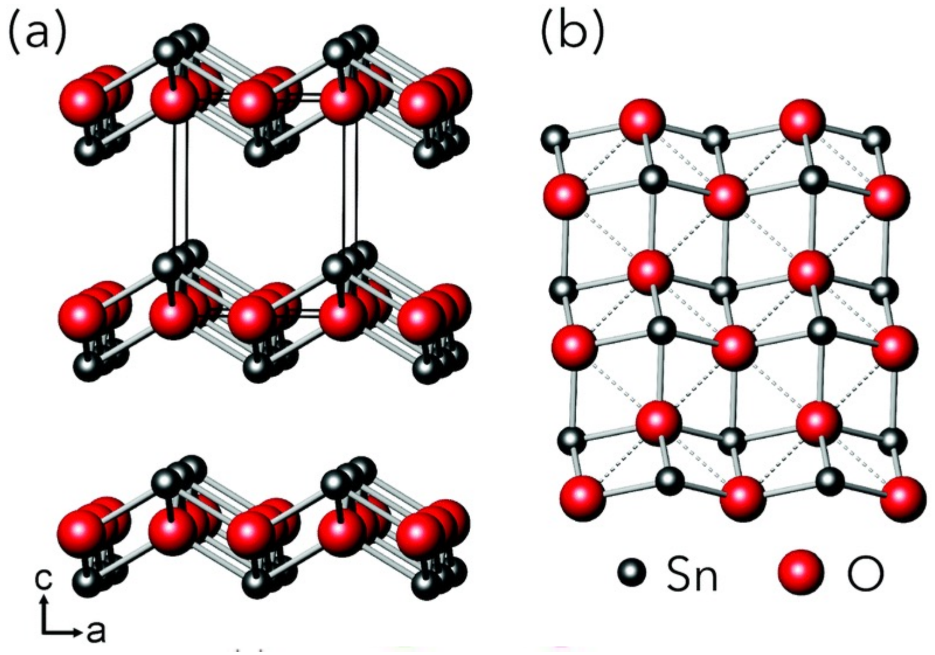
  B. as an additional control group, the shell model was also compared, and LPM shows better agreement with the DFT refined nanocluster structures.

  C. in the level of clusters, the effect of lone pairs on the structural deformation was demonstrated.

Overview: cations of potential sp-lone pair formation & applications

sp-lone pair is generally found in materials, which are including Sn(II), Pb(II), Bi(III) etc;

Electronic configuration of the valence shell : $d^{10}\ s^{2}\ p^{0}$



Octahdral *Fm3m* > Distorted *P4/nmm*

Applications

Materials Related with Lone Pair Effects	
SnO, PbO	Thermo/Photo Electrics
*M*TiO$_3$, *M*=Sn,Pb	Ferro/Piezo Electrics
*M*Tl*X*$_3$, *M*=Rb,Cs, X=F,Br,Cl	Superconductivity
Cs*M*Br3, *M*=Sn,Pb	Optoelectrics

1. L. Liang et. al; *J. Mater. Chem. A*, 2014, 2, 10647-10653. 2. S.A Miller et. al; *J. Mater. Chem. C.*, 2017, 5, 8854-8861. 3. Walsh et. al; *Journal of Solid State Chemistry.,* 178 (2005) 1422–1428
4. Fabini et. al; *J. Am. Chem. Soc.*, 2016, 138, 11820−11832. 5. Pitike et al; *Physical Review B.,* 91, 035112 (2015)

Modelling Approach: theoretical background

One-Centre Hamiltonian Approach

Basis functions of one and three orbitals are enough to describe sp-lone pair effect.

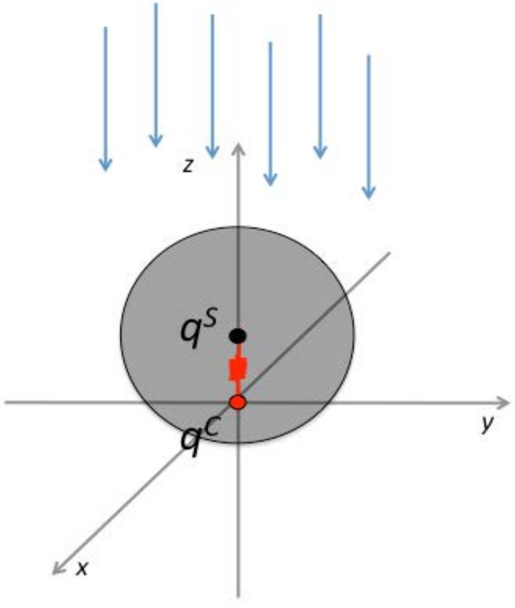
One-Centre Hamiltonian Approach

$$|\psi\rangle = c_1|s\rangle + c_2|px\rangle + c_3|py\rangle + c_4|pz\rangle.$$

by a linear combination of basis functions, *sp*-hybridisation and its polarisation can be described.

Shell model is typically adopted to describe ionic polarisation in IP methods.

Two point charges are connected with a harmonic spring.



Shell Model

$$\varepsilon_{shell} = \frac{1}{2}kr^2$$

$$\varepsilon_{anharmonic} = \frac{1}{2}k_2r^2 + \frac{1}{24}k_4r^4$$

$$E_{\text{spherical}} = \sum_{i,j} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + A_{ij}\exp(-r_{ij}/\rho_{ij}) - \frac{C_{ij}}{r_{ij}^6}$$

Buckingham potential popular in IP methods.

However, shell model can only reproduce a potential of spherical shape

Angular terms in the basis funciton

$$\Gamma_s = 1$$
$$\Gamma_{p_x} = \sin\theta\cos\phi$$
$$\Gamma_{p_y} = \sin\theta\sin\phi$$
$$\Gamma_{p_z} = \cos\theta$$

Modelling Approach: *energy calculation*

Fixed point iteration algorithm (SCF-LIKE)

A system with more than two sp-lone pairs needs SCF-like convergence to determine its energy !

It cannot determine all states at the same time.

```
Init  $|\psi_\alpha^k\rangle$.      usually set  $|\psi_\alpha^1\rangle = |s\rangle$.
while   $k$ :1, 2, …   do
    for   $\alpha$ :1, 2, … $\alpha$ max   do      $\alpha$ max: number of sp-cations.
        begin evaluate:
            $\mathrm{H}_{\alpha;\mu\nu}^{k} = \sum_{\mu\nu}\left\{\mathrm{H}_{\mu\nu}^{\alpha;0} + \sum_A \mathrm{H}_{\alpha A;\mu\nu}^{c} + \sum_{\beta\neq\alpha}\left(\left\langle\mu\middle|\widehat{\mathrm{H}}_{\alpha\beta}^{spc}\middle|\nu\right\rangle + \sum_{\lambda\sigma} c_\lambda^\beta c_\sigma^\beta \left\langle\mu\middle|\left\langle\lambda\middle|\widehat{\mathrm{H}}_{\alpha\beta}^{spe}\middle|\sigma\right\rangle\middle|\nu\right\rangle\right)\right\}.$
            solve   $\mathbf{HC} = \mathbf{CE}$  for each sp-lone pair cation ($\alpha$) gives  $|\psi_\alpha^{k+1}\rangle$  and  $\varepsilon_\alpha^{k+1}$.
    end $\alpha$
    if
        $\sum_\alpha\left(|\psi_\alpha^{k+1}\rangle - |\psi_\alpha^{k}\rangle\right) <$ eigenvector-tolerance.   .AND.   $\sum_\alpha(\varepsilon_\alpha^{k+1} - \varepsilon_\alpha^{k}) <$ energy-tolerance.
    then
        set $|\psi_\alpha^{SCF}\rangle = |\psi_\alpha^{k}\rangle$.   Exit.
end $k$
```

On-site Energy Term

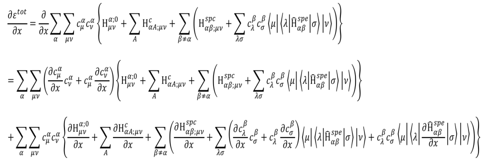
Interaction with non-lone pair species

Interaction with core of other lone pair cations

Interaction with other lone pair electron densities

Modelling Approach: *geometric derivative calculation*

Fixed point iteration algorithm (SCF-LIKE)



Derivative calculation is important to calculate forces action on each species in the system, and using the information one can carry out geometric optimisation. Popel et al., *International Journal of Quantum Chemistry : Quantum Chemistry Symposium* 13,225-241 (1979)

eqn(1).

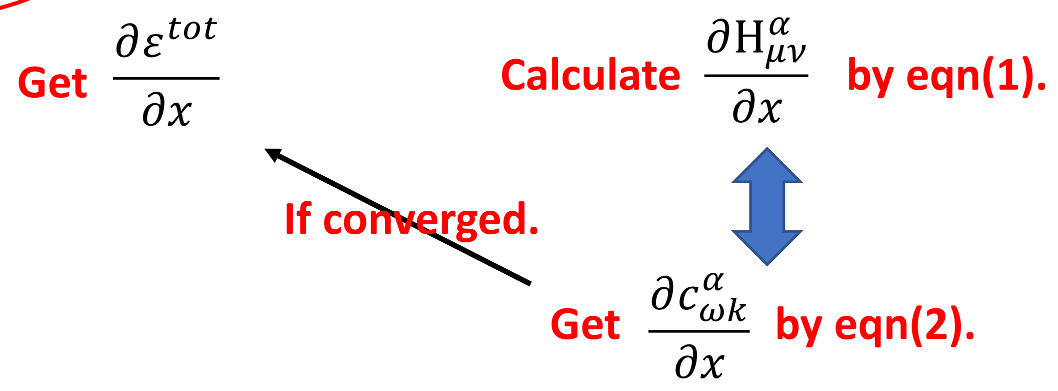
$$\frac{\partial \varepsilon^{tot}}{\partial x} = \frac{\partial}{\partial x}\sum_{\alpha}\sum_{\mu\nu} c_{\mu}^{\alpha} c_{\nu}^{\alpha}\left\{\mathrm{H}_{\mu\nu}^{\alpha;0} + \sum_{A}\mathrm{H}_{\alpha A;\mu\nu}^{c} + \sum_{\beta\neq\alpha}\left(\mathrm{H}_{\alpha\beta;\mu\nu}^{spc} + \sum_{\lambda\sigma} c_{\lambda}^{\beta} c_{\sigma}^{\beta}\left\langle\mu\middle|\left\langle\lambda\middle|\hat{\mathrm{H}}_{\alpha\beta}^{spe}\middle|\sigma\right\rangle\middle|\nu\right\rangle\right)\right\}$$

$$= \sum_{\alpha}\sum_{\mu\nu}\boxed{\left(\frac{\partial c_{\mu}^{\alpha}}{\partial x} c_{\nu}^{\alpha} + c_{\mu}^{\alpha}\frac{\partial c_{\nu}^{\alpha}}{\partial x}\right)}\left\{\mathrm{H}_{\mu\nu}^{\alpha;0} + \sum_{A}\mathrm{H}_{\alpha A;\mu\nu}^{c} + \sum_{\beta\neq\alpha}\left(\mathrm{H}_{\alpha\beta;\mu\nu}^{spc} + \sum_{\lambda\sigma} c_{\lambda}^{\beta} c_{\sigma}^{\beta}\left\langle\mu\middle|\left\langle\lambda\middle|\hat{\mathrm{H}}_{\alpha\beta}^{spe}\middle|\sigma\right\rangle\middle|\nu\right\rangle\right)\right\}$$

$$+ \sum_{\alpha}\sum_{\mu\nu} c_{\mu}^{\alpha} c_{\nu}^{\alpha}\left\{\frac{\partial \mathrm{H}_{\mu\nu}^{\alpha;0}}{\partial x} + \sum_{A}\frac{\partial \mathrm{H}_{\alpha A;\mu\nu}^{c}}{\partial x} + \sum_{\beta\neq\alpha}\left(\frac{\partial \mathrm{H}_{\alpha\beta;\mu\nu}^{spc}}{\partial x} + \sum_{\lambda\sigma}\boxed{\left(\frac{\partial c_{\lambda}^{\beta}}{\partial x} c_{\sigma}^{\beta} + c_{\lambda}^{\beta}\frac{\partial c_{\sigma}^{\beta}}{\partial x}\right)}\left\langle\mu\middle|\left\langle\lambda\middle|\hat{\mathrm{H}}_{\alpha\beta}^{spe}\middle|\sigma\right\rangle\middle|\nu\right\rangle + c_{\lambda}^{\beta} c_{\sigma}^{\beta}\left\langle\mu\middle|\left\langle\lambda\middle|\frac{\partial \hat{\mathrm{H}}_{\alpha\beta}^{spe}}{\partial x}\middle|\sigma\right\rangle\middle|\nu\right\rangle\right)\right\}$$

geometric eigenvector derivatives can also be iteratively calculated

eqn(2). $$\frac{\partial c_{\omega k}^{\alpha}}{\partial x} = \sum_{j\neq k}\sum_{\mu\nu}\frac{c_{\omega j}^{\alpha} c_{\omega k}^{\alpha}}{\varepsilon_{j}^{\alpha} - \varepsilon_{k}^{\alpha}}\left(c_{\nu k}^{\alpha}\frac{\partial \varepsilon_{k}^{\alpha}}{\partial x}\delta_{\mu\nu} - c_{\nu k}^{\alpha}\boxed{\frac{\partial \mathrm{H}_{\mu\nu}^{\alpha}}{\partial x}}\right)$$



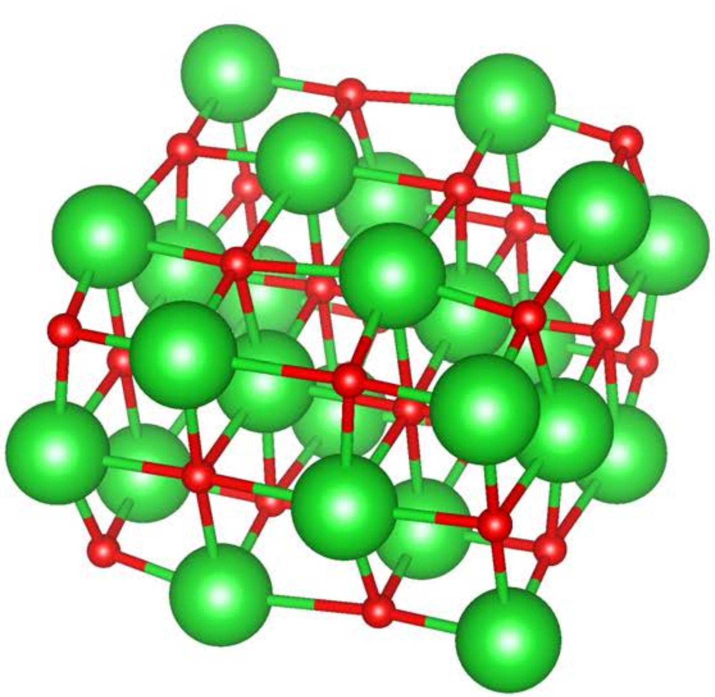
Get $\frac{\partial \varepsilon^{tot}}{\partial x}$

Calculate $\frac{\partial \mathrm{H}_{\mu\nu}^{\alpha}}{\partial x}$ **by eqn(1).**

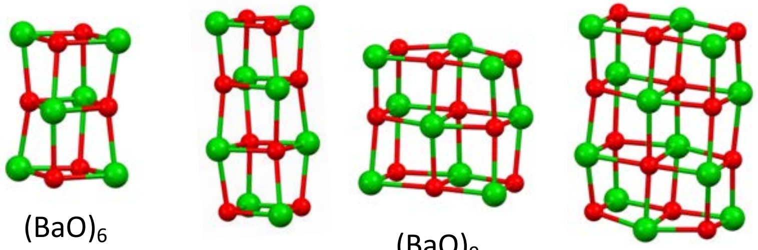
If converged.

Get $\frac{\partial c_{\omega k}^{\alpha}}{\partial x}$ **by eqn(2).**

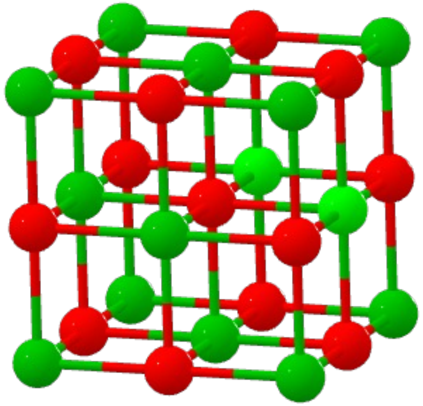
How to model *sp*-lone pair cations?



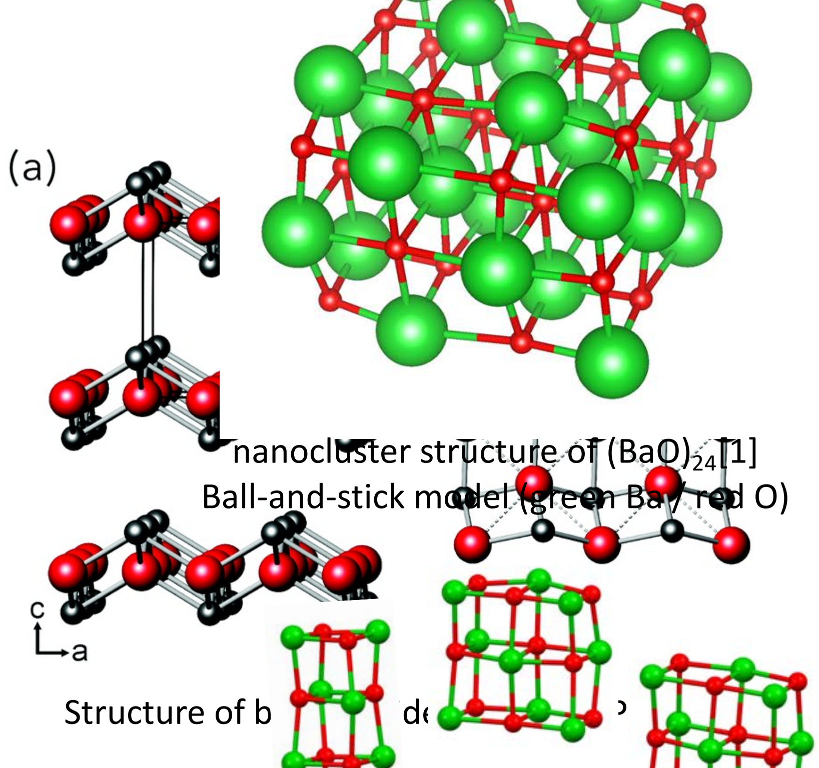
nanocluster structure of $(BaO)_{24}$[1]
Ball-and-stick model (green Ba / red O)



$(BaO)_6$ $(BaO)_8$ $(BaO)_9$ $(BaO)_{12}$

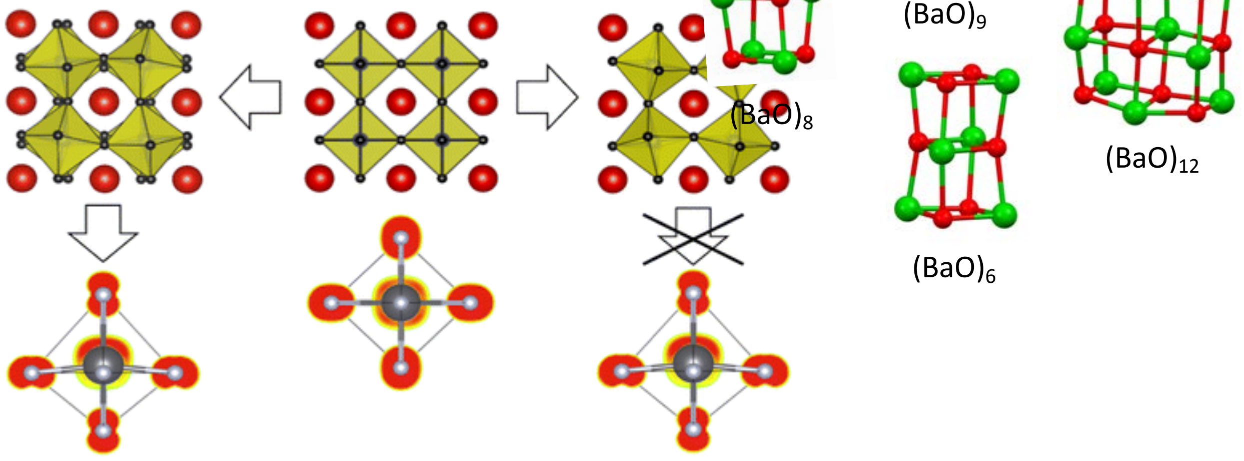


Alkali earth metal oxides
SrO and BaO



nanocluster structure of $(BaO)_{24}$[1]
Ball-and-stick model (green Ba / red O)

Structure of b de

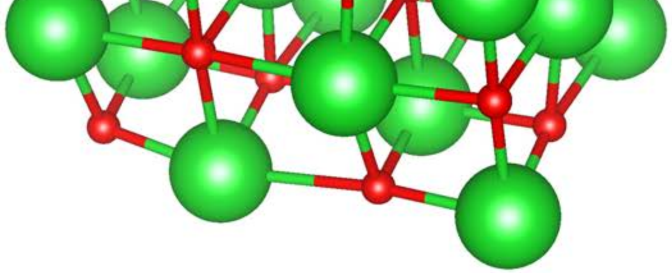


Lone pair induced distortions in halide perovskites

[1] S.G.E.T. Escher, T. Lazauskas, M.A. Zwijnenburg, S.M. Woodley, Comput. Theor. Chem 1107 (2017) 74–81
[2] Miller et. Al; J. Mater. Chem. C., 2017, 5. 10.1039
[3] E. H. Smith et. al; *Inorg. Chem*., 2015, 54, 8536–8543

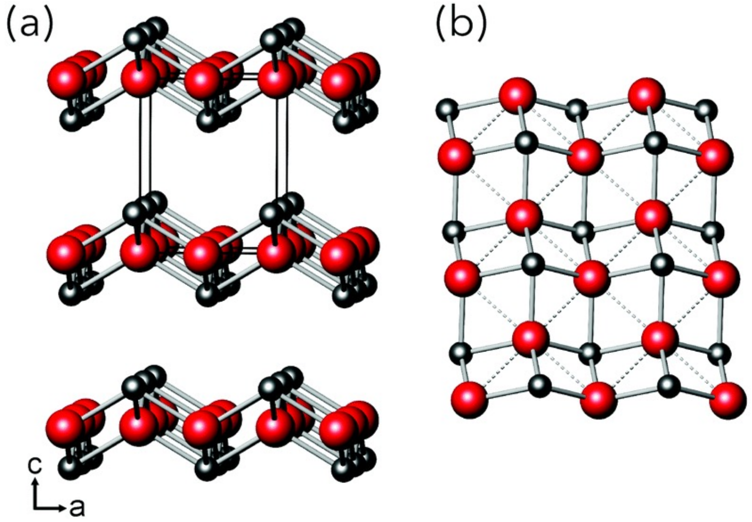
structural distortions caused by stereo-actice lone pairs

How to model *sp*-lone pair cations?



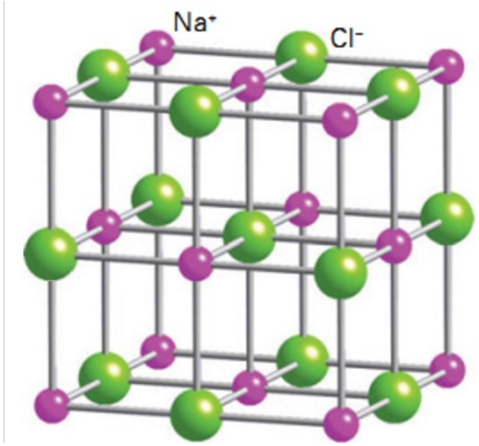
1.1 Research Motivation

- Modelling non-spherical electron density with high-polarisability.
- Species: Sn^{+2}, Pb^{+2}, Bi^{3+} etc. with electronic configuration of **d^{10}** s^2p^0

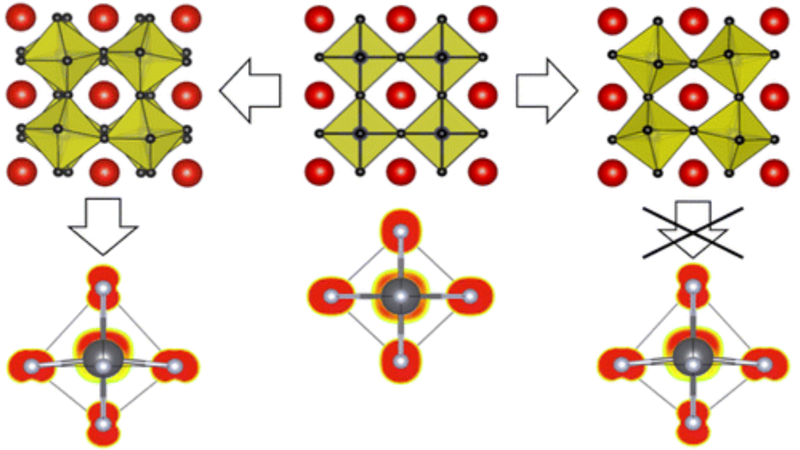


Structure of binary oxides: SnO and PbO

Miller et. Al; *J. Mater. Chem. C.*, 2017, **5**. 10.1039/C7TC01623A.



Rocksalt structure



Lone pair induced distortions in halide perovskites

E. H. Smith et. al; *Inorg. Chem.*, 2015, **54**, 8536–8543

Structural distortions are induced due to the presence of stereo-active lone pair electron density

Widely ranging applications

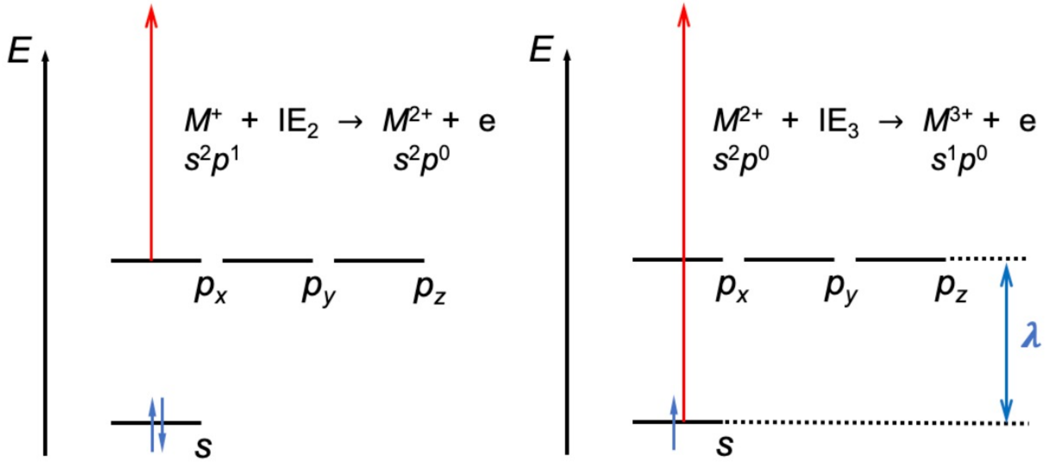
SnO/PbO photo-conductive/voltaic devices; Bi_2O_3 ionic conductor in photovoltaic devices; $(Sn/Pb)X_2$ optical devices; $(Sn/Pb)TiO_3$ piezo-electrics; $Cs(Sn/Pb)X_3$ opto-electrics.

Modelling *sp*-lone pair cation

1.2 Modelling the effective valence state

The effective valence state of lone pair cations: **s^2p^0**

treated as a two-level system – given that the inner **d** states are relatively inert.



(a) The second ionisation and the ground state of M^{2+}

(b) The third ionisation and the ground state of M^{3+}

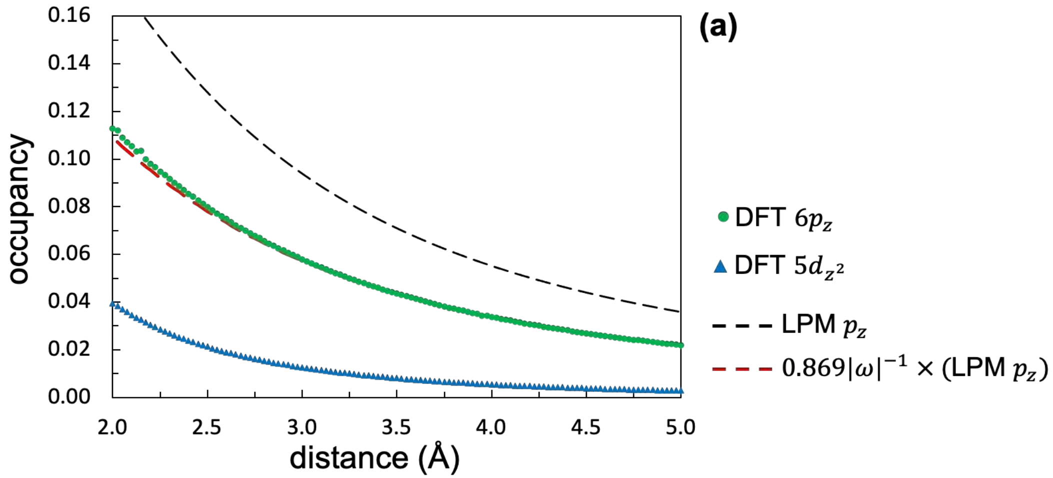
Figure 2.1 Energy diagrams of the valence states for an isolated lone pair cation *M* (e.g., *M* = Sn or Pb) in vacuum: (a) shows two electrons occupying the *s* state is occupied by lone pair electrons and the three *p* states left empty after the 2nd ionisation occurs; (b) shows one electron occupying the s state after the 3rd ionisation occurs where the energy difference between *s* and *p* states is marked with a Greek letter λ.

Model effective valence state

represented by a single molecular orbital

$$|\psi\rangle = c_1|s\rangle + c_2|p_x\rangle + c_3\left|p_y\right\rangle + c_4|p_z\rangle$$

Molecular orbital approach with minimal number of basis functions



Orbital occupancy of Pb2+ cation interacting with a point charge(e) as a function of their separation distance; calculated by DFT and LPM.

$$s = R_s(r)\Gamma_s(\theta,\phi)$$

$$p_x = R_p(r)\Gamma_x(\theta,\phi)$$

$$p_y = R_p(r)\Gamma_y(\theta,\phi)$$

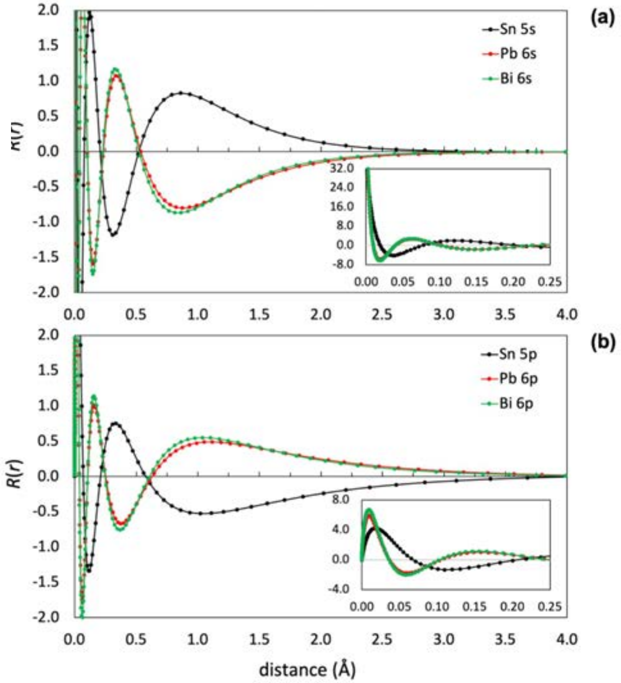
$$p_z = R_p(r)\Gamma_z(\theta,\phi)$$

$$\Gamma_s = \frac{1}{2}\left(\frac{1}{\pi}\right)^{1/2}$$

$$\Gamma_x(\theta,\phi) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi$$

$$\Gamma_y(\theta,\phi) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\sin\phi$$

$$\Gamma_z(\theta,\phi) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

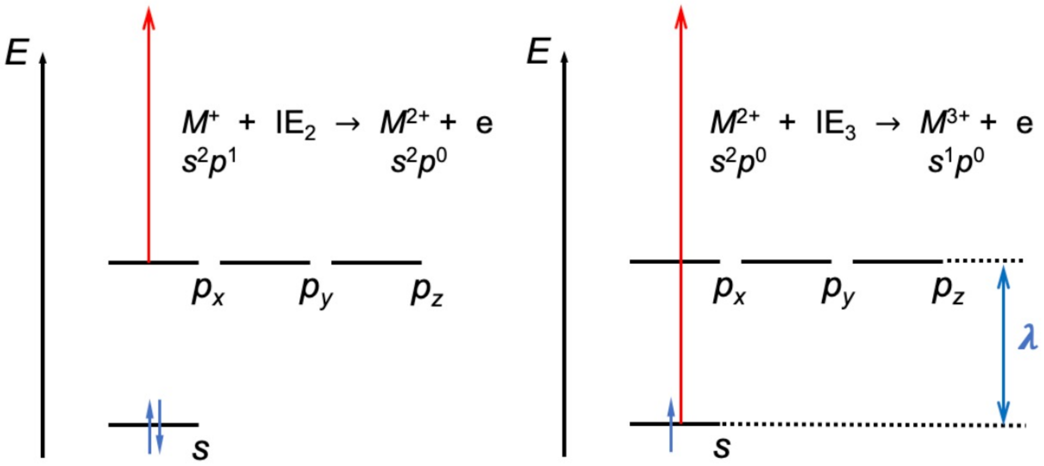


Modelling *sp*-lone pair cation

1.2 Modelling the effective valence state

The effective valence state of lone pair cations: **s^2p^0**

treated as a two-level system – given that the inner **d** states are relatively inert.



(a) The second ionisation and the ground state of M^{2+}

(b) The third ionisation and the ground state of M^{3+}

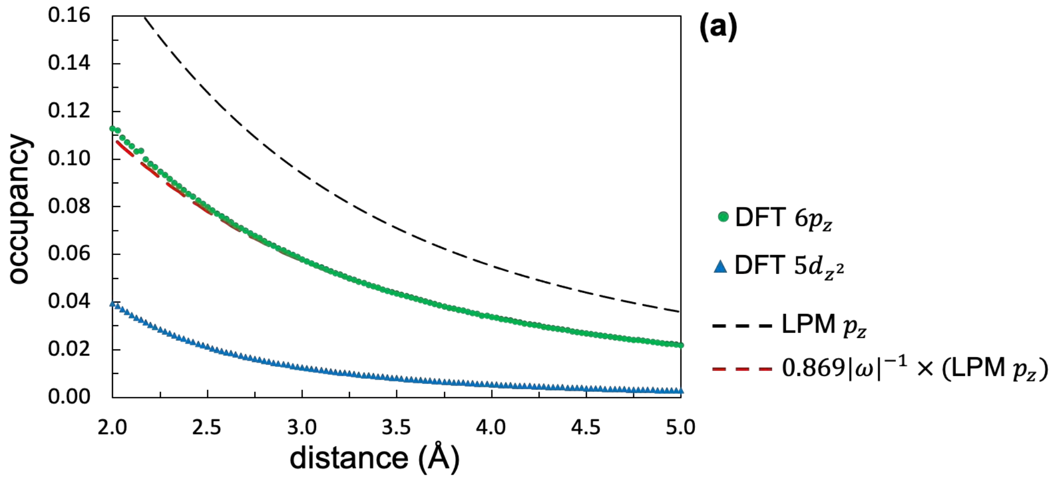
Figure 2.1 Energy diagrams of the valence states for an isolated lone pair cation M (e.g., M = Sn or Pb) in vacuum: (a) shows two electrons occupying the s state is occupied by lone pair electrons and the three p states left empty after the 2nd ionisation occurs; (b) shows one electron occupying the s state after the 3rd ionisation occurs where the energy difference between s and p states is marked with a Greek letter λ.

Model effective valence state

represented by a single molecular orbital

$$|\psi\rangle = c_1|s\rangle + c_2|p_x\rangle + c_3\,|p_y\rangle + c_4|p_z\rangle$$

Molecular orbital approach with minimal number of basis functions



Orbital occupancy of Pb2+ cation interacting with a point charge(e) as a function of their separation distance; calculated by DFT and LPM.

Energy of lone pair density:

$$E_{\rm LP} = \langle\psi|\hat{\rm H}|\psi\rangle \quad \text{or}$$

$$E_{\rm LP} = \sum_{\mu,\nu} c_\mu c_\nu \langle\mu|\hat{\rm H}|\nu\rangle = \sum_{\mu,\nu} c_\mu c_\nu H_{\mu\nu}.$$

Hamiltonian of the electron lone pair is:

$$\hat{\rm H} = \hat{\rm H}^0 + \hat{\rm H}^1$$

$$H^0_{\mu\nu} \equiv \langle\mu|\hat{\rm H}^0|\nu\rangle = \begin{cases} \lambda, & \text{if } \mu = \nu = p_x, p_y \text{ and } p_z \\ 0, & \text{otherwise.} \end{cases}$$

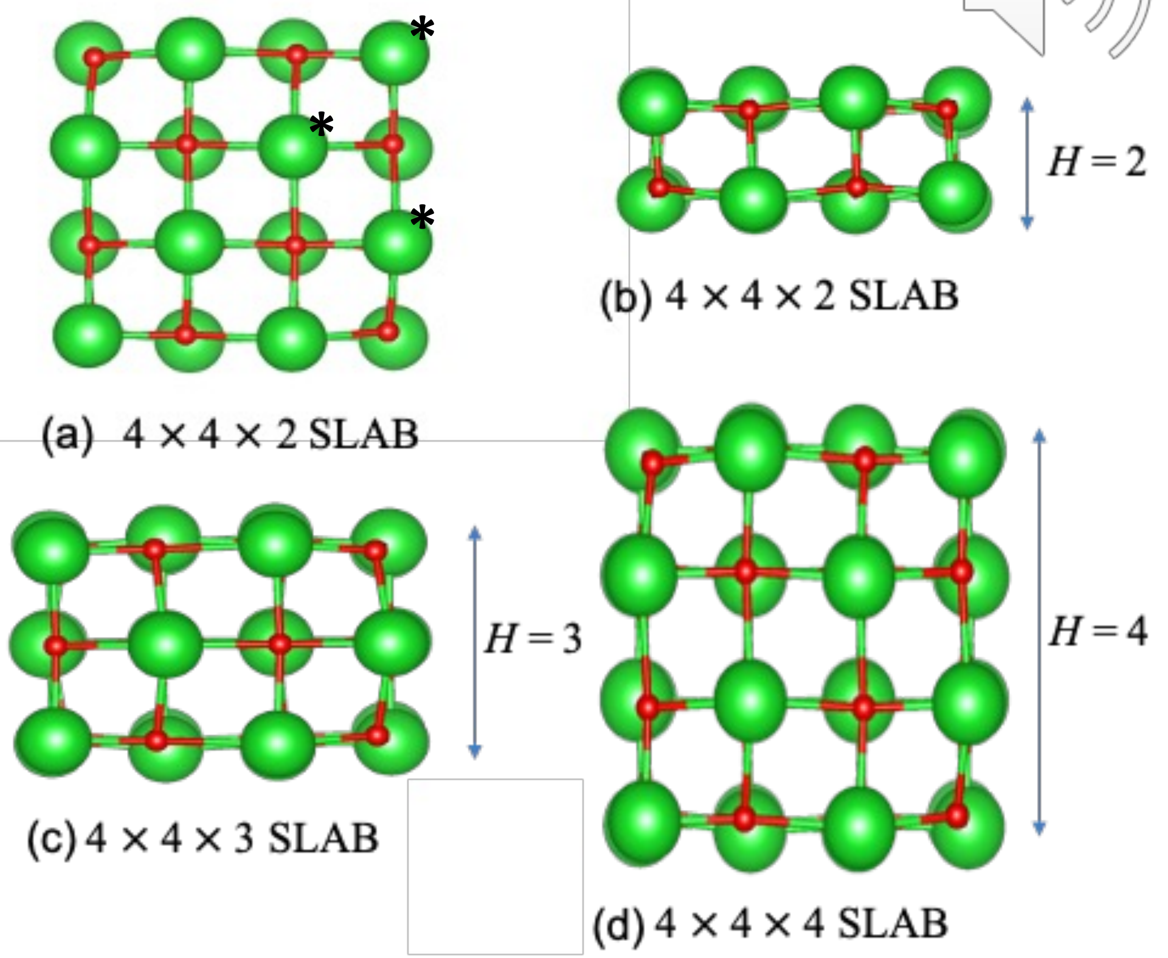
Ground state model Hamiltonian and $\hat{\rm H}^1$ is …

Model Application: Sn^{2+} impurity in barium oxide molecular cluster (1)

Barium oxide nanoclusters are known to have rocksalt like structures, which resembles their bulk [1], and thus clear to investigate structural distortions induced by lone pair density.

❑ Objectives

- ➢ BaO nanocluster slabs in different sizes denoted by using $K \times L \times H$ notation – see fig 1.
- ➢ Each BaO nanocluster has unique Ba sites, where we replace the Ba cation into Sn lone piar cation.
- ➢ We relaxed the clusters with Sn cation impurity by using three different models – DFT(PBEsol), the lone pair model and IP.
- ➢ We compared the model results with that of DFT and IP



(a) 4 × 4 × 2 SLAB

(b) 4 × 4 × 2 SLAB

(c) 4 × 4 × 3 SLAB

(d) 4 × 4 × 4 SLAB

Fig 1. Various barium oxide nanoclusters in rocksalt-like shapes. (a) and (b) show top and side views of 4×4×2 slab, respectively. (c) and (d) show side views of the corresponding slab sizes.

computational detail.
BaO IP potential take from [2]
Keeping O-O potential from BaO
IP Sn-O potential parameters are fitted to α-SnO

[1] *J. Phys. Chem. C* 2009, *113,* 20486–20492
[2] *Computational and Theoretical Chemistry* 1107 (2017) 74–81

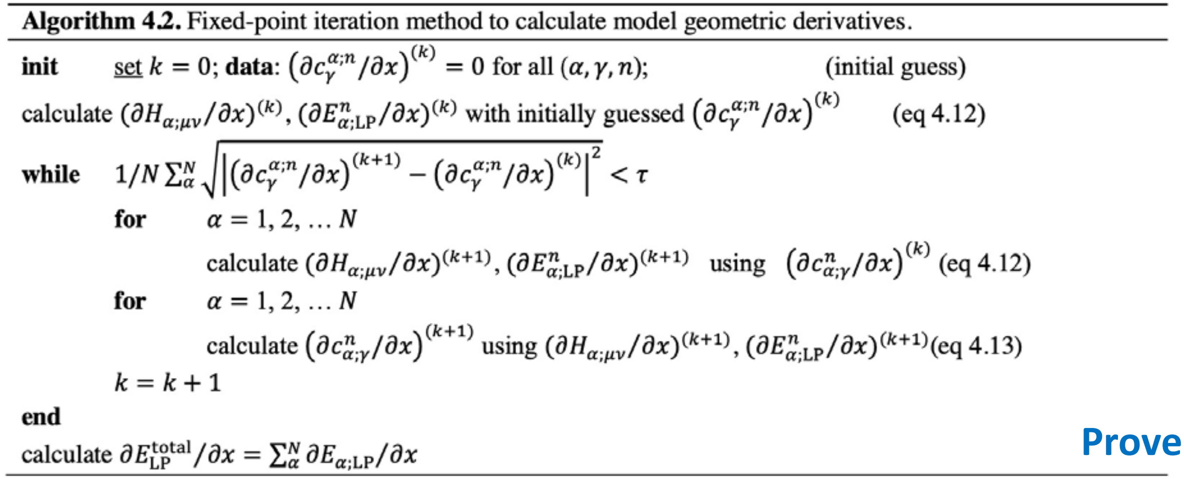
Model Development/Implementation

Energy / Force calculations in the LPM

2.2b Nanocluster System Modelling for Simulation

Modelling $\mathbf{F}_{\boldsymbol{i}} = -\nabla_i E(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$

Force Calculation Algorithm



Algorithm 4.2. Fixed-point iteration method to calculate model geometric derivatives.

```
init    set $k = 0$; data: $(\partial c_\gamma^{\alpha;n}/\partial x)^{(k)} = 0$ for all $(\alpha, \gamma, n)$;      (initial guess)
calculate $(\partial H_{\alpha;\mu\nu}/\partial x)^{(k)}$, $(\partial E_{\alpha;\mathrm{LP}}^n/\partial x)^{(k)}$ with initially guessed $(\partial c_\gamma^{\alpha;n}/\partial x)^{(k)}$      (eq 4.12)
while   $1/N \sum_\alpha^N \sqrt{\left|(\partial c_\gamma^{\alpha;n}/\partial x)^{(k+1)} - (\partial c_\gamma^{\alpha;n}/\partial x)^{(k)}\right|^2} < \tau$
        for     $\alpha = 1, 2, \ldots N$
                calculate $(\partial H_{\alpha;\mu\nu}/\partial x)^{(k+1)}$, $(\partial E_{\alpha;\mathrm{LP}}^n/\partial x)^{(k+1)}$ using $(\partial c_{\alpha;\gamma}^n/\partial x)^{(k)}$ (eq 4.12)
        for     $\alpha = 1, 2, \ldots N$
                calculate $(\partial c_{\alpha;\gamma}^n/\partial x)^{(k+1)}$ using $(\partial H_{\alpha;\mu\nu}/\partial x)^{(k+1)}$, $(\partial E_{\alpha;\mathrm{LP}}^n/\partial x)^{(k+1)}$(eq 4.13)
        $k = k + 1$
end
calculate $\partial E_{\mathrm{LP}}^{\mathrm{total}}/\partial x = \sum_\alpha^N \partial E_{\alpha;\mathrm{LP}}/\partial x$
```

Taken from UCL report

Once the energy and force established,
binding with local optimiser (BFGS, LS etc) is straightforward.

Electronic force by the lone pair electron densities

$$\frac{\partial E_{\mathrm{LP}}^{\mathrm{total}}}{\partial x} = \sum_\alpha \frac{\partial E_{\alpha;\mathrm{LP}}}{\partial x} = \sum_\alpha \left\langle \psi_\alpha \middle| \frac{\partial \widehat{H}_\alpha}{\partial x} \middle| \psi_\alpha \right\rangle$$

$$= \sum_\alpha \sum_{\mu,\nu} c_\mu^\alpha c_\nu^\alpha \left[\sum_A \frac{\partial H_{\alpha A;\mu\nu}^{MM}}{\partial x} + \sum_{\beta \neq \alpha} \sum_{\lambda,\sigma} \left\{ \frac{\partial c_\lambda^\beta}{\partial x} c_\sigma^\beta \langle \mu_\alpha | \widetilde{\Phi}_{\alpha\beta;\lambda\sigma} | \nu_\alpha \rangle + \frac{1}{2} c_\lambda^\beta c_\sigma^\beta \left\langle \mu_\alpha \middle| \frac{\partial \widetilde{\Phi}_{\alpha\beta;\lambda\sigma}}{\partial x} \middle| \nu_\alpha \right\rangle \right\} \right]$$

This term does not disappear …

(this does not cause an issue when there is a single lone pair cation in a system)

coupled relation

$$\frac{\partial c_\gamma^{\alpha;n}}{\partial x} = \sum_{m \neq n} \sum_{\mu,\nu} \frac{c_\mu^{\alpha;m} c_\gamma^{\alpha;m}}{E_{\alpha;\mathrm{LP}}^m - E_{\alpha;\mathrm{LP}}^n} \left(c_\nu^{\alpha;n} \frac{\partial E_{\alpha;\mathrm{LP}}^n}{\partial x} \delta_{\mu\nu} - c_\gamma^{\alpha;n} \frac{\partial H_{\alpha;\mu\nu}}{\partial x} \right)$$

Coupled Perturbed Hartree-Fock (**CPHF**) equation

Proved that the problem can be reduced into the form below

$$\mathbf{B}\,\mathbf{c}^{(k)} + \mathbf{d} = \mathbf{c}^{(\mathrm{k+1})}$$

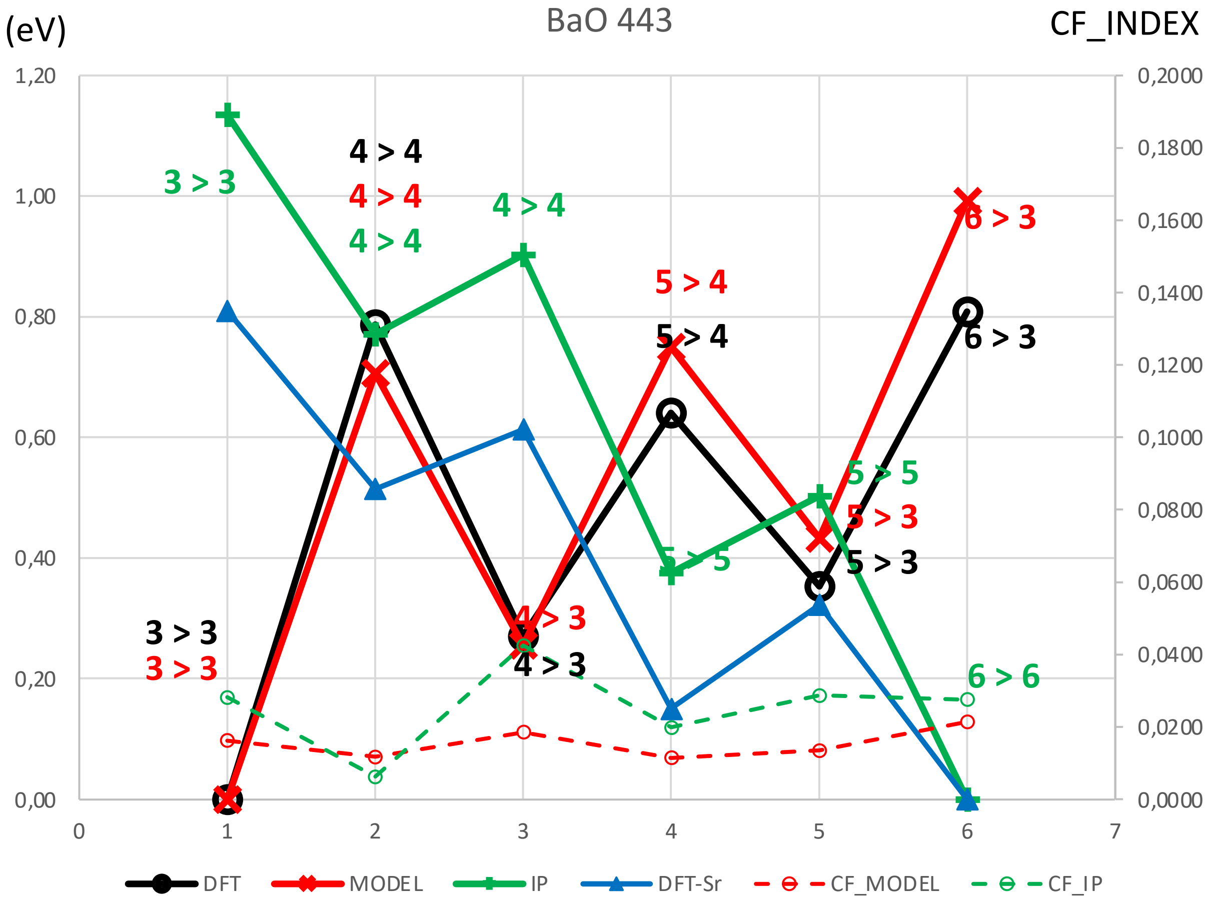
where the unknowns are in the vector **c**, and the iterative method generates a sequence of approximations, $\mathbf{c}^{(1)}$,$\mathbf{c}^{(2)}$, … with initially guessed $\mathbf{c}^{(0)}$ until the approximation meets the termination criteria.

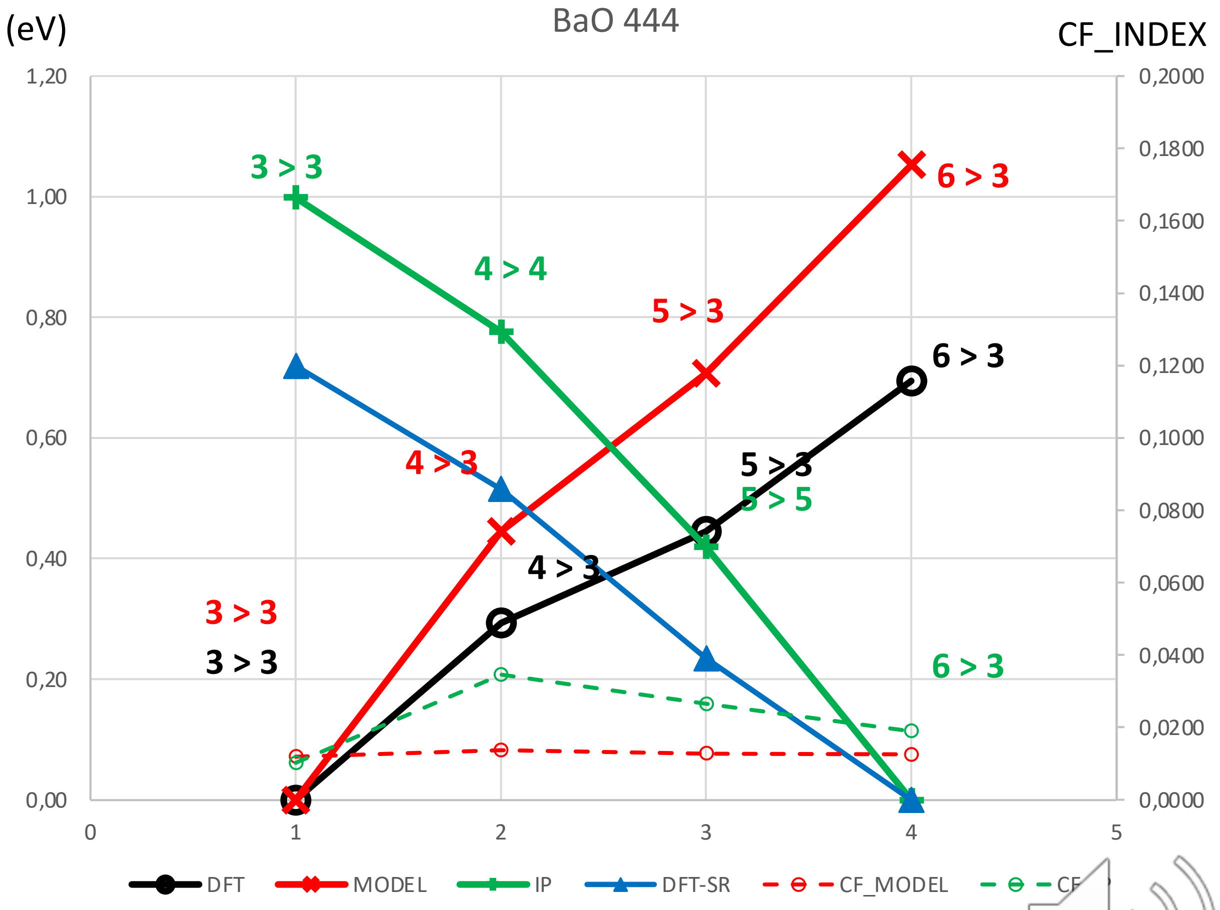
can be solved using an iterative method

- **The whole development process will be a milestone for others trying to use the similar approach.**
- **Indeed, the experience now giving great help for developing the periodic extension of LPM.**

Model Application: Sn^{2+} impurity in barium oxide molecular cluster (3)

2020 VIRTUAL MRS® SPRING/FALL MEETING & EXHIBIT

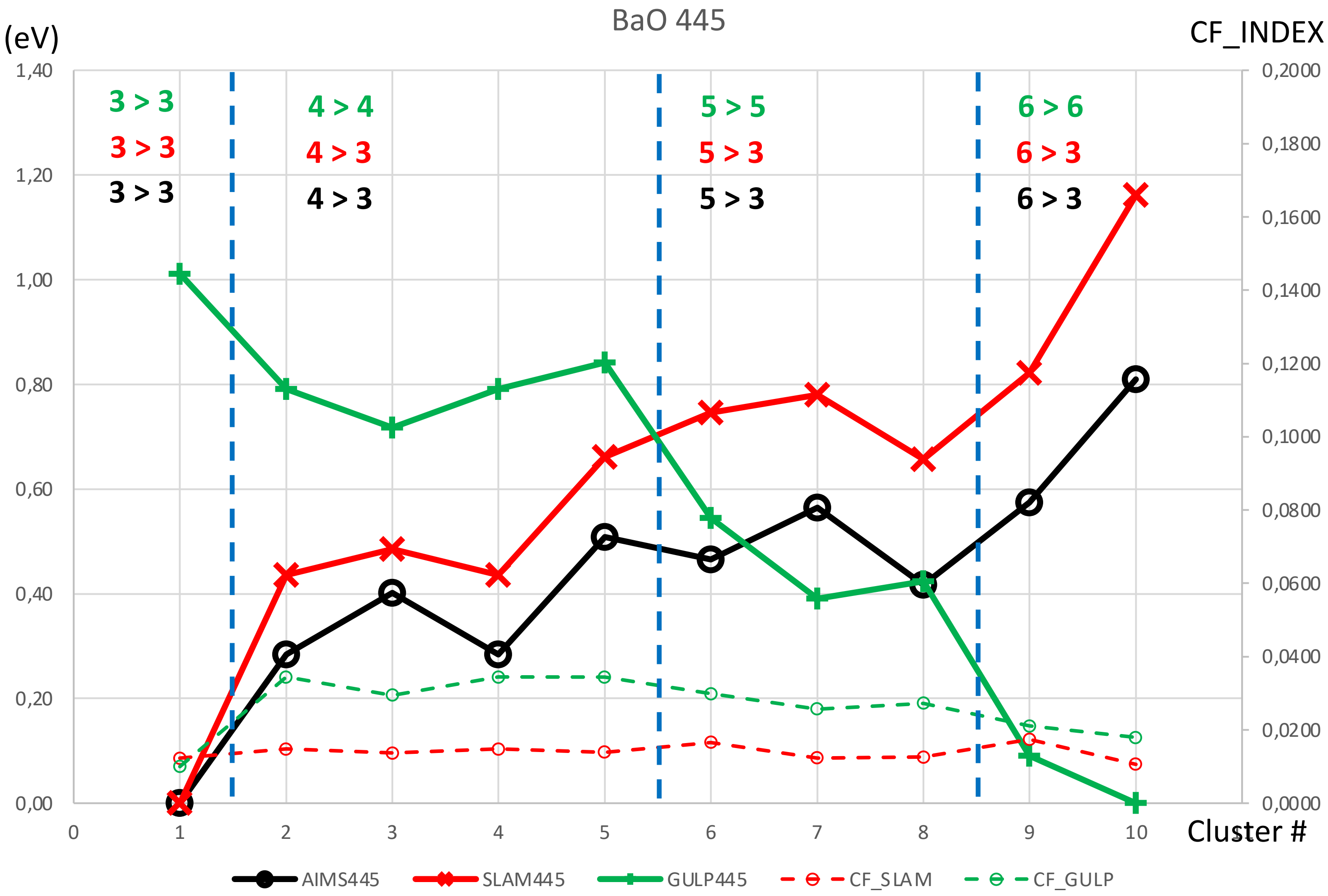




- In general, the model results show better agreement with DFT – in terms of bond dissociation and energetics
- The IP results behave more like DFT-Sr, which implies that the IP cation is rather prouncing asymmetrical lone pair (shell) but behaves more like spherical entity.

Creating a lone pair cation impurity in BaO molecular cluster:

BaO 445

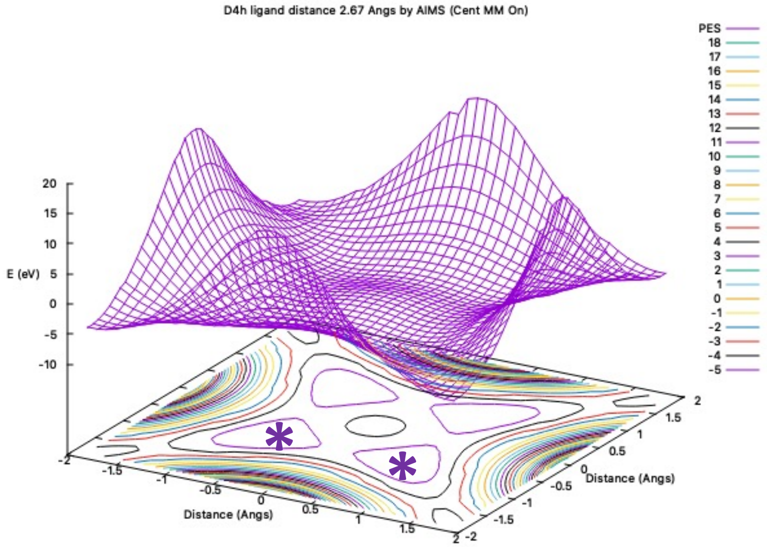


Results

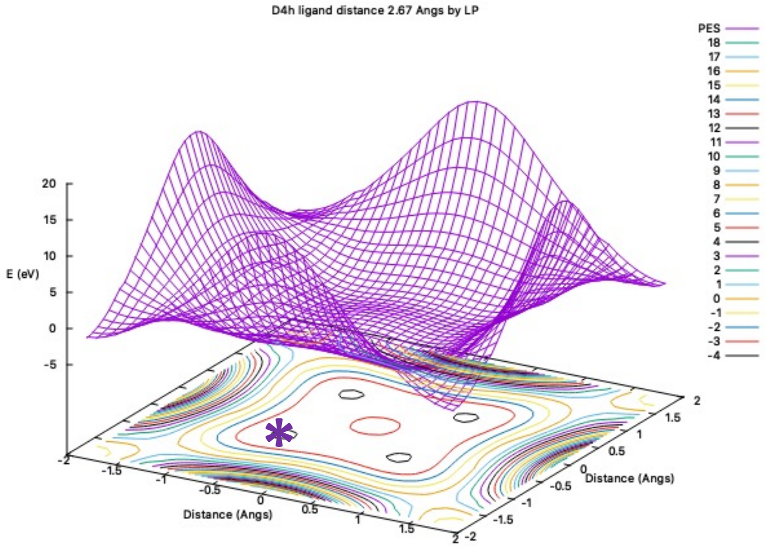
- ☐ ***One can observe, the lone pair cation by DFT / SLAM prefer to form coordination number of 3.***
- ☐ ***When lone pair cation is located at the corner, it shows the most stable energy, since it does not need to break any bonds.***
- ☐ ***When lone pair cation is located at Oh environment (6 > 3), then it shows the highest energy cost, since it needs to push out the surrounding Ba/O ions to make bond dissociations.***
- ☐ ***GULP (shell model) prefers to keep a rocksalt-like symmetric structure (bond dissociations are not observed).***

Model application I.

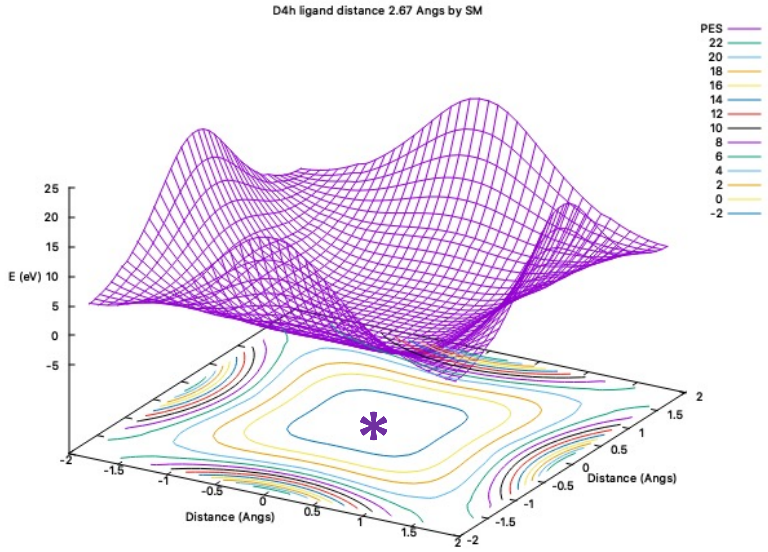
Creating a single Sn(II) defect on BaO nanoclusters



DFT



Model



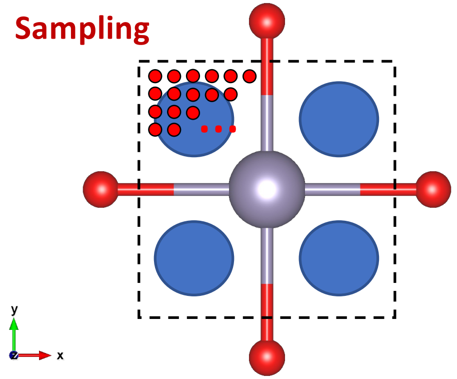
Shell Model

cavity size (2.67 Å) centre to ligand distance,(Ba-O) bond length (2.67 Å) of 664 BaO cluster

- ❑ By using the toy-system in fig 1, we investigated the inert lone pair effect

DFT and Model results has four local minima around the vertices, however IP shows one minimum at the centre point.

- ➢ *The lone pair model has better performace to approximate the PES of DFT and also inert lone pair effect.*

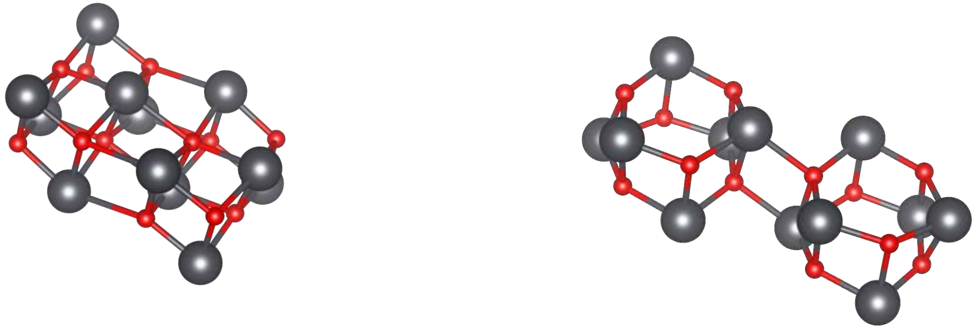


Sn(II) (grey ball) in surrounded by 4 O anions (red balls)

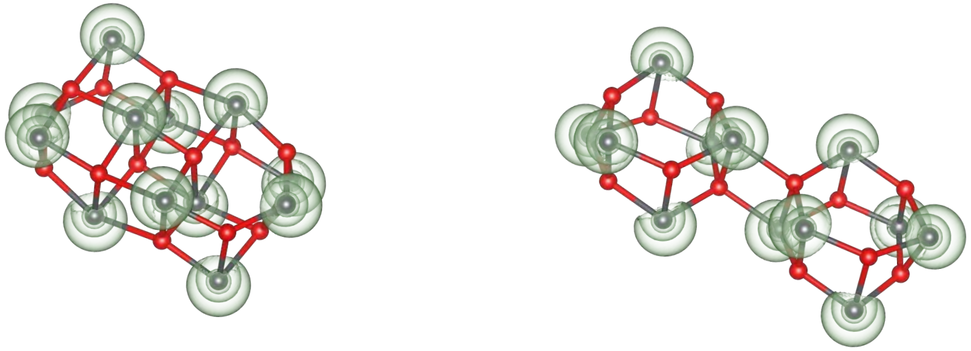
Model application II. Characterisation of nanoclusters PbO

Optimising **tetromino structures** on energy landscapes of the **DFT** and the **Lone pair mode**

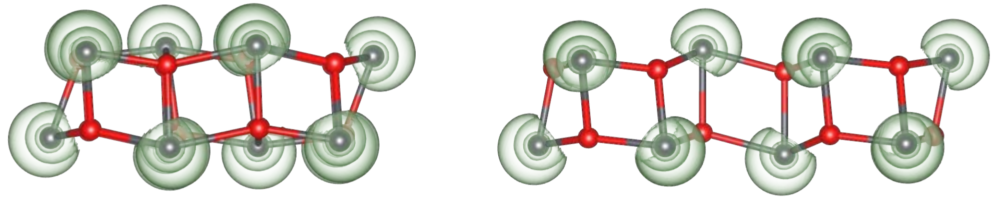
DFT



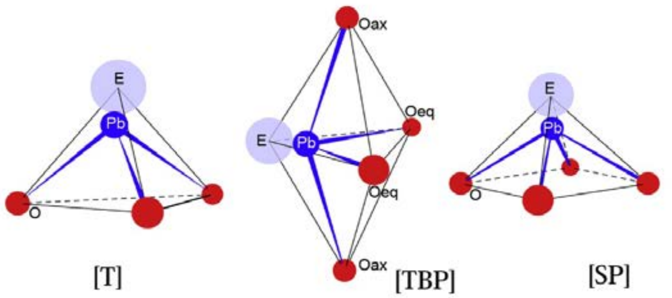
LPM



LPM
side view



- Lone pair caiton Pb(II) prefers to have specific local coordination environments [1].



Local coordination environment of lone pair cation

- Extra coordination sites (to be 5 or 6 coordinations by oxygen ligands) are occupied by the stereo-active lone pairs.

[1] J. Galy, S.F. Matar, Prog. Solid. State Ch. 44 (2016) 35–58.