A Calculation of the $\dfrac{N_{Pb}}{N_{Se}}$ ratio for various cluster shapes

- **Octahedron** (Oh)

  The volume of an octahedron with edge L is

$$V_{Oh} = \frac{\sqrt{2}}{3} L^3. \tag{A.1}$$

  Since in this case all the faces have the same crystallographic index, the total surface of (111) faces, S_{111}, is equal to the total lateral surface:

$$S_{111,Oh} = S_{Oh} = 8S_{tr} = 8\frac{\sqrt{3}}{4} L^2 = 2\sqrt{3} L^2. \tag{A.2}$$

  where S_{tr} is the area of each triangle forming the solid surface (see also figure 4 in the text).

  The octahedron edge L can be expressed as a function of the cluster diameter d, $L = d/\sqrt{2}$, so that eqs. A.1, A.2 become

$$V_{Oh} = \frac{d^3}{6} \tag{A.3}$$

  and

$$S_{111,Oh} = \sqrt{3} d^2 \tag{A.4}$$

  Inserting eqs. A.3 and A.4 in eq. 4 in the text:

$$\left(\frac{N_{Pb}}{N_{Se}}\right)_{Oh} = \frac{d + \frac{3}{4}\sqrt{3}a}{d - \frac{3}{4}\sqrt{3}a} \tag{A.5}$$

  recalling that a is the periodic lattice constant.

  Since eq. A.5 has been obtained for ideal solids (i.e. neglecting the edge effects which can be important in real atomic clusters), we checked its reliability by extracting from the PbSe bulk several octahedral clusters, and fitting their Pb/Se atomic ratio with eq. A.5. The comparison is shown in figure A.1.

- **Truncated octahedron** (TOh)

  The volume of a truncated octahedron with edge L is

$$V_{TOh} = 8\sqrt{2} L^3. \tag{A.6}$$

  In this case the S_{111} portion is not equal to the total lateral surface. We have

$$S_{111,TOh} = 8S_{hex} = 8\left(\frac{3}{2}\sqrt{3}L^2\right) = 12\sqrt{3} L^2. \tag{A.7}$$

  where S_{hex} is the area of one of the hexagons on the solid surface (see figure 4 in the text).

The edge can be expressed as a function of the cluster diameter d as $L = d/2\sqrt{2}$, so that

$$V_{TOh} = \frac{d^3}{2} \tag{A.8}$$

and

$$S_{111,TOh} = \frac{3}{2}\sqrt{3}d^2. \tag{A.9}$$

Then the Pb/Se ratio becomes

$$\left(\frac{N_{Pb}}{N_{Se}}\right)_{TOh} = \frac{d + \frac{3}{8}\sqrt{3}a}{d - \frac{3}{8}\sqrt{3}a} \tag{A.10}$$

In Figure A.2 we report the fit of the Pb/Se ratio of several truncated octahedra clusters with eq. A.10.

- **Cuboctahedron** (COh)

  The volume of a cuboctahedron with edge L is

$$V_{COh} = \frac{5}{3}\sqrt{2}L^3. \tag{A.11}$$

  In this case the surface of the (111) faces is

$$S_{111,COh} = 8S_{tr} = 8\left(\frac{\sqrt{3}}{4}L^2\right) = 2\sqrt{3}L^2. \tag{A.12}$$

  where S_{tr} is the area of one of the triangular portions of the surface (see figure 4 in the text).

  The edge is $L = d/2$, so that

$$V_{COh} = \frac{5}{24}\sqrt{2}d^3, \tag{A.13}$$

$$S_{111,COh} = \frac{\sqrt{3}}{2}d^2 \tag{A.14}$$

  and

$$\left(\frac{N_{Pb}}{N_{Se}}\right)_{COh} = \frac{d + \frac{3}{20}\sqrt{6}a}{d - \frac{3}{20}\sqrt{6}a} \tag{A.15}$$

  As above, the Pb/Se ratio computed in several cuboctahedral clusters extracted from the PbSe crystal has been fitted with eq. A.15, as shown in figure A.3.

Then for all the solids considered here, the Pb/Se ratio can be written

$$\frac{N_{Pb}}{N_{Se}} = f(d) = \frac{d + \beta a}{d - \beta a} \tag{A.16}$$

where d is the cluster diameter and β a shape parameter. The values of β are reported in table 1, corresponding to table 4 in the text.

Shape	β
Octahedron	$3/4\sqrt{3}$
Truncated Octahedron	$3/8\sqrt{3}$
Cuboctahedron	$3/20\sqrt{6}$

Table 1: Shape parameters for three model solids

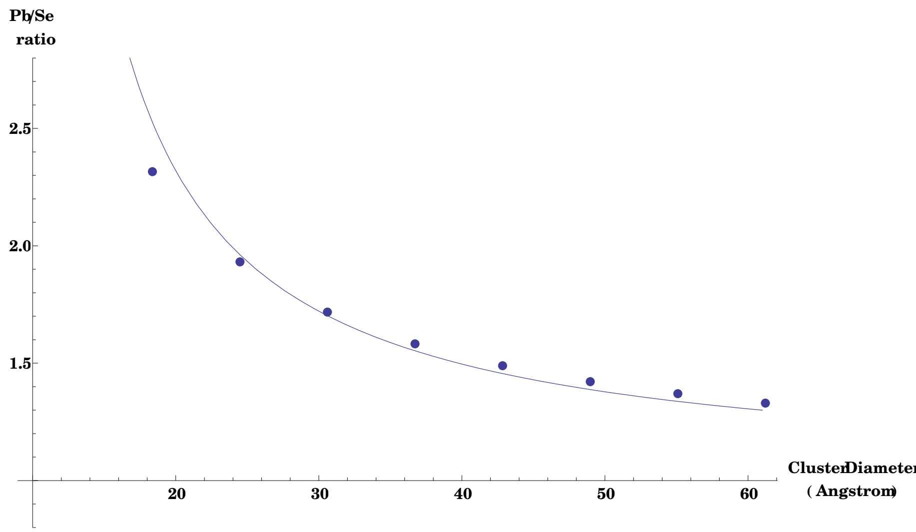

Figure A.1: Fitting of the actual Pb/Se ratio for octahedral clusters with function A.5

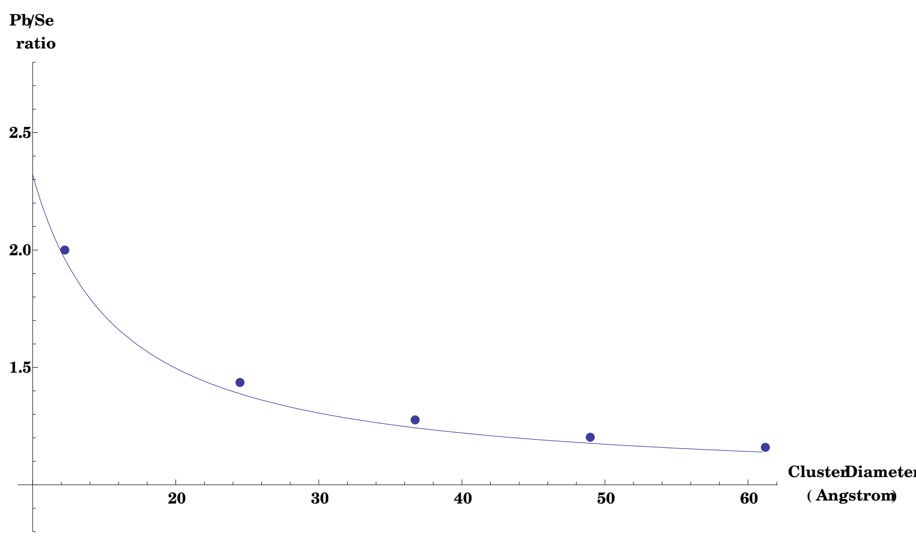

Figure A.2: Fitting of the actual Pb/Se ratio for truncated octahedral clusters with function A.10

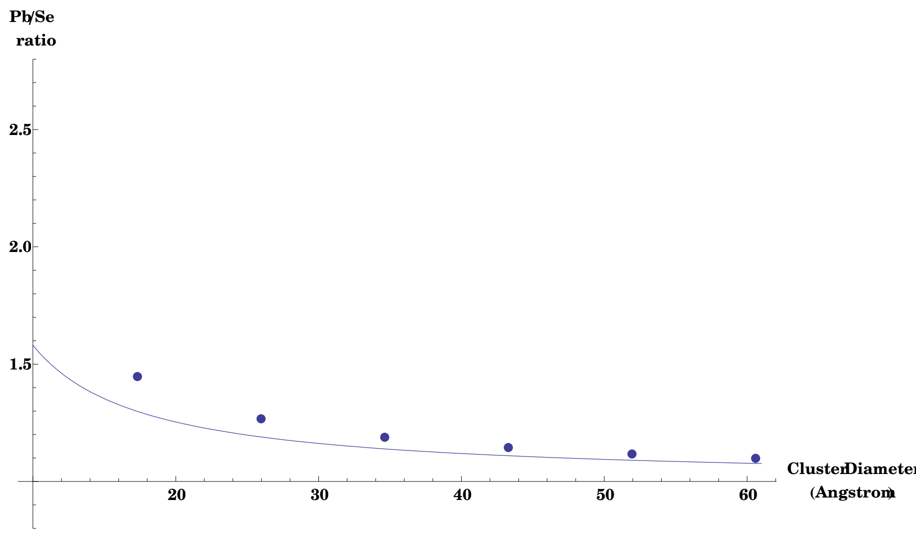

Figure A.3: Fitting of the actual Pb/Se ratio for cuboctahedral clusters with function A.15