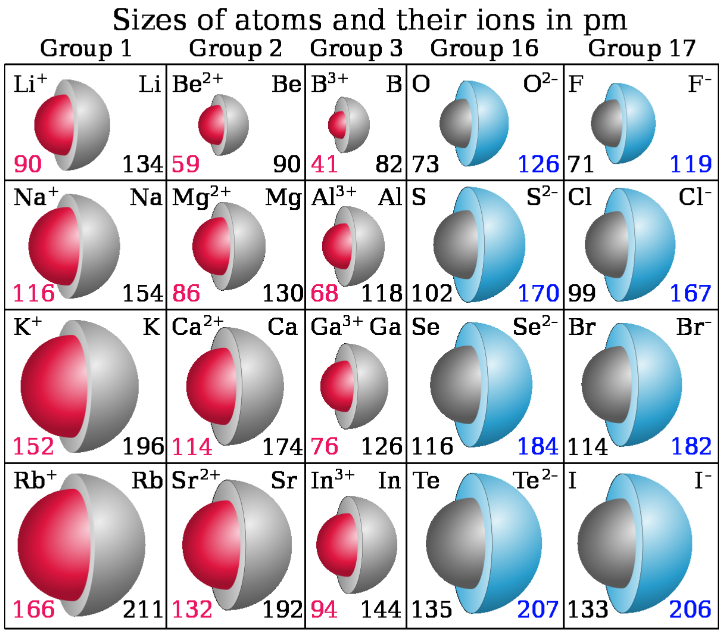
Ionic radius

Ionic radius, r_{ion}, is the radius ascribed to an atom's ion. Although neither atoms nor ions have sharp boundaries, it is useful to treat them as if they are hard spheres with radii such that the sum of ionic radii of the cation and anion gives the distance between the ions in a crystal lattice. Ionic radii are typically given in units of either picometers (pm) or Angstroms (Å), with 1 Å = 100 pm. Typical values range from 30 pm (0.3 Å) to over 200 pm (2 Å).

Trends in ionic radii

X^-	NaX	AgX
F	464	492
Cl	564	555
Br	598	577
Unit cell parameters (in pm, equal to two M–X bond lengths) for sodium and silver halides. All compounds crystallize in the NaCl structure.		

Ions may be larger or smaller than the neutral atom, depending on the ion's charge. When an atom loses an electron to form a cation, the lost electron no longer contributes to shielding the other electrons from the charge of the nucleus; consequently, the other electrons are more strongly attracted to the nucleus, and the radius of the atom gets smaller. Likewise, when an electron is added to an atom, forming an anion, the added electron shields the other electrons from the nucleus, with the result that the size of the atom increases.



Relative sizes of atoms and ions. The neutral atoms are colored gray, cations red, and anions blue.

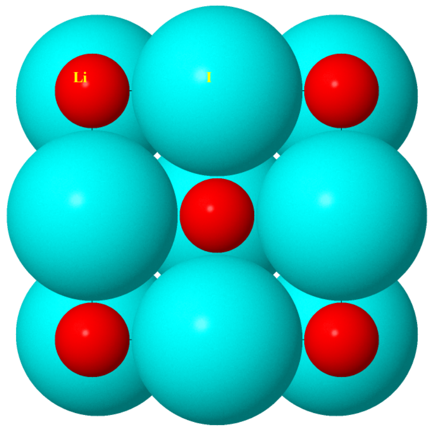
The ionic radius is not a fixed property of a given ion, but varies with coordination number, spin state and other parameters. Nevertheless, ionic radius values are sufficiently transferable to allow periodic trends to be recognized. As with other types of atomic radius, ionic radii increase on descending a group. Ionic size (for the same ion) also increases with increasing coordination number, and an ion in a high-spin state will be larger than the same ion in a low-spin state. In general, ionic radius decreases with increasing positive charge and increases with increasing negative charge.

An "anomalous" ionic radius in a crystal is often a sign of significant covalent character in the bonding. No bond is *completely* ionic, and some supposedly "ionic" compounds, especially of the transition metals, are particularly covalent in character. This is illustrated by the unit cell parameters for sodium and silver halides in the table. On the basis of the fluorides, one would say that Ag^+ is larger than Na^+, but on the basis of the chlorides and bromides the opposite appears to be true.[1] This is because the greater covalent character of the bonds in AgCl and AgBr reduces the bond length and hence the apparent ionic radius of Ag^+, an effect which is not present in the halides of the more electropositive sodium, nor in silver fluoride in which the fluoride ion is relatively unpolarizable.

Determination of ionic radii

The distance between two ions in an ionic crystal can be determined by X-ray crystallography, which gives the lengths of the sides of the unit cell of a crystal. For example, the length of each edge of the unit cell of sodium chloride is found to be 564.02 pm. Each edge of the unit cell of sodium chloride may be considered to have the atoms arranged as Na^+•••Cl^-•••Na^+, so the edge is twice the Na-Cl separation. Therefore, the distance between the Na^+ and Cl^- ions is half of 564.02 pm, which is 282.01 pm. However, although X-ray crystallography gives the distance between ions, it doesn't indicate where the boundary is between those ions, so it doesn't directly give ionic radii.

Landé[2] estimated ionic radii by considering crystals in which the anion and cation have a large difference in size, such as LiI. The lithium ions are so much smaller than the iodide ions that the lithium fits into holes within the crystal lattice, allowing the iodide ions to touch. That is, the distance between two neighboring iodides in the crystal is assumed to be twice the radius of the iodide ion, which was deduced to be 214 pm. This value can be used to determine other radii. For example, the inter-ionic distance in RbI is 356 pm, giving 142 pm for the ionic radius of Rb^+. In this way values for the radii of 8 ions were determined.



Front view of the unit cell of a LiI crystal, using Shannon's crystal data (Li^+ = 90 pm; I^- = 206 pm). The iodide ions nearly touch (but don't quite), indicating that Landé's assumption is fairly good.

Wasastjerna estimated ionic radii by considering the relative volumes of ions as determined from electrical polarizability as determined by measurements of refractive index.[3] These results were extended by Victor Goldschmidt[4] Both Wasastjerna and Goldschmidt used a value of 132 pm for the O^{2-} ion.

Pauling used effective nuclear charge to proportion the distance between ions into anionic and a cationic radii.[5] His data gives the O^{2-} ion a radius of 140 pm.

A major review of crystallographic data led to the publication of revised ionic radii by Shannon.[6] Shannon gives different radii for different coordination numbers, and for high and low spin states of the ions. To be consistent with Pauling's radii, Shannon has used a value of $r_{ion}(O^{2-})$ = 140 pm; data using that value are referred to as "effective" ionic radii. However, Shannon also includes data based on $r_{ion}(O^{2-})$ = 126 pm; data using that value are referred to as "Crystal" ionic radii. Shannon states that "it is felt that crystal radii correspond more closely to the physical size of ions in a solid."[6] The two sets of data are listed in the two tables below.

Crystal ionic radii in pm of elements in function of ionic charge and spin (*ls* = low spin, *hs*= high spin). Ions are 6-coordinate unless indicated differently in parentheses (e.g. 146 (4) for 4-coordinate N^{3-}).[6]

Number	Name	Symbol	3–	2–	1–	1+	2+	3+	4+	5+	6+	7+	8+
3	Lithium	Li				90							
4	Beryllium	Be					59						
5	Boron	B						41					
6	Carbon	C							30				
7	Nitrogen	N	132 (4)					30		27			
8	Oxygen	O		126									

9	Fluorine	F			119							22	
11	Sodium	Na				116							
12	Magnesium	Mg					86						
13	Aluminum	Al						67.5					
14	Silicon	Si							54				
15	Phosphorus	P						58		52			
16	Sulfur	S		170					51		43		
17	Chlorine	Cl			167					26 (3py)		41	
19	Potassium	K				152							
20	Calcium	Ca					114						
21	Scandium	Sc						88.5					
22	Titanium	Ti					100	81	74.5				
23	Vanadium	V					93	78	72	68			
24	Chromium	Cr					87 *ls*; 94 *hs*	75.5	69	63	58		
25	Manganese	Mn					81 *ls*; 97 *hs*	72 *ls*; 78.5 *hs*	67	47 (4)	39.5 (4)	60	
26	Iron	Fe					75 *ls*; 92 *hs*	69 *ls*; 78.5 *hs*	72.5		39 (4)		
27	Cobalt	Co					79 *ls*; 88.5 *hs*	68.5 *ls*; 75 *hs*	67 *hs*				
28	Nickel	Ni					83	70 *ls*; 74 *hs*	62 *ls*				
29	Copper	Cu				91	87	68 *ls*					
30	Zinc	Zn					88						
31	Gallium	Ga						76					
32	Germanium	Ge					87		67				
33	Arsenic	As						72		60			
34	Selenium	Se		184					64		56		
35	Bromine	Br			182			73 (4sq)		45 (3py)		53	
37	Rubidium	Rb				166							
38	Strontium	Sr					132						
39	Yttrium	Y						104					
40	Zirconium	Zr							86				
41	Niobium	Nb						86	82	78			
42	Molybdenum	Mo						83	79	75	73		
43	Technetium	Tc							78.5	74		70	
44	Ruthenium	Ru						82	76	70.5		52 (4)	50 (4)
45	Rhodium	Rh						80.5	74	69			
46	Palladium	Pd				73 (2)	100	90	75.5				
47	Silver	Ag				129	108	89					
48	Cadmium	Cd					109						
49	Indium	In						94					
50	Tin	Sn							83				

51	Antimony	Sb						90		76			
52	Tellurium	Te		207					111		70		
53	Iodine	I			206					109		67	
54	Xenon	Xe											62
55	Caesium	Cs				181							
56	Barium	Ba					149						
57	Lanthanum	La						117.2					
58	Cerium	Ce						115	101				
59	Praseodymium	Pr						113	99				
60	Neodymium	Nd					143 (8)	112.3					
61	Promethium	Pm						111					
62	Samarium	Sm					136 (7)	109.8					
63	Europium	Eu					131	108.7					
64	Gadolinium	Gd						107.5					
65	Terbium	Tb						106.3	90				
66	Dysprosium	Dy					121	105.2					
67	Holmium	Ho						104.1					
68	Erbium	Er						103					
69	Thulium	Tm					117	102					
70	Ytterbium	Yb					116	100.8					
71	Lutetium	Lu						100.1					
72	Hafnium	Hf							85				
73	Tantalum	Ta						86	82	78			
74	Tungsten	W							80	76	74		
75	Rhenium	Re							77	72	69	67	
76	Osmium	Os							77	71.5	68.5	66.5	53 (4)
77	Iridium	Ir						82	76.5	71			
78	Platinum	Pt					94		76.5	71			
79	Gold	Au				151		99		71			
80	Mercury	Hg				133	116						
81	Thallium	Tl				164		102.5					
82	Lead	Pb					133		91.5				
83	Bismuth	Bi						117		90			
84	Polonium	Po							108		81		
85	Astatine	At										76	
87	Francium	Fr				194							
88	Radium	Ra					162 (8)						
89	Actinium	Ac						126					
90	Thorium	Th							108				

91	Protactinium	Pa						116	104	92			
92	Uranium	U						116.5	103	90	87		
93	Neptunium	Np					124	115	101	89	86	85	
94	Plutonium	Pu						114	100	88	85		
95	Americium	Am					140 (8)	111.5	99				
96	Curium	Cm						111	99				
97	Berkelium	Bk						110	97				
98	Californium	Cf						109	96.1				

Effective ionic radii in pm of elements in function of ionic charge and spin (*ls* = low spin, *hs*= high spin). Ions are 6-coordinate unless indicated differently in parentheses (e.g. 146 (4) for 4-coordinate N^{3-}).[6]

Number	Name	Symbol	3–	2–	1–	1+	2+	3+	4+	5+	6+	7+	8+
3	Lithium	Li				76							
4	Beryllium	Be					45						
5	Boron	B						27					
6	Carbon	C							16				
7	Nitrogen	N	146 (4)					16		13			
8	Oxygen	O		140									
9	Fluorine	F			133							8	
11	Sodium	Na				102							
12	Magnesium	Mg					72						
13	Aluminum	Al						53.5					
14	Silicon	Si							40				
15	Phosphorus	P						44		38			
16	Sulfur	S		184					37		29		
17	Chlorine	Cl			181					12 (3py)		27	
19	Potassium	K				138							
20	Calcium	Ca					100						
21	Scandium	Sc						74.5					
22	Titanium	Ti					86	67	60.5				
23	Vanadium	V					79	64	58	54			
24	Chromium	Cr					73 *ls*; 80 *hs*	61.5	55	49	44		
25	Manganese	Mn					67 *ls*; 83 *hs*	58 *ls*; 64.5 *hs*	53	33 (4)	25.5 (4)	46	
26	Iron	Fe					61 *ls*; 78 *hs*	55 *ls*; 64.5 *hs*	58.5		25 (4)		
27	Cobalt	Co					65 *ls*; 74.5 *hs*	54.5 *ls*; 61 *hs*	53 *hs*				
28	Nickel	Ni					69	56 *ls*; 60 *hs*	48 *ls*				
29	Copper	Cu				77	73	54 *ls*					

30	Zinc	Zn					74						
31	Gallium	Ga						62					
32	Germanium	Ge					73		53				
33	Arsenic	As						58		46			
34	Selenium	Se		198					50		42		
35	Bromine	Br			196			59 (4sq)		31 (3py)		39	
37	Rubidium	Rb				152							
38	Strontium	Sr					118						
39	Yttrium	Y						90					
40	Zirconium	Zr							72				
41	Niobium	Nb						72	68	64			
42	Molybdenum	Mo						69	65	61	59		
43	Technetium	Tc							64.5	60		56	
44	Ruthenium	Ru						68	62	56.5		38 (4)	36 (4)
45	Rhodium	Rh						66.5	60	55			
46	Palladium	Pd				59 (2)	86	76	61.5				
47	Silver	Ag				115	94	75					
48	Cadmium	Cd					95						
49	Indium	In						80					
50	Tin	Sn							69				
51	Antimony	Sb						76		60			
52	Tellurium	Te		221					97		56		
53	Iodine	I			220					95		53	
54	Xenon	Xe											48
55	Caesium	Cs				167							
56	Barium	Ba					135						
57	Lanthanum	La						103.2					
58	Cerium	Ce						101	87				
59	Praseodymium	Pr						99	85				
60	Neodymium	Nd					129 (8)	98.3					
61	Promethium	Pm						97					
62	Samarium	Sm					122 (8)	95.8					
63	Europium	Eu					117	94.7					
64	Gadolinium	Gd						93.5					
65	Terbium	Tb						92.3	76				
66	Dysprosium	Dy					107	91.2					
67	Holmium	Ho						90.1					
68	Erbium	Er						89					
69	Thulium	Tm					103	88					

70	Ytterbium	Yb					102	86.8					
71	Lutetium	Lu						86.1					
72	Hafnium	Hf							71				
73	Tantalum	Ta						72	68	64			
74	Tungsten	W							66	62	60		
75	Rhenium	Re							63	58	55	53	
76	Osmium	Os							63	57.5	54.5	52.5	39 (4)
77	Iridium	Ir						68	62.5	57			
78	Platinum	Pt					80		62.5	57			
79	Gold	Au				137		85		57			
80	Mercury	Hg				119	102						
81	Thallium	Tl				150		88.5					
82	Lead	Pb					119		77.5				
83	Bismuth	Bi						103		76			
84	Polonium	Po							94		67		
85	Astatine	At										62	
87	Francium	Fr				180							
88	Radium	Ra					148 (8)						
89	Actinium	Ac						112					
90	Thorium	Th							94				
91	Protactinium	Pa						104	90	78			
92	Uranium	U						102.5	89	76	73		
93	Neptunium	Np					110	101	87	75	72	71	
94	Plutonium	Pu						100	86	74	71		
95	Americium	Am					126 (8)	97.5	85				
96	Curium	Cm						97	85				
97	Berkelium	Bk						96	83				
98	Californium	Cf						95	82.1				

Non-spherical Ions

The concept of ionic radii is based on the assumption of a spherical ion shape. However, from a group-theoretical point of view the assumption is only justified for ions that reside on high-symmetry crystal lattice sites like Na and Cl in halite or Zn and S in sphalerite. A clear distinction can be made, when the point symmetry group of the respective lattice site is considered,[7] which are the cubic groups O_h and T_d in NaCl and ZnS. For ions on lower-symmetry sites significant deviations of their electron density from a spherical shape may occur. This holds in particular for ions on lattice sites of polar symmetry, which are the crystallographic point groups C_1, C_{1h}, C_n or C_{nv}, n = 2, 3, 4 or 6.[8] A thorough analysis of the bonding geometry was recently carried out for pyrite-type disulfides, where monovalent sulfur ions reside on C_3 lattice sites. It was found that the sulfur ions have to be modeled by ellipsoids with different radii in direction of the symmetry axis and perpendicular to it.[9] Remarkably, it turned out in this case that it is not the ionic radius, but the ionic volume that remains constant in different crystalline compounds.

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[1] On the basis of conventional ionic radii, Ag^+ (129 pm) is indeed larger than Na^+ (116 pm)

[2] Landé, A. (1920). "Über die Größe der Atome" (http://springerlink.com/content/j862631p43032333/). *Zeitschrift für Physik* **1** (3): 191–197. . Retrieved 1 June 2011.

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