

Energies of electrons in atoms

Notes on General Chemistry

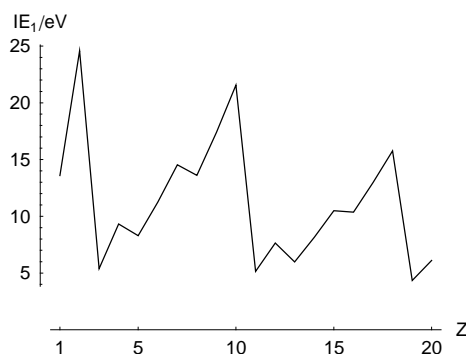
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...[quote]...

■ Atomic first ionization energies

Here is a chart showing the first ionization energy of the atoms hydrogen through calcium.



First ionization energy, in eV, of the atoms hydrogen through calcium.

Based on the chart above, what is the trend in ionization energies for the alkalis, the elements in the left most column of the periodic table? Hint: Circle the points corresponding to the alkalis and then connect just those points with a line.

Based on the chart above, what is the trend in ionization energies for the noble gases, the elements in the rightmost column of the periodic table?

Based on the chart above, what is the trend in ionization energies for the elements in any particular column of the periodic table?

Based on the chart above, what is the trend in ionization energies for the elements in any particular row of the periodic table?

Based on the chart above and your answers to the previous questions, make a sketch of how you think the chart would continue for gallium ($Z = 31$) to strontium ($Z = 38$).

■ Atomic electron configurations

We can use the pattern of relative changes in atomic ionization energies to uncover how electrons are arranged in many electron atoms. The place to start is expressions for the average distance and for the energy of an electron in a one-electron atom.

The average distance from the nucleus of an electron in the orbital $n\ell$, with $\ell = n - 1$ (1s, 2p, 3d, 4f, etc.), in a one-electron atom that has nuclear charge $+Ze$ is.

$$r_{\text{avg}} = a_0 n^2 / Z$$

where $a_0 = 0.529 \text{ \AA} = 0.0529 \text{ nm}$. The energy of an electron in a one-electron atom that has nuclear charge $+Ze$ is

$$E_n = -13.6 \text{ eV } Z^2 / n^2.$$

This energy is relative to the energy of the electron when it is very far away from the nucleus, corresponding to very large values of n .

The first ionization energy of hydrogen is 13.60 eV. The first ionization energy of helium is 24.59 eV. If the additional electron in helium were in the $n = 2$ shell, it would be easier to remove than the electron in hydrogen, since it would be farther from the nucleus and the nuclear charge would be reduced by about one unit by the shielding of the first, 1s electron. The fact that the helium ionization energy is higher rather than lower suggests that the added electron in helium is in the same 1s orbital as the electron in hydrogen.

The first ionization energy of lithium is 5.39 eV. Reasoning in the same way as for helium, the fact that the lithium ionization energy is lower than for either hydrogen or helium suggests that the added electron in lithium is in the $n = 2$ shell. At this point we do not have enough information to know whether it is in a 2s or a 2p orbital.

The first ionization energy of beryllium is 9.23 eV. Again, reasoning in a way analogous to what we did for helium, the fact that the beryllium ionization energy is higher than that for lithium suggests that the added electron in lithium is again in the $n = 2$ shell. However, we still do not have enough information to know whether it is in a 2s or a 2p orbital.

The first ionization energy of boron is 8.30 eV. Since this value is less than that for beryllium, but not much less, suggests that the added electron in boron is again in the $n = 2$ shell, but in a *different* subshell. Using Pauli's rule, based on other experimental evidence, that only two electrons may be in the same orbital, the data suggests that the added electrons in lithium and beryllium are in the 2s subshell and that the added electron in boron is in the 2p subshell. That is, we can conclude that the configuration of electrons in lithium is $1s^2 2s^1$, in beryllium is $1s^2 2s^2$, and in boron $1s^2 2s^2 2p^1$.

The first ionization energy continues to increase (except for a slight drop at oxygen) to neon, whose first ionization energy is 21.57 eV. This suggests that the added electrons are filling the 2p orbitals and so that the configuration of electrons in neon is $1s^2 2s^2 2p^6$.

The first ionization energy of the next element, sodium, is 5.14 eV. This very large drop is analogous to that between helium and lithium. Taking into account what we have learned so far, this suggests the configuration of electrons in sodium is $1s^2 2s^2 2p^6 3s^1$. This in turn suggest there should be an increase in ionization energy of the next element, magnesium, with configuration $1s^2 2s^2 2p^6 3s^2$, and then a drop in ionization energy of the next element, aluminum, with configuration $1s^2 2s^2 2p^6 3s^2 3p^1$. Indeed, the first ionization energy of magnesium is 7.65 eV, an increase from sodium, and the first ionization energy of aluminum is 5.99 eV, a decrease from magnesium.

Make a sketch of how you think the chart of second ionization energies would look, for the ions He^+ through Mg^+ .

Compare your predicted pattern of second ionization energies with the actual pattern constructed using measured second ionization energies as reported on WebElements.

■ Electron shielding

By analyzing the pattern of first ionization energies we have learned that the principle quantum number, $n = j + \ell$, where j is the number of radial loops in the wavefunction and ℓ is the number of angular planes in the wavefunction, determines the coarse scale of relative electron energies: The energy of an electron in an atom is greater, the greater the principle quantum number of its wavefunction. The number of angular planes sets the fine scale of relative electron energies. The energy ordering (lower energy, more stable \rightarrow higher energy, less stable) is determined first by the value of n , and then, for a given n , by the value of ℓ , as follows:

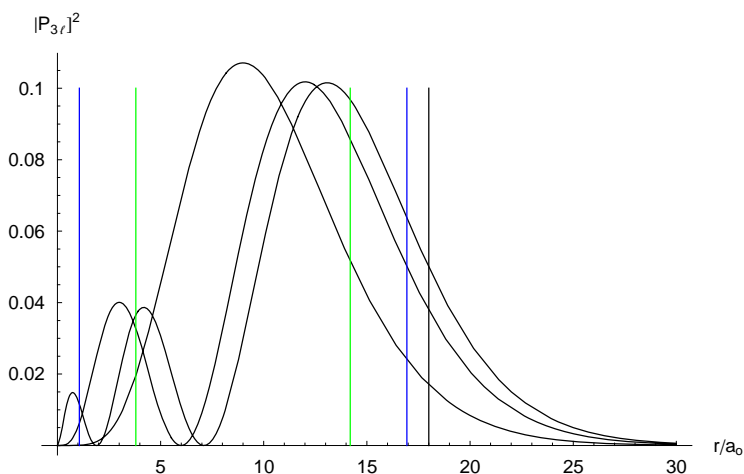
$$1s < 2s < 2p < 3s < 3p < 3d < 4s < 4p < 4d < 4f < \text{etc. (atomic electron energy ordering)}.$$

You should memorize this energy ordering. There are exceptions to this ordering but it is largely correct.

The reason orbitals increase in energy as n increases is because of the combined effect of the average distance increasing as n^2 and the shielding of nuclear charge by electron closer to the nucleus. The reason the 2p orbitals are less stable than the 2s orbital is because of the inner loop of the 2s wavefunction. This inner loop means that a 2s electron is shielded slightly less than a 2p electron, and so experience slightly greater nuclear charge.

Shielding reflects wavefunctions details near the nucleus

We would like to understand the relative stability of many-electron subshells (fixed n but different ℓ) in terms of the distribution of electron density for the different subshells. Here are the electron densities for the $n = 3$ electrons in a hydrogen atom.



Hydrogen atom 3s (three peaks), 3p (two peaks) and 3d (one peak) shell densities. Distance is in units of the Bohr radius, a_0 . The vertical lines are the classical turning points (green for 3d, blue for 3p and black for 3s; the inner turning point for 3s is at $r = 0$), and so bracket the classically allowed region for each shell density.

The vertical lines mark the allowed region of each subshell. Since the allowed region for the 3d is bracketed by that for the 3p, which in turn is bracketed by that for the 3s, we expect the average

distance of the 3d electron to be *closest* to the nucleus, followed by the average distance of the 3p electron, and the 3s electron to *farthest* from the nucleus. The actual average distances, computed as

$$\langle r_{3\ell} \rangle = \int_0^{\infty} |P_{3\ell}(r)|^2 r dr,$$

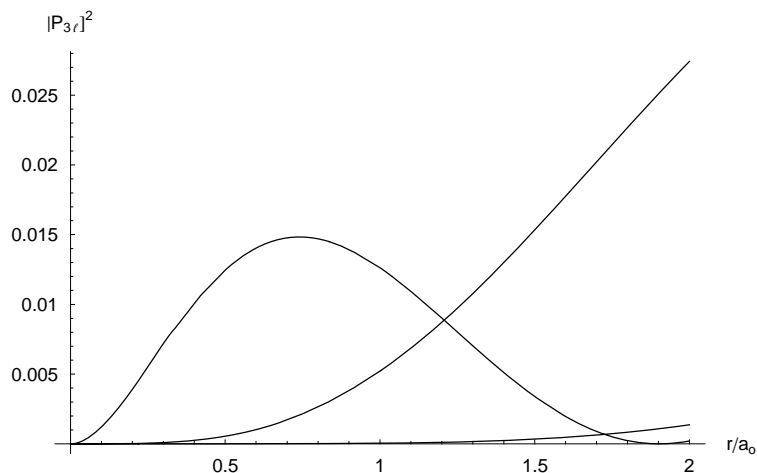
are

3s	13.5
3p	12.5
3d	10.5

Average distance, in $a_0 = 0.527 \text{ \AA}$, from the nucleus of hydrogen $n = 3$ electrons.

This ordering of average distances may seem surprising, since we know in many-electron atoms, the 3s subshell is more stable than the 3p subshell, which is more stable than the 3d subshell, and this in turn might lead us to believe that in many electron atoms the 3s electron would be *closest* to the nucleus.

In fact, the origin of the greater stability of the 3s is due not to the average distance of the electron but instead to the *relative amount of the electron density close to the nucleus* in the different subshells. Here is a plot of the hydrogen 3s, 3p and 3d shell densities near the nucleus,



Hydrogen atom 3s (peak), 3p (quadratic rise from $r = 0$) and 3d (cubic rise from zero) shell densities near the nucleus. Distance is in units of the Bohr radius, a_0 .

and here is the fraction of electron density in each subshell within $1 a_0$ of the nucleus.

3s	0.0099
3p	0.0013
3d	6.5×10^{-6}

Fraction of hydrogen $n = 3$ electron density within $1 a_0$ of the nucleus.

The results show that within $1 a_0$ of the nucleus the 3p shell density is only 13% of the 3s shell density, and the 3d shell density is essentially zero.

This means that both 3s and 3p electrons are present, a 3p electron will see less nuclear charge than a 3s electron, due to the shielding of the nucleus by the fraction of the 3s electron that is closer to the nucleus than the 3p electron. Similarly, a 3d electron will be shielded by both 3s and 3p electrons and so will see still less nuclear charge than a 3p electron. Since a 3d electron is shielded most, it will see the least nuclear charge and so be the least tightly bound. In this way we can understand why in many-electron atoms that within a shell, subshells fill in the order s, p, d,

Here is the fraction of electron density all of the subshells through $n = 4$ within $1 a_0$ of the nucleus.

1s	0.32
2s	0.034
3s	0.0099
4s	0.0041
2p	0.0037
3p	0.0013
4p	0.00056
3d	6.5×10^{-6}
4d	3.9×10^{-6}
4f	3.4×10^{-9}

Fraction of hydrogen electron density within $1 a_0$ of the nucleus for the $n = 1, 2, 3,$ and 4 subshells.

See if you use these fractional electron densities to understand the filling order $1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p$.

Estimating shielding: Effective nuclear charge

We can estimate the effect of shielding by replacing the atomic number Z by an effective atomic number, $Z_{\text{eff}} = Z - s$, that has been reduced by a *shielding constant* s . That is, if we assume the energy of an electron in an atom is given by the formula

$$E_n = -13.6 \text{ eV } Z_{\text{eff}}^2 / n^2,$$

then we can use the measured first ionization energy,

$$\text{IE}_1 = E_{\infty} - E_n = -13.6 \text{ eV } Z_{\text{eff}}^2 / \infty^2 - (-13.6 \text{ eV } Z_{\text{eff}}^2 / n^2) = 13.6 Z_{\text{eff}}^2 / n^2,$$

to determine the effective atomic number and so the shielding constant. If the shielding constant is zero, this means the electron that is ionized experiences the full charge on the nucleus. Here are the effective charge and shielding constants determined from the first ionization energies of the elements up through potassium.

element	configuration	n	IE/eV	Z	s	Z_{eff}
H	$1s^1$	1	13.6	1	0.	1.
He	$1s^2$	1	24.59	2	0.6553	1.345
Li	$1s^2 2s^1$	2	5.392	3	1.741	1.259
Be	$1s^2 2s^2$	2	9.323	4	2.344	1.656
B	$1s^2 2s^2 2p^1$	2	8.298	5	3.438	1.562
C	$1s^2 2s^2 2p^2$	2	11.26	6	4.18	1.82
N	$1s^2 2s^2 2p^3$	2	14.53	7	4.932	2.068
O	$1s^2 2s^2 2p^4$	2	13.62	8	5.999	2.001
F	$1s^2 2s^2 2p^5$	2	17.42	9	6.736	2.264
Ne	$1s^2 2s^2 2p^6$	2	21.57	10	7.481	2.519
Na	$1s^2 2s^2 2p^6 3s^1$	3	5.139	11	9.156	1.844
Mg	$1s^2 2s^2 2p^6 3s^2$	3	7.646	12	9.75	2.25
Al	$1s^2 2s^2 2p^6 3s^2 3p^1$	3	5.986	13	11.01	1.99
Si	$1s^2 2s^2 2p^6 3s^2 3p^2$	3	8.152	14	11.68	2.323
P	$1s^2 2s^2 2p^6 3s^2 3p^3$	3	10.49	15	12.37	2.635
S	$1s^2 2s^2 2p^6 3s^2 3p^4$	3	10.36	16	13.38	2.619
Cl	$1s^2 2s^2 2p^6 3s^2 3p^5$	3	12.97	17	14.07	2.93
Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$	3	15.76	18	14.77	3.23
K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	4	4.341	19	16.74	2.26

Effective charge and shielding constant determined from the first ionization energies of the elements up through potassium.

Verify the values for Z_{eff} and s for neon and sodium.

Propose an explanation for why the effective charge of beryllium is greater than that of lithium.

Propose an explanation for why the effective charge of beryllium is greater than that of boron.

Propose an explanation for why the effective charge of carbon is greater than that of boron.

Propose an explanation for why the effective charge of neon is greater than that of sodium.

The effective charge for lithium is 1.26, for sodium is 1.84 and for potassium is 2.26. Propose an explanation for why the effective charge increases even though the ionized electron is increasingly in a higher shell.

The effective charge for boron is 1.56 and that for aluminum is 1.99. Propose an explanation for why the effective charge increases even though the ionized electron is increasingly in a higher shell.

■ Shielding in excited states

Electron shielding in atoms is most effective when the shielded electron is mostly farther away from the nucleus than the electrons that shield it. This means an electron should be increasingly shielded as when it is in a higher energy orbital, since the average distance of the electron from the nucleus increases as the square of the principal quantum number. The set of excited states for a given value of ℓ is known as a *Rydberg series*.

Li atom Rydberg series

Here are the first ionization energies and effective nuclear charges for the lithium $1s^2 ns$ Rydberg series.

n	IE/eV	Z_{eff}
2	5.392	1.25941
3	2.0189	1.15596
4	1.0511	1.1121
5	0.6075	1.05683
6	0.4342	1.07216
7	0.31263	1.06139
8	0.23585	1.05359
9	0.18425	1.04763
10	0.1477	1.0422

First ionization energies and effective nuclear charges for the lithium $1s^2 ns$ Rydberg series.

Propose a reason why the effective nuclear charge drops rapidly to near 1.

Here are the first ionization energies and effective nuclear charges for the lithium $1s^2 np$ Rydberg series.

n	IE/eV	Z_{eff}
2	3.5442	1.02106
3	1.55774	1.01539
4	0.87035	1.01197
5	0.554685	1.00985
6	0.384172	1.0085
7	0.281698	1.00752
8	0.215456	1.00701
9	0.169998	1.0063
10	0.137652	1.00613

First ionization energies and effective nuclear charges for the lithium $1s^2 np$ Rydberg series.

Propose a reason why the effective nuclear charge is near 1 even for the lowest energy excited state, while this was not the case for the ns lithium Rydberg series.

Here are the first ionization energies and effective nuclear charges for the lithium $1s^2 nd$ Rydberg series.

n	IE/eV	Z_{eff}
3	1.51339	1.00083
4	0.85128	1.00083
5	0.544843	1.00085
6	0.378411	1.00091
7	0.27808	1.00103
8	0.21302	1.0013
9	0.16838	1.0015
10	0.1364	1.00154

First ionization energies and effective nuclear charges for the lithium $1s^2 nd$ Rydberg series.

Propose a reason why the effective charge is so much closer to 1 than in either the ns or the np lithium Rydberg series.

Na atom Rydberg series

Here are the first ionization energies and effective nuclear charges for the sodium $1s^2 2s^2 2p^6 ns$ Rydberg series.

n	IE/eV	Z_{eff}
3	5.139	1.84426
4	1.94765	1.51383
5	1.02264	1.37118
6	0.629369	1.29082
7	0.426106	1.23914
8	0.307519	1.20306
9	0.232342	1.17644
10	0.181705	1.15597
11	0.145983	1.13974
12	0.119843	1.12655
13	0.10014	1.1156
14	0.084922	1.10637

Propose a reason why the lowest energy member of this Rydberg series has so much larger an effective charge than the lowest energy member of the lithium ns Rydberg series.

Here are the first ionization energies and effective nuclear charges for the sodium $1s^2 2s^2 2p^6 np$ Rydberg series.

n	IE/eV	Z_{eff}
3	3.036	1.41754
4	1.386	1.27704
5	0.7945	1.20859
6	0.5148	1.16744
7	0.3606	1.13992
8	0.2666	1.12017
9	0.2051	1.10532
10	0.16266	1.09371
11	0.13215	1.0844
12	0.10948	1.07674
13	0.09218	1.07035
14	0.07867	1.06487

Propose a reason why the low energy members of this Rydberg series has so much larger an effective charge than the low energy members of the lithium np Rydberg series.

Here are the first ionization energies and effective nuclear charges for the sodium $1s^2 2s^2 2p^6 nd$ Rydberg series.

n	IE/eV	Z_{eff}
3	1.52203	1.00368
4	0.855502	1.00331
5	0.547027	1.00285
6	0.379585	1.00246
7	0.278702	1.00215
8	0.213267	1.00188
9	0.168433	1.00166
10	0.136381	1.00147
11	0.11267	1.00129
12	0.094635	1.00108
13	0.08061	1.00092
14	0.069484	1.00077

Propose a reason why the all of the members of this Rydberg series have so much smaller effective charge than the low energy members of the sodium np Rydberg series.