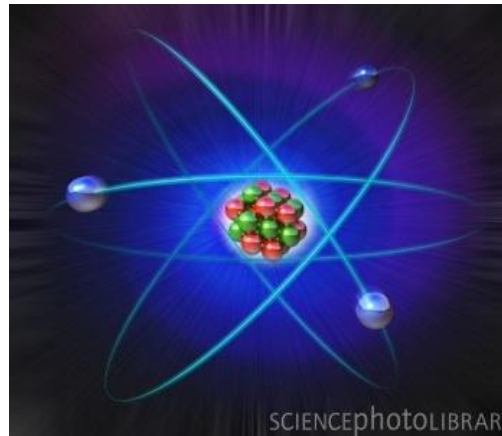


Atomic Structure-II

BSc. 1st Sem (Core)



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Quantum numbers

- Schrodinger's Equation (1D) on applying boundary condition gives a quantum number
- Schrodinger's Equation (3D) on applying boundary condition gives three quantum numbers.
- These quantum numbers **come out of the theory** rather than being put into the theory as Bohr did.
- From Chemistry, four quantum numbers were required, instead of the three that the Schrodinger's Equation predicts.
- The fourth quantum number (spin) can be predicted from a relativistic quantum theory, where the equation is called the *Dirac Equation*.
- In the hydrogen atom spherical coordinates (r, θ, ϕ) is used instead of cartesian (x, y, z) .
- The solution of the Schrodinger's equation in spherical coordinates gives us three quantum numbers: n , l , and m_l
- n is related to the r and hence is related to **energy**, l is related to the θ -**equation** and hence related to **angular momentum**, **and** m_l is related to the ϕ **equation** and is related to the **z-component of angular momentum**, which is related to the magnetic properties of the state.

- The fourth quantum number, m_s is a relativistic quantum phenomenon. It is related to magnetic behavior, and classically related to the electron “spinning”, so that its spinning charge creates a magnetic field.
- Thus, one needs three (Why three? 3 dimensions) quantum numbers to define a given wavefunction

Symbol	Name	Values	Role
n	Principal	1, 2, 3, . . .	Determines the major part of the energy
l	Angular momentum*	0, 1, 2, . . . , $n - 1$	Describes angular dependence and contributes to the energy
m_l	Magnetic	0, ± 1 , ± 2 , . . . , $\pm l$	Describes orientation in space (angular momentum in the z direction)
m_s	Spin	$\pm \frac{1}{2}$	Describes orientation of the electron spin (magnetic moment) in space

Principal Quantum Number, n

- The principal quantum number, n , describes the **energy level** on which the orbital resides.
- Largest E difference is between E levels
- The values of n are integers > 0
- 1, 2, 3,... n .

Azimuthal Quantum Number, l

- defines shape of the orbital
- Allowed values of l are integers ranging from 0 to $n-1$.
- We use letter designations to communicate the different values of l and, therefore, the shapes and types of orbitals.
- So each of these letters corresponds to a shape of orbital.

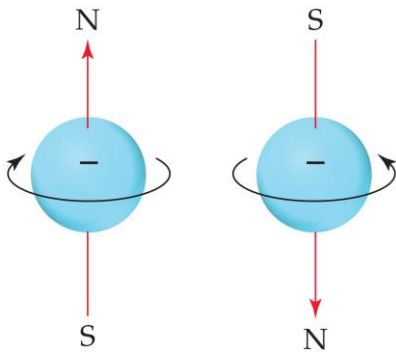
Value of l	0	1	2	3
Type of orbital	s	p	d	f

Magnetic Quantum Number, m_l

- Describes the three-dimensional orientation of the orbital.
- Values are integers ranging from $-l$ to l : $-l, \dots, 0, \dots, l$

Spin Quantum Number, m_s

- This leads to a fourth quantum number, the spin quantum number m_s .
- The spin quantum number has only 2 values $+1/2$ and $-1/2$
- Describes magnetic field vector of electron



n	Possible Values of l	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1s	0	1	1
2	0	2s	0	1	4
	1	2p	1, 0, -1	3	
3	0	3s	0	1	
	1	3p	1, 0, -1	3	9
	2	3d	2, 1, 0, -1, -2	5	
4	0	4s	0	1	
	1	4p	1, 0, -1	3	16
	2	4d	2, 1, 0, -1, -2	5	
	3	4f	3, 2, 1, 0, -1, -2, -3	7	

Symmetric & Antisymmetric wave function

How do we extend the quantum theory to systems beyond the hydrogen atom?

- For systems of 2 electrons, Ψ depends on time, and on the coordinates of each of the two electrons: $\Psi(x_1, y_1, z_1, x_2, y_2, z_2, t)$.
- The Schrodinger's equation has two kinetic energies instead of one.
- It turns out that the Schrodinger Equation can again be separated:

$$\Psi = \Psi_a(x_1, y_1, z_1) * \Psi_b(x_2, y_2, z_2) * T(t)$$

This is like having electron one in state a, and having electron two in state b.

- From the Heisenberg Uncertainty Principle and dual character of matter it is difficult to identify the electrons (which is electron 1 and which is electron 2). This means that the wavefunction must also reflect this uncertainty.
- There are two ways of making the wavefunction reflect the indistinguishability of the two electrons:

$$\Psi_{\text{sym}} = [\Psi_a(r_1) * \Psi_b(r_2) + \Psi_b(r_1) * \Psi_a(r_2)] * T(t) \quad (\text{symmetric})$$

and $\Psi_{\text{anti}} = [\Psi_a(r_1) * \Psi_b(r_2) - \Psi_b(r_1) * \Psi_a(r_2)] * T(t) \quad (\text{antisymmetric}).$

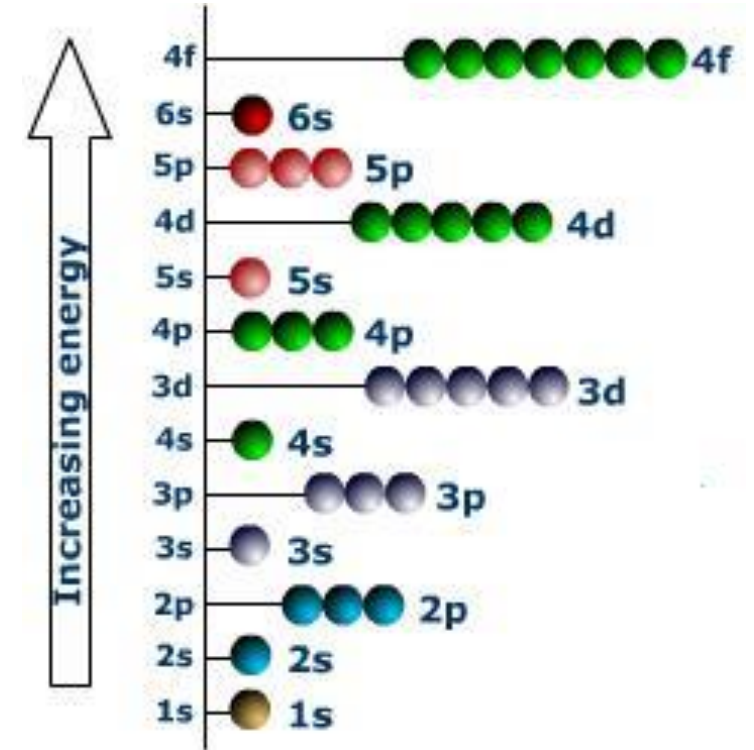
Which (if either) possibility agrees with experiment?

- It turns out that some particles are explained nicely by the symmetric, and some are explained by the antisymmetric.
- Particles that work with the **symmetric** form are called **Bosons** and have **integer spin**.
- If particle 1 and particle 2 both have the same state, $\Psi > 0$. This means that both particles **Can** be in the same state at the same location at the same time.
- Particles that work with the **anti-symmetric** form are called **Fermions** and have **half-integer spin**.
- If particle 1 and particle 2 both have the same state, $\Psi = 0$ and so Probability = 0. This means that both particles **Cannot** be in the same state at the same location at the same time.
- **Bosons:** Photons and alpha particles ($2n + 2p$) are bosons. These particles can be in the same location with the same energy state at the same time. This occurs in a laser beam, where all the photons are at the same energy (monochromatic).

- Fermions: Electrons, protons and neutrons are fermions. These particles cannot be in the same location with the same energy state at the same time.
- This means that two electrons going around the same nucleus cannot both be in the exact same state at the same time!
This is known as the Pauli Exclusion Principle!
- If all the electrons could be in the same state in an atom, then there would be no difference chemically between any of the elements!
- Thus, the possibility of chemistry is explained by the wave/particle duality of light and matter, and electrons acting as fermions!
- Two identical neighboring atoms CAN each have an electron in the same state, since those two electrons are NOT in the same area of space.

Sequence of Energies levels

- The energy of the hydrogenic orbitals is found to depend on n and l
- Orbital energies increase as $(n + l)$ increases
- If two orbitals possess same $(n + l)$, the one with the smaller n has lower energy
- For a given energy level (n), Energy: $s < p < d < f$
- This generalization is valid only for the one electron wave functions for each separate orbital



- For a multielectron system, effective nuclear charge gets modified (penetration & shielding) and energy of an orbital is given by total energy of the atomic system before and after addition of electron and requisite nucleons.
- Generally, energies of different orbitals drop to different extent with increase in atomic number.

Pauli's Exclusion Principle (1925)

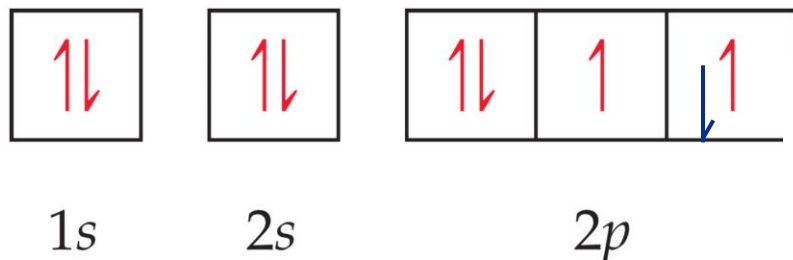
- According to *Pauli's Exclusion Principle*, no two electrons in an atom can have identical sets of quantum numbers.
- Alternatively, the same set of values for all four quantum numbers cannot be assigned to more than one electron in an atom.
- No two electrons in the same atom can have exactly the same energy.
- No more than two electrons may occupy a single orbital and, if two do occupy a single orbital, then their spins must be paired
- The principle restricts the maximum number of electrons which may be assigned to a given orbital (s, p, d and f-orbital can accommodate maximum 2, 6, 10 and 14 electrons respectively)
- The exclusion principle, thus helps to write down the electronic configuration of an atom. As soon as the maximum capacity of an orbital is reached, the next electron has to be placed in higher energy orbital.

Aufbau Principle

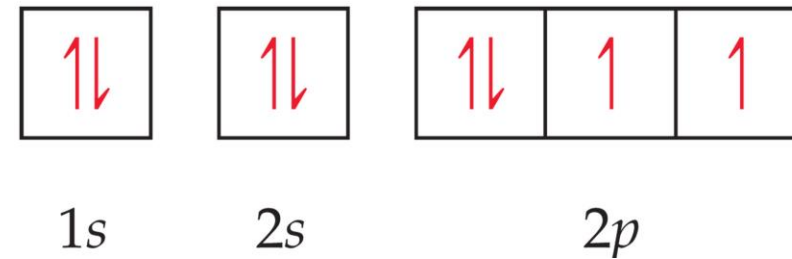
- Aufbau principle concerns gradual building up of the electron configuration of multielectron atoms starting from hydrogen
- Rule 1: A system of particles is stable when its total energy is minimum. Accordingly, electrons are assigned to the orbitals to give the lowest total energy for the atom. These atomic orbitals are acceptable solution of Schrodinger equation.
- Rule 2: Only one electron can exist in any particular quantum state in an atom. This follows from Pauli's exclusion principle
- Rule 3: The ground state of an atom is one with maximum total spin possible i.e., one having maximum number of parallel spins within a subshell

Hund's rule of maximum multiplicity

- 'For degenerate orbitals, the lowest energy is attained when the number of electrons with the same spin is maximized.'
- The ground state of an atom should contain the maximum number of unpaired electron (within the same subshell) with their parallel spin
- The most stable configuration of an atom corresponds to maximum spin multiplicity. Multiplicity is given by $2S+1$, where S is the resultant of all individual spin quantum numbers

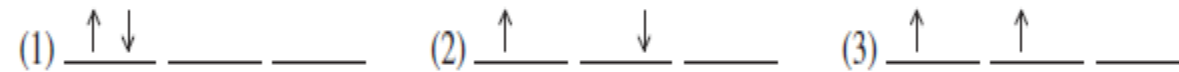


wrong



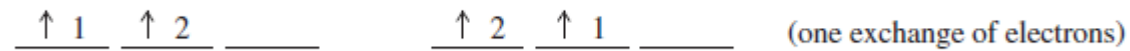
correct

- Hund's rule is a consequence of the energy required for pairing electrons in the same orbital. When two negatively charged electrons occupy the same region of space (same orbital) in an atom, they repel each other, with a Coulombic energy of repulsion (Π_c) per pair of electrons. As a result, this repulsive force favors electrons in different orbitals (different regions of space) over electrons in the same orbitals
- In addition, there is an exchange energy (Π_e), which arises from purely quantum mechanical considerations. This energy depends on the number of possible exchanges between two electrons with the same energy and the same spin. For example, the electron configuration of C-atom is $1s^2 2s^2 2p^2$. The $2p$ electrons can be placed in the p orbitals in three ways:



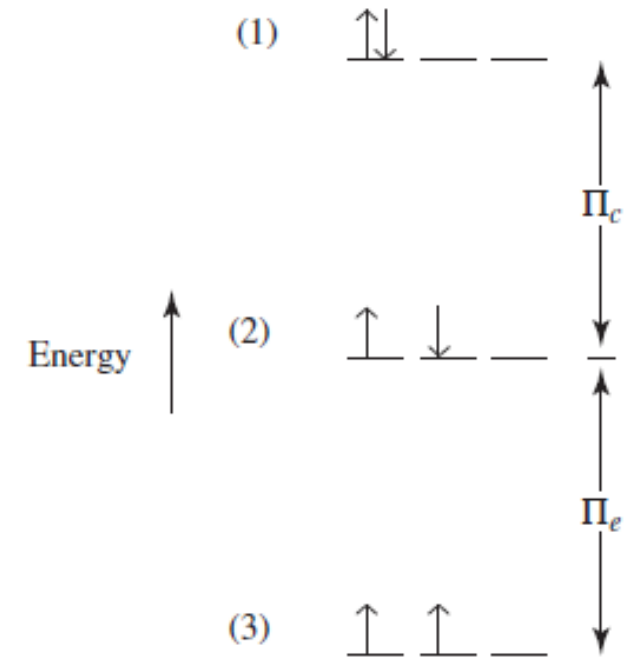
- Each of these corresponds to a state having a particular energy. State (1) involves Coulombic energy of repulsion (Π_c), because it is the only one that pairs electrons in the same orbital. The energy of this state is higher than that of the other two by (Π_c) as a result of electron-electron repulsion.

- In the second state, there is only one possible way to arrange the electrons to give the same diagram, because there is only a single electron in each having + or – spin; these electrons can be distinguished from each other on this basis.
- In the third state, the electrons have the same spin and are therefore indistinguishable from each other. Therefore, there are two possible ways in which the electrons can be arranged:



- Because there are two possible ways in which the electrons in state (3) can be arranged, we can say that there is *one pair* of possible exchanges between these arrangements, described as *one exchange of parallel electrons*. The energy involved in such an exchange of parallel electrons is designated Πe ; each exchange stabilizes (lowers the energy of) an electronic state, favoring states with more parallel spins (Hund's rule). Therefore, state (3), which is stabilized by one exchange of parallel electrons, is lower in energy than state (2) by Πe .

- The results of considering the effects of Coulombic and exchange energies for the p^2 configuration may be summarized in an energy diagram
- State (3) is the most stable; its electrons are in separate orbitals and have parallel spin; because state (3) has one possible exchange of electrons with parallel spin, it is lower in energy than state (2) by Π_e . State (1) is highest in energy because it has two electrons in the same orbital and is therefore higher in energy than state (2) by Π_c . Neither state (1) nor state (2) is stabilized by exchange interactions (zero Π_e).
- Π_c is a consequence of repulsion between electrons in the same orbital; the greater the number of such paired electrons, the higher the energy of the state.
- Π_e is a consequence of parallel electron spins in separate orbitals; the greater the number of such parallel spins (greater the number of exchanges), the lower the energy of the state.
- Both Π_c and Π_e energies must be taken into account when comparing the energies of different electronic states.



Oxygen

With four p electrons, oxygen could have two unpaired electrons ($\uparrow \downarrow \uparrow \underline{\hspace{0.5cm}}$), or it could have no unpaired electrons ($\uparrow \downarrow \uparrow \downarrow \underline{\hspace{0.5cm}}$).

a. Determine the number of electrons that could be exchanged in each case, and find the Coulombic and exchange energies.

$\uparrow \downarrow \uparrow \underline{\hspace{0.5cm}}$ This configuration has one pair, energy contribution Π_c .

$\uparrow \downarrow \uparrow \underline{\hspace{0.5cm}}$ One electron with $\downarrow$ spin and no possibility of exchange.

$\uparrow \downarrow \uparrow \underline{\hspace{0.5cm}}$ Four possible arrangements for electrons with $\uparrow$ spin; three exchange possibilities (1-2, 1-3, 2-3), shown below; energy contribution $3\Pi_e$.

$\uparrow 1 \uparrow 2 \uparrow 3 \quad \uparrow 2 \uparrow 1 \uparrow 3 \quad \uparrow 3 \uparrow 2 \uparrow 1 \quad \uparrow 1 \uparrow 3 \uparrow 2$

Overall, $3\Pi_e + \Pi_c$.

$\uparrow \downarrow \uparrow \downarrow \underline{\hspace{0.5cm}}$ has two pairs in the same orbitals and one exchange possibility for each spin pair.

Overall, $2\Pi_e + 2\Pi_c$.

b. Which state, $\uparrow \downarrow \uparrow \underline{\hspace{0.5cm}}$, or $\uparrow \downarrow \uparrow \downarrow \underline{\hspace{0.5cm}}$, is lower in energy?

The state $\uparrow \downarrow \uparrow \underline{\hspace{0.5cm}}$ is lower in energy because it has less Coulombic energy of repulsion (Π_c in comparison with $2\Pi_c$) and is stabilized by a greater number of exchanges ($3\Pi_e$ in comparison with $2\Pi_e$).

EXERCISE 2.4 A third possible state for the p^4 configuration would be $\underline{\uparrow \downarrow} \underline{\uparrow} \underline{\downarrow}$. Determine the Coulombic and exchange energies of this state, and compare its energy with the energies of the states determined in the preceding example. Draw a sketch showing the relative energies of these three states for oxygen's p^4 configuration.

EXERCISE 2.5 A nitrogen atom, with three $2p$ electrons, could have three unpaired electrons ($\underline{\uparrow} \underline{\uparrow} \underline{\uparrow}$), or it could have one unpaired electron ($\underline{\uparrow \downarrow} \underline{\uparrow} \underline{}$).

- Determine the number of electrons that could be exchanged in each case and the Coulombic and exchange energies. Which state would be lower in energy?
- A third possible state for a $2p^3$ configuration would be $\underline{\uparrow} \underline{\uparrow} \underline{\downarrow}$. Determine its Coulombic and exchange energies, and compare the energy of this state with the energies determined in part **a**.

When the orbitals are degenerate (have the same energy), both Coulombic and exchange energies favor unpaired configurations over paired configurations.

Element	Z	Configuration
H	1	$1s^1$
He	2	$1s^2$
Li	3	$[\text{He}] 2s^1$
Be	4	$[\text{He}] 2s^2$
B	5	$[\text{He}] 2s^2 2p^1$
C	6	$[\text{He}] 2s^2 2p^2$
N	7	$[\text{He}] 2s^2 2p^3$
O	8	$[\text{He}] 2s^2 2p^4$
F	9	$[\text{He}] 2s^2 2p^5$
Ne	10	$[\text{He}] 2s^2 2p^6$
Na	11	$[\text{Ne}] 3s^1$
Mg	12	$[\text{Ne}] 3s^2$
Al	13	$[\text{Ne}] 3s^2 3p^1$
Si	14	$[\text{Ne}] 3s^2 3p^2$
P	15	$[\text{Ne}] 3s^2 3p^3$
S	16	$[\text{Ne}] 3s^2 3p^4$
Cl	17	$[\text{Ne}] 3s^2 3p^5$
Ar	18	$[\text{Ne}] 3s^2 3p^6$
K	19	$[\text{Ar}] 4s^1$
Ca	20	$[\text{Ar}] 4s^2$
Sc	21	$[\text{Ar}] 4s^2 3d^1$
Ti	22	$[\text{Ar}] 4s^2 3d^2$
V	23	$[\text{Ar}] 4s^2 3d^3$
Cr	24	$*[\text{Ar}] 4s^1 3d^5$
Mn	25	$[\text{Ar}] 4s^2 3d^5$
Fe	26	$[\text{Ar}] 4s^2 3d^6$
Co	27	$[\text{Ar}] 4s^2 3d^7$
Ni	28	$[\text{Ar}] 4s^2 3d^8$
Cu	29	$*[\text{Ar}] 4s^1 3d^{10}$
Zn	30	$[\text{Ar}] 4s^2 3d^{10}$

- Some irregularities occur when there are enough electrons to half-fill s and d orbitals on a given row.
- For instance, the electron configuration for Chromium, is $[\text{Ar}] 4s^1 3d^5$ rather than the expected $[\text{Ar}] 4s^2 3d^4$.
- Attributed to special stability of half-filled subshells.
- This occurs because the $4s$ and $3d$ orbitals are very close in energy.
- These anomalies occur in f -block atoms, as well.

Element	Z	Configuration
Ge	32	$[\text{Ar}] 4s^2 3d^{10} 4p^2$
As	33	$[\text{Ar}] 4s^2 3d^{10} 4p^3$
Se	34	$[\text{Ar}] 4s^2 3d^{10} 4p^4$
Br	35	$[\text{Ar}] 4s^2 3d^{10} 4p^5$
Kr	36	$[\text{Ar}] 4s^2 3d^{10} 4p^6$
Rb	37	$[\text{Kr}] 5s^1$
Sr	38	$[\text{Kr}] 5s^2$
Y	39	$[\text{Kr}] 5s^2 4d^1$
Zr	40	$[\text{Kr}] 5s^2 4d^2$
Nb	41	$*[\text{Kr}] 5s^1 4d^4$
Mo	42	$*[\text{Kr}] 5s^1 4d^5$
Tc	43	$[\text{Kr}] 5s^2 4d^5$
Ru	44	$*[\text{Kr}] 5s^1 4d^7$
Rh	45	$*[\text{Kr}] 5s^1 4d^8$
Pd	46	$*[\text{Kr}] 4d^{10}$
Ag	47	$*[\text{Kr}] 5s^1 4d^{10}$
Cd	48	$[\text{Kr}] 5s^2 4d^{10}$
In	49	$[\text{Kr}] 5s^2 4d^{10} 5p^1$
Sn	50	$[\text{Kr}] 5s^2 4d^{10} 5p^2$
Sb	51	$[\text{Kr}] 5s^2 4d^{10} 5p^3$
Te	52	$[\text{Kr}] 5s^2 4d^{10} 5p^4$
I	53	$[\text{Kr}] 5s^2 4d^{10} 5p^5$
Xe	54	$[\text{Kr}] 5s^2 4d^{10} 5p^6$

Element	Z	Configuration
Cs	55	[Xe] 6s ¹
Ba	56	[Xe] 6s ²
La	57	*[Xe] 6s ² 5d ¹
Ce	58	*[Xe] 6s ² 4f ¹ 5d ¹
Pr	59	[Xe] 6s ² 4f ³
Nd	60	[Xe] 6s ² 4f ⁴
Pm	61	[Xe] 6s ² 4f ⁵
Sm	62	[Xe] 6s ² 4f ⁶
Eu	63	[Xe] 6s ² 4f ⁷
Gd	64	*[Xe] 6s ² 4f ⁷ 5d ¹
Tb	65	[Xe] 6s ² 4f ⁹
Dy	66	[Xe] 6s ² 4f ¹⁰
Ho	67	[Xe] 6s ² 4f ¹¹
Er	68	[Xe] 6s ² 4f ¹²
Tm	69	[Xe] 6s ² 4f ¹³
Yb	70	[Xe] 6s ² 4f ¹⁴
Lu	71	[Xe] 6s ² 4f ¹⁴ 5d ¹
Hf	72	[Xe] 6s ² 4f ¹⁴ 5d ²
Ta	73	[Xe] 6s ² 4f ¹⁴ 5d ³
W	74	[Xe] 6s ² 4f ¹⁴ 5d ⁴
Re	75	[Xe] 6s ² 4f ¹⁴ 5d ⁵
Os	76	[Xe] 6s ² 4f ¹⁴ 5d ⁶
Ir	77	[Xe] 6s ² 4f ¹⁴ 5d ⁷
Pt	78	*[Xe] 6s ¹ 4f ¹⁴ 5d ⁹
Au	79	*[Xe] 6s ¹ 4f ¹⁴ 5d ¹⁰
Hg	80	[Xe] 6s ² 4f ¹⁴ 5d ¹⁰
Tl	81	[Xe] 6s ² 4f ¹⁴ 5d ¹⁰ 6p ¹
Pb	82	[Xe] 6s ² 4f ¹⁴ 5d ¹⁰ 6p ²
Bi	83	[Xe] 6s ² 4f ¹⁴ 5d ¹⁰ 6p ³
Po	84	[Xe] 6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁴
At	85	[Xe] 6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁵
Rn	86	[Xe] 6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁶

Element	Z	Configuration
Fr	87	$[\text{Rn}] 7s^1$
Ra	88	$[\text{Rn}] 7s^2$
Ac	89	* $[\text{Rn}] 7s^2 6d^1$
Th	90	* $[\text{Rn}] 7s^2 6d^2$
Pa	91	* $[\text{Rn}] 7s^2 5f^2 6d^1$
U	92	* $[\text{Rn}] 7s^2 5f^3 6d^1$
Np	93	* $[\text{Rn}] 7s^2 5f^4 6d^1$
Pu	94	$[\text{Rn}] 7s^2 5f^6$
Am	95	$[\text{Rn}] 7s^2 5f^7$
Cm	96	* $[\text{Rn}] 7s^2 5f^7 6d^1$
Bk	97	$[\text{Rn}] 7s^2 5f^9$
Cf	98	* $[\text{Rn}] 7s^2 5f^9 6d^1$
Es	99	$[\text{Rn}] 7s^2 5f^{11}$
Fm	100	$[\text{Rn}] 7s^2 5f^{12}$
Md	101	$[\text{Rn}] 7s^2 5f^{13}$
No	102	$[\text{Rn}] 7s^2 5f^{14}$
Lr	103	$[\text{Rn}] 7s^2 5f^{14} 6d^1$
Rf	104	$[\text{Rn}] 7s^2 5f^{14} 6d^2$
Db	105	$[\text{Rn}] 7s^2 5f^{14} 6d^3$
Sg	106	$[\text{Rn}] 7s^2 5f^{14} 6d^4$
Bh	107	$[\text{Rn}] 7s^2 5f^{14} 6d^5$
Hs	108	$[\text{Rn}] 7s^2 5f^{14} 6d^6$
Mt	109	$[\text{Rn}] 7s^2 5f^{14} 6d^7$
Ds	110	* $[\text{Rn}] 7s^1 5f^{14} 6d^9$
Rg	111	* $[\text{Rn}] 7s^1 5f^{14} 6d^{10}$
Cn ^a	112	$[\text{Rn}] 7s^2 5f^{14} 6d^{10}$