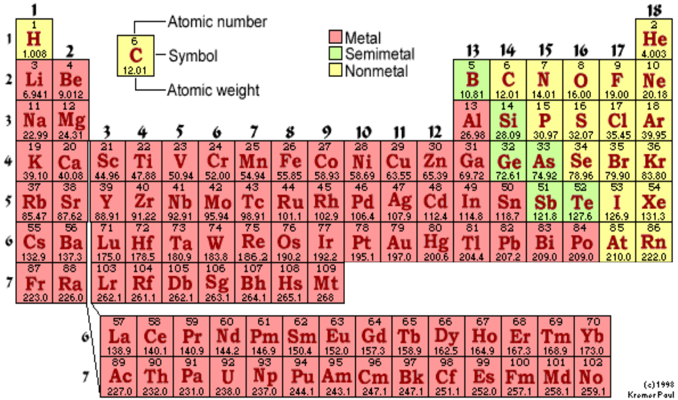
Multielectron atoms, Pauli Exclusion Principle, and the Periodic Table

- The last homework set is available. It has 9 problems but should be straightforward. It is due at 12:50pm on Thursday 4/30
- Final is on 5/2 from 1:30pm-4:00pm in G125 (this room)
- Rest of the semester:
  - Today we will cover multielectron atoms, the Pauli Exclusion Principle and figure out the Periodic table.
  - Monday will be the fundamentals of quantum mechanics.
  - Wednesday and Friday of next week will be review.

Wolfgang Pauli
1900 – 1958



6
C
12.01 — Atomic number / Symbol / Atomic weight

🟥 Metal
🟩 Semimetal
🟨 Nonmetal

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	71 Lu 175.0	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 209.0	85 At 210.0	86 Rn 222.0
7	87 Fr 223.0	88 Ra 226.0	103 Lr 262.1	104 Rf 261.1	105 Db 262.1	106 Sg 263.1	107 Bh 264.1	108 Hs 265.1	109 Mt 268									

6	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 146.9	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0
7	89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 244.1	95 Am 243.1	96 Cm 247.1	97 Bk 247.1	98 Cf 251.1	99 Es 252.0	100 Fm 257.1	101 Md 258.1	102 No 259.1

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http://www.colorado.edu/physics/phys2170/

Atomic wavefunctions and quantum numbers

Each atomic electron can be identified by four quantum numbers:

n = 0, 1, 2, … = principal quantum number

ℓ gives total orbital angular momentum: $L = \sqrt{\ell(\ell+1)}\hbar$

m gives z-component of orbital angular momentum: $L_z = m\hbar$

m_s = ±½ gives the z-component of spin: $S_z = m_s\hbar$

The atom itself has angular momentum which is the vector sum of orbital and intrinsic angular momenta of the electrons. $\vec{J} = \vec{L} + \vec{S}$

Thus, the Stern-Gerlach experiment actually measures the z-component of the total angular momentum: $J_z = L_z + S_z$

Useful information for homework problem 3

Approximations for multielectron atoms

When there are multiple electrons we have to consider the effect of the electrons on each other. This is difficult to do precisely.

So we need to make approximations.

The outer electrons are *screened* by the inner electrons so the effective charge they feel is less than Ze which we can write as $Z_{\text{eff}}e$. If one electron is well outside of the other $Z-1$ electrons it feels a charge of just $1e$ (i.e. $Z_{\text{eff}} = 1$).

The innermost electrons feel nearly the full charge of Ze so $Z_{\text{eff}} \approx Z$.

We can use our findings for hydrogen-like ions by replacing Z with Z_{eff} so the energy is $E_n = -Z_{\text{eff}}^2 E_R / n^2$ and the most probable radius is $r_{\text{mp}} \approx n^2 a_B / Z_{\text{eff}}$

Clicker question 1

Set frequency to DA

Lithium has Z=3. Two electrons are in a 1s state and one electron is in a 2p state. About how many times farther out is the 2p electron compared to the 1s electrons?

A. 3
B. 4
C. 6
D. 8
$\boxed{\text{E. 12}}$

$$E_n = -Z_{\text{eff}}^2 E_R / n^2$$

$$r_{\text{mp}} \approx n^2 a_B / Z_{\text{eff}}$$

The 1s state is always closest to the nucleus and thus will feel nearly the full force of all Z protons so $Z_{\text{eff}} \approx Z$. This gives a radius of $r_{1\text{s}} \approx a_B / 3$

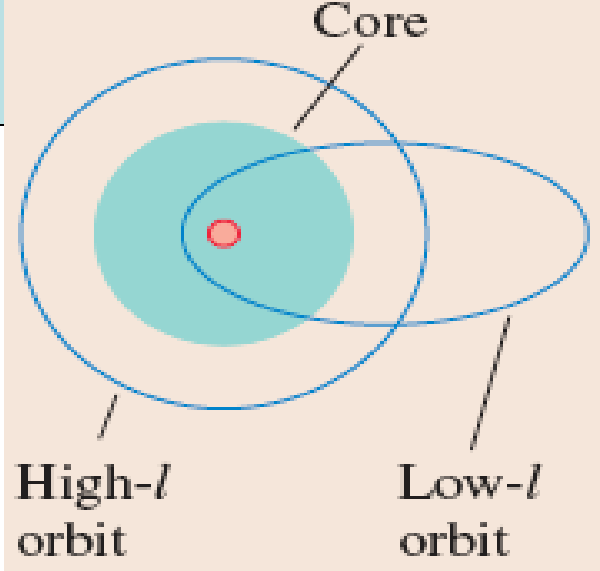
The 2p electron will be screened by the two 1s electrons and will only feel a net charge of 1e. So Z_{eff} = 1. So $r_{2\text{s}} \approx 4a_B$.

Taking the ratio we find r_{2p}/r_{1s} = 12.

For hydrogen and hydrogen-like ions this ratio is only n^2 = 4.

Multielectron atom energy levels

For a given principal quantum number *n*, the ℓ states have different radial distributions.



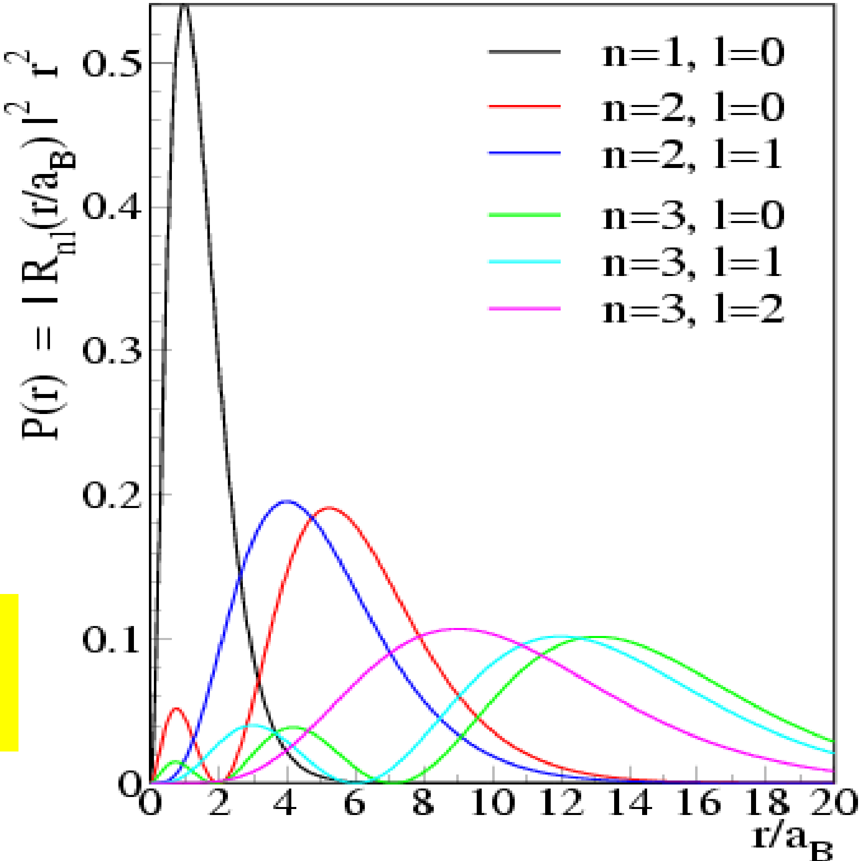
Since Z_{eff} depends on how far out the electron is, different ℓ states have different energies for the same value of *n*.

The main criterion is how close the electrons get to the nucleus.

The closer the electrons get to the nucleus, the higher Z_{eff} is and the lower (more negative) the energy.

$$\boxed{E_n = -Z_{\text{eff}}^2 E_R / n^2}$$

Higher ℓ electrons don't get close to the nucleus so Z_{eff} is smaller.



Clicker question 2

Set frequency to DA

Lithium has *Z*=3. Two electrons are in a 1s state and one electron is excited into the 3d state. How does the energy of this excited electron compare to the energy of the electron in a hydrogen atom which is also in the 3d state?

A. The lithium electron energy is significantly higher (less negative)

B. The lithium electron energy is significantly lower (more negative)

[✓ C. The lithium electron energy is about the same]

D. Impossible to tell

$$E_n = -Z_{\text{eff}}^2 E_R / n^2$$

$$r_{\text{mp}} \approx n^2 a_B / Z_{\text{eff}}$$

The outermost electron in lithium will be screened by the two 1s electrons and will only feel a net charge of 1*e*. So $Z_{\text{eff}} = 1$. This is the same as for the hydrogen atom!

So in both cases, $E_3 = -E_R / 9$

Experimentally it is -1.513 eV for lithium and -1.512 eV for hydrogen

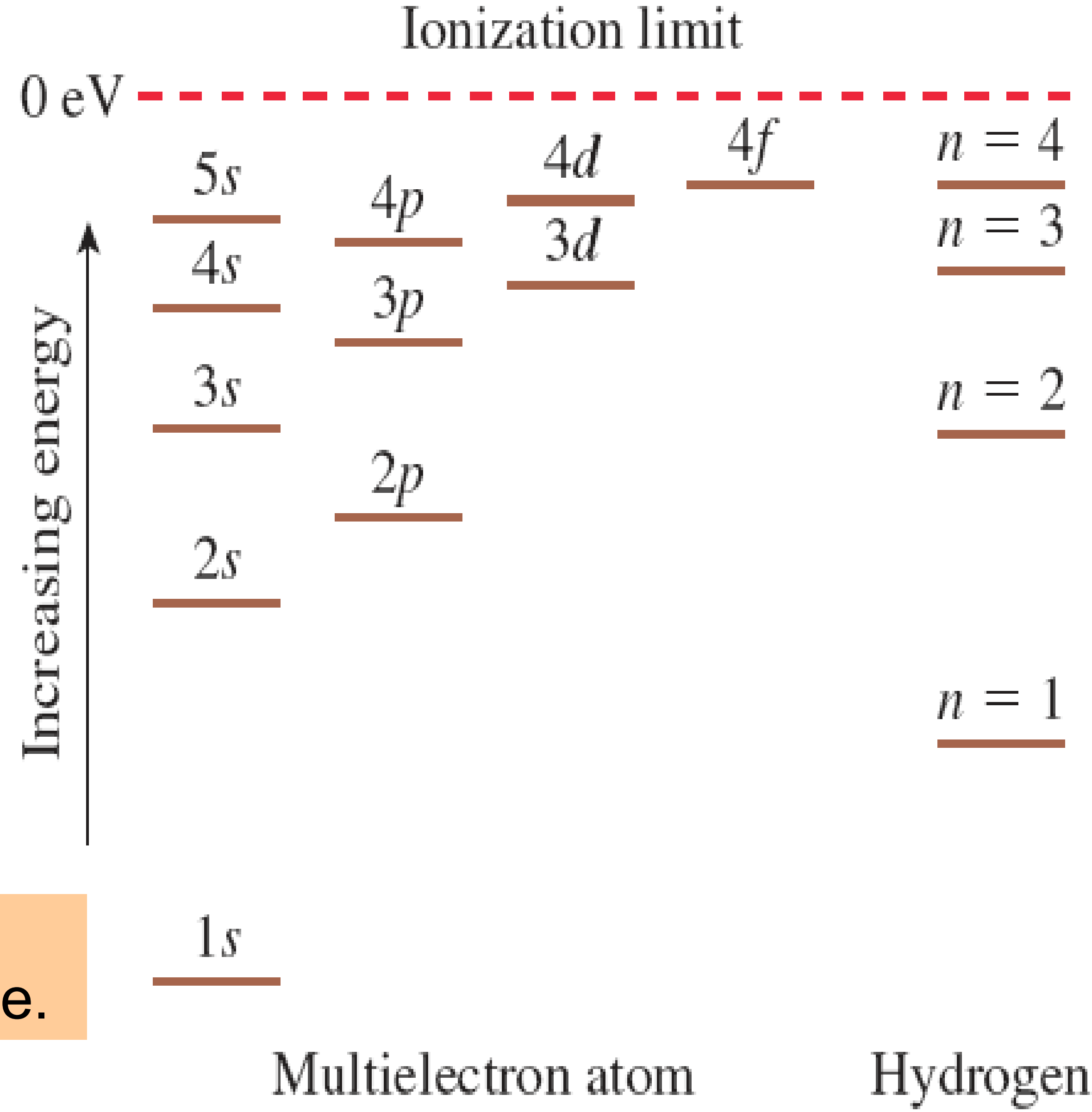
Related to homework problem 5

Energy levels for multielectron atoms

For a given *n*, as ℓ increases, the energy increases (becomes less negative).

So energy depends on both *n* and ℓ for multielectron atoms.

There are now more energy levels so the degeneracy of each level is less.



Note that the 4s state is actually *below* the 3d state.

Building up electron configurations

We know the hydrogen ground state is 1s.

Makes sense: electrons want to be in the lowest potential energy state.

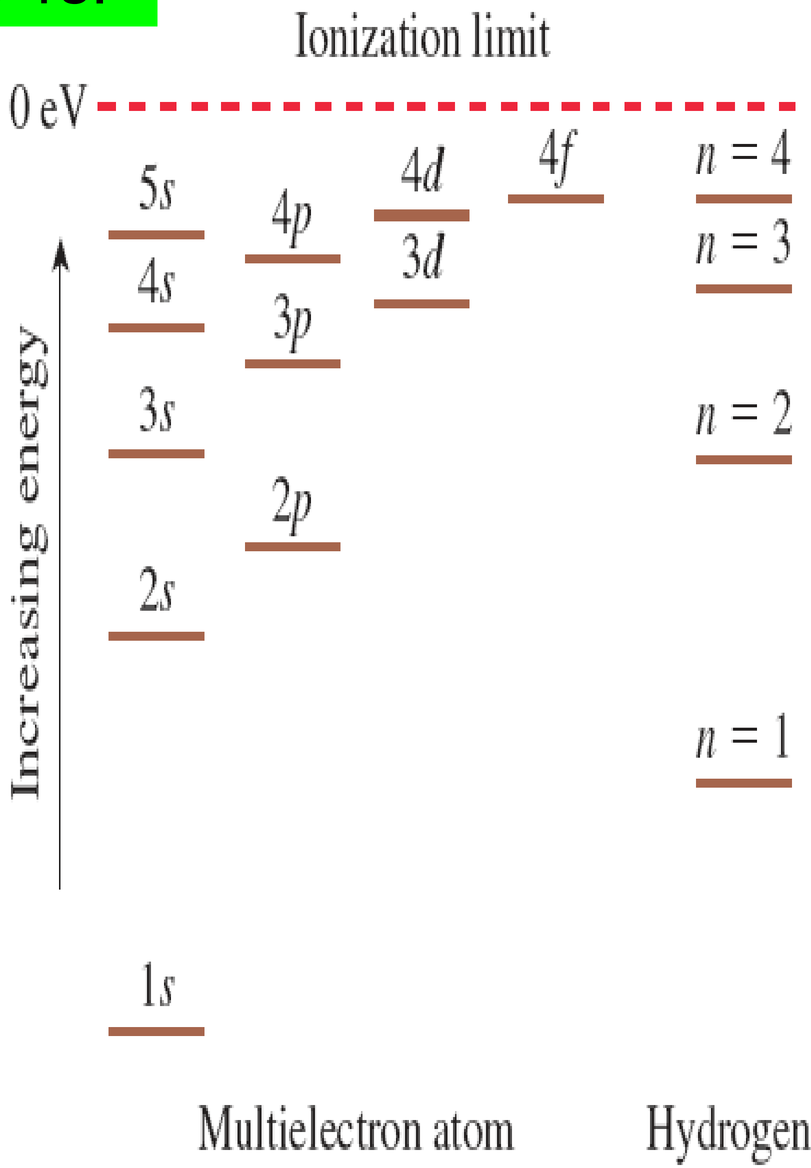
Helium has two electrons.
What are their energy states?

Both helium electrons are in the 1s state (lowest potential energy).

Lithium has three electrons.
What are their energy states?

Two electrons are in the 1s state but one electron is in the 2s state!

Why aren't all 3 electrons in the 1s state?!



Reading quiz 1

Set frequency to DA

Please answer this question on your own.

Q. In 1925, Wolfgang Pauli came up with the Pauli Exclusion Principle which states …

A. The position and momentum of a particle cannot both be precisely known.

B. No two electrons in a quantum system can occupy the same quantum state.

C. Two components of an atom's angular momentum cannot both be precisely known.

D. Multiple bosons in a quantum system can have the same quantum numbers.

E. None of the above

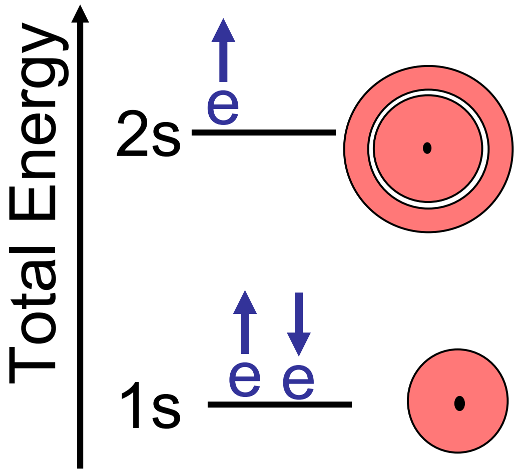
Incidentally, A-D are all true statements.

As far as understanding atoms, this means that no two electrons in an atom can have the same quantum numbers.

Filling orbitals

For multielectron atoms, energy levels are specified by n and ℓ.
A specification of $n\ell m$ is termed the *orbital*.

Electrons fill the lowest energy orbitals but have to obey the Pauli Exclusion Principle so there are at most two electrons per orbital.



Hydrogen (H): $n=1, \ell=0, m=0, m_s=\pm\frac{1}{2}$

Total angular momentum = ±½

Helium (He): $\begin{cases} n=1, \ell=0, m=0, m_s=+\frac{1}{2} \\ n=1, \ell=0, m=0, m_s=-\frac{1}{2} \end{cases}$

Total angular momentum = 0

Lithium (Li): $\begin{cases} n=1, \ell=0, m=0, m_s=+\frac{1}{2} \\ n=1, \ell=0, m=0, m_s=-\frac{1}{2} \\ n=2, \ell=0, m=0, m_s=\pm\frac{1}{2} \end{cases}$

Total angular momentum = ±½

Filling orbitals

We can continue filling orbitals.

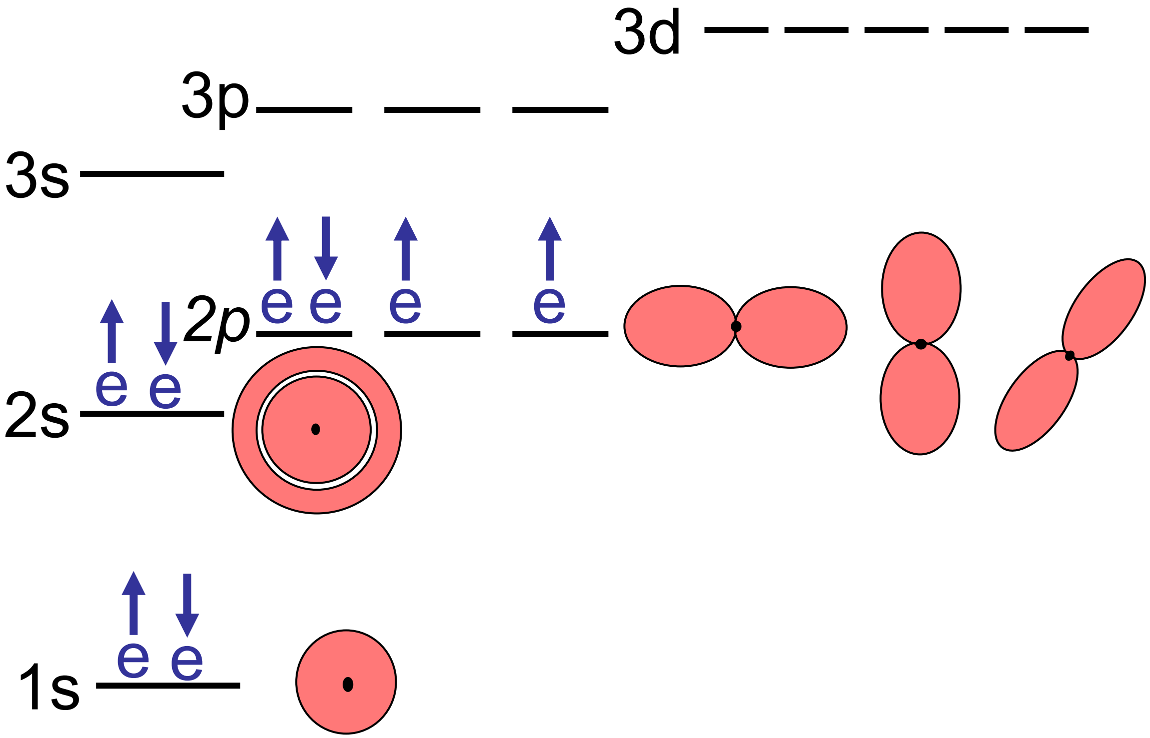
The electron configuration is given by writing the *nℓ* value and a superscript with the number of electrons for the energy level.

Oxygen: $1s^2 2s^2 2p^4$

B C N O

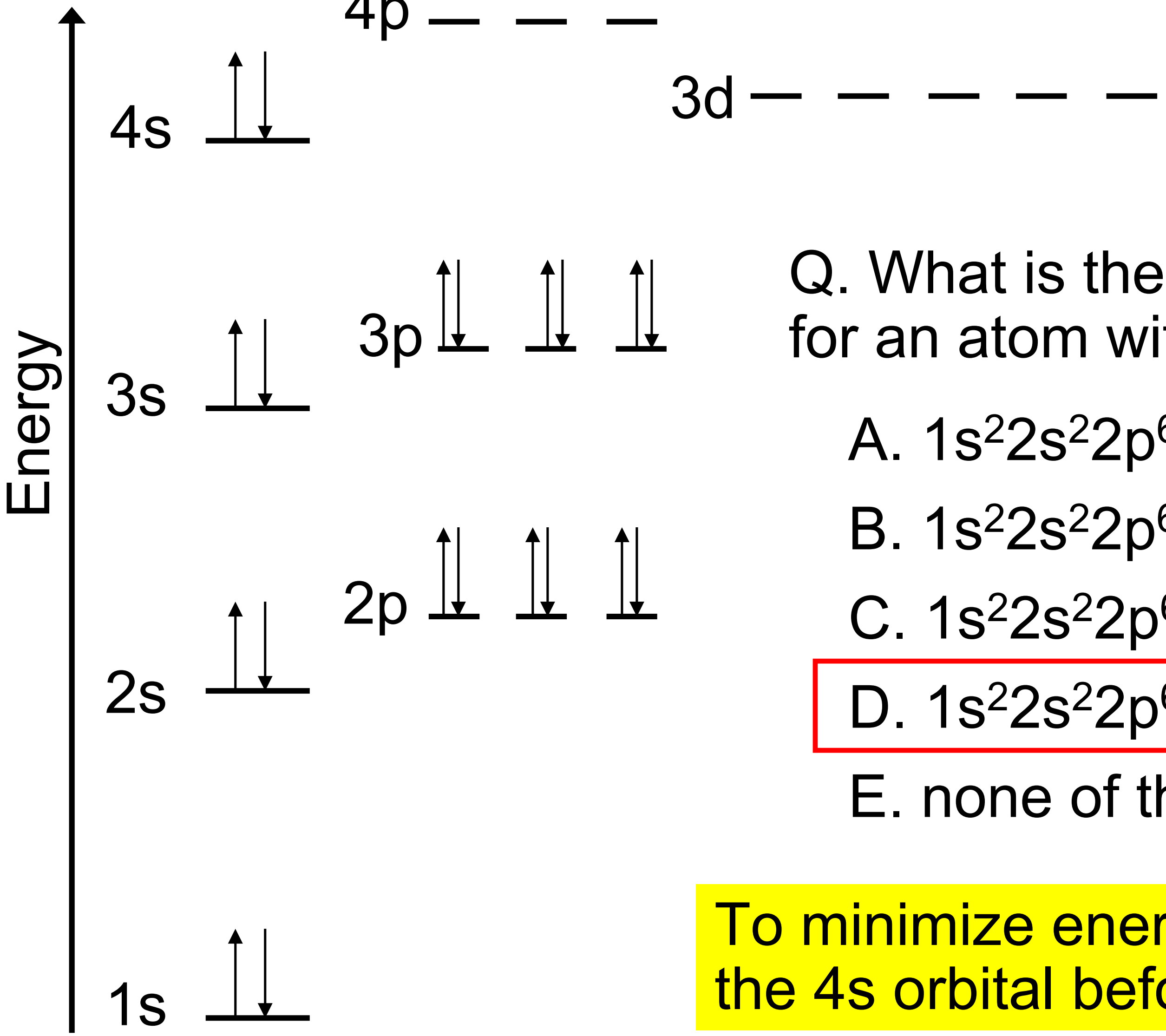
Li: $1s^2 2s^1$ Be: $1s^2 2s^2$

H: $1s^1$ He: $1s^2$



Clicker question 3

Set frequency to DA



Q. What is the electron configuration for an atom with 20 electrons?

A. $1s^2 2s^2 2p^6 3s^2 3p^4$

B. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$

C. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

D. $\boxed{1s^2 2s^2 2p^6 3s^2 3p^6 4s^2}$

E. none of the above

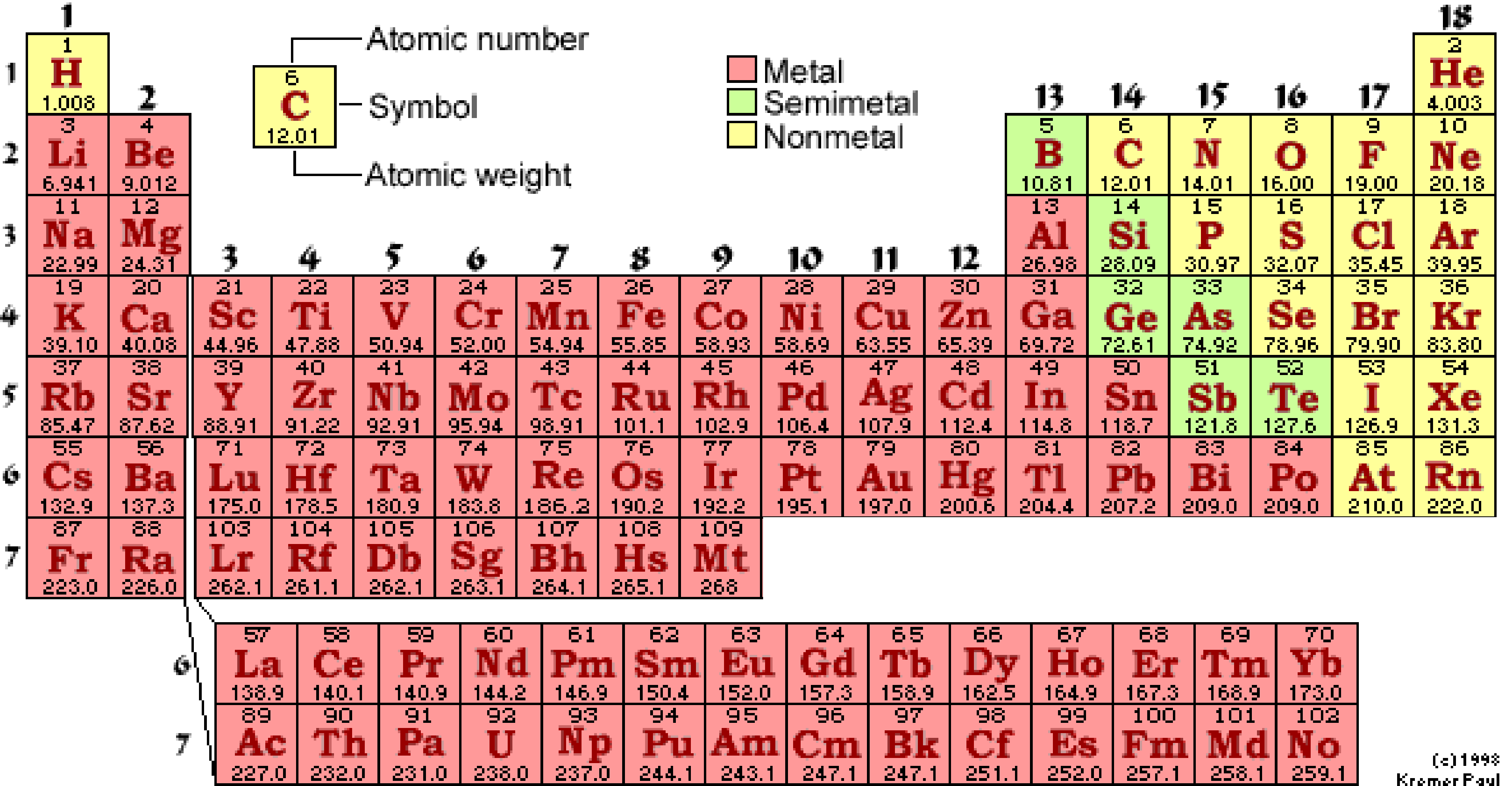
To minimize energy, two electrons fill the 4s orbital before the 3d orbital.

Periodic table of the elements

Periodic table created by Dmitri Mendeleev in 1869.

He grouped elements which behaved similarly.

Big success was predicting new elements which were later found.



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Periodic table of the elements

Chemical behavior is generally determined by the outer (loosely bound) electrons.

Elements in the same column have similar outer electrons and similar energies so they behave similarly.

So quantum mechanics can *explain* the periodic table!