

LECTURE 16/36 OCT-11-02

HYDROGEN ATOM

ORBITALS

MULTI ELECTRON ATOMS

BACK GROUND: OXToby CH 15

READ: TODAY'S LEE GRAY CH 21-28

NEXT LEE GRAY CH 2p42-56

FOR HYDROGEN  $Z=1$

$$\psi_{1,0,0} \equiv \psi_{1s}(r,\theta,\phi) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

( $l=0 \rightarrow s$ )

$$|\psi_{1s}|^2 = \frac{1}{\pi a_0^3} e^{-\frac{2r}{a_0}}$$

WHERE

$$a_0 \equiv \frac{\epsilon_0 h^2}{\pi \mu |e|^2} = \text{BOHR RADIUS}$$

MOST PROBABLE DISTANCE =  $a_0$

$$\langle r_{1s} \rangle = \frac{3}{2} a_0$$

AVERAGE DISTANCE  
FROM THE ORIGIN

$$\psi_{n,l,m}(r, \theta, \varphi) = R_{n,l}(r) Y_l^m(\theta, \varphi)$$

$R_{n,l}(r)$  IS A REAL FUNCTION

$Y_l^m(\theta, \varphi)$  IN GENERAL IS A COMPLEX FUNCTION

IF WE WANT A 3-D PICTURE OF THESE WAVE FUNCTION DESCRIBING THE ELECTRONIC CHARGE, WE NEED A REAL FUNCTION.

WE HAVE TWO OPTIONS

- a) DENSITY PLOTS  
INCLUDE THE RADIAL PART
- b) POLAR PLOTS  
ONLY THE ANGULAR PART

# ORBITALS $\Leftrightarrow$ LINEAR COMBINATION OF WAVE FUNCTIONS

$n$  = SPECIFIES THE SIZE OR EXTENT OF AN ORBITAL

$l$  = SPECIFIES THE SHAPE

- $l=0 \rightarrow s$
- $l=1 \rightarrow p$
- $l=2 \rightarrow d$
- $l=3 \rightarrow f$
- $l=4 \rightarrow g$  (AND ALPHABETICAL)

$1s \leftrightarrow R_{1,0}$

$y_0^0$

$2s \leftrightarrow R_{2,0}$

$y_0^0$

$2p \leftrightarrow R_{2,1}$

$y_1^{-1}$

$y_1^0$

$y_1^{+1}$

$3s \leftrightarrow R_{3,0}$

$y_0^0$

$3p \leftrightarrow R_{3,1}$

$y_1^{-1}$

$y_1^0$

$y_1^{+1}$

$3d \leftrightarrow R_{3,2}$

$y_2^{-2}$

$y_2^{-1}$

$y_2^0$

$y_2^{+1}$

$y_2^{+2}$

$4s \leftrightarrow R_{4,0}$

$y_0^0$

$4p \leftrightarrow R_{4,1}$

$y_1^{-1}$

$y_1^0$

$y_1^{+1}$

$4d \leftrightarrow R_{4,2}$

$y_2^{-2}$

$y_2^{-1}$

$y_2^0$

$y_2^{+1}$

$y_2^{+2}$

$4f \leftrightarrow R_{4,3}$

$y_3^{-3}$

$y_3^{-2}$

$y_3^{-1}$

$y_3^0$

$y_3^{+1}$

$y_3^{+2}$

$y_3^{+3}$

POLAR PLOTS

SINCE WE ARE NOT INCLUDING THE RADIAL PART OF THE WAVE FUNCTION, WE ONLY HAVE S, P AND d ORBITALS.

$$s \equiv Y_0^0(\theta, \varphi)$$

$$p_z \equiv Y_1^0(\theta, \varphi)$$

$$p_x \equiv \frac{1}{\sqrt{2}} (Y_1^{+1} + Y_1^{-1})$$

$$p_y \equiv \frac{1}{\sqrt{2}} (Y_1^{+1} - Y_1^{-1})$$

$$d_{z^2} \equiv Y_2^0$$

$$d_{xz} \equiv \frac{1}{\sqrt{2}} [Y_2^1 + Y_2^{-1}]$$

$$d_{yz} \equiv \frac{1}{\sqrt{2}} [Y_2^1 - Y_2^{-1}]$$

$$d_{x^2-y^2} \equiv \frac{1}{\sqrt{2}} [Y_2^2 + Y_2^{-2}]$$

$$d_{xy} \equiv \frac{1}{\sqrt{2}} [Y_2^2 - Y_2^{-2}]$$

and

$$|Y_1^{-1}(\theta, \phi)|^2 = \frac{3}{8\pi} \sin^2 \theta$$

Because  $Y_1^1(\theta, \phi)$  and  $Y_1^{-1}(\theta, \phi)$  correspond to the same energy, we know from Section 4-5 that any linear combination of  $Y_1^1$  and  $Y_1^{-1}$  is also an energy eigenfunction with the same energy. It is customary to use the combinations

$$\begin{aligned} p_x &= \frac{1}{\sqrt{2}}(Y_1^1 + Y_1^{-1}) = \left(\frac{3}{4\pi}\right)^{1/2} \sin \theta \cos \phi \\ p_y &= \frac{1}{\sqrt{2}i}(Y_1^1 - Y_1^{-1}) = \left(\frac{3}{4\pi}\right)^{1/2} \sin \theta \sin \phi \end{aligned} \quad (6-124)$$

Plots of  $p_x$  and  $p_y$  are shown in Figure 6-11. They have the same shape as the  $p_z$  function except that they are directed along the  $x$  and  $y$  axes. The three functions  $p_x$ ,  $p_y$ , and  $p_z$  are often used as the angular part of hydrogen atomic wave functions because they are real and have easily visualized directional properties.

For the  $l = 2$  case,  $m = 0, \pm 1$ , and  $\pm 2$ , and so there are five  $d$  orbitals. We have already considered the  $m = 0$  value previously. For the other values of  $m$ , we take linear combinations like we did above for the  $p$  functions. The customary linear combinations are

$$\begin{aligned} d_{z^2} &= Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1) \\ d_{xz} &= \frac{1}{\sqrt{2}}(Y_2^1 + Y_2^{-1}) = \left(\frac{15}{4\pi}\right)^{1/2} \sin \theta \cos \theta \cos \phi \\ d_{yz} &= \frac{1}{\sqrt{2}i}(Y_2^1 - Y_2^{-1}) = \left(\frac{15}{4\pi}\right)^{1/2} \sin \theta \cos \theta \sin \phi \\ d_{x^2-y^2} &= \frac{1}{\sqrt{2}}(Y_2^2 + Y_2^{-2}) = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2 \theta \cos 2\phi \\ d_{xy} &= \frac{1}{\sqrt{2}i}(Y_2^2 - Y_2^{-2}) = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2 \theta \sin 2\phi \end{aligned} \quad (6-125)$$

The angular parts of the five  $d$  orbitals are shown in Figure 6-15. Note that the last four orbitals given in Eqs. 6-125 differ only in their orientation. Figure 6-15 suggests the rationale of the notation of the  $d$  orbitals;  $d_{z^2}$  lies along the  $z$  axis,  $d_{x^2-y^2}$  lies along the  $x$  and  $y$  axes;  $d_{xy}$  lies in the  $x$ - $y$  plane;  $d_{xz}$  lies in the  $x$ - $z$  plane, and  $d_{yz}$  lies in the  $y$ - $z$  plane. Most chemists use the five  $d$  orbitals given by Eqs. 6-125 rather than the spherical harmonics, because the functions in Eqs. 6-125 are real and have convenient directional properties. The real representations of the hydrogen atomic wave functions are given in Table 6-6. The

By, we know from  
an energy eigen-  
combinations

(6-124)

same shape as the  
axes. The three  
hydrogen atomic  
normalized directional

are five  $d$  orbitals.  
the other values  
 $p$  functions. The

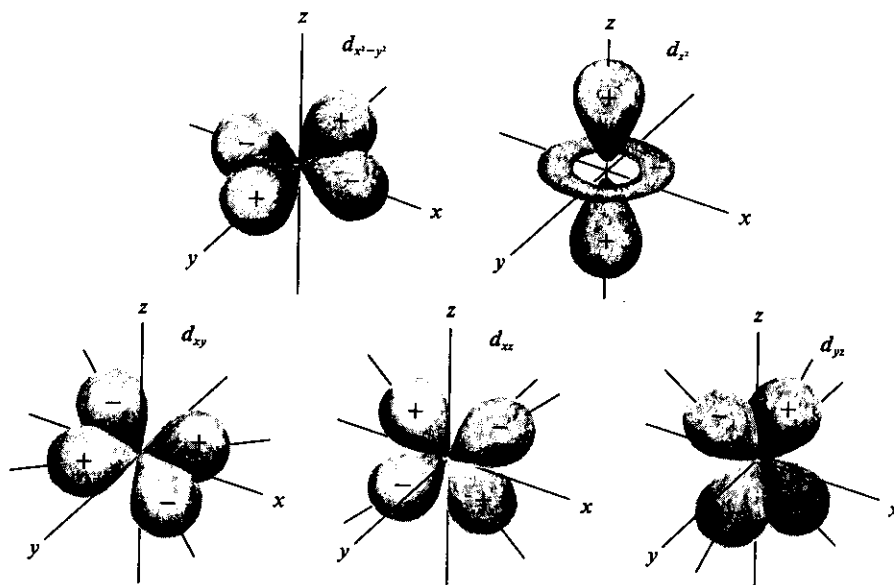


Figure 6-15. Three-dimensional polar plots of the angular part of the real representation of the hydrogen atomic wave functions for  $l = 2$ . Such plots show the directional character of these orbitals but are not good representations of the shape of these orbitals because the radial functions are not included.

$\cos \phi$

$\sin \phi$  (6-125)

$2\phi$

$2\phi$

15. Note that the  
tion. Figure 6-15  
along the  $z$  axis,  
 $d_{xz}$  lies in the  $x-z$   
 $d$  orbitals given  
the functions in  
The real repre-  
Table 6-6. The

functions in Table 6-6 are the linear combinations of the complex wave functions in Table 6-5. Both sets are equivalent, but chemists normally use the real functions in Table 6-6. We shall see in later chapters that molecular wave functions can be built out of atomic orbitals and if the atomic orbitals have a definite directional character, it is possible to use chemical intuition to decide which are the more important atomic orbitals to use to describe molecular orbitals.

### 6-11 The Energy Levels of a Hydrogen Atom Are Split by a Magnetic Field

In this section, we shall discuss a hydrogen atom in an external magnetic field. Before doing so, however, we shall review some facts and equations concerning magnetic dipoles and magnetic fields. The motion of an electric charge around a closed loop produces a magnetic dipole  $\mu$  whose magnitude is given by

$$\mu = iA \tag{6-126}$$

FOR THE HYDROGEN ATOM

8  
16

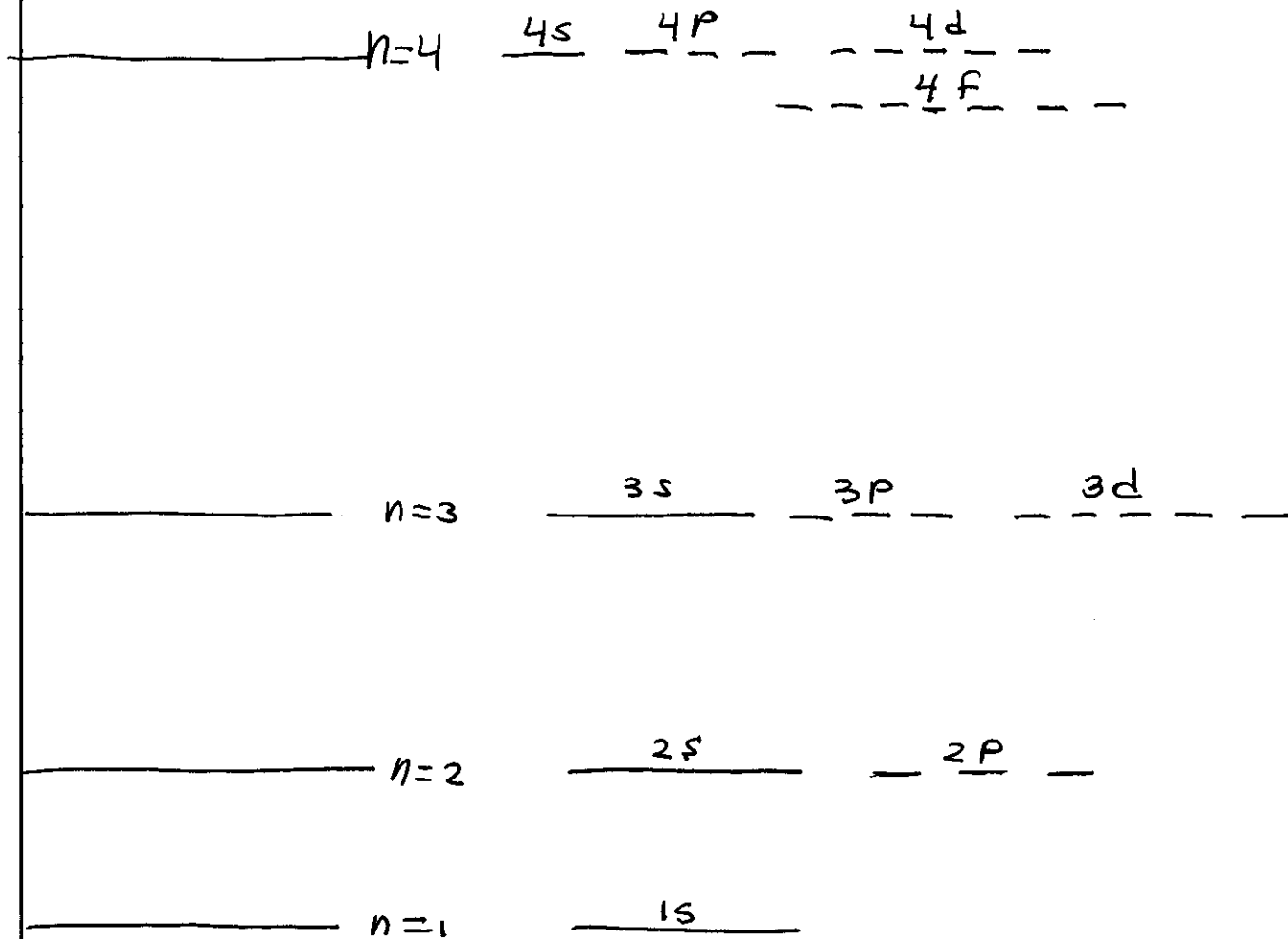




Table 6-6 The allowed values of  $\ell$  and  $m_\ell$  for  $n = 1$  through 4

$n$	$\ell$	$m_\ell$	Orbital	Number of orbitals
1	0	0	1s	1
2	0	0	2s	1
		1, 0, -1	2p	3
3	0	0	3s	1
		1, 0, -1	3p	3
		2, 1, 0, -1, -2	3d	5
4	0	0	4s	1
		1, 0, -1	4p	3
		2, 1, 0, -1, -2	4d	5
		3, 2, 1, 0, -1, -2, -3	4f	7

9  
T6

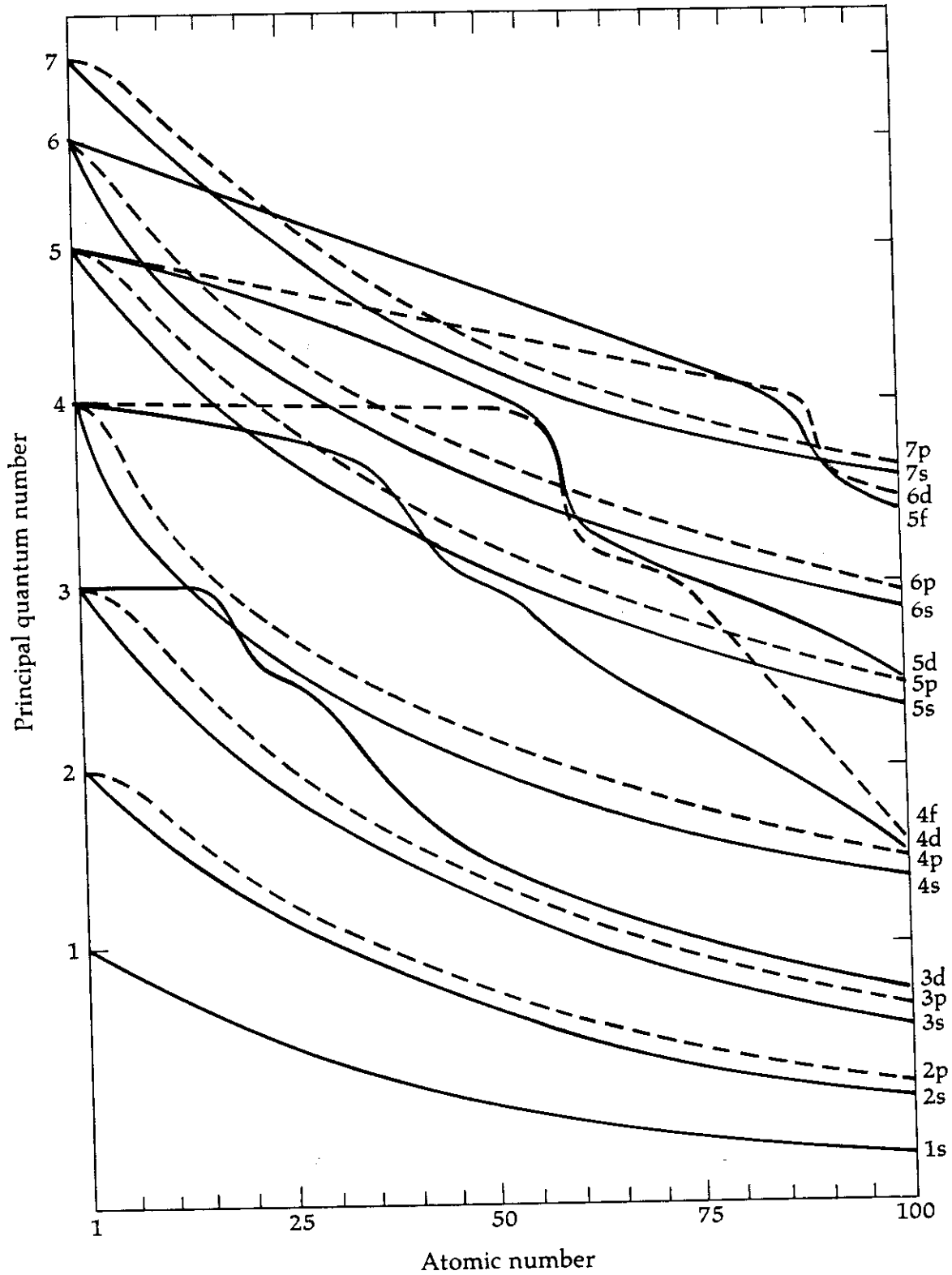
FOR MULTI ELECTRON ATOMS WE NEED TO INCLUDE THE electron-electron INTERACTION THAT SPLITS THE HYDROGEN ENERGY LEVELS. ALSO WE NEED TO INCLUDE A FOURTH QUANTUM NUMBER ASSOCIATED TO A QUANTUM MECHANICAL PROPERTY CALLED SPIN. THIS PROPERTY TAKES ON VALUES OF  $\frac{1}{2}$  (UP) OR  $-\frac{1}{2}$  (DOWN).

### PAULI EXCLUSION PRINCIPLE

NO TWO ELECTRONS CAN HAVE THE SAME QUANTUM NUMBERS

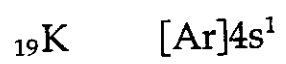
### HUND'S RULE

FOR ANY SET OF ORBITALS OF EQUAL ENERGY THE ELECTRONIC CONFIGURATION WITH MAX # OF PARALLEL SPINS RESULTS IN THE LOWEST ELECTRON-ELECTRON REPULSION.

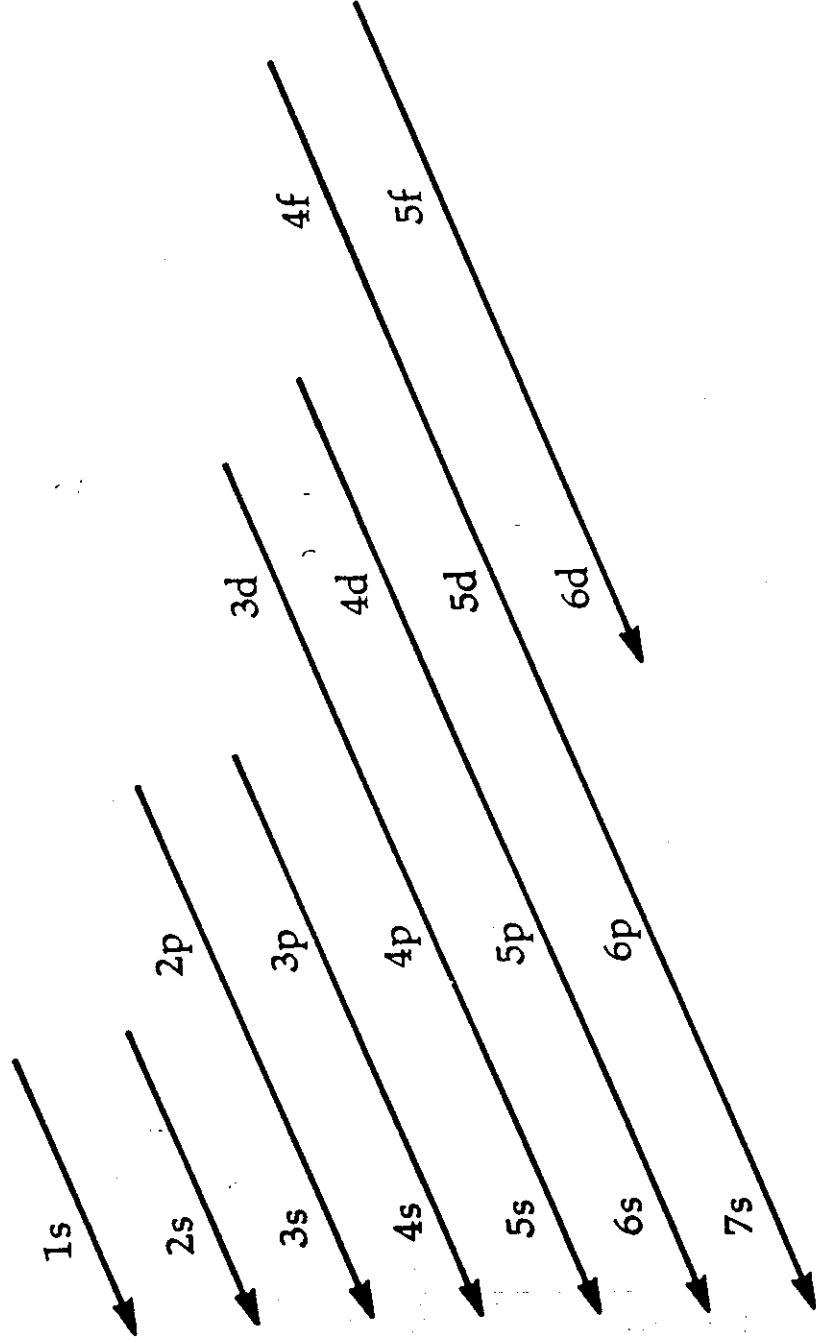


**FIGURE 6.9** Orbital energies in neutral atoms as a function of atomic number. As in Figure 6.7, the energies are not shown to scale.

mences at  $Z = 19$ , the atom has a lower energy when the 19th and 20th electrons occupy the 4s rather than the 3d orbital. As a result, the electronic configurations of potassium and calcium are



and



**FIGURE 6.8** Orbital filling sequence. Atomic orbitals are generally filled in the order indicated by the arrows, starting at the top. Deviations from this sequence are discussed in the text.

chemical inertness to the elements whose atoms possess this configuration; the elements with closed-shell configurations are known as the noble gases.

The next element, lithium, has the configuration

$$1s^2 2s^1$$

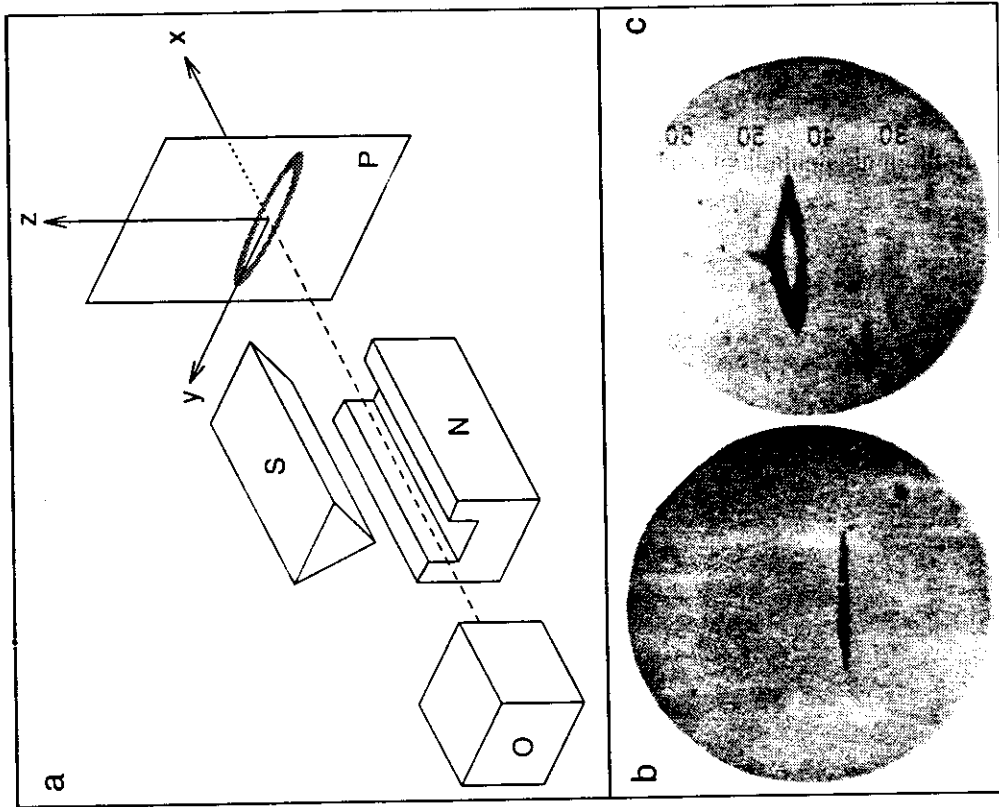


Fig. 1.4. Stern-Gerlach experiment. Experimental setup with oven O, magnet pole shoes N and S, and glass screen P (a). Silver deposit on screen without field (b) and with field (c) as shown in Stern's and Gerlach's original publication. The splitting is largest in the middle and gets smaller to the left and the right of the picture because the field inhomogeneity is largest in the  $x, z$  plane.

Source: (b) and (c) from W. Gerlach and O. Stern, *Zeitschrift für Physik* 9 (1922) 349 © 1922 by Springer-Verlag, Berlin, reprinted by permission.

H	$1s^1$			
He	$1s^2$			
Li	$1s^2 2s^1$			
Be	$1s^2 2s^2$			
B	$1s^2 2s^2 2p^1$	$p_x$ ↑	$p_y$ —	$p_z$ —
C	$1s^2 2s^2 2p^2$	↑	↑	—
N	$1s^2 2s^2 2p^3$	↑	↑	↑
O	$1s^2 2s^2 2p^4$	↑↓	↑	↑
F	$1s^2 2s^2 2p^5$	↑↓	↑↓	↑
Ne	$1s^2 2s^2 2p^6$	↑↓	↑↓	↑↓

$1s$   $2s$   $2p$   $3s$   $3p$   $4s$   $3d$   $4p$   $5s$   $4d$   $5p$   $6s$   $4f$   $5d$   
 $6p$   $7s$   $5f$   $6d$

