

Chapter 5 (Lecture 11-12)

Hydrogen Atom

The explanation of spectroscopic data was one of the first great victories of quantum theory. In modern science and technology, the mastery of atomic physics is responsible for decisive progress ranging from laser technology to the exploration of the cosmos.

The particular case of the hydrogen atom is perhaps the most striking. Its particularly simple spectrum delivered the first clues of quantum laws.

We now consider the specific case of the hydrogen atom. Here, we consider the problem in its first approximation, where we neglect spin effects. We consider the problem of a particle of mass m_e in the Coulomb field of the proton, which is considered infinitely massive (the reduced mass correction is straightforward):

$$V(r) = -\frac{1}{4\pi\epsilon_0} \frac{q^2}{r} = -\frac{e^2}{r}$$

Note that for the atoms including more than one proton in its nucleus the potential energy of the system can be obtained by $q \rightarrow Zq$, where Z is number of proton in the nucleus or atomic number. The radial equation is

$$\frac{\hbar^2}{2m} \left(-\frac{\partial^2 R}{\partial r^2} - \frac{2}{r} \frac{\partial R}{\partial r} + \frac{l(l+1)}{r^2} R \right) + V(r)R = ER$$

Where m is mass of electron. It is convenient to transform the variable into the dimensionless form. Length is measure in atomic units

$$a_0 = \frac{\hbar^2}{me^2} = 5.29 \times 10^{-11} m = 1 \text{ bohr.}$$

Energy in hartrees

$$\frac{e^2}{a_0} = 4.358 \times 10^{-18} J = 27.211 \text{ eV}$$

Rewriting the Schrödinger equation in atomic units

$$\frac{\hbar^2}{2m} \left(-\frac{\partial^2 R}{\partial r^2} - \frac{2}{r} \frac{\partial R}{\partial r} + \frac{l(l+1)}{r^2} R \right) - \frac{1}{4\pi\epsilon_0} \frac{q^2}{r} R = ER$$

Remember that angular parts of the equation have been solved in previous sections. The construction of a solution is broken into two parts. The first part is called the *asymptotic behavior*, referring to the solution at very large distance from the proton or very close to the proton. The asymptotic behavior of the equation

$$r \rightarrow \infty; \frac{1}{2} \left(-\frac{\partial^2 R}{\partial r^2} - \frac{2}{r} \frac{\partial R}{\partial r} \right) \rightarrow ER$$

Then

$$R \rightarrow \frac{e^{\pm\sqrt{-2E}r}}{r}$$

The other asymptotic of the equation is:

$$r \rightarrow 0; \frac{1}{2} \left(-\frac{\partial^2 R}{\partial r^2} + \frac{l(l+1)}{r^2} R \right) \rightarrow 0$$

Then

$$R \rightarrow r^{l+1}$$

The substitution of $R = r^l e^{\pm\sqrt{-2E}r} f(r)$ gives us

$$r f'' + 2(1 + l - \sqrt{-2E}r) f' + 2r(-1 + \sqrt{-2E}(l+1)) f = 0$$

Therefore we obtain a series solution. Then general solution of radial equation is given by

$$R_{nl} = r^l e^{-\frac{r}{n+l}} L_{n-l-1}^{2l+1} \left(\frac{2r}{n} \right)$$

Where $l = 0, 1, 2, \dots, n-1$, n is called principal quantum number. For each values of l there are $2l+1$ values of magnetic quantum number m . Energy of the oscillator is given by

$$E = -\frac{E_0}{2(n)^2}; E_0 = m \left(\frac{e^2}{4\pi\epsilon_0 \hbar} \right)^2 = 27.2 \text{ eV}$$

The negative energy E indicates that the electron and proton are bound together.

The boundary conditions requires $n > l, n = 1, 2, 3, \dots$. Total wave function is given by

$$\psi_{nlm} = N_{nl} r^l e^{-\frac{r}{n+l}} L_{n-l-1}^{2l+1} \left(\frac{2r}{n} \right) Y_{lm}(\theta, \phi)$$

Experimental observations in the 19th century showed that one can group the lines in series which were given names according to their aspect. In the case of sodium, after the theory had been understood, it turned out that these series correspond to the following transitions,

$$\text{the sharp series } \hbar\omega = E_{n,l=0} - E_{3,1}$$

$$\text{the principal series } \hbar\omega = E_{n,l=1} - E_{3,0}$$

$$\text{the diffuse series } \hbar\omega = E_{n,l=2} - E_{3,1}$$

$$\text{the fundamental series } \hbar\omega = E_{n,l=3} - E_{3,2}$$

Orbital angular momentum quantum number

Each of these four series corresponds to transitions from a state of given l (and various values of n) to a well-defined state. Consequently, the tradition consists of attributing to a given value of l the initial of the corresponding series (spectroscopic notation):

Symbolic letter	s	p	d	f	g	h
Corresponding value of l	0	1	2	3	4	5

A state of well-defined energy is then denoted by a number (the value of n) followed by a letter (corresponding to the value of l):

$n = 1, l = 0$: state $1s$; $n = 3, l = 2$: state $3d$.

Restriction of quantum numbers are:

$$n = 1, 2, 3 \dots; l = 0, 1, 2, \dots, n - 1; m_l = -l, \dots, l.$$

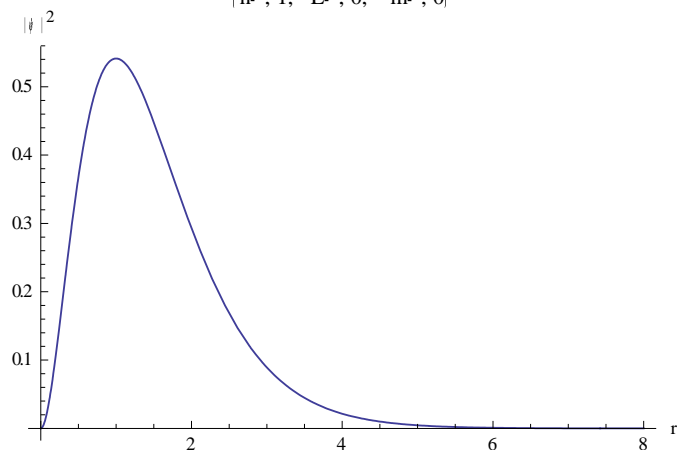
Table: Values of Laguerre polynomial $L_{n-l-1}^{2l+1}(r)$

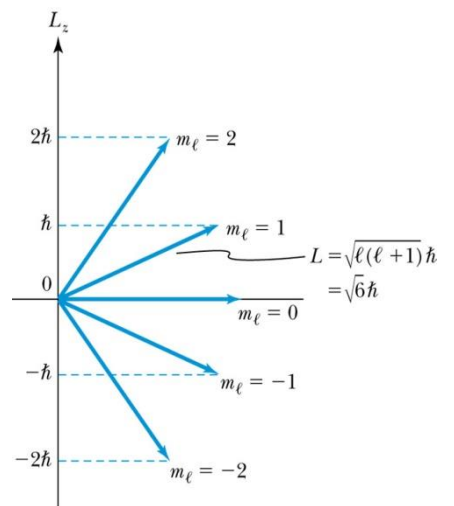
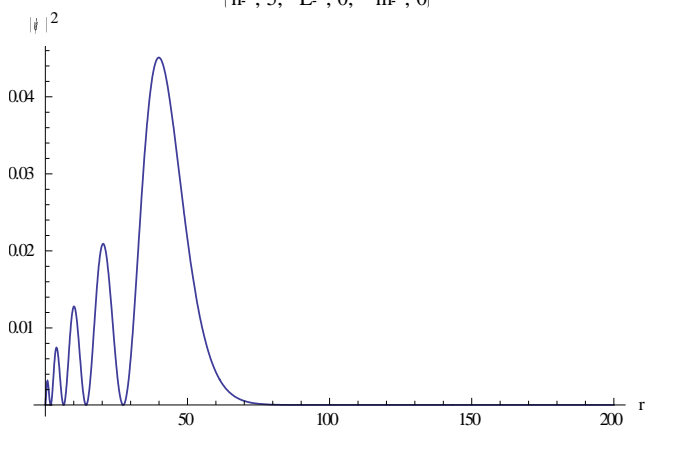
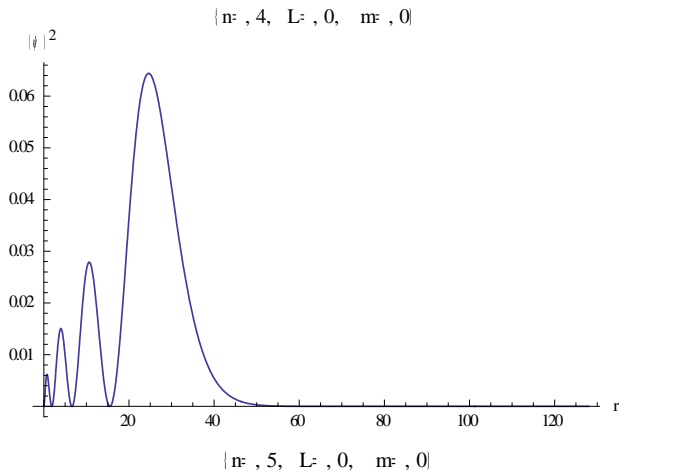
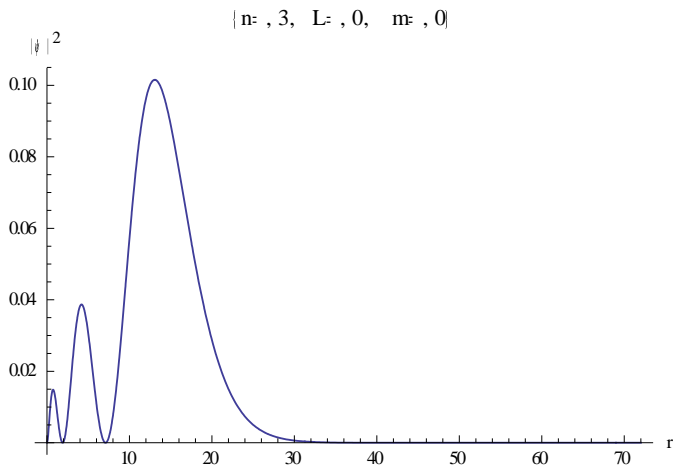
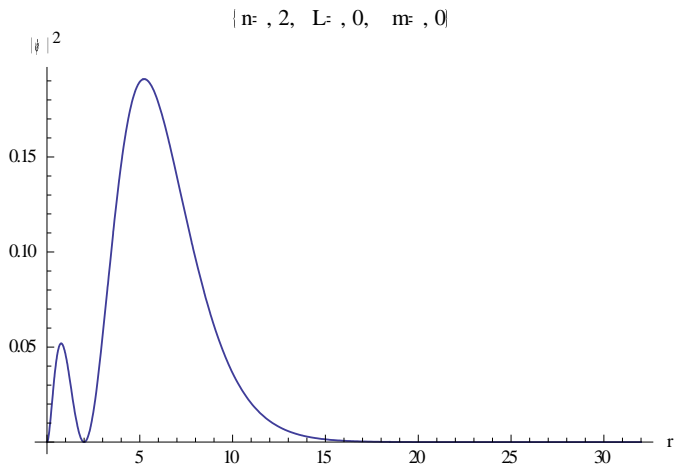
$n \backslash l$	0	1	2	3
1	1			
2	$2 - r$	1		
3	$\frac{1}{9}(27 - 18r + 2r^2)$	$4 - \frac{2r}{3}$	1	
4	$\frac{1}{48}(192 - 144r + 24r^2 - r^3)$	$\frac{1}{8}(80 - 20r + r^2)$	$6 - \frac{r}{2}$	1

Probability distribution of wave function.

$$\int_0^{\infty} r^2 R_{nl}(r) dr$$

$|n=1, l=0, m=0\rangle$





Magnetic quantum number

The angle ϕ is a measure of the rotation about the z axis.

The solution specifies that m_l is an integer and related to the z component of L .

$$L_z \Phi = m_l \Phi$$

We expect the average of the angular momentum components squared to be

$$\langle L_x^2 \rangle = \langle L_y^2 \rangle = \langle L_z^2 \rangle$$

$$\langle L^2 \rangle = 3\langle L_z^2 \rangle = \frac{1}{2l+1} \sum_{m_l=-l}^l m_l^2 \hbar^2 = l(l+1)\hbar^2$$

Spin

In quantum mechanics, **spin** is a fundamental characteristic property of quantum particles. All elementary particles of a given kind have the same **spin quantum number**, an important part of a particle's quantum state. When combined with the spin-statistics theorem, the spin of electrons results in the Pauli exclusion principle, which in turn underlies the periodic table of chemical elements. Wolfgang Pauli was the first to propose the concept of spin, but he did not name it.

Spin is a type of angular momentum. Since spin is a type of angular momentum, it has the same units: J·s in SI units. In practice, however, SI units are almost never used to describe spin: Instead, it is written as a multiple of the reduced Planck's constant \hbar .

We assume that it will behave like orbital angular momentum, and will obey the same commutator relations and satisfy similar eigenvalue equations. Thus if S_x, S_y , and S_z are the components of the intrinsic spin operator S , the eigenfunctions of S^2 and S_z satisfy

$$S^2 \chi_{s,m_s} = s(s+1)\hbar^2 \chi_{s,m_s}$$

and

$$S_z \chi_{s,m_s} = m_s \hbar \chi_{s,m_s}$$

where

$$s = 0, \frac{1}{2}, \frac{3}{2}, \dots,$$

$$m_s = -s, -s+1, \dots, s-1, s$$

Just like the angular momentum operators,

$$[S_x, S_y] = i\hbar S_z; [S_y, S_z] = i\hbar S_x; [S_z, S_x] = i\hbar S_y$$

$$[S^2, S_x] = [S^2, S_y] = [S^2, S_z] = 0$$

Experimentally, it is found two spin states for an electron, so we must have $m_s = \pm 1/2$, and so $s = 1/2$. We say that the electron has spin one-half. Only two normalized spin eigenfunctions exist for this system:

$$\chi_+ \equiv \chi_{\frac{1}{2}, \frac{1}{2}}; \chi_- \equiv \chi_{\frac{1}{2}, -\frac{1}{2}}$$

These two states are spin eigenstates with "spin up" and "spin down" respectively. Since $m_s = \pm 1/2$ only, there are only two (2) eigenstates of \hat{S}^2 and \hat{S}_z : χ_+ and χ_- . These are sometimes called *spinors*.

$$S^2 \chi_{\pm} = \hbar^2 \frac{1}{2} \left(\frac{1}{2} + 1 \right) \chi_{\pm}; \quad S_z \chi_{\pm} = \hbar \left(\pm \frac{1}{2} \right) \chi_{\pm}$$

Spin operators

The operators and spinors can be represented by matrices. Let the spinors be represented by column matrices: $\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$. The operators are 2×2 square matrices, which can be figured out, knowing the eigenvalues. Suppose

$$S^2 \chi_+ = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{3}{4} \hbar^2 \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad S^2 \chi_- = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{3}{4} \hbar^2 \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

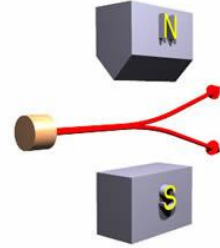
Carrying out the multiplications yields

$$S^2 = \frac{3}{4} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Similarly we obtain

$$S_z = \frac{1}{2} \hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Using commutation relations we obtain



$$S_x = \frac{1}{2} \hbar \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \text{ and } S_y = \frac{1}{2} \hbar \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

Note that the spin eigenfunctions contain only information about the spin state — they tell you nothing about space distributions. The spin state may be represented as a two-component column vector, and the spin operators by two-by-two matrices, as discussed by B & J. For particles with spin larger than 1/2 (quite possible), the number of basic spin eigenstates and the dimensions of the matrices are larger. Like angular momentum, spin may be described qualitatively with the aid of a simple vector model.

Total angular momentum (Optional)

As in classical physics, the total angular momentum of a particle is

$$J = L + S.$$

L operates in ordinary space only; S operates only in spin space. All components of L commute with all components of S , and both satisfy the same commutation relations.

Thus J satisfies the same commutation relations as L and S . It is shown that simultaneous eigenfunctions of J^2 and J_z satisfy

$$J^2 \psi_{jm_j} = j(j+1) \hbar^2 \psi_{jm_j}$$

and

$$J_z \psi_{jm_j} = m_j \hbar \psi_{jm_j},$$

where j is an integer or half-integer, and m_j ranges between $-j$ and j . Because L^2 , L_z , S^2 , and S_z all commute, they have simultaneous eigenfunctions, given by

$$\psi_{lsm_l m_s} = Y_{lm_l}(\theta, \varphi) \chi_{s, m_s}.$$

Alternatively, the four operators L^2 , L_z , S^2 , and S_z form a commuting set. Their simultaneous eigenfunctions are linear combinations of the $\psi_{lsm_l m_s}$. For given l and s the values of j are $|l - s|$ up to $|l + s|$, and m_j can take on values from $-j$ to j .

When more than one particle is present, we need first to add orbital angular momenta, then spin angular momenta and finally we obtain the total angular momentum.

$$L = \sum_i L_i; \quad S = \sum_i S_i; \quad J = L + S$$

A total of four quantum numbers are used to describe completely the movement and trajectories of each electron within an atom. The combination of all quantum numbers of all electrons in an atom is described by a wave function that complies with the Schrödinger equation. Each electron in an atom has a unique set of quantum numbers; according to the [Pauli Exclusion Principle](#), no two electrons can share the same combination of four quantum numbers. Quantum numbers are important because they can be used to determine the electron configuration of an atom and the probable location of the atom's electrons. Quantum numbers are also used to understand other characteristics of atoms, such as ionization energy and the atomic radius.

Physicists use letter names for the various ℓ values:

$\ell =$	0	1	2	3	4	5 . . .
Letter =	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	<i>h</i> . . .

Atomic states are usually referred to by their values of n and ℓ .

A state with $n = 2$ and $\ell = 1$ is called a $2p$ state.

Energy levels are **degenerate** with respect to ℓ , m_l and m_s (the energy is independent of ℓ , m_l and m_s).

Selection rules

The Selection Rules governing transitions between electronic energy levels of transition are:

1. $\Delta m_s = 0$ The Spin Rule
2. $\Delta l = \pm 1$ The Orbital Rule
3. $\Delta m_l = 0, \pm 1$

The first rule says that allowed transitions must involve the promotion of electrons without a change in their spin.

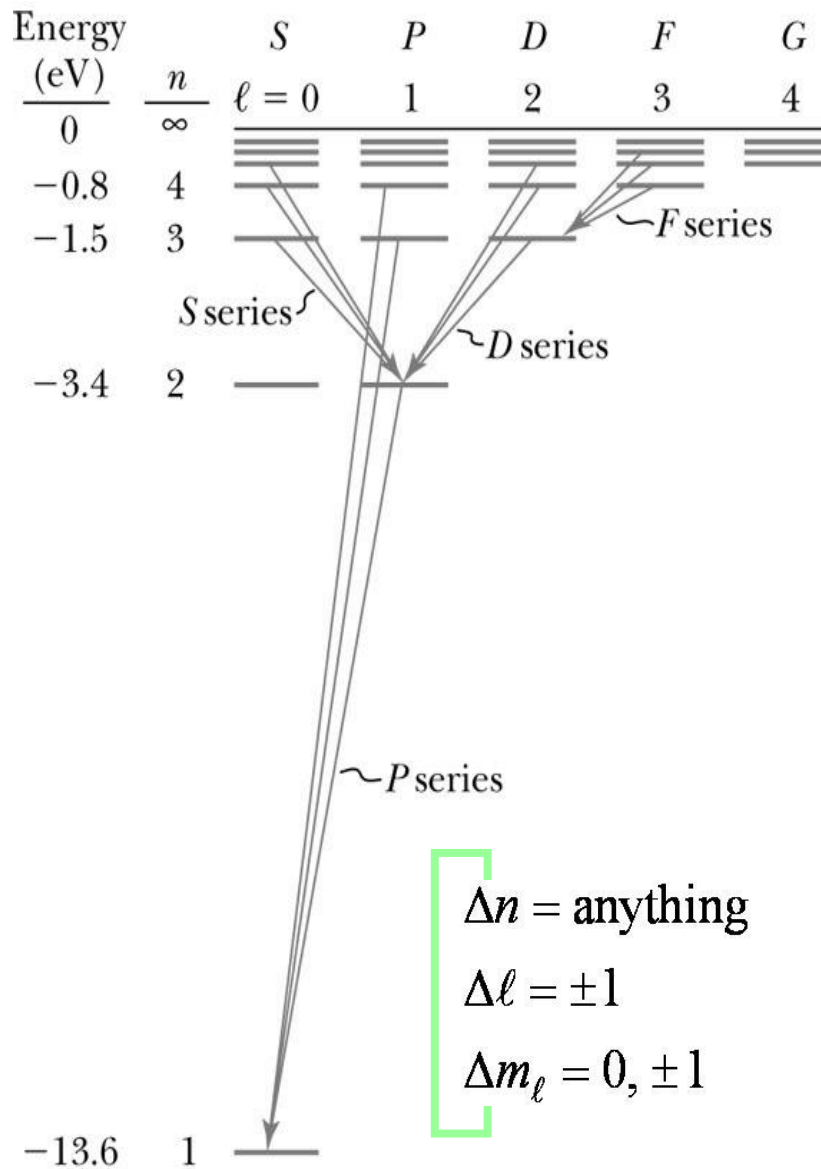
The second rule says that if the molecule has a centre of symmetry, transitions within a given set of p or d orbitals (i.e. those which only involve a redistribution of electrons within a given subshell) are forbidden.

Allowed transitions:

Electrons that absorb or emit photons can change states only when $\Delta l = \pm 1$ and $\Delta m_s = 0, \pm 1, \Delta m_s = 0$.

Forbidden transitions:

Other transitions are possible but occur with much smaller probabilities.



Dirac notation

The bra-ket notation provides a convenient short-hand notation for H states. Since $n, l, m_l,$ and m_s determine the state, we can write a state as a ket:

$$\psi_{nlm_l m_s} = |nlm_l m_s\rangle$$

Because the intrinsic spin quantum number is constant $s=1/2$, it does not appear in the bra-ket.

Action of the operators on the state:

$$\begin{aligned}
 H|nlm_l m_s\rangle &= -\frac{E_0}{2n^2} |nlm_l m_s\rangle \\
 L^2|nlm_l m_s\rangle &= l(l+1)\hbar^2 |nlm_l m_s\rangle \\
 L_z|nlm_l m_s\rangle &= m_l \hbar |nlm_l m_s\rangle \\
 S_z|nlm_l m_s\rangle &= m_s \hbar |nlm_l m_s\rangle
 \end{aligned}$$

Where $E_0 = 27.2\text{eV}$. The quantum numbers takes the values

$$n = 1, 2, 3, \dots$$

$$l = 1, 2, 3, \dots, n - 1$$

$$m_l = -l, \dots, +l$$

$$m_s = \pm \frac{1}{2}$$

Example: Superposition of a state of H-atom is given by:

$$|nlm_l m_s\rangle = \frac{1}{\sqrt{2}} |210 \left(\frac{1}{2}\right)\rangle + A |210 \left(-\frac{1}{2}\right)\rangle$$

- Find the constant A.
- Find expectation values of H, L^2, L_z and S_z .

Answer: $A = \frac{1}{\sqrt{2}}$; $\langle H \rangle = -\frac{27.2}{2 \times 2^2}$; $\langle L^2 \rangle = 2\hbar^2$; $\langle L_z \rangle = 0$; $\langle S_z \rangle = 0$

Example: For the principal quantum number $n = 4$, find number of degeneracy of the state.

Solution: Energy of the electron for given quantum number is $E = -\frac{27.2}{32} eV$

$$n = 3, \text{ then } l = 0, 1, 2, 3$$

$$l = 0; m_l = 0; m_s = \frac{1}{2}, -\frac{1}{2}; 2 \text{ degeneracy}$$

$$l = 1; m_l = -1, 0, 1; m_s = \frac{1}{2}, -\frac{1}{2}; 6 \text{ degeneracy}$$

$$l = 2; m_l = -2, -1, 0, 1, 2; m_s = \frac{1}{2}, -\frac{1}{2}; 10 \text{ degeneracy}$$

$$l = 3; m_l = -3, -2, -1, 0, 1, 2, 3; m_s = \frac{1}{2}, -\frac{1}{2}; 14 \text{ degeneracy}$$

Total: 32 degeneracy.