January 27

Energy Spectra of Real Atoms

In the previous lecture, I derived the spectrum of bound states of the Hydrogen atom. In this lecture, I will explain what the solution of this mathematical problem has to do with the discrete energy spectrum of real atoms.

You probably know that, in 1885, Johan Balmer brought some order to the confusing systematics of line spectra of hot gases by pointing out that the positions of the visible lines in the spectrum of Hydrogen followed a formula

$$\nu = (\text{const.}) \cdot \left(\frac{1}{4} - \frac{1}{n^2}\right) \qquad n = 3, 4, 5 \cdots$$

Later, other related series were found, obeying

$$\nu = (\text{const.}) \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \begin{matrix} n_1, n_2 = 1\ 2\ 3 \cdots \\ n_1 < n_2 \end{matrix}$$

These series, for $n_1 = 1, 2, 3$, are called the Lyman, Balmer, and Paschen series, respectively. Lyman is in the UV, Paschen is in the IR. The UV line at $n_1 = 1$, $n_2 = 2$, called *Lyman* α), is the dominant emission line in starlight.

It was found that the frequencies of light emitted by other atoms also had the form

$$\nu = T_1 - T_2$$

where T_1 and T_2 (called *terms*) are definite frequencies characteristic of the particular atom involved. The *Rydberg-Ritz combination principle* states that all emission frequencies have this structure. After Planck wrote the formula $E = h\nu$, it was natural to interpret the terms T_i as the energies of discrete atomic energy levels. In 1913, Bohr made his great breakthrough in the understanding of atomic spectra by putting forward a primitive atomic model for the Hydrogen atom that predicted the terms quantitatively. His model gave

$$E = \hbar\omega = -\frac{1}{2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{m}{\hbar^3}\,\frac{1}{n^2} = -\frac{R_y}{n^2}$$

where

$$R_y = 13.6\,eV \qquad \nu = \frac{R_y}{h} = 3.1\times 10^{15}/\text{sec}$$

The energy levels are the same as would be found many years later in the solution to the Schrödinger equation. The value agreed with the best experimental measurements of the time.

Bohr went on to make a further prediction. In hot Helium gas, a set of levels were known that also satisfied the Balmer formula; these had been discovered by Pickering in sunlight and, in 1912, by Fowler in Helium discharge tubes. Bohr interpreted these as the transitions in the one-electron atom He$^+$. Since, for a nucleus with charge Z, the Rydberg energy is

$$R_y = Z^2 \cdot \frac{1}{2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{m}{\hbar^2}$$

Bohr predicted

$$R_y(He)/R_y(H) = 4$$

Fowler wrote an angry letter to the Proceedings of the Royal Society that Bohr must be wrong, since his measurements gave

$$R_y(\mathrm{He}) / R_y(\mathrm{H}) = 4.0016$$

Bohr solved this problem with the following insight: Consider the classical mechanics problem of two bodies with masses M and m interacting through a central force. This problem can be rewritten as a 1-body problem in the relative coordinate $\vec{r}$, with the masses replaced by the *reduced mass*

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

This gives

$$R_y(A) = \frac{R_y}{m_e} \cdot \left(\frac{m_e}{1 + m_e/m_A} \right)$$

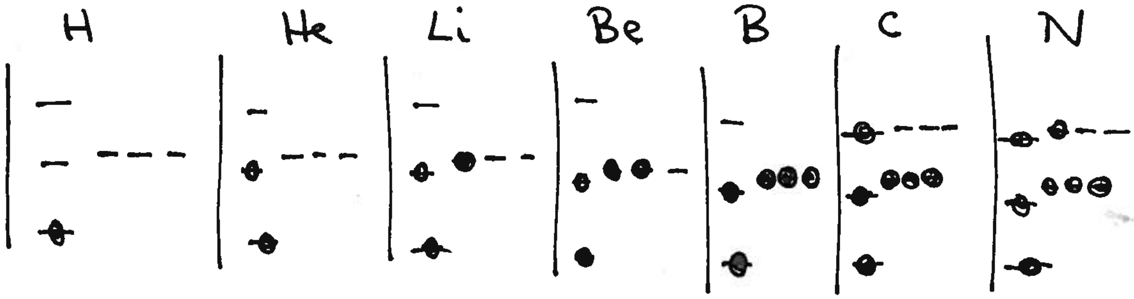
which gave exactly Fowler's result. This was by far the most accurate prediction ever made in spectroscopy and was a triumph for Bohr's theory. The formula for R_A also explains the spectra of other one-electron atoms — Li^{+2}, Be^{+3}, etc.

Close examination of the spectra of Hydrogen and other one-electron systems reveals very small splittings of the exact equality or *degeneracy* of levels predicted by the Schrödinger equation. For example, the $\ell = 1$ states actually split into two groups, with splitting in energy of the order of

$$\Delta E \approx \alpha^3 mc^2$$

This *fine structure* (and also *hyperfine structure*) of Hydrogen will be discussed in Physics 131.

The solution for the Hydrogen atom wavefunctions suggests an explanation for the periodic table of the elements, the idea of Mendeleev that the chemical properties of elements repeat periodically. One possible way to build a multi-electron atom would be to put all of the electrons into the lowest energy Schrödinger wavefunction. However, what if it were only possible to put one electron into each wavefunction? Then the electronic structure of an atom would be built up by filling the various wavefunctions sequentially, starting from the bottom. The first elements in the periodic table would then have atoms with the structure



The principle that only one electron can occupy each distinct quantum state was proposed by Wolfgang Pauli and is called the *Pauli exclusion principle* (in German, "Paulische Äquivalenzverbot").

Because the various states of the same n but different ℓ have the same energy in Schrödinger's solution, it is not clear in what order we should fill these states. This requires looking more closely into the structure of multi-electron atoms. First, we should give these states their proper names. The integer n is called the *principal quantum number* and runs over $n = 1, 2, 3, \ldots$. For each n, $\ell = 0, 1, \ldots, (n-1)$. The states of different ℓ are assigned names as follows:

$\ell = 0$ S states
$\ell = 1$ P states
$\ell = 2$ D states
$\ell = 3$ F states
$\ell = 4$ G states

Thus, we speak of 1S, 2S, 2P levels, and so on.

In a multi-electron atom, each electron feels the electrostatic potential not only due to the nucleus but also due to the other electrons. The electrons are negatively charged, so the inner electrons *screen* the nuclear charge. Thus, the outer electrons see a potential with a smaller charge. The wavefuntions of the innermost electrons might be well described by a Schrödinger equation with charge Z. However, if there are N electrons close to the nucleus, the electrons outside this group might feel a Coulomb potential with charge $(Z - N)$. The outermost electrons feel a central charge close to 1. Since, the Rydberg depends on Z as

$$Ry(Z) = Z^2 \cdot Ry$$

the innermost electrons are much more deeply bound that the outer electrons. Similarly, since the characteristic size of wavefunctions is

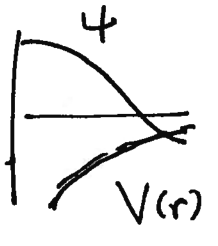
$$a_0(Z) = \frac{1}{Z} a_0$$

all atoms, from Hydrogen to Uranium, have roughly the same size, of the order of

$$a_0(Z \cong 1) = a_0 = \frac{1}{2} \mathring{A}$$

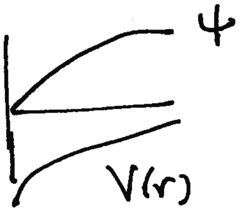
The Coulomb potential is strongest near $r = 0$, so the wavefunctions that are large near $r = 0$ are pulled down in energy more strongly by the inner nuclear charge. That is, the S states, with

$$\psi(r) \sim r^0$$

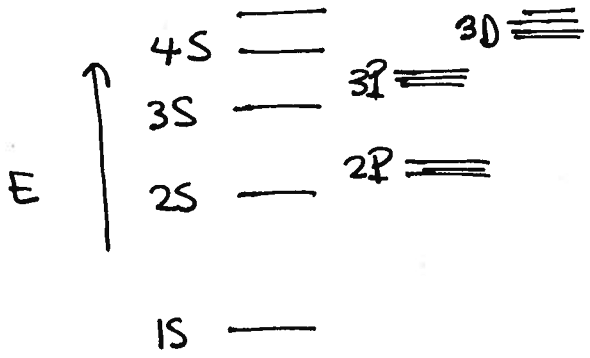


should be lowest in energy, while the P and D states, with

$$\psi(r) \sim r^1 \quad \text{for P}$$
$$\psi(r) \sim r^2 \quad \text{for D}$$



should be higher. It turns out that, in the solution of a multi-electron problem, the first D state (3D) has a higher energy than the 4S state. Similarly, the 4F state has a higher energy than the 6S state.



This justifies the order of filling of states shown above.

When a group of states is completely filled, we call this a *closed shell.* Intuitively, atoms with closed shells should be chemically inert, while atoms with electrons and open states at the same level should be chemically reactive. These ideas predict that chemical properties repeat periodically.

However, the model above gives the wrong periodicity. It predicts that H, B, Si should be inert, while He, N, P are highly reactive.

Fortunately, there is one more ingredient that should be added to the story. In 1925, two Dutch graduate students, Samuel Goudsmit and George Uhlenbeck, noticed that many atomic spectral lines seemed to come in pairs. They proposed that electrons carry an extra quantum number m_s which takes two values, conventionally,

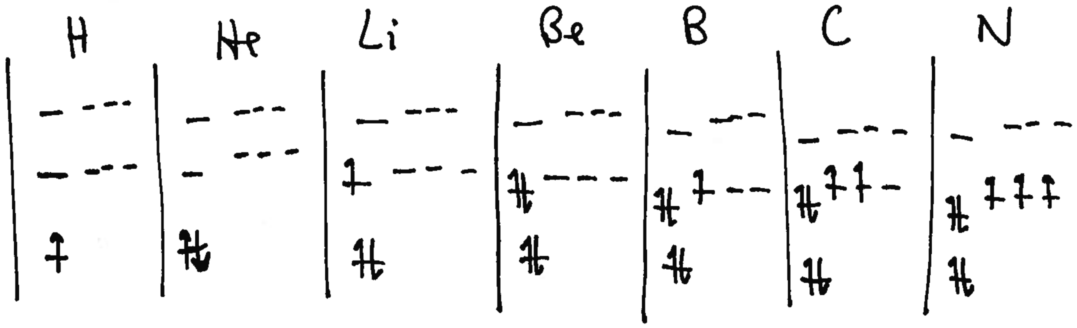
$$m_s = \pm \frac{1}{2}$$

Goudsmit and Uhlenbeck identified m_s as associated with the internal angular momentum of the electron. This idea is very non-obvious, but it turns out to be correct. I will give an explanation of this quantum number later in the course. For now, I will refer to m_s as *spin.* I will represent the two spin states of an electron as

$$m_s = \frac{1}{2} \quad \uparrow \qquad\qquad m_s = -\frac{1}{2} \quad \downarrow$$

An electron in a Hydrogen atom then has four quantum numbers: n, ℓ, m, m_s.

When Pauli found out about the spin quantum number, he saw that his exclusion principle would give the correct periodicity to explain the chemical properties of atoms. We can now put *two* electrons in each Hydrogen atom wavefunction, one with spin up ($m_s = +\frac{1}{2}$), one with spin down ($m_s = -\frac{1}{2}$). Then the filling pattern becomes



Filling of all S and P states at a given level n gives a closed shell. This predicts that the atoms

He , Ne , Ar , . . .

are inert. These are precisely the noble gases. The alkali metals Li, Na, K, etc., with one electron in an otherwise empty shell, would be predicted to be especially reactive, and, indeed, they are.

The presence of D and F states shifted upward in energy with respect to the S and P states with the same n explains the other oddity of the periodic table. The transition metals Sc through Zn arise by filling of the 3D states. The number of these states is $5 \times 2 = 10$. The rare earths La through Lu correspond to filling of the 4F states. The number of these states is $7 \times 2 = 14$.

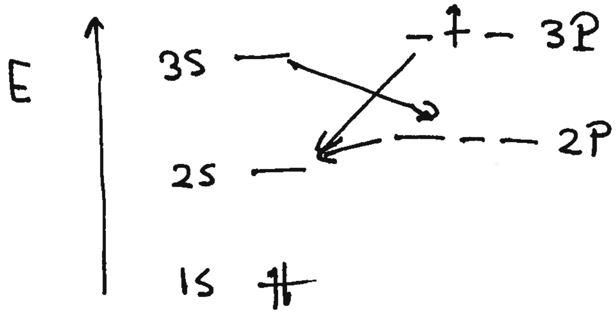
We can test these hypotheses further by looking at the excited states of the atoms in the first row of the periodic table. Begin with Helium. The lowest state or *ground state* of Helium is the closed shell

Above this state, one finds a Hydrogen-like spectrum observed through radiative transitions.

In fact, there are two sets of states, with no prominent transitions between one set and the other. The energy level diagram, and the transitions from which it is inferred, is shown in the figure, from G. Herzberg, *Atomic Spectra and Atomic Structure*. The second set of levels is lower than the first by about 4In the second set of levels, the major transition line from the 2P to the 1S is not observed! The 2S state in this system is metastable, with a lifetime more than 10^4 times longer than the typical lifetimes of excited states of Hydrogen. These systems are called *parahelium* and *orthohelium*, respectively.

The model with electron spin gives an explanation of this structure. In the lowest-energy excited states of Helium, one electron remains in the 1S state while the other goes into a higher level. These spins may have parallel or antiparallel spins. The strongest radiative transitions do not flip the spin—and, also, always change ℓ by 1 unit. Transitions that flip the spin can occur but at much smaller rates; we say that they are "forbidden". In parahelium, the spin of the excited electron has a spin opposite to that of the electron in the 1S. Then the transitions from the 2P and higher states to the 1S is allowed. In orthohelium, the excited electron has a spin parallel to that of the electron in the 1S. Then the transition from the higher states to the 1S cannot occur, by the Pauli principle, without a spin flip. Also, without a spin flip, all radiative transitions must stay inside the same system of levels, either para- or ortho-.

Lithium has an excitation spectrum similar to that of Hydrogen. Two electrons remain in the closed shell 1S. The electron in the 2S can jump to the 2P and to higher states, and, if the electron is in a higher level, it can transition down to the 2S.



Similar patterns for radiative transitions are seen in the other alkali metals (Na, K, etc.).

The alkali earths (Be, Mg, Ca, etc.) have similar patterns of radiative transitions, with para- and ortho- systems of energy levels similar to those of He. Boron has a series of levels beginning with one electron in the 2P, treating the 1S and 2S as closed shells.

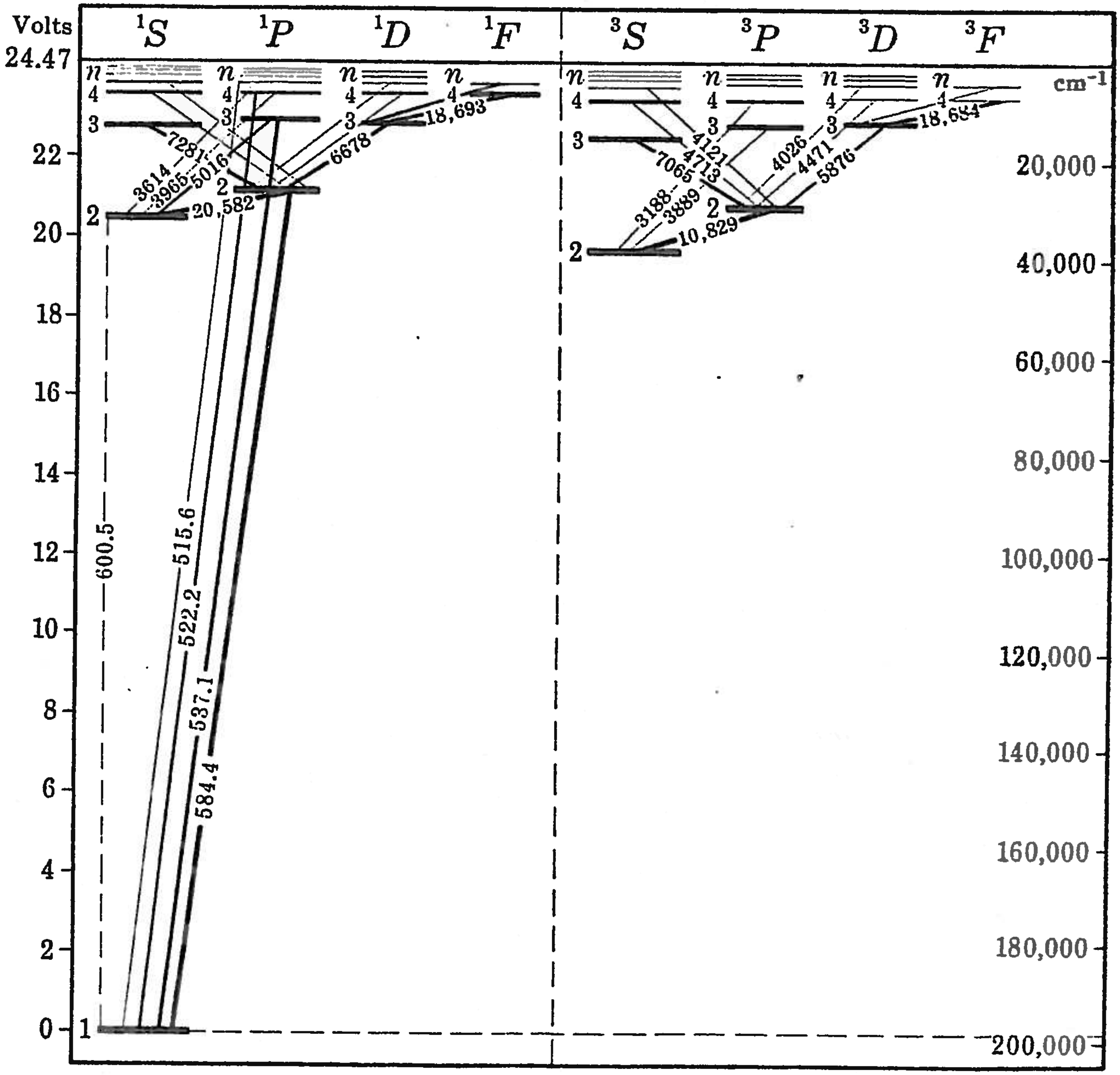


Fig. 27. Energy Level Diagram for Helium. The running numbers ar true principal quantum numbers of the emission electron are here identica The series in the visible and near ultraviolet regions correspond to the indicate transitions between terms with $n \geqq 2$.

Carbon gives an interesting new case. The ground state has two electrons in the 2P state. A single electron in the 2P states has 6 possible states — 3 orbital states ($m = -1, 0, 1$) and, for each of these, 2 spin states. For two identical electrons, the number of states is

$$\frac{6 \cdot 5}{2!} = 15$$

For the m_s configuration

$$\uparrow\uparrow$$

the Pauli principle requires that the two electrons be in different orbital states. In all, there are 9 states with parallel spin configurations, all of which turn out to have the same energy

$$(m_{s1}\ m_{s2}) = \qquad\qquad (m_1 m_2) =$$

$$(\uparrow\uparrow,\ \uparrow\downarrow,\ \downarrow\downarrow) \times ((1,0)\ (1,-1)\ (0,-1))$$

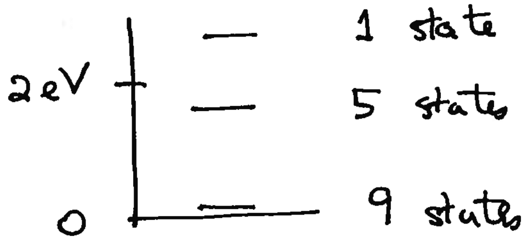
The remaining 6 states have an antiparallel spin configuration

$$\uparrow\downarrow$$

and one of the orbital configurations

$$m_1 m_2 = \quad (1\ 1)\ (0\ 0)\ (-1\ -1)\ (1\ 0)\ (0\ -1)\ (1\ -1)$$

The states with parallel spins and different orbital configurations are lower in energy because electrons repel one another by electrostatic forces and thus prefer to be in different orbital states. The actual pattern of energies for the lowest-lying states of C is



A more complete energy spectrum for C is shown in the figure, taken again from Herzberg's book.

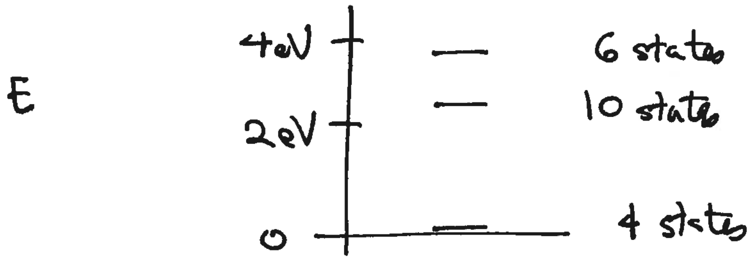
For Nitrogen, we have 3 electrons in the 2P levels. The number of possible electron states is

$$\frac{6\cdot 5\cdot 4}{3!} = 20$$

As in C, the lowest energy state has the electrons in all different orbital states, with a parallel spin configuration There are 4 states of this type, with equal energy,

$$((\uparrow\uparrow\uparrow), (\uparrow\uparrow\downarrow), (\uparrow\downarrow\downarrow), (\downarrow\downarrow\downarrow)) \times (1, 0, -1)$$

The remaining states form two groups with some antiparallel spins



A more complete spectrum for N, from Herzberg's book, is shown in the figure.

For Oxygen, we have 4 identical electrons in the 2P states. The number of possible quantum states is

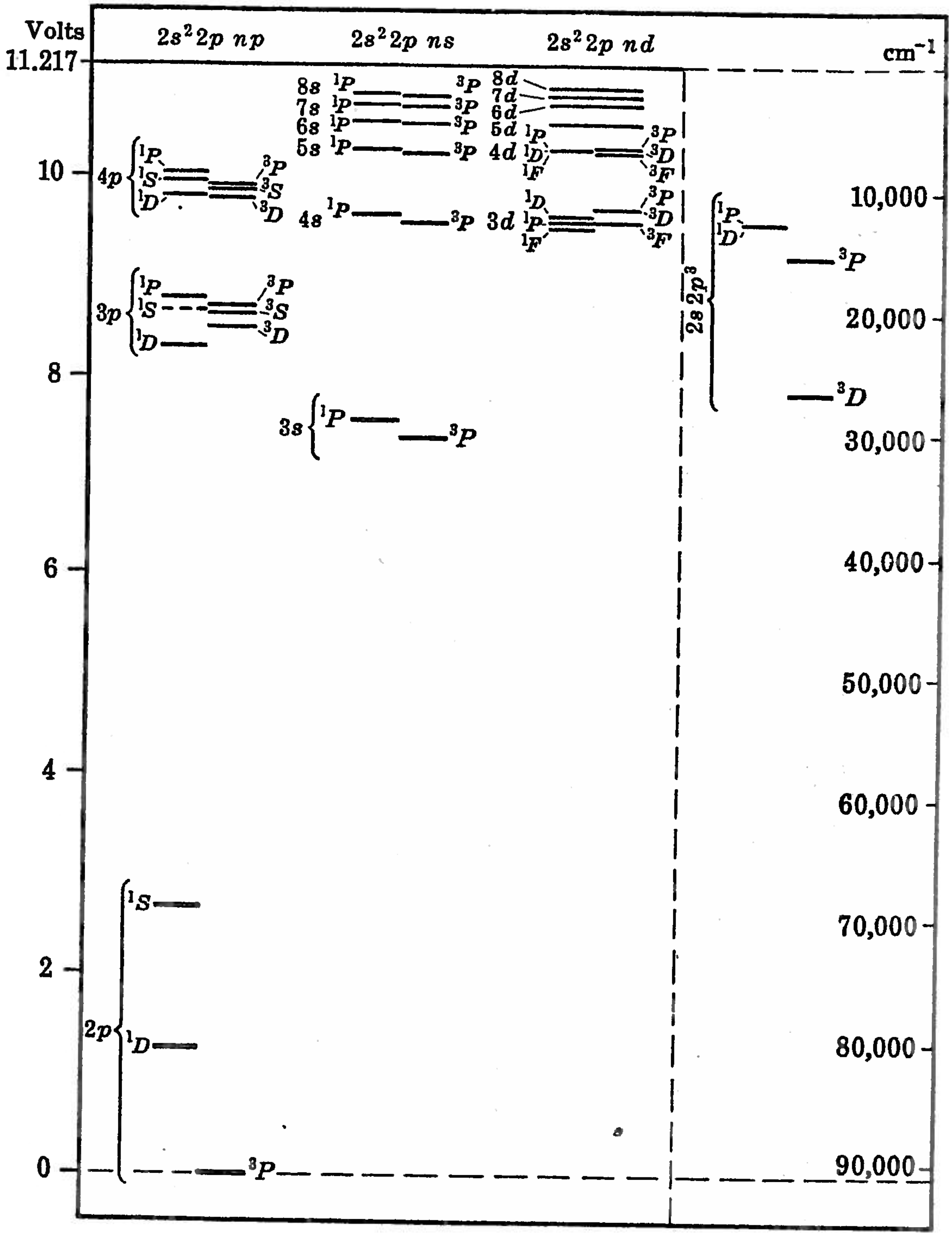


Fig. 55. Energy Level Diagram for C I. The unobserved $3p\ ^1S$ term is cated with a dotted line.

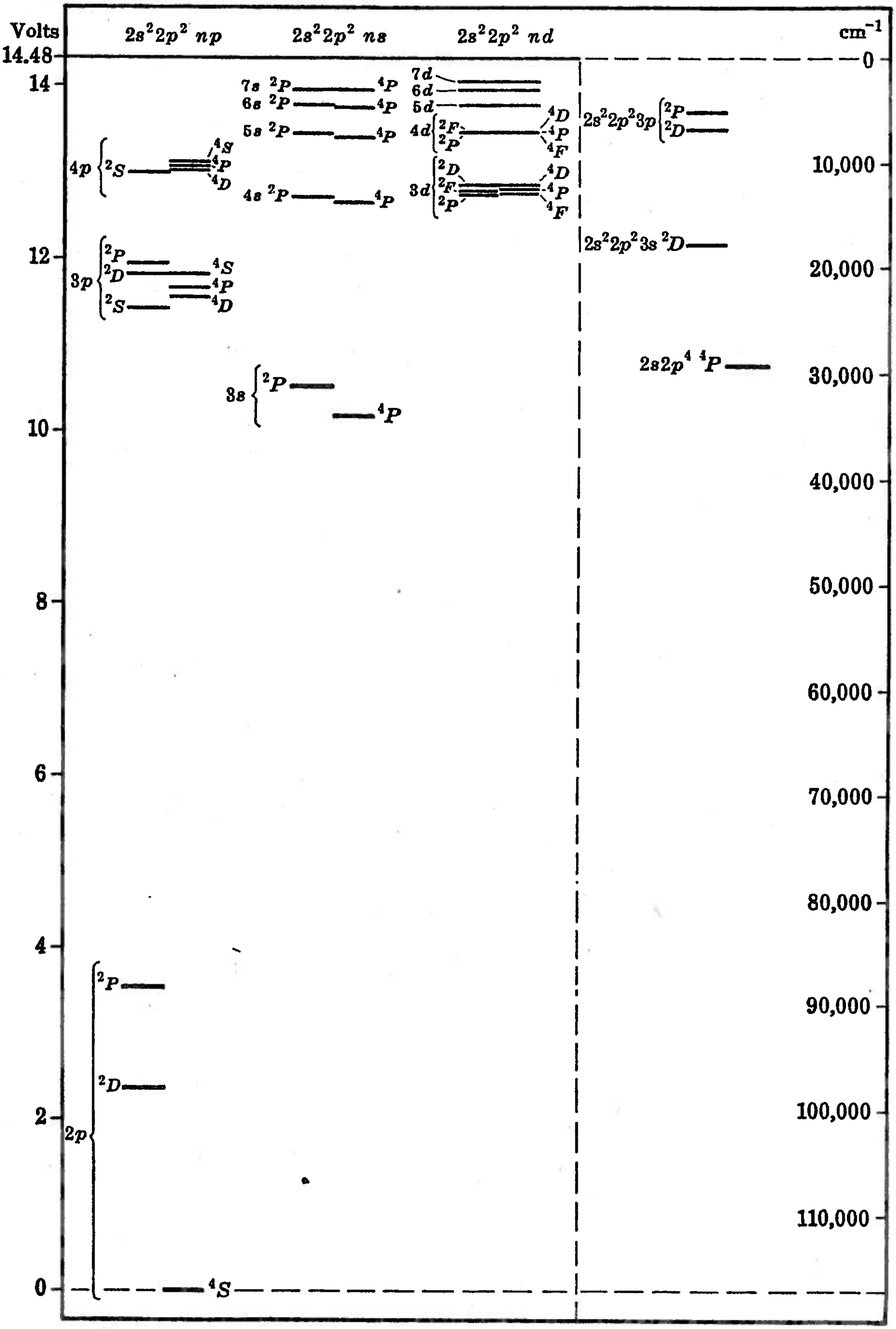


Fig. 56. Energy Level Diagram for N I.

$$\frac{6 \cdot 5 \cdot 4 \cdot 3}{4!} = 15$$

For Fluorine, the number of states is

$$\frac{6 \cdot 5 \cdot 4 \cdot 3 \cdot 2}{5!} = 6$$

We can work out the energy levels most easily by regarding the 2P states in these cases as closed 2P shells with 1 hole, for F, and 2 holes, for O. The holes have $m_s = \mp\frac{1}{2}$ and can occupy any of the three m levels. We then find the same pattern for the lowest-lying states as we found in B and C. You know from chemistry that the single hole in a closed shell in F is as reactive as the single electron in a closed shell that we found in Li.

There is more to say about Schrödinger theory, but we can already see that we are in a position of diminishing returns. In particular, we have met two new concepts—the Pauli exclusion principle and electron spin—that we cannot discuss fully without going to a deeper level of understanding of quantum mechanics. So, in the next lecture, we will start over and begin our approach to the foundations of the theory.