Chapter 4
Atomic Structure

4.1 The Nuclear Atom

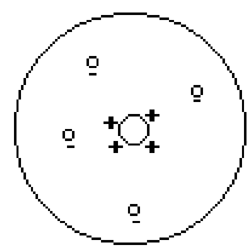
J. J. Thomson found electrons in atoms (1897) by extracting them from a gaseous discharge and bending them in magnetic fields. This let him find their charge/mass ratio.

Thomson suggested (1898) that atoms consist of positively charged lumps of matter with electrons embedded in them. ("Raisin pudding.")

> This model may seem silly now, but, as we will see soon, some of the later, more sophisticated models of the atom led to some very serious problems.

Geiger and Marsden (1911) shot alpha particles at thin (much less than the thickness of a human hair) gold foils. Alpha particles are helium atoms minus their electrons, so they have a charge of +2e.

> In the Thomson model, the electric charge is smeared out over the atomic volume, and no (or very weak) interaction is expected between the charged alpha particles and the gold atoms. That's because there is no local electric field to deflect a charged particle.
>
> Most of the alpha particles went on through with no interaction, but some of them scattered at large angles, and some even scattered through an angle of 180°.
>
> That result was totally unexpected. The experiment led Rutherford to develop his model for the atom, in which the atom's positive charge and mass are concentrated in a very small nucleus, with the electrons some distance away.
>
> Here's the picture of Rutherford's atom, which you're probably familiar with...



> The concentration of charge at the nucleus allowed for large enough electric fields to deflect the alpha particles.

Rutherford developed a theory of alpha particle scattering by nuclei.

> We won't cover the mathematics of the Rutherford model and Rutherford scattering, contained in the appendix to chapter 4. The mathematics is not difficult, but it is (to me, anyway) rather tedious. One comment is worth noting, however:
>
> The Rutherford model is entirely classical. That's one reason I skip it, because...
>
> In dealing with alpha particles and nuclei, we would expect classical models to break down.
>
> As Beiser points out, the alpha particle doesn't get close enough to the nucleus for its wave nature to become significant. Rutherford's calculations worked because of that. Who knows

what direction physics would have taken had Rutherford's classical calculations not been in correspondence with quantum mechanical reality.

Nuclear Dimensions

This section can be confusing if you don't read it carefully. Beiser estimates the size of a nucleus based on how close a highly energetic alpha particle can get.

It may not be clear at first why the distance of closest approach of a particular alpha particle to the nucleus should tell us much about nuclear size.

The alpha particle used in this section happens to have an energy of 7.7 MeV. Beiser calculates the distance of closest approach for this alpha particle. Below is how he does it.

The alpha particle has 7.7 MeV of energy. It has a charge of +2. If it approaches the positively charged nucleus (charge Ze), it will feel a coulomb repulsion. We can calculate the potential energy due to this repulsion.

$$U = \frac{1}{4\pi\varepsilon_0}\frac{2eZe}{r}.$$

At closest approach, $r=r_0$ and the kinetic energy, K=7.7 MeV, has been completely converted to potential energy. We solve the above equation for r_0, plug in the numbers, and get, for gold (as an example) $r_0=3.0\text{x}10^{-14}$ m.

Here's the question. What does this have to do with nuclear size? Wouldn't a more energetic alpha particle get closer?

It would, of course. It just turns out that the 7.7 MeV alpha particle is energetic enough to get reasonably close to the nucleus, so that the above number is a fairly good estimate.

Thus, this section doesn't really calculate nuclear dimensions--it just gives an upper bound on their dimensions.

4.2 Electron Orbits

The Rutherford model requires electrons separated by large distances from the positively charged nuclei. Does anybody see any problems here?

We might expect that the electrons would be sucked into the positively charged nucleus (after all, unlike charges do attract, and the electrostatic force is a very strong one).

Otherwise, they must be far enough away to not feel any attraction, in which case they ought just to go off on their own. The electrons certainly can't just sit around doing nothing.

Also, what holds the positive charges in the nucleus together? After all, unlike charges repel.

This is a problem we won't solve until later in the course.

Dynamically stable orbits, like those of the planets around the sun, would allow electrons to remain "attached" to nuclei. So let's calculate such an orbit.

As you learned in Physics 23, there must be a centripetal force holding anything in circular motion (remember, circular motion is accelerated motion).

In atoms, that force is the Coulomb attraction between electrons and nuclei:

$$F = \frac{e^2}{4\pi \varepsilon_0 r^2} = \frac{mv^2}{r}.$$

We can readily solve for electron velocity:

$$v = \frac{e}{\sqrt{4\pi \varepsilon_0 mr}}.$$

The electron's kinetic energy is $K=mv^2/2$ and its potential energy is

$$U = -\frac{e^2}{4\pi \varepsilon_0 r}.$$

Its total energy E is just E=K+U. Adding kinetic and potential energies gives

$$E = -\frac{e^2}{8\pi \varepsilon_0 r}.$$

The total energy is negative, meaning the electron is bound to the nucleus. As this section in Beiser points out, this total energy is actually shared between electron and nucleus.

Example: use the ionization energy of hydrogen to calculate the velocity and radius of the electron orbit.

The ionization energy is 13.6 eV, so the binding energy is -13.6 eV, or $-2.2\text{x}10^{-18}$ Joules.

Solve the preceding equation for r:

$$r = -\frac{e^2}{8\pi \varepsilon_0 E} = -\frac{(1.6x10^{-19})^2}{(8\pi)(8.85x10^{-12})(-2.2x10^{-18})} = 5.3x10^{-11} m.$$

The electron velocity is calculated to be $2.2\text{x}10^6$ m/s. It is interesting that the electron velocity is far from relativistic. This is not the case in heavier atoms.

Does anybody see some problems here?

This is a classical derivation, based on Newton's and Coulomb's laws. It contradicts electromagnetic theory, which says that the accelerated electron should radiate (i.e. lose) energy and rapidly spiral into the nucleus.

The explanation? We simply can't use classical physics to explain the atom. We need to consider the wave nature of electrons.

Aside: why, then, did the Rutherford model work (in the parts of the text that we skipped)?

Answer: λ=h/mv.

For an alpha particle with v=$2x10^7$ m/s and m=$6.6x10^{-27}$ kg, λ=$5x10^{-15}$ m. (A "typical" small nuclear size.)

The alpha particle was estimated above to get within 6 of these de Broglie wavelengths of the nucleus. Apparently 6 wavelengths is far enough away for classical physics to work.

4.3 Atomic Spectra

The idea behind this section is that there existed a body of data on atomic spectra which the Bohr model of the atom (which we will do next) was able to explain.

Much of this data existed for several decades before the Bohr model.

This section looks at the data. The next section looks at the Bohr model.

Kinds of atomic spectra:

Emission spectra: an atomic gas is excited, usually by an electric current, and emits radiation of specific wavelengths.

Absorption spectra: an atomic gas absorbs radiation of specific wavelengths.

Of course, molecules can have emission and absorption spectra too.

For example, if we put a high voltage current through hydrogen gas, we see light.

The light is not a continuous spectrum, but a series of discrete, monoenergetic lines.

The first series of lines was discovered by Balmer, and the wavelengths are given by

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad n = 3,4,5,...$$

R is a constant whose value we will calculate later. This is an empirical equation, which we would like to explain with the laws of Physics. We can't explain it with classical physics.

There are other series of spectral lines. I am not particularly interested in having you memorize their names or formulas. They all follow something like

$$\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \qquad n_i = n_f + 1, n_f + 2, n_f + 3, \ldots$$

The important idea is that the next section will explain these experimental observations.

4.4 The Bohr Atom (1913)

Beiser notes that this is not the approach Bohr took in his work, because de Broglie and his particle waves didn't come for another decade.

Note that this is a model for the ***hydrogen*** atom.

Why choose the hydrogen atom...

Consider the orbital wavelength of an electron.

An electron in orbit around hydrogen nucleus has wavelength $\lambda = h/mv$ and a velocity as given previously:

$$v = \frac{e}{\sqrt{4\pi \varepsilon_0 m r}}.$$

You can solve these two equations for the wavelength:

$$\lambda = \frac{h}{e}\sqrt{\frac{4\pi \varepsilon_0 r}{m}}.$$

Plugging in the electron mass, $r = 5.3 \times 10^{-11}$ m for the radius of an electron orbit in hydrogen, $e = 1.6 \times 10^{-19}$ C, and $\varepsilon_0 = 8.85 \times 10^{-12}$, you get a wavelength $\lambda = 33 \times 10^{-11}$ m, which is the circumference of the electron orbit.

So what?

We have taken an electron and calculated its wavelength. We find that its wavelength exactly corresponds to one orbit of the hydrogen atom. See Figure 4.12.

This provides us with a clue as to how to construct electron orbits.

Remember our vibrating string? If waves going down and coming back are out of phase, we have destructive interference; that particular wavelength can't "fit" into the vibrating string. We achieved resonance only for particular masses hanging on the string (i.e., for particular tensions in the string).

Similarly, if an electron wave going around a nucleus "meets itself" out of phase after one revolution, destructive interference will take place. Actually, instead of "destroying" itself, such an electron simply can't fit into an orbit. It must either gain or lose energy, so as to have a velocity which gives it a wavelength which fits into the orbit.

We thus arrive at the postulate that ***an electron can orbit a nucleus only if its orbit contains an integral number of de Broglie wavelengths.***

Note that Bohr didn't know about de Broglie waves when he worked out his model for the hydrogen atom, so he couldn't have made this postulate.

Expressed mathematically:

$$n\lambda = 2\pi r_n \qquad n = 1,2,3,...$$

Combining this expression for λ with the one we obtained earlier in this section gives us an equation for r_n, the orbital radii in the Bohr atom.

$$r_n = \frac{n^2 h^2 \varepsilon_0}{\pi m e^2} \qquad n = 1,2,3,...$$

The integer n is called the ***quantum number*** of the orbit.

When n=1,

$$r_1 = \frac{h^2 \varepsilon_0}{\pi m e^2} = \frac{(6.62x10^{-34})^2(8.85x10^{-12})}{\pi(9.11x10^{-31})(1.6x10^{-19})^2} = 5.292x10^{-11} m.$$

This value of r_1 is the radius of the innermost orbit. It is called the Bohr radius, a_0, of the hydrogen atom, and a_0=5.292x10^{-11} m. The other radii are given by $r_n=n^2a_0$.

4.5 Energy Levels and Spectra

We are now in a position to understand energy levels and atomic spectra.

Plugging r_n into our expression for the energy of an electron in an orbit gives

$$E_n = -\frac{m e^4}{8 \varepsilon_0^2 h^2}\left(\frac{1}{n^2}\right) = \frac{E_1}{n^2} \qquad n = 1,2,3,...$$

These are the ***energy levels*** of the hydrogen atom. Electrons in hydrogen atoms are restricted to these energies. The negative sign indicates the electrons are bound.

The lowest energy level E_1 is called the ***ground state*** of the atom, and higher states are called ***excited states***.

When n=∞ then E=0 and the electron is no longer bound. Electrons with energies ***greater than*** E=0 are not restricted to quantum states.

The ionization energy of hydrogen is E_1=-13.6 eV.

Electrons in hydrogen only exist in the above energy levels, and not in states in between. Electrons change energy levels by absorbing a photon (and gaining energy) or emitting a photon (and losing energy).

The difference between the initial and final electron energy is equal to the photon energy:

$$E_i - E_f = hf.$$

Let n_i and n_f be the quantum numbers for the initial and final electron states.

Then it is easy to show that the wavelength of the photon emitted in this transition is

$$\frac{1}{\lambda} = -\frac{E_1}{hc}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right).$$

This says that emission and absorption spectra for hydrogen will contain only the wavelengths given by the equation above.

If n_f=1, a series of spectral lines known as the Lyman series is observed. These phenomena are discussed in the chapter. I'm skipping them because they are easy to follow in the text, not because I think they are unimportant.

Finally, the factor $-E_1/hc$ is equal to the constant R in the experimentally observed spectral series, which I mentioned last time.

Our conclusion is that the Bohr model does an excellent job of explaining spectral lines.

Be aware, however, that the Bohr model is not really correct.

4.6 Correspondence Principle

It would be a good idea for you to read this section for ideas.

Quantum physics in the limit of large quantum numbers should give the same results as classical physics.

I won't test you specifically over the material in this section.

4.7 Nuclear motion

Again, it would be a good idea to read this section for ideas, but I won't test you over it.

The main idea is that electrons and nuclei orbit each other. The much more massive nucleus moves very little, just as the earth does most of the orbiting around the sun. However, on the atomic scale, the corrections for nuclear motion are big enough to be measurable.

4.8 Atomic Excitation

Atoms can be excited to energy levels above their ground state by:

(1) collisions with other atoms, ions, etc. which transfer kinetic energy, and

(2) photons.

Here we are talking about electronic energy levels. The electrons are absorbing the energy.

Transitions back to the ground state occur via photon emission. Typically this occurs within about 10^{-8} s of excitation (a ballpark figure).

What object is most effective at giving its kinetic energy to an electron? (Draw picture of objects of different masses colliding and take a vote.)

Conclusion: electrons are most effective at transferring kinetic energy to other electrons.

An example of (1) above is a neon lamp. An electric field applied across a gas-filled tube accelerates electrons and ions. Collisions excite atomic energy levels.

An example of (2) is hydrogen absorbing photons of wavelength 121.7 nm and being excited from the n=1 to n=2 state.

The Franck-Hertz Experiment

This is a famous experiment which demonstrated atomic energy levels.

Accelerated electrons colliding with atoms give up energy to atomic electrons, provided their energy is sufficient to promote an atomic electron from one energy level to a higher one.

Things I might ask on a test: what did this experiment demonstrate? Given figure 4.22, interpret the dips in the current versus voltage curve.

4.9 Lasers

Facts about lasers

(1) laser light is coherent; i.e. all waves are exactly in phase,
(2) laser light is (nearly) monochromatic,
(3) the divergence of the laser light is controlled by the size of the aperture through which it leaves; the divergence can be made extremely small,
(4) the laser beam is very intense (10^{30} K, whatever a temperature that high really means).

Required for a laser:

(1) metastable states in the lasing material,
(2) an optical cavity,
(3) method of pumping metastable states to achieve a population inversion.

Absorption and emission:

(1) Induced absorption -- what we have talked about; a photon raises an atom to an excited state.
(2) Spontaneous emission -- what we have talked about; at atom in an excited state drops back to the ground state via emission of a photon.
(3) Induced emission -- a photon of the energy required to produce induced absorption can induce an atom to drop from the excited state back to the ground state -- the probability of this occurring is same as the probability of (1) occurring.

Beiser points out induced emission is like stopping a pendulum by applying a force 180° out of phase with the swings--nothing mysterious.

Some terms

(1) metastable state -- a relatively long-lifetime excited state
 atoms live a long time in metastable states
(2) population inversion -- majority of atoms are in excited states
 if minority of atoms are in excited states, then absorption rather than emission is more probable
(3) optical pumping -- using photons to create a population inversion

The simplest kind of laser is a three-level laser (optical pumping would depopulate a two-level system).

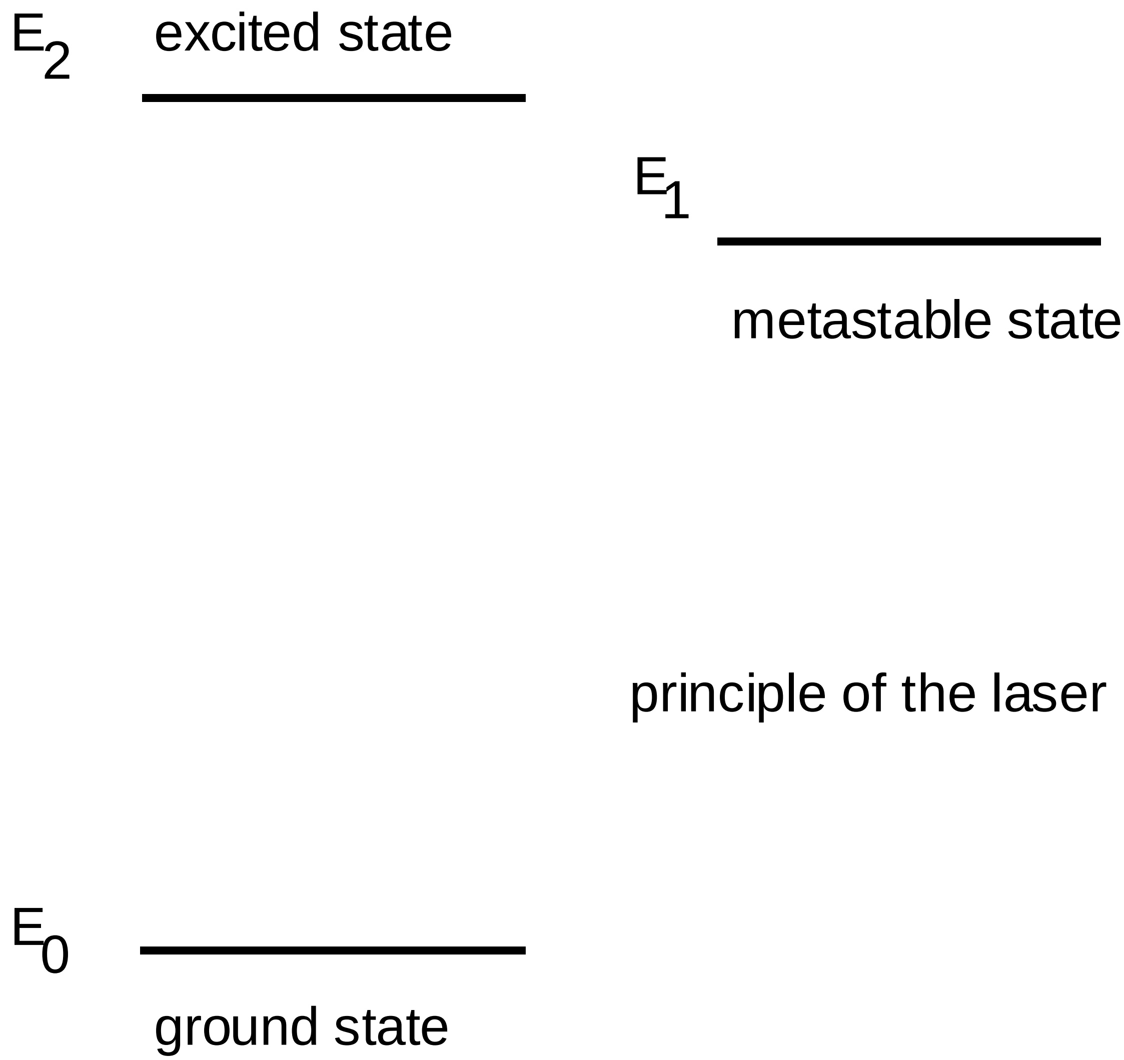
Explain figure 4.26.

Read about the 4-level laser.

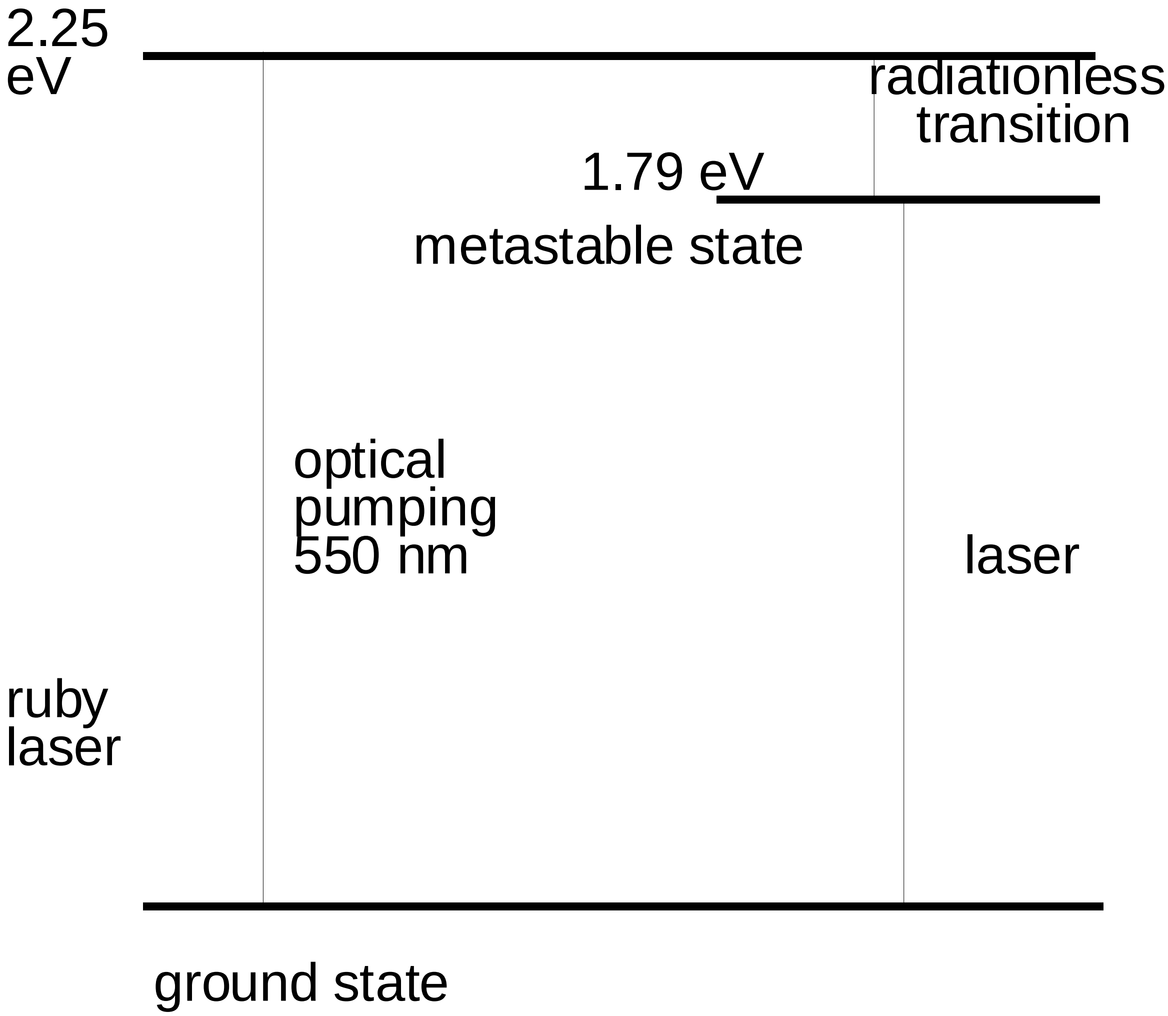
Explain figure 4.27 with ruby laser details.

A red pulse of light is produced after each flash of the lamp.

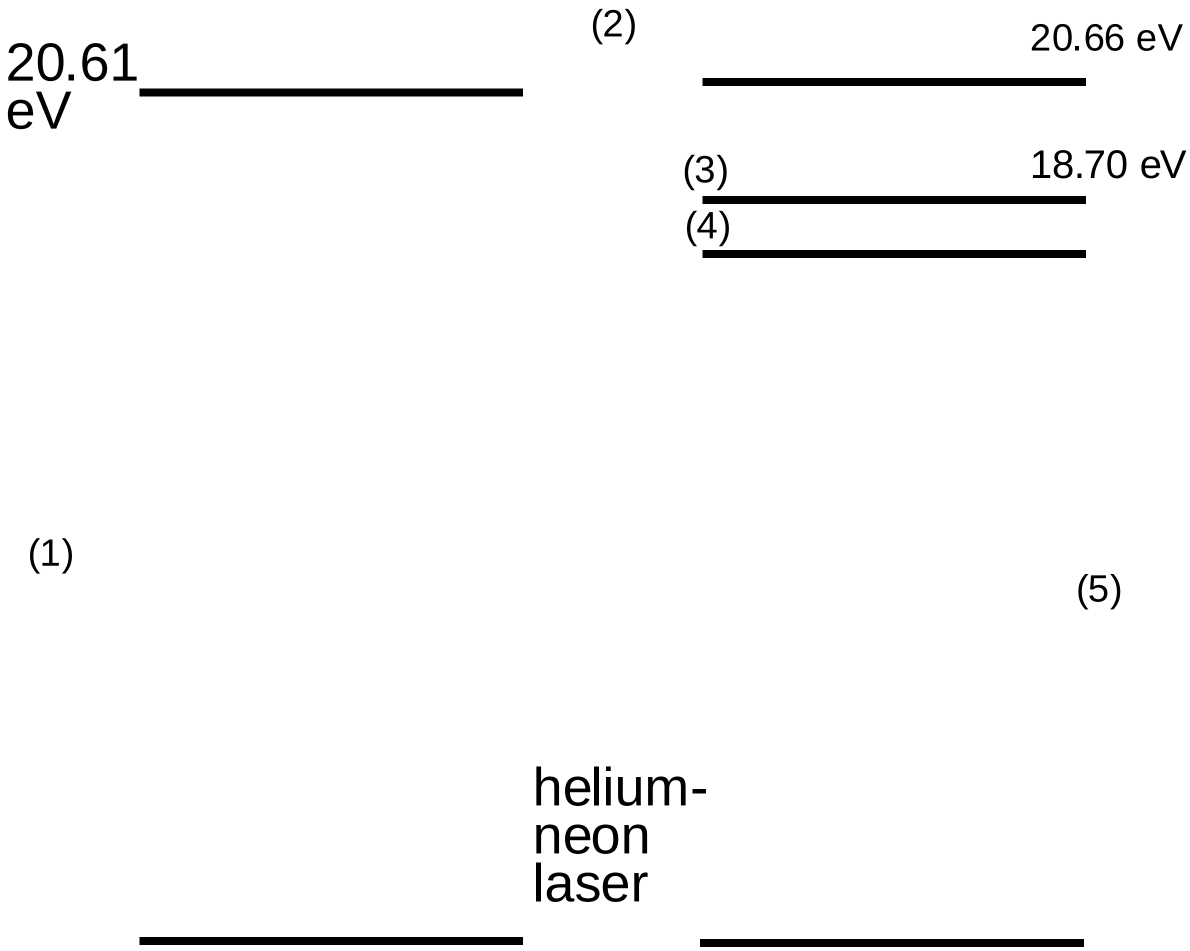
Explain figure 4.29 with He-Ne laser details. This is neat because it is a continuous process.



Principle of the laser.



The ruby laser.



(1) electron impact
(2) collision
(3) laser transition 632.8 nm
(4) spontaneous emission
(5) radiationless transition

A four level laser.