

## Schrödinger, 5

### Transitions

An energy eigenstate of the Schrödinger Equation is always of the form  $\Psi(\vec{r}, t) = \psi(\vec{r}) \exp(-iEt/\hbar)$ . Such an eigenstate is “permanent” in the sense that  $|\Psi|^2$  is independent of time. In order to achieve a transition from one allowed state to another, the potential energy has to change in time:  $U = U_0 + U'(t)$ , where  $U_0$  is the original potential energy and  $U'(t)$  is the change—in formal language, a “time-dependent perturbation.” (See the discussion in the Appendix below for more details about how quantum mechanics describes transitions.) Probably the most important example is the so-called “electric dipole” perturbation for electrons in an atom. The electric dipole potential energy is of the form

$$U' = [e\mathcal{E}_0 \cos(\omega t)] r \cos\theta.$$

The stuff inside the square brackets is a force resulting from a spatially uniform, but oscillating electric field. The stuff outside results from taking the dot product of this force (assumed to point in the  $z$ -direction) with the electron’s position vector. If this perturbation is applied to the eigenstates of an electron in hydrogen, characterized by some initial values of  $nlm_l$ , we get **transitions to states with different values of  $nlm_l$  provided the following are true.**

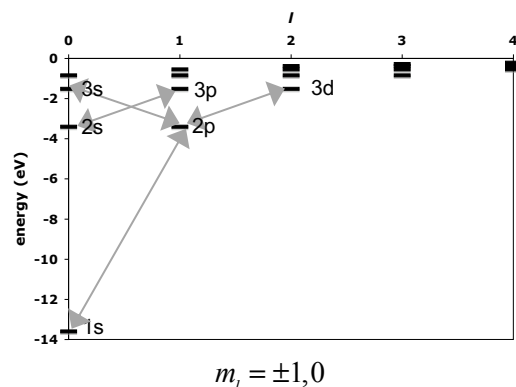
(1) The “driving frequency” has to satisfy  $\omega = \frac{|E_{nf} - E_{ni}|}{\hbar}$ . In other words,  $\Delta n \neq 0$ . If the energy difference is positive the final state has higher energy and the interpretation is that a photon is absorbed; if the difference is negative, a photon is emitted. The change in energy arises because the time-dependence of the perturbations doesn’t allow time to be separated out of the Schrödinger Equation; the electron energy is not conserved.

(2) The presence of the angle  $\theta$  in the perturbation also means that the electron angular momentum is not conserved. The rules for the latter are  $\Delta l = \pm 1$  and  $\Delta m_l = \pm 1, 0$ . The angular momentum change of the electron is associated with the photon: **photons always carry one unit of angular momentum. This intrinsic angular momentum is called “spin.”**

In summary, **electric dipole transitions in sanitized hydrogen require**

$$\Delta n \neq 0, \Delta l = \pm 1, \Delta m_l = 0, \pm 1.$$

Transitions to the ground state,  $1s$ , in hydrogen can occur from the  $p$  states only;  $2p \rightarrow 1s$  and  $3p \rightarrow 1s$  are allowed, but  $2s \rightarrow 1s$ ,  $3s \rightarrow 1s$ , and  $3d \rightarrow 1s$  are not (because of the  $\Delta l = \pm 1$  rule). (Note that the ground state can be excited to a higher energy state but not to a lower one, because there are no lower energy states.) The figure to the right shows a piece of the energy level diagram for hydrogen. The arrows show allowed transitions between  $n=2$  and  $n=1$  and between  $n=3$  and  $n=2$ . Note that the arrows connecting  $s$  and  $p$  states are really three arrows each because the  $p$  states are three-fold degenerate (having



substates). The transition  $3d \rightarrow 2p$  involves *nine*  $m_l$  transitions, namely,  $2 \rightarrow 1, -2 \rightarrow -1, 1 \rightarrow 1, 1 \rightarrow 0, -1 \rightarrow -1, -1 \rightarrow 0, 0 \rightarrow 0, 0 \rightarrow 1, 0 \rightarrow -1$ ; the other six possibilities are forbidden by the  $\Delta m_l = \pm 1, 0$  rule. The  $n = 2$  to  $n = 1$  transitions involve a change in energy of  $-10.2$  eV, which results in emission of UV photons. All of the  $n = 3$  to  $n = 2$  transitions shown involve a change in energy of  $-1.89$  eV ( $E_3$  to  $E_2$ ). This produces  $1.89$  eV photons, which are red. Green photons ( $2.55$  eV) come from  $n = 4$  to  $n = 2$  transitions, while blue photons ( $2.86$  eV) come from  $n = 5$  to  $n = 2$  and violet photons ( $3.02$  eV) come from  $n = 6$  to  $n = 2$ . Transitions from higher energy states to  $n \geq 3$  states are all in the infrared. Explaining the stability of H (and all atoms) and the origin of the observed colors of excited hydrogen gas was the first shining (sorry for the pun) achievement of quantum mechanics.

Visible hydrogen atom spectrum:



### Appendix I: How transitions occur in the Schrodinger Equation

Eigenstates of the unperturbed Schrödinger Equations are *not* solutions to the perturbed equation. A solution of the latter, however, can be expressed as a time-changing superposition (mixture) of the original eigenstates:  $\Psi = \sum_{\sigma} a_{\sigma}(t) \Psi_{\sigma}$ . Here  $\sigma$  means “eigenstate” and is shorthand for a set of quantum numbers—for example, for the electron in sanitized hydrogen  $\sigma = \{nlm_l\}$ ; provided  $\sum_{\sigma} |a_{\sigma}(t)|^2 = 1$ ,  $|a_{\sigma}(t)|^2$  can be interpreted as the probability that  $\Psi$  is in state  $\Psi_{\sigma}$  at time  $t$ .

Now,  $E_{op} \Psi_{\sigma} = (K_{op} + U_0) \Psi_{\sigma}$ , whereas  $E_{op} \Psi = (K_{op} + U_0) \Psi + U' \Psi$ . Plugging  $\Psi = \sum_{\sigma} a_{\sigma}(t) \Psi_{\sigma}$  into the latter equation leads to

$$\sum_s \left[ (E_{op} a_s) \Psi_{\sigma} + a_s (E_{op} \Psi_{\sigma}) \right] = \sum_{\sigma} a_{\sigma} \left[ (K_{op} + U_0) \Psi_{\sigma} + U' \Psi_{\sigma} \right].$$

(There are two terms on the left-hand side because the energy operator is a derivative in time and  $a$  depends on time.) According to the former equation, the second term on the left-hand side cancels with the first term on the right-hand side. Multiplying what is left by  $\Psi_{\sigma_i}^*$  (where  $\sigma_i$  is one of the eigenstates of the unperturbed Schrödinger Equation) and integrating over all space produces

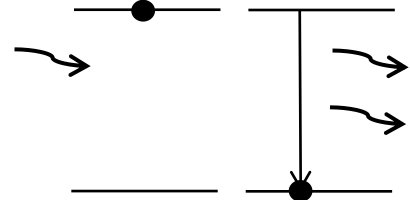
$$E_{op} a_{\sigma_i} = i\hbar \frac{da_{\sigma_i}}{dt} = \sum_{\sigma} a_{\sigma} \int \Psi_{\sigma_i}^* U' \Psi_{\sigma} dV.$$

There is only one term on the left-hand side because  $\int \Psi_{\sigma_i}^* \Psi_{\sigma} dV$  equals zero for every  $\sigma$  except  $\sigma_i$ . The right-hand side doesn't have to reduce to just the  $\sigma_i$  term if  $U'$  depends on position. In that case,  $U'$  causes an “overlap” of some states  $\sigma$  with  $\sigma_i$ . The interpretation of

this is that if the particle described here is known to be in state  $\sigma_i$  at  $t = 0$ , then  $|a_{\sigma_i}(0)|^2 = 1$  and all the other  $|a_{\sigma}(0)|^2 = 0$  (where  $\sigma$  is not  $\sigma_i$ ); the differential equation for  $a$  then tells how  $|a_{\sigma_i}(t)|^2$  decreases and other  $|a_{\sigma}(t)|^2$  grow. That's a quantum mechanical transition. Which states  $\sigma_i$  can evolve to depend on what the wavefunctions are and what the perturbation is.

### Appendix II: Stimulated emission

An oscillating electric field of just the right frequency can cause a transition from a higher energy electronic state to a lower one, producing in turn an emitted photon. Such an electric field might be associated with another photon—a “stimulating” photon. Because the frequencies of the two photons are equal, so are their energies. In fact, the photons emerge in identical states. The figure to the right is a cartoon representation of this **stimulated emission** process. In a **laser** (a device that employs **L**ight **A**mplification by **S**timulated **E**mission of **R**adiation) the excitation process that precedes the left part of the figure is fast compared with the de-excitation process on the right. The laser has many atoms, a continuing excitation mechanism, and a way of partially confining the photons. As a result, the density of identical photons can build up to a very high value. Because the photons leaking out of the laser are all in the same state, the beam is highly collimated, very bright, and coherent. This permits numerous applications in medicine, material processing, information storage and retrieval, and precision measurements, worth perhaps \$200B per year.



*(Historical comment: The enormous economic impact of laser technology has been driven by over 50,000 patents. Not all of these have rewarded the inventor, of course. An interesting story about the laser patent saga focuses on Gordon Gould. Gould was a graduate student at Columbia University in the 1950s when he conceived the idea of using “optical pumping” as the excitation source for a device to amplify light intensity. Gould wanted to patent his idea but believed he had to actually build a working model in order to do so. In order to do that, he left Columbia and joined a company with more resources. In 1959, he began applying for a patent for a “LASER” (Gould was the first person to use this acronym), but his project was declared classified by the US government (which was funding his work). Meanwhile, two other researchers (one of whom had a lab close to Gould’s at Columbia!) submitted a patent application for a device similar to Gould’s and were awarded a patent in 1960 (they did *not* call their device LASER). The important aspect of this story is that as a student, Gould kept careful notebooks on his research work, including writing down and defining the LASER acronym. After work every night he had his notes notarized by the owner of his neighborhood candy store. Eventually, after the government released its hold on his project, Gould used his notebooks as the basis for several patent applications. To make a very long story short, he eventually succeeded, had a long career in engineering (he was inducted into the National Inventors Hall of Fame in 1991), and made a lot of money. *The lesson: keep careful notebooks describing what you are thinking about dear readers.*)*

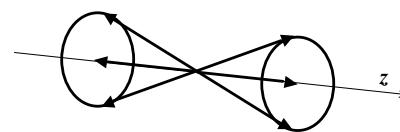
### Appendix III: “Spontaneous” emission

In Fn3, we briefly mentioned that “quantum field theory” is a more general description of matter than Schrödinger quantum mechanics. In quantum field theory, the Coulomb interaction between an electron and a proton in a hydrogen atom is only an approximation. The actual

interaction is nonlinear and can be thought of as consisting of the exchange of infinitely many photons between the electron and proton. These photons have infinitely many different frequencies. Thus, if the electron in a hydrogen atom is in an excited Schrödinger state, such exchange photons with just the right frequency will **stimulate** the decay of that state. Thus, no excited Schrödinger state is an eigenstate of the actual interaction, and will, even in isolation, spontaneously decay without the help of an external photon. The spontaneously emitted photon will obey all of the same electric dipole transition rules noted above.

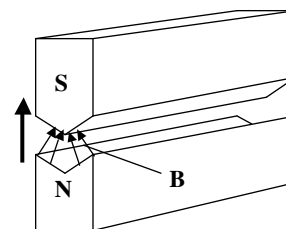
### Spin of the photon

The angular momentum transition rule,  $\Delta l = \pm 1$ , for electric dipole transitions in hydrogen suggests that the photon involved carries “one unit of angular momentum” so that total angular momentum can be conserved. This bit of angular momentum can’t be turned off (as long as the photon exists): it is an *intrinsic* property of the photon. The intrinsic angular momentum of the photon is whimsically called its “spin.” We say, “photons have spin-1” (pronounced “spin one”). In analogy with orbital angular momentum, the magnitude of the photon’s spin angular momentum is  $\sqrt{s(s+1)}\hbar = \sqrt{2}\hbar$ , where its spin quantum number is defined as  $s = 1$ . Orbital angular momentum has quantized directions in space ( $z$ ). This is true for photon spin as well. For photons,  $m_s = \pm 1$  (there’s no 0 value as you would expect for orbital angular momentum with  $l = 1$ ). So, where is this  $z$ -axis? It turns out you can use the direction of the photon propagation. See the figure to the right. The photon is “at” the place where the vertices of the cones come together. If the photon’s  $m_s = +1$ ,  $S_z$  points in the direction of propagation and  $\vec{S}$  can be anywhere on the sides of the forward cone;  $m_s = -1$  gives the opposite result. The  $m_s$  values can be interpreted as states of **circular polarization** of the electric and magnetic fields that describe the probability of detecting the photon. Positive  $m_s$  corresponds to a counterclockwise circulation of the fields when viewed down the propagation direction (i.e., in the  $-z$ -direction). If you point your right thumb in the propagation direction for this case and curl your right fingers in the direction of circulation you get counterclockwise. Thus, a photon with positive  $m_s$  is “right handed;” with negative  $m_s$  it is “left handed.” In order to have  $m_s = 0$  would require electric and magnetic fields circulating along the  $z$ -direction, but photons only have transverse fields—perpendicular to  $z$ . Thus, photons have no  $m_s = 0$  state.



### Spin of the electron: Stern-Gerlach experiment

In 1921, before any of this was known for photons, Otto Stern and Walter Gerlach did an experiment that showed that *electrons* also have spin. Their experiment tested the hypothesis that charged particles carry little permanent magnetic fields, *even when they are at rest*. A Stern-Gerlach (SG) apparatus is a long, inhomogeneous magnet that can be used to measure the strength and orientation of such particle permanent magnets. An SG apparatus is depicted to the right. (The N and S poles are two ends of a big horseshoe magnet, the body of which is not shown.) The shape of the apparatus is designed to produce a gradient of  $\vec{B}$  pointing in the direction of the bold arrow. Let’s call it the  $z$ -direction. A permanent magnet



with magnetic moment  $\vec{\mu}$  experiences a force in the  $z$ -direction given by  $F_z = \mu_z \frac{dB}{dz}$ , where  $\mu_z$  is the component of  $\vec{\mu}$  along the bold arrow direction.

Surprisingly, when an electron travels down the long axis of an SG apparatus (you have to keep the electron in the apparatus by applying an electric field perpendicular to the direction of motion because  $\vec{F} = q\vec{v} \times \vec{B}$  gives a horizontal force), it deflects either upward or downward by the same amount. This is equivalent to saying that  $\mu_z$  is either + some value or – that value, never anything else. The electron’s magnet orients in such a way that  $\mu_z$  takes on one of two possible values. The vertical deflection of the electron is *not* due to its translational motion. Even an electron at rest (if that were possible) would deflect up or down in an SG apparatus. On the other hand, magnetism requires charge in motion. So to account for its permanent magnet, the electron is said to be incessantly “spinning.” Like mass and charge, *spin* is an intrinsic property of all microscopic matter. As in the case of the photon, electron spin is a strange little bit of angular momentum that can neither be slowed down nor speeded up. For an electron, spin can have two orientations when placed in an external magnetic field—“up” or “ $\uparrow$ ” or “+1/2” and “down” or “ $\downarrow$ ” or “–1/2.” (The value 1/2 comes from the general rule that there are  $2s+1$  possible  $z$ -orientations of an angular momentum vector whose magnitude is  $\sqrt{s(s+1)}\hbar$ . The magnitude of spin angular momentum for “spin-1/2” [pronounced “spin one half”] particles is  $\sqrt{\frac{1}{2}(\frac{1}{2}+1)}\hbar = \frac{1}{2}\sqrt{3}\hbar$ .)

The picture that the electron’s magnetic moment arises from it being a spinning ball of charge shouldn’t be taken seriously. The magnitude of magnetic moment is the product of current times area. The smaller the area the bigger the current has to be to get the same moment. For a spinning sphere of charge, the smaller is the radius of the sphere the faster a point on its equator has to travel. As  $c$  is the fastest such a point could travel, no smaller sphere is possible. The magnitude of the electron’s magnetic moment is measured to be about  $6 \times 10^{-5}$  eV/T. (T stands for tesla, the strength of a magnetic field. 1 T is a very strong magnetic field: large MRI magnets usually produce a few T.) The smallest possible spinning sphere with a charge  $e$ , the charge of the electron, would have a radius about 100 times bigger than that of a proton. The effective radius of an electron is measured to be *many times smaller* (perhaps zero?) than that of a proton, so the spinning sphere of charge idea isn’t right. Nonetheless, like many other attempts to understand quantum mechanics through classical models, it persists in the minds of us humans who live in a seemingly classical world.

Importantly, protons and neutrons also have intrinsic magnetic moments and spins—both, spin-1/2. Simple arguments suggest that both of these *nucleonic* magnetic moments should be about 1800 times smaller than that of the electron. The magnetic moment of the proton is of opposite sign to that of the electron (because it is positively charged) but its actual magnitude is 2.8 times bigger than would be expected (i.e.,  $2.8 \times 6 \times 10^{-5}$  eV/T/1800). The neutron is electrically neutral and might be expected to have a zero magnetic moment. Instead, it has the *same* sign as that of the electron and a magnitude of about  $1.9 \times 6 \times 10^{-5}$  eV/T/1800. The funny values of the magnetic moments of the proton and neutron are attributed to the reasonably well-confirmed hypothesis that each is made of smaller particles—the “up” and “down” quarks, which are also spin-1/2 particles, and “gluons,” which are spin-1 particles that “glue” the quarks to one another. We now know that all particles either have integer spin (called “bosons”) or odd half-integer spin (“fermions”).

(*Historical comment:* As we will see more clearly in a bit, the results of the Stern-Gerlach experiment are profoundly important. One would expect the experiment to have merited Nobel Prizes for the two collaborators. Curiously, none were awarded immediately. Eventually, World War II happened. During the War, Gerlach stayed in Germany as a pro-Nazi scientist, perhaps working on the German atomic bomb project. Stern left Germany in 1933 shortly after Hitler came to power, winding up at the Carnegie Institute in Pittsburgh. The Nobel Prize was suspended in 1939, but was awarded again in 1943 while the War was still going on, with Stern receiving the first resurrected Physics Prize. He won for *measuring the magnetic moment of the proton*, which Gerlach had not participated in. The citation by the Nobel committee does not mention the original Stern-Gerlach experiment, presumably as a pointed comment about Gerlach's politics.)

Because electrons and protons carry intrinsic magnetism, the sanitized hydrogen atom cannot be exactly correct. But how wrong are its predictions? To see, we note, as above, that an external magnetic field can exert force on a magnetic moment. This force can be derived from a magnetic potential energy of the form  $U_{\text{magnetic}} = -\mu_z B_{\text{external}}$ , where the direction of  $B_{\text{external}}$  determines what is meant by the  $z$ -axis. As the magnitude of the electron's magnetic moment is  $6 \times 10^{-5}$  eV/T the electron would have to experience a magnetic field due the proton of about 1000 T to significantly alter the colors of hydrogen photons, for example. Is that possible? One hint comes from deep space. ***Large clouds of neutral hydrogen atoms in the interstellar medium emit strong radio signals. This radiation has a characteristic wavelength of 21 cm and is believed to result when the magnetic moment of an electron in the 1s state in hydrogen flips direction from aligned with the proton's magnetic moment to anti-aligned (due to atom-atom collisions).*** The energy of a 21 cm wavelength photon is about  $6 \times 10^{-6}$  eV. Thus, even though the 1s electron actually passes through the proton the average magnetic field it feels is only on the order of 0.1 T. Though magnetic effects on hydrogen transitions can be measured by high precision modern optics techniques, they are really pretty weak.