

Schrödinger, 3

The 3D infinite square well: quantum dots, wells, and wires

In the preceding discussion of the Schrödinger Equation the particle of interest was assumed to be “moving in the x -direction.” Of course, it is not possible for a particle to be moving in one spatial direction only. If that were true, according to the HUP it could be anywhere in the y - and z -directions and therefore be undetectable with finite volume detectors. Now, we consider the more realistic case of motion in all three spatial directions. For this purpose, we start with the **3D infinite square well**. This model provides a useful conceptual framework for understanding a burgeoning “nano-industry,” namely the production and use of “quantum dots.” The 3D infinite square well is a “rigid rectangular solid box.” The potential energy of a particle trapped inside is given by $U(x,y,z) = 0$, if $0 < x < L_1, 0 < y < L_2, 0 < z < L_3$, and ∞ , otherwise. The particle’s momentum now has three components and its kinetic energy is $K = (p_x^2 + p_y^2 + p_z^2)/2m$. After replacing each momentum component with an appropriate differential operator, the wavefunction satisfies the 3D Schrödinger Equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi \quad (1)$$

inside the well and its eigenstates can be separated into $\Psi(x,y,z,t) = X(x)Y(y)Z(z)T(t)$, where, as before, $T(t) \propto \exp(-iEt/\hbar)$, and X, Y , and Z are sine functions that vanish on the “walls” of the well:

$$\Psi_{n_x, n_y, n_z}(x, y, z, t) = A \sin(n_x \pi x / L_1) \sin(n_y \pi y / L_2) \sin(n_z \pi z / L_3) \exp(-iE_{n_x, n_y, n_z} t / \hbar).$$

In this expression, all the n s are positive integers (i.e., 1, 2, 3, ...) and the energy eigenvalues are

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_1^2} + \frac{n_y^2}{L_2^2} + \frac{n_z^2}{L_3^2} \right). \quad (2)$$

The normalization constant A is determined by requiring $\iiint |\Psi|^2 dx dy dz = 1$, where the integrals are over all possible values of x, y , and z : $A = \sqrt{L_1 L_2 L_3} / 8$.

Example: Suppose the trapped particle is an electron and the dot is cubical with $L = 1$ nm. What is the electron’s ground state energy?

Solution: The ground state has the lowest energy, corresponding to all of the n s being equal to 1. Thus, $E_{111} = 3(\hbar c)^2 \pi^2 / 2mc^2 L^2$, about 1 eV. By choosing dot sizes correctly, one can create

dots that absorb or emit photons of well-defined energies. The image to the right (best viewed in color) shows a dozen vials contained CdSe quantum dots of different sizes in solution. After absorbing UV radiation these dots emit in the colors



shown. By coating the CdSe dots with proteins that attach to specific cell membrane molecules it is possible to trace out cell structures by illuminating the cells in white light and looking at the emission at the appropriate wavelengths. This technique has been shown to be effective in

mapping tumors in test animals (Nature Biotechnology, **22**, 93-97 (2004)) and holds great promise for clinical application for humans. Also see, “Dazzling Dots,” Science News, pp 22-25, July 11, 2015.

Note that the states of a particle in a 3D well are associated with *three* quantum numbers—one for each way the particle can move in space. A short table of lowest energy eigenvalues for a cubical well is

n_x	n_y	n_z	E	n_x	n_y	n_z	E
1	1	1	3	2	2	2	12
1	1	2	6	1	2	3	14
1	2	1	6	1	3	2	14
2	1	1	6	2	1	3	14
1	2	2	9	2	3	1	14
2	1	2	9	3	1	2	14
2	2	1	9	3	2	1	14
1	1	3	11	2	2	3	17
1	3	1	11	2	3	2	17
3	1	1	11	3	2	2	17

In the table E is measured in units of $\hbar^2\pi^2/2mL^2$. In the table, E has a single entry for two states, (111) and (222), otherwise all other entries have 3 or 6 different states with the same E . This situation is called *degeneracy*. An energy level that has N possible states is said to be *N -fold degenerate*. Thus, the energy levels in the table with two 1s and a 2 are 3-fold degenerate; the levels with all possible combinations of 1, 2, and 3 are 6-fold degenerate. Levels that have only one possible state are *nondegenerate*.

Degeneracy arises from two causes: symmetry and an arithmetic accident. In all of the cases in the table, the degeneracy arises from the fact that for a cube you can switch the labels of the $x, y,$ and z -axes without changing anything. But that’s not true if the sides of the rectangular solid are unequal. If, instead of $L_1 = L_2 = L_3 = L$ as in the table, we have

$L_1 = L, L_2 = L/\sqrt{2}, L_3 = L/\sqrt{3}$ (so that the nice cubical symmetry is removed) then only the states (112) and (221) in the table are degenerate (with $E = 15$), and that is merely a numerical accident having nothing to do with symmetry.

A 3D well becomes effectively a 2D well if one of the sides is much smaller than the other two. For example, suppose $L_1 = L_2 = L, L_3 = L/10$. The energy levels would then be, $E = E_0(n_x^2 + n_y^2 + 100n_z^2)$, where $E_0 = \hbar^2\pi^2/2mL^2$. Thus there would be lots (a few hundred) of combinations of different n_x and n_y values with $n_z = 1$ that would have lower energies than for (112), the lowest energy state with the first level of excitation in the z -direction. At low energies, the z motion is effectively frozen, and the well acts as if it were 2D. That’s a so-called “quantum well.” A similar thing happens if two of the sides are much smaller than the third. Then at low energy two of the motions are frozen and only the third has the possibility of excitation. In that case, that’s a 1D “quantum wire” (a physical realization of an infinite square well).

The sanitized hydrogen atom

Though they provide useful qualitative understanding, the square well potential energies we have studied are simple approximations to the real interactions between particles. We now apply what we have learned about the quantum behavior of particles with square well potential energies to understanding the atomic structure of matter. Atoms are bound systems of negatively charged electrons and positively charged nuclei. The most elementary kind of atom is hydrogen consisting of one electron (with electric charge $-e$, where $e = 1.6 \times 10^{-19}$ C) and one proton (with electric charge $+e$). The simplest version of the hydrogen atom assumes the electron interacts with a point-like proton sitting motionless at the origin of some coordinate system via the attractive Coulomb (electrostatic) potential energy

$$U(r) = -\frac{k_E e^2}{r}, \quad (3)$$

where r is the instantaneous distance between the electron and proton and $k_E = 1/4\pi\epsilon_0$ is the electrostatic force-constant.

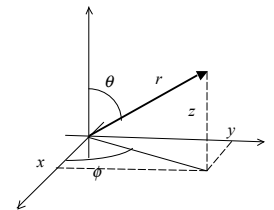
*(Historical comment: When a hydrogen atom was first understood as an electron bound to a proton, it was assumed to be a kind of planetary system with the electron in a classical orbit about the proton. In its orbit, the electron is continuously pulled toward the proton; it continuously accelerates. This model is incompatible with Maxwell's Equations. Maxwell requires that accelerating charges radiate electromagnetic waves. As they radiate, the electrons lose energy and fall inward toward the proton. A typical infall time is about a microsecond or so. Thus, no H atom should last long enough to be around very long. Moreover, the radiation emitted by the infalling electron should continuously shift to shorter and shorter wavelengths. But a tube of excited H atoms steadily glows a nice pink color; when this light is passed through a diffraction grating it breaks up into red, green, blue, and violet colors of constant wavelength. There are also constant wavelength UV and IR "colors" as well. Obviously, the classical picture of hydrogen is badly incorrect. Perhaps you have studied a cartoon model of the hydrogen atom known as the "Bohr atom." In it, the electron orbits the proton in certain allowed classical circular orbits that are kludged in just the right way to "explain" hydrogen's emission spectra. Unfortunately, this cartoon model gets hydrogen's *observed* angular momenta completely wrong. The Bohr atom was invented before Schrödinger quantum mechanics and, though it predicts quantized energy values, is actually incompatible with it. For example, a classical circular orbit has a precisely defined radius. But the Heisenberg Uncertainty Principle dictates that zero uncertainty in radius requires total uncertainty in radial momentum and, therefore, orbital kinetic energy. In quantum mechanics it is not possible to know both simultaneously. If you've previously studied the Bohr atom, please try to forget it.)*

The simple picture described by (3) ignores the facts that the electron's motion has relativistic corrections, the proton has a finite size (indeed, consists of smaller particles called *quarks* and *gluons*) and actually moves as the electron moves (in fact, it can't be at rest at an exact position because that violates the uncertainty principle), and that the proton and electron interact magnetically, through the weak force, and through gravity (which, compared with the Coulomb interaction, are small, really small, and really, really small, respectively). All of these ignored aspects produce only minor modifications to the great triumphs of the Schrödinger description of hydrogen, namely, its stability and evaluation of the electron's energy and angular momentum eigenvalues.

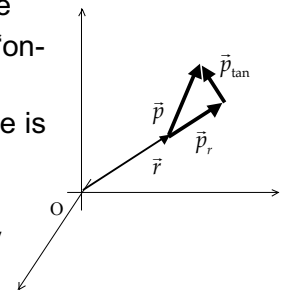
As (a) total mechanical energy equals kinetic plus potential energies and (b) the electron in the hydrogen atom moves in three dimensions, it seems plausible that the Schrödinger Equation for the hydrogen problem is just equation (1) above with the potential energy in equation (3) added to the right-hand side. But there's a mathematical complication. In Cartesian coordinates, $r = \sqrt{x^2 + y^2 + z^2}$. Thus, there are infinitely many different $x, y,$ and z values that can be combined to give the same r . The Coulomb potential energy depends only on the length of the electron's position vector, not on its direction; it is *spherically symmetric*. This potential energy mixes $x, y,$ and z in a complicated way. As a result, the Schrödinger Equation for the Coulomb potential energy cannot be solved by separation of variables if Cartesian coordinates are used. **In general, whenever the potential energy is spherically symmetric one has to use spherical coordinates:** r, θ, ϕ .

Spherical and Cartesian coordinates are related as shown in the figure to the right. The coordinates of the tip of the position vector are either (x, y, z) or (r, θ, ϕ) , where the two are related by

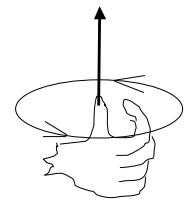
$$\begin{aligned}x &= r \sin \theta \cos \phi \\y &= r \sin \theta \sin \phi \\z &= r \cos \theta\end{aligned}$$



A classical particle moving in 3D has a momentum \vec{p} that, in spherical coordinate language, is partly radial (along a line passing through the origin of coordinates, “on-center”) and partly tangential (“off-center”): $\vec{p} = \vec{p}_r + \vec{p}_{\text{tan}}$, where \vec{p}_r and \vec{p}_{tan} are perpendicular to each other (see right). The classical kinetic energy of the particle is given by $K = \frac{p^2}{2m} = \frac{\vec{p} \cdot \vec{p}}{2m} = \frac{p_r^2}{2m} + \frac{p_{\text{tan}}^2}{2m} = K_r + K_{\text{tan}}$, that is, a part due to radial motion and a part due to off-center motion (i.e., around the origin). The latter is naturally associated with *angular momentum*.



Angular momentum is defined as $\vec{L} = \vec{r} \times \vec{p}$. It is a measure of motion about the point that \vec{r} emerges from. Because the cross product of two vectors that lie along the same line is zero, $\vec{r} \times \vec{p}_r = \vec{0}$ and, hence, $\vec{L} = \vec{r} \times \vec{p}_{\text{tan}}$. The magnitude of \vec{L} is the product of the magnitudes of \vec{r} and \vec{p}_{tan} (because the angle between them is 90°): $L = r p_{\text{tan}}$. For a circular orbit \vec{L} , calculated about the center of the circle, is perpendicular to the plane of the orbit and points along your right thumb if you curl your right-hand fingers in the direction of the motion [see right].



In general, $\frac{d\vec{L}}{dt} = \frac{d}{dt}(\vec{r} \times \vec{p}) = \frac{d\vec{r}}{dt} \times \vec{p} + \vec{r} \times \frac{d\vec{p}}{dt}$. The first term on the rightmost side is zero because $\frac{d\vec{r}}{dt} = \frac{\vec{p}}{m}$. The second term is the *torque*: $\vec{\tau} = \vec{r} \times \vec{F}_{\text{net}}$. In the hydrogen problem, the Coulomb force of the proton on the electron points directly down the radial direction, so $\frac{d\vec{L}}{dt} = \vec{0}$. As the electron orbits the proton its orbital angular momentum is a constant (both in direction and

magnitude). We can replace p_{\tan} by L/r in the particle kinetic energy to obtain: $K = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2}$.

When that's done, the Schrödinger Equation for the sanitized hydrogen problem is formally

$$E_{op} \Psi = K_{op} \Psi + U\Psi = K_{r,op} \Psi + K_{orb,op} \Psi + U\Psi = K_{r,op} \Psi + L_{op}^2 \Psi / 2mr^2 - k_E e^2 \Psi / r. \quad (4)$$

After replacing (that is, after doing a lot of uninformative algebra) the derivatives with respect to (x, y, z) in the Schrödinger Equation by derivatives with respect to (r, θ, ϕ) (e.g., using

$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x} \frac{\partial}{\partial \phi}$, and so on) we obtain

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \Psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \Psi}{\partial \phi^2} \right] - \frac{k_E e^2}{r} \Psi. \quad (5)$$

Identifying the operators in (4) with the derivatives in (5) yields:

$$E_{op} = i\hbar \frac{\partial}{\partial t}$$

$$K_{r,op} = -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right)$$

$$L_{op}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

Separating the variables in (5) via the product $\Psi(r, \theta, \phi, t) = R(r)\Theta(\theta)\Phi(\phi)T(t)$ reveals the secrets of the (sanitized) hydrogen atom.