Elementary Quantum Mechanics[1]

1. (One-particle) Schrödinger equation.

Physics form:

$$(1) \qquad i\hbar\Psi_t = -\frac{\hbar^2}{2m}\boldsymbol{\Delta}\Psi + U(\Psi),$$

where $\hbar = 1.05 \cdot 10^{-34} J \cdot s$ is `Planck's constant` [connecting energy and *angular* frequency] and m is the mass of the particle.

Math form:

$$(2) \qquad iu_t + \boldsymbol{\Delta}u + U(u) = 0,$$

which one can get from (1) after a linear change of variables. [You can take it further and consider imaginary time $\tau = it$, and then (2) becomes a heat equation.]

Abstract form:

$$(3) \qquad i\hbar\psi_t = H(\psi),$$

"Classical"[2] quantum mechanics: H is a linear self-adjoint operator [known as the `Hamiltonian` on a (complex) Hilbert space $\mathbb{H}$; eigenvalues of H are the energy level of the particle; eigenfunctions of H are the observable states of the particle; ψ is known as the `wave function` and $|\psi|^2$ is the probability density function (pdf) describing the state of the particle. Note that (1) is a particular case of (3), with

$$H = -\frac{\hbar^2}{2m}\boldsymbol{\Delta} + U;$$

the $-\frac{\hbar^2}{2m}\boldsymbol{\Delta}$ part represents the kinetic energy and U represents the potential energy. If we use separation of variables and look for the solution of (3) in the form

$$\psi(t) = e^{-iEt/\hbar}\varphi, \ \varphi \in \mathbb{H},$$

then

$$(4) \qquad H(\varphi) = E\varphi,$$

that is, φ has to be an eigenfunction of the operator H, with the corresponding eigenvalue E. If we are "lucky" so that there are countable many solutions to (4) and the corresponding eigenfunctions $\varphi_k, \ k \geq 1$ form an orthonormal basis in $\mathbb{H}$, then the general solution of (3) is

$$\psi(t) = \sum_k e^{-iE_k t/\hbar}a_k\varphi_k, \ a_k \in \mathbb{C},$$

and the "physical" solutions are those satisfying

$$\|\psi(t)\|_{\mathbb{H}}^2 = 1,$$

that is,

$$\sum_k |a_k|^2 = 1.$$

The main two examples: (quantum) harmonic oscillator and the hydrogen atom; in both cases we get "lucky".

Harmonic oscillator: $\mathbb{H} = L_2(\mathbb{R})$,

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{m^2\omega^2 x^2}{2},$$

where ω is the frequency of the corresponding classical oscillator

$$(5) \qquad \ddot{x}(t) + \omega^2 x(t) = 0.$$

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[2]As opposed to relativistic, non-linear, etc.

In this case, (4) becomes

$$-\frac{\hbar^2}{2m}\varphi''(x) + \frac{m^2\omega^2 x^2}{2}\varphi(x) = E\varphi(x),$$

which, after changing the variables $z = x/a$,

$$a = \sqrt{\frac{\hbar}{m\omega}},$$

and $v(z) = \varphi(x)$, becomes

$$v''(z) - z^2 v(z) + \lambda v(z) = 0, \ \ \lambda = \frac{2E}{\hbar\omega},$$

which, in turn, after a change of variables $u(z) = v(z)e^{z^2/2}$ becomes the `Hermite differential equation`:

$$u''(z) - 2zu'(z) + (\lambda - 1)u(z) = 0,$$

which we solve using the power series method to conclude that the only physically relevant solutions are polynomials corresponding to

$$\lambda_k = 2k + 1, \ \ k = 0, 1, 2, \ldots.$$

In particular, the lowest energy, also known as the `ground state`, corresponding to $k = 0$ is

$$E_0 = \frac{\hbar\omega}{2}$$

and the corresponding `wave function`

$$\psi_0(t, x) = \frac{1}{(\pi a^2)^{1/4}} e^{-\mathrm{i}E_0 t/\hbar} e^{-x^2/(2a^2)}$$

means that the pdf describing the position of the particle in the ground state is Gaussian with mean zero and variance $a^2/2 = \dfrac{\hbar}{4m\omega}$:

$$|\psi_0(t, x)|^2 = \frac{1}{a\sqrt{\pi}} e^{-x^2/a^2}.$$

The result illustrates

- The `Bohr correspondence principle`: as $\hbar \to 0$, we have $a \to 0$ meaning that the particle is at rest at $x = 0$, which, with zero energy E_0, is consistent with (5) describing the classical harmonic oscillator. Another way to have $a \to 0$ is to have $m \to \infty$ (or, more generally, to have $m\omega$ much bigger than $\hbar = 1.05 \cdot 10^{-34} J \cdot s$, which is what we have in classical mechanics anyway.
- The `Heisenberg uncertainty principle`, in both position-momentum and time-energy forms: if we think of a as the measure of the uncertainty $\triangle x$ in the location of the particle and $\triangle t = 1/\omega$ as the basic time scale, then $\triangle p = m\triangle x/\triangle t$ is the uncertainty in the measurement of the momentum, and

$$\triangle x \triangle p = m\omega a^2 = \frac{\hbar}{2} = \triangle t E_0.$$

Hydrogen atom: $\mathbb{H} = L_2(\mathbb{R}^3)$,

$$(6) \qquad\qquad H = -\frac{\hbar^2}{2m}\boldsymbol{\Delta} - \frac{\mathrm{e}^2}{4\pi\varepsilon_0 r},$$

where e is the elementary charge, ε_0 is the electric permittivity of vacuum, and $r = \sqrt{x^2 + y^2 + z^2}$.

Here, an electron moving around a proton, some preliminary estimates must be carried out to ensure that subsequent computations make sense, at least to some extend:

(1) The proton is about 1800 times heavier than the electron and therefore can be assumed not moving;
(2) If a is the distance between the proton and the electron, m is the mass of the electron, and p is the momentum, then

$$E(a) = \frac{p^2}{2m} - \frac{\mathrm{e}^2}{4\pi\varepsilon_0 a}$$

is the energy of the electron. By the uncertainty principle, $pa \sim \hbar$, so that

$$E(a) \sim \frac{\hbar^2}{2ma^2} - \frac{e^2}{4\pi\varepsilon_0 a}$$

and the minimal value of the right-hand side is achieve when

(7)
$$a = a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{me^2} \approx 0.5 \cdot 10^{-10} \text{ meters,}$$

the `Bohr radius` of the hydrogen atom: the (approximate) closest distance between the proton and electron. The corresponding value of the energy is

(8)
$$E_0 = -\frac{\hbar^2}{2ma_0^2}$$

Further analysis will show a_0 and E_0 are the "natural" distance and energy scales of the problem. The speed v of the electron satisfies

$$v = \frac{p}{m} \sim \frac{\hbar}{a} \sim \frac{e^2}{4\pi\varepsilon_0 \hbar} \sim \frac{c}{137},$$

where c is the speed of light in vacuum. In other words, no relativistic corrections [which are of order $(v/c)^2 \sim 10^{-4}$] are necessary.

Now the objective is to compute the eigenvalues and eigenfunctions of the operator (6), that is, to compute non-zero solutions of

$$-\frac{\hbar^2}{2m}\mathbf{\Delta}\varphi - \frac{e^2}{4\pi\varepsilon_0 r}\varphi = -\lambda\varphi, \ \lambda > 0,$$

that are physically relevant, that is, satisfy

$$\int_{\mathbb{R}^3} |\varphi|^2 dV < \infty.$$

Note that we expect the energy levels to be negative: it is the negative energy that keeps electron from flying away and thus keeps the atom together.

STEP 1. Write $\mathbf{\Delta}$ in spherical coordinates (r, θ, ϕ).

STEP 2. Separation of variables: look for solutions in the form

$$\varphi = A(r)B(\theta)G(\phi),$$

and get the equation

(9)
$$\frac{r^2 A'' + 2r A'}{A} + \frac{B''}{B \sin^2 \phi} + \frac{G'' + G' \cot \phi}{G} + \frac{2r}{a_0} - \frac{\lambda}{E_0}\frac{r^2}{a_0^2} = 0;$$

as was promised a few line above, a_0 is the Bohr radius (7) and E_0 is the corresponding energy (8).

STEP 3. Use physical reasoning [similar to the analysis of the drum/timpani]: because of the spherical symmetry of the problem, we expect $B(\theta) = B(\theta + 2\pi)$ and $G(\phi) = G(\phi + 2\pi)$. The 2π-periodicity of B immediately implies

(10)
$$B(\theta) = e^{in\theta}$$

and introduces the first important parameter into the problem: the integer number n.

STEP 4. Go back to (9), with (10) in mind, to conclude that

(11)
$$G'' + G' \cot \phi = \left(\frac{n^2}{\sin^2 \phi} - \beta\right)G$$

for some number β. The define $v(z)$ by $G(\phi) = v(\cos\phi)$ to get

$$(1 - z^2)v'' - 2zv' = \left(\frac{n^2}{1 - z^2}\right)v$$

and then continue to $w(z) = (1 - z^2)^{-n/2}v(z)$ for the end result:

$$(1 - z^2)w'' - 2(n + 1)xw' + (\beta - n(n + 1))w = 0.$$

The physically relevant solutions of this equation are polynomials [`generalized Legendre polynomials`]; such polynomial solutions exist exactly when

$$\beta = \ell(\ell+1)$$

for some $\ell \geq |n|$. All other solutions have "bad" singularities when $z = \pm 1$ [that is, when $\phi = 0$ or $\phi = \pi$]. The integer ℓ becomes the second important parameter of the problem. Writing $P_{\ell,n}$ to denote those polynomial solutions, we re-trace the steps to conclude that

$$G(\phi) = \sin^n(\phi)P_{\ell,n}(\cos\phi).$$

STEP 5. Now determine the function A. To this end, define

$$\kappa = \sqrt{\frac{\lambda}{E_0}}.$$

Then define the function $u = u(z)$ by

$$A(r) = \left(\frac{r}{a_0}\right)^\ell e^{-\kappa r/a_0}\, u(2\kappa r/a_0).$$

Keeping in mind that (9) and (11) imply

$$\frac{r^2 A'' + 2rA'}{A} + \frac{2r}{a_0} - \frac{\lambda}{E_0}\frac{r^2}{a_0^2} = \beta = \ell(\ell+1),$$

derive the following equation for u:

$$zu'' + (2\ell+2-z)u' + (\kappa^{-1} - (\ell+1))u = 0,$$

known as the `associated Laguerre differential equation`. The polynomial (physically relevant) solutions of this equation exist if and only if

$$\frac{1}{\kappa} = N = 1, 2, 3\ldots,$$

and are known as the `generalized Laguerre polynomials` $L_{N+\ell}^{(2\ell+1)}$. The third parameter of the problem N represents the energy levels of the system:

$$E_N = \frac{E_0}{N^2};$$

keeping in mind that $E_0 < 0$, we see that the energy E_N is increasing with N while staying negative. There is also a somewhat confusing convention $E_1 = E_0$.

STEP 6. Put everything together and write the wave functions of the hydrogen atom at the energy level N:

$$(12) \qquad \psi(t, r, \theta, \phi) = C_{N,\ell,n}e^{-\mathrm{i}tE_N/\hbar}e^{\mathrm{i}n\theta}\sin^n(\phi)P_{\ell,n}(\cos\phi)(r/a_0)^\ell e^{-r/(a_0 N)}L_{N+\ell}^{(2\ell+1)}(2r/(a_0 N)).$$

The number $C_{N,\ell,n}$ ensures that

$$\int_0^\infty \int_0^{2\pi}\int_0^\pi |\psi(t,r,\theta,\phi)|^2 \sin\phi d\phi\, d\theta\, r^2 dr = 1.$$

Of course, (12) looks totally incomprehensible when thrown at you in a physics or chemistry book. On the other hand, in many physics and chemistry books, equation (12) is the *starting point*. Also, the notations for the angles can be different.

A few comments:

- The state of the hydrogen atom is determined by three numbers: `principal quantum number` $N = 1, 2, \ldots$, the `azimuthal (orbital) number` $\ell = 0, 1, \ldots, N-1$, and the `magnetic number` $n = 0, \pm 1, \ldots, \pm\ell$. The magnetic number n determines the orientation of electron's trajectory in space. The orbital number ℓ determines the shape of electron's orbit and is often denotes by a letter [$s = 0, p = 1, d = 2, f = 3$], which certainly adds to the confusion. Similar procedures are used to study more complicated atoms, leading to similar results and notations such as $5s^2p^1$, meaning there are $2 + 1 = 3$ electrons at the energy level $N = 5$, two of them have $\ell = 0$ and one has $\ell = 1$.

- The wave function in the ground state is

$$\psi_0(t, r, \theta, \phi) = \frac{1}{\sqrt{\pi}} e^{-\mathrm{i}t E_0/\hbar} a_0^{-3/2} e^{-r/a_0}.$$

  You are welcome to confirm that

$$\int_0^\infty \int_0^{2\pi} \int_0^\pi |\psi_0(t, r, \theta, \phi)|^2 \sin\phi d\phi \; d\theta \; r^2 dr = 1,$$

  and also

$$\int_0^\infty \int_0^{2\pi} \int_0^\pi r|\psi_0(t, r, \theta, \phi)|^2 \sin\phi d\phi \; d\theta \; r^2 dr = 3a_0/2,$$

  that is, in the ground state, the average distance between the proton and the electron is $3a_0/2$, but, with very small probabilities, the electron can come arbitrarily close to or get arbitrarily far from the proton.

  In other words, there is no such thing as "the" size of the hydrogen [or any other] atom, although, for hydrogen, 10^{-10} meters is a good "ballpark value".
- The number

$$\alpha = \frac{\mathrm{e}^2}{4\pi\varepsilon_0 c\hbar} \approx \frac{1}{137}$$

  is known as the `fine structure constant`; it has no units [check it!].
- A bit of history. Max Plank [age 43] came up with the relation $E = \hbar\omega$ while studying black body radiation in 1901; Niels Bohr [age 28] came up with a model of the hydrogen atop while studying spectral lines in 1913, well before Erwin Schrödinger [age 37] *postulated* his equation in 1924. It was Max Born [age 45] who interpreted the square of the absolute value of the solution of the Schrödinger equation as the probability density function in 1927; Hiesenberg [age 26] introduced the uncertainty principle also in 1927. From 1927 to about 1933, various famous and very famous people (Dirac, Weyl, von Neumann, etc.) developed the mathematical foundations of quantum mechanics.