The Schrödinger equation

Combining the classical Hamilton function for a free particle (with mass $m$), $H = p^2/(2m)$, with the de Broglie relation $p = \hbar k$ and the Planck relation $E = \varepsilon = \hbar \omega$ leads to

$$H = E = T = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \hbar \omega, \quad k^2 = k_x^2 + k_y^2 + k_z^2$$

(20)

With eq. (19), this relation is readily transferred into an operator identity for a differential equation (wave equation?):

$$\frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = \hbar \omega$$

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

$$\hat{H} = -\frac{\hbar^2}{2m} \left[ \left( \frac{\partial}{\partial x} \right)^2 + \left( \frac{\partial}{\partial y} \right)^2 + \left( \frac{\partial}{\partial z} \right)^2 \right] = \frac{(-i \hbar \nabla)^2}{2m} = i \hbar \frac{\partial}{\partial t}$$

(21)
This operator identity can be applied to a suitable mathematical object, e.g. a complex-valued scalar function $\psi(r, t)$ of position $r$ and time $t$, to give the **time-dependent Schrödinger equation**:

$$\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t} \quad \Leftrightarrow \quad \left( \hat{H} - i\hbar \frac{\partial}{\partial t} \right) \psi = 0 \quad (22)$$

The function $\psi(r, t)$ is called ‘state function’, or ‘wave function’.

As in classical mechanics, where the Hamilton function includes kinetic and potential energies, $H = T + V$, the Hamilton operator is extended to include parts for both kinetic and potential energy, $\hat{H} = \hat{T} + \hat{V}$. For application to scalar functions $\psi(r, t)$ we thus have:

$$p \rightarrow \hat{p} = -i\hbar \nabla \quad (23)$$

$$T = \frac{p^2}{2m} \rightarrow \hat{T} = \frac{(-i\hbar \nabla)^2}{2m} = -\frac{\hbar^2}{2m} \nabla^2 = -\frac{\hbar^2}{2m} \Delta \quad (24)$$

$$V = V(r, t) \rightarrow \hat{V} = V(r, t) \times \quad (25)$$

Gradient operator $\nabla$ and Laplace operator $\Delta$ in cartesian coordinates:

$$\nabla = \left( \begin{array}{c} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{array} \right), \quad \Delta = \nabla^2 = \nabla \cdot \nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

From eq. (22) and its complex conjugate (assuming $V$ to be real),

$$\left( \hat{T} + \hat{V} - i\hbar \frac{\partial}{\partial t} \right) \psi = 0 \quad \left( \hat{T} + \hat{V} + i\hbar \frac{\partial}{\partial t} \right) \psi^* = 0 \quad (26)$$

follows

$$\psi^* \left( \hat{T} + \hat{V} - i\hbar \frac{\partial}{\partial t} \right) \psi = 0 \quad \psi \left( \hat{T} + \hat{V} + i\hbar \frac{\partial}{\partial t} \right) \psi^* = 0 \quad (27)$$

The difference of these two expressions is (the terms with $V$ cancel)

$$\psi^* \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \psi - i\hbar \psi^* \frac{\partial \psi}{\partial t} - \psi \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \psi^* - i\hbar \psi \frac{\partial \psi^*}{\partial t} = 0 \quad (28)$$
When the Hamilton operator (Hamiltonian) does not depend on time, i.e. \( \mathcal{H} = \mathcal{H}(t) \), eq. (22) has solutions of the form
\[
(r; t) = (r) \exp(iE t) \quad \text{(33)}
\]
which represent stationary states, provided the spatial part \((r)\) satisfies the \textbf{time-independent Schrödinger equation}:
\[
\mathcal{H}(r) = E(r) \quad \Leftrightarrow \quad (\mathcal{H} - E) \phi = 0 \quad \text{(34)}
\]
The separation constant \( E \) is the energy of the stationary state.

The probability density for stationary states does not depend on time:
\[
\rho = \psi^*(r, t) \psi(r, t) = \phi^*(r) \phi(r) \quad \text{(35)}
\]

Solving eq. (34) is equivalent to a variation principle, applied to the integral (functional of \( \phi \))
\[
H[\phi] = \int \phi^* \mathcal{H} \phi \, dr \quad \text{(36)}
\]

* This is an application of a general theorem from the theory of partial differential equations (PDE): If the partial differential operator is a sum of terms, where each term acts on a different coordinate (or set of coordinates), then there are solutions in product form, and the PDE can be split into lower-dimensional parts.
under the condition that \( \phi \) remains normalized (use Lagrange’s method of undetermined multipliers).

Consider the functional

\[
L[\phi] = H[\phi] - \lambda \left( \int \phi^* \phi \, dr - 1 \right) = \int \phi^* \hat{H} \phi \, dr - \lambda \left( \int \phi^* \phi \, dr - 1 \right) (37)
\]

(\( \lambda \) is a yet undetermined Lagrange parameter)

Condition for stationarity: \( \delta L = 0 \), with

\[
\delta L = \int (\delta \phi)^* \hat{H} \phi \, dr + \int \phi^* \hat{H} \delta \phi \, dr - \lambda \left( \int (\delta \phi)^* \phi \, dr + \int \phi^* \delta \phi \, dr \right)
= \int (\delta \phi)^* (\hat{H} - \lambda) \phi \, dr + \int \left[ (\hat{H} - \lambda) \phi^* \right] \delta \phi \, dr (38)
\]

The first integral is the complex conjugate of the second integral (if \( \hat{H}^* = \hat{H} \)).

Since \( \delta L = 0 \) shall hold for arbitrary variations \( \delta \phi \), it follows:

\[
(\hat{H} - \lambda) \phi = 0 \quad \Rightarrow \quad \lambda = E (39)
\]

Together with boundary conditions for \( \phi \), the time-independent Schrödinger equation thus constitutes an eigenvalue problem, which has to be solved for pairs \( (E, \phi) \) of eigenvalues \( E \) and eigenfunctions \( \phi \).

Again a situation comparable to e.g. classical mechanics is found: There exists a variation principle behind the working equations.

In classical mechanics, the working equations are the Lagrange (or Hamilton) equations (one equation, or a pair of equations, for every degree of freedom), whereas in quantum mechanics, the working equation (for stationary states of the system under study) is the time-independent Schrödinger equation.
The free particle

This is the quantum mechanical analogue of the situation considered with Newton's first law of motion: The potential energy $V$ is constant (may be set to zero), and the particle (with mass $m$) has only kinetic energy, so that

$$\hat{V} = 0, \quad \hat{H} = \hat{T} + \hat{V} = \hat{T} = -\frac{\hbar^2}{2m} \nabla^2$$

(40)

It follows immediately from our ‘derivation’ of the time-dependent Schrödinger equation (22), that plane waves are acceptable solutions

$$\psi(r, t) = C \exp \left[ i(k \cdot r - \omega t) \right], \quad E = h \omega = \frac{(\hbar k)^2}{2m} \geq 0$$

(41)

which are also eigenfunctions to the linear momentum (vector) operator $\hat{p}$ with eigenvalue (vector) $\hbar k$:

$$\hat{p} \psi = -i \hbar \nabla \psi = \hbar \mathbf{k} \psi$$

(42)

The probability density is constant, $\rho = \psi^* \psi = C^* C = |C|^2$, everywhere and at every time. This is O.K. for a plane wave.

The most general solution is obtained by continuous superposition (note the relation to Fourier transformation)

$$\psi(r, t) = \int C(k) e^{i(k \cdot r - \omega t)} \, dk, \quad \omega(k) = \frac{\hbar k^2}{2m}$$

(43)

since integration in $k$-space can be interchanged with differentiation with respect to ordinary space coordinates or time.

A suitable choice for $C(k)$ leads to a valid representation of a ‘free particle’ (a ‘well located’ object), which is also known as a ‘wave packet’.
The particle in a box

This is the quantum mechanical analogue of a classical particle (with mass $m$) confined to a 1-, 2- or 3-dimensional region of space: The potential energy $V$ is constant (may be set to zero) within this region, but infinitely high outside. For a 3-dimensional rectangular box with lengths $L_x$, $L_y$, and $L_z$:

$$\tilde{V} = \begin{cases} 0 & 0 \leq x \leq L_x, \ 0 \leq y \leq L_y, \ 0 \leq z \leq L_z \\ \infty & \text{elsewhere} \end{cases}$$  \hspace{1cm} (44)

Inside the box, the time-dependent Schrödinger equation has the form

$$\left(\hat{H} - i \hbar \frac{\partial}{\partial t}\right) \psi = \left(-\frac{\hbar^2}{2m} \nabla^2 - i \hbar \frac{\partial}{\partial t}\right) \psi = 0$$  \hspace{1cm} (45)

which has stationary solutions of the form

$$\psi(r,t) = \phi(r) e^{-iEt/\hbar}, \quad \phi(r) = X(x) Y(y) Z(z), \quad E = E_x + E_y + E_z$$  \hspace{1cm} (46)

and $\phi(r)$ has to vanish at the boundaries of the box.

The problem can be reduced to one-dimensional problems of the following form:

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - E_x\right) X(x) = 0$$  \hspace{1cm} \hspace{1cm} \hspace{1cm} (47)

with boundary conditions $X(0) = 0$ and $X(L_x) = 0$. The general solution of the ordinary differential equation (47) is

$$X(x) = c_1 e^{ik_xx} + c_2 e^{-ik_xx} = A \cos(k_xx) + B \sin(k_xx)$$  \hspace{1cm} (48)

with $A = c_1 + c_2$, $B = i(c_1 - c_2)$. The boundary conditions lead to $A = 0$ (from $X(0) = 0$) and $k_xx = n\pi$ with $n \in \mathbb{Z}$ (from $X(L_x) = 0$), so that the acceptable solutions are

$$X_n(x) = B \sin(k_xx), \quad k_xx = \frac{n\pi}{L_x}, \quad E_x = \frac{(\hbar k_xx)^2}{2m} = \frac{\hbar^2}{8m} \left(\frac{n}{L_x}\right)^2$$  \hspace{1cm} (49)

with $n > 0$.$^\dagger$

$^\dagger n = 0$ gives $X_0(x) \equiv 0$, while $n < 0$ gives the same energy and probability density, since $X_{-n} = -X_n$. 

---

The coefficient $B$ is determined by normalization of the probability density:

$$1 = \int_{0}^{L_x} X^*(x) X(x) \, dx = B^2 \int_{0}^{L_x} \sin^2 (k_x x) \, dx \quad \rightarrow \quad B = \sqrt{\frac{2}{L_x}}$$

(50)

The **boundary conditions** lead to **quantization**. This is a general result, as well as the fact, that the number of zeros (nodes) of the solutions $X_n(x)$ increases with the energy (compare with a string).

The energies (eigenvalues) grow quadratically as a function of $n$, $E_x(n) \propto n^2$, and the lowest energy is higher than the potential energy minimum, $E_x(n = 1) > 0$. The 'particle in a 1-dimensional box' has at least this energy, even at temperature $T = 0K$ (**zero-point energy**).
Energy levels $E_{nkl}$ and degrees of degeneracy $g$ for a particle in a 3-dimensional cubic box

$$E_{nkl} = \frac{\hbar^2}{8m} \left( n^2 \left( \frac{x}{L_x} \right)^2 + k^2 \left( \frac{y}{L_y} \right)^2 + l^2 \left( \frac{z}{L_z} \right)^2 \right)$$

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Whenever there is a rational relation between any two (or all three) squared lengths $L_x^2$, $L_y^2$, and $L_z^2$, degeneracies occur, i.e. several state functions belong to the same energy eigenvalue. E.g. in the case of a cubic box ($L_x = L_y = L_z = L$): $E_{nnn}$ is non-degenerate, $E_{nnl}$ ($n \neq l$) is triply degenerate, and $E_{nkl}$ ($n$, $k$, $l$ all different) is sixfold degenerate.

Extension to the general case of a 3-dimensional rectangular box is straightforward:

$$\phi_{nkl}(r) = \sqrt{\frac{8}{L_x L_y L_z}} \sin \left( \frac{n\pi x}{L_x} \right) \sin \left( \frac{k\pi y}{L_y} \right) \sin \left( \frac{l\pi z}{L_z} \right)$$

$$E_{nkl} = E_x + E_y + E_z = \frac{\hbar^2}{8m} \left( \frac{n^2}{L_x^2} + \frac{k^2}{L_y^2} + \frac{l^2}{L_z^2} \right)$$

The ground state (i.e. the state with lowest possible energy):

$$\phi_{111}(r) = \sqrt{\frac{8}{L_x L_y L_z}} \sin \left( \frac{\pi x}{L_x} \right) \sin \left( \frac{\pi y}{L_y} \right) \sin \left( \frac{\pi z}{L_z} \right)$$

$$E_{111} = \frac{\hbar^2}{8m} \left( \frac{1}{L_x^2} + \frac{1}{L_y^2} + \frac{1}{L_z^2} \right)$$
Special functions

The confluent hypergeometric function (Kummer\textsuperscript{§} function):

\[ 1F_1(a; c; x) = \sum_{k=0}^{\infty} \frac{(a)_k}{(c)_k} \frac{x^k}{k!} = 1 + \frac{a}{c} x + \frac{a(a+1)}{c(c+1)} \frac{x^2}{2!} + \ldots \]

is a solution of the Kummer differential equation

\[ x y'' + (c - x) y' - a y = 0 \]

The Gauß' hypergeometric function:

\[ 2F_1(a, b; c; x) = \sum_{k=0}^{\infty} \frac{(a)_k(b)_k}{(c)_k} \frac{x^k}{k!} \]

\[ = 1 + \frac{ab}{c} x + \frac{a(a+1)b(b+1)}{c(c+1)} \frac{x^2}{2!} + \ldots \]

is a solution of the Gauß differential equation

\[ x (1 - x) y'' + [ c - (a + b + 1) x ] y' - ab y = 0 \]

\textsuperscript{§} E. E. Kummer (1810-1893)
The harmonic oscillator

The 1-dimensional harmonic oscillator is the quantum mechanical analogue of a classical particle (with mass $m$), moving in a parabolic potential or, equivalently, moving under a restoring force given by Hooke’s law (with force constant $K$)

$$V(x) = \frac{1}{2}Kx^2 \quad \Leftrightarrow \quad F_x = -\frac{dV}{dx} = -Kx \quad (55)$$

Classically, the particle can oscillate with arbitrary energy, the oscillating frequency $\nu$ being related to the force constant $K$ through

$$\omega = 2\pi\nu = \sqrt{\frac{K}{m}} \quad \Rightarrow \quad K = m\omega^2 \quad (56)$$

Quantum mechanically, the Schrödinger equation, corresponding to the potential energy $V(x)$ given above, has to be solved.

Stationary states $\phi(x)$, with $-\infty \leq x \leq \infty$, are solutions of

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}Kx^2 - E\right)\phi(x) = 0 \quad (57)$$

$$\left(\frac{d^2}{dx^2} + k^2 - \lambda^2 x^2\right)\phi(x) = 0 \quad (58)$$

with

$$k^2 = \frac{2m}{\hbar^2}E, \quad \lambda = \frac{m\omega}{\hbar}$$

The variable transformation $\xi = \sqrt{\lambda}x$ gives

$$\left(\frac{d^2}{d\xi^2} + \varepsilon - \xi^2\right)\phi(\xi) = 0, \quad \varepsilon = \frac{k^2}{\lambda} = \frac{2E}{\hbar\omega} \quad (59)$$

Physically acceptable (i.e. normalizable) solutions of this ordinary differential equation exist only for

$$\varepsilon_n = 2n + 1, \quad n = 0, 1, 2, \ldots \quad \Rightarrow \quad E_n = (2n + 1)\frac{\hbar\omega}{2} \quad (60)$$

Quantization, due to boundary conditions ($\phi(\xi) \to 0$ for $|\xi| \to \infty$).
These solutions are, in explicit form,

$$\phi_n(x) = N_n H_n(\xi) \exp\left(-\frac{1}{2} \xi^2\right), \quad \xi = \sqrt{\frac{m \omega}{\hbar}} x, \quad \omega = \sqrt{\frac{K}{m}}$$ \quad (61)

$$N_n = \left(\frac{1}{2^n n! \sqrt{\frac{m \omega}{\pi \hbar}}}\right)^{1/2}, \quad E_n = (2n+1) \frac{\hbar \omega}{2}, \quad n = 0, 1, 2, \ldots$$

As the mass $m$ increases, the energy spacing $E_{n+1} - E_n = \hbar \omega$ decreases. Thus, the classical behaviour is recovered in the limit $m \to \infty$ (and also for $\hbar \to 0$).

The Hermite polynomials $H_n(\xi)$ can be expressed in terms of confluent hypergeometric functions, and obey a recurrence relation:

$$H_{2k}(\xi) = (-1)^k \frac{(2k)!}{k!} \, _1F_1(-k; 1/2; \xi^2)$$ \quad (62)

$$H_{2k+1}(\xi) = (-1)^k \frac{(2k+1)!}{k!} (2\xi) \, _1F_1(-k; 3/2; \xi^2)$$ \quad (63)

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - 2nH_{n-1}(\xi) \quad (n \geq 1)$$ \quad (64)

\*Ch. Hermite (1822-1901)
The state function for the ground state \((n = 0)\) is a Gauß function \(\phi_0(x) = \exp(-\xi^2/2)/\sqrt[4]{\pi}\), with energy \(E_0 = \hbar \omega/2\) (zero-point energy).

State functions \(\phi_n(x)\) and probability density distributions \([\phi_n(x)]^* \phi_n(x)\) (for \(n = 0, 1, 2, 3, 4, \text{ and } 5\)) for the 1-dimensional harmonic oscillator.
The general molecule

After these one-particle examples the step to the case of an arbitrary molecule can be done quite easily, if we restrict ourselves to the non-relativistic treatment, and omit external (electric or magnetic) fields.

Hamilton operator for an arbitrary molecule, built from $N$ nuclei (with charges $Z_K$ and masses $M_K$), and $n$ electrons (definition of the system under study, in \textit{space-fixed coordinates}):

$$\hat{H} = \hat{T} + \hat{V}$$  \hspace{1cm} (65)

Kinetic energy operator (based on single-particle kinetic energy):

$$\hat{T} = \hat{T}_n + \hat{T}_e, \quad \hat{T}_n = \sum_{K=1}^{N} \left(-\frac{\hbar^2}{2M_K}\right) \Delta_K, \quad \hat{T}_e = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{n} \Delta_i$$  \hspace{1cm} (66)

Potential energy operator (based on the Coulomb potential energy):

$$\hat{V} = \hat{V}_{nn} + \hat{V}_{en} + \hat{V}_{ee}$$  \hspace{1cm} (67)

$$\hat{V}_{nn} = +\frac{e^2}{\kappa_0} \sum_{K=1}^{N-1} \sum_{L=K+1}^{N} \frac{Z_K Z_L}{R_{KL}}$$  \hspace{1cm} (68)

$$\hat{V}_{en} = -\frac{e^2}{\kappa_0} \sum_{i=1}^{n} \sum_{K=1}^{N} \frac{Z_K}{r_{iK}}$$  \hspace{1cm} (69)

$$\hat{V}_{ee} = +\frac{e^2}{\kappa_0} \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{1}{r_{ij}}$$  \hspace{1cm} (70)

One can try to separate motions related to the various degrees of freedom, as in classical mechanics. This can be done exactly for the overall translation of the center of total molecular mass, but a separation of the internal nuclear motions (molecular rotation and nuclear vibration) from the electronic motion is possible only in an approximate way.
Switching to molecule-fixed coordinates, and making a sequence of well-defined steps (adiabatic ansatz, adiabatic approximation, Born-Oppenheimer approximation) leads to the so-called ‘electronic Schrödinger equation for space-fixed (or clamped) nuclei’:

\[ \hat{H}_{el} \psi_k = E_k \psi_k , \quad k = (0), 1, 2, \ldots \]  

(71)

The ‘electronic Hamiltonian’ can be split into zero-, one- and two-electron parts:

\[ \hat{H}_{el} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2 \]  

(72)

\[ \hat{H}_0 = \frac{e^2}{\kappa_0} \sum_{K=1}^{N-1} \sum_{L=K+1}^{N} \frac{Z_K Z_L}{R_{KL}} \]

\[ \hat{H}_1 = \sum_{i=1}^{n} \left( -\frac{\hbar^2}{2m_e} \Delta_i - \frac{e^2}{\kappa_0} \sum_{K=1}^{N} \frac{Z_K}{r_{iK}} \right) \]

\[ \hat{H}_2 = \frac{e^2}{\kappa_0} \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{1}{r_{ij}} \]

The zero-electron part \( \hat{H}_0 \) contributes only an additive constant to the total energy (and is thus sometimes excluded from \( \hat{H}_{el} \)).

The electronic energies \( E_k \) (eigenvalues) and the corresponding electronic state functions \( \psi_k \) (eigenfunctions) depend parametrically on the internal coordinates of the nuclear configuration.

In addition to this parametrical dependence on nuclear configuration, the state functions are functions of the (space and spin) coordinates of all \( n \) electrons (i.e. all those coordinates which have to or may appear due to the form of the Hamilton operator \( \hat{H}_{el} \)):

\[ \psi_k = \psi_k(x_1, x_2, \ldots, x_n) , \]

(73)

\( x = (r, \sigma) \) combines space and spin coordinates (the latter can take only two values: \( \sigma = +\frac{1}{2} \) for \( \uparrow \) or \( \alpha \) spin, \( \sigma = -\frac{1}{2} \) for \( \downarrow \) or \( \beta \) spin).

The electronic energy \( E_k \), also known as potential energy hypersurface (PES), is a scalar function in an \( f \)-dimensional space, where \( f \) depends
on the number of nuclei $N$:

- non-linear molecule: $f = 3N - 6$
- linear molecule: $f = 3N - 5$

For a diatomic molecule ($N = 2$) $f = 1$, and the electronic energy simply reduces to potential energy curves $E_k(R)$, where $R$ denotes the internuclear distance.

All quantum chemical program codes only determine approximate solutions $(E_k, \Psi_k)$ to eq. (71). A quantum mechanical treatment of nuclear motion, where the PES $E_k$ would appear as (a part of) an effective potential energy operator, is not attempted.

Most of present-day quantum mechanical methods only differ
(1) in the degree of sophistication applied to approximate the state functions $\Psi_k$ and/or
(2) the presence or absence of further approximations made with respect to the electronic Hamiltonian $\hat{H}_{el}$ and the evaluation of the energies $E_k$ (this statement excludes methods based on density functional theory, DFT).