

1.3: The Schrödinger Equation

The Time-Dependent Schrödinger Equation

How to extract from $\Psi(q_j, t)$ knowledge about momenta is treated, where the structure of quantum mechanics, the use of operators and wavefunctions to make predictions and interpretations about experimental measurements, and the origin of 'uncertainty relations' such as the well known Heisenberg uncertainty condition dealing with measurements of coordinates and momenta are also treated.

Before moving deeper into understanding what quantum mechanics 'means', it is useful to learn how the wavefunctions Ψ are found by applying the basic equation of quantum mechanics, the *Schrödinger equation*, to a few exactly soluble model problems. Knowing the solutions to these 'easy' yet chemically very relevant models will then facilitate learning more of the details about the structure of quantum mechanics because these model cases can be used as 'concrete examples'.

The Schrödinger equation is a differential equation depending on time and on all of the spatial coordinates necessary to describe the system at hand (thirty-nine for the H_2O example cited above). It is usually written

$$\mathbf{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

where $\Psi(q_j, t)$ is the unknown wavefunction and \mathbf{H} is the operator corresponding to the total energy physical property of the system. This operator is called the Hamiltonian and is formed, as stated above, by first writing down the classical mechanical expression for the total energy (kinetic plus potential) in Cartesian coordinates and momenta and then replacing all classical momenta p_j by their quantum mechanical operators $p_j = -i\hbar \frac{\partial}{\partial q_j}$.

For the H_2O example used above, the classical mechanical energy of all thirteen particles is

$$E = \sum_i \left(\frac{p_i^2}{2m_e} + \frac{1}{2} \sum_j \frac{e^2}{r_{i,j}} - \sum_a Z_a \frac{e^2}{r_{i,a}} \right) + \sum_a \left(-\frac{\hbar^2}{2m_a} \frac{\partial^2}{\partial q_a^2} + \frac{1}{2} \sum_b Z_a Z_b \frac{e^2}{r_{a,b}} \right)$$

where the indices i and j are used to label the ten electrons whose thirty cartesian coordinates are $\{q_i\}$ and a and b label the three nuclei whose charges are denoted $\{Z_a\}$, and whose nine cartesian coordinates are $\{q_a\}$. The electron and nuclear masses are denoted m_e and $\{m_a\}$, respectively.

The corresponding Hamiltonian operator is

$$\mathbf{H} = \sum_i \left(-\left(\frac{\hbar^2}{2m_e}\right) \frac{\partial^2}{\partial q_i^2} + \frac{1}{2} \sum_j \frac{e^2}{r_{i,j}} - \sum_a Z_a \frac{e^2}{r_{i,a}} \right) + \sum_a \left(-\left(\frac{\hbar^2}{2m_a}\right) \frac{\partial^2}{\partial q_a^2} + \frac{1}{2} \sum_b Z_a Z_b \frac{e^2}{r_{a,b}} \right).$$

Notice that \mathbf{H} is a second order differential operator in the space of the thirty-nine Cartesian coordinates that describe the positions of the ten electrons and three nuclei. It is a second order operator because the momenta appear in the kinetic energy as p_j^2 and p_a^2 , and the quantum mechanical operator for each momentum $\mathbf{p} = i\hbar \frac{\partial}{\partial q}$ is of first order.

The Schrödinger equation for the H_2O then reads

$$\sum_i \left[-\left(\frac{\hbar^2}{2m_e}\right) \frac{\partial^2}{\partial q_i^2} + \frac{1}{2} \sum_j \frac{e^2}{r_{i,j}} - \sum_a Z_a \frac{e^2}{r_{i,a}} \right] \Psi + \sum_a \left[-\left(\frac{\hbar^2}{2m_a}\right) \frac{\partial^2}{\partial q_a^2} + \frac{1}{2} \sum_b Z_a Z_b \frac{e^2}{r_{a,b}} \right] \Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

*If the Hamiltonian operator contains the time variable explicitly, one must solve the time-dependent Schrödinger equation. If the Hamiltonian operator does **not** contain the time variable explicitly, one can solve the time-independent Schrödinger equation*

The Time-Independent Schrödinger Equation

In cases where the classical energy, and hence the quantum Hamiltonian, do **not** contain terms that are explicitly time dependent (e.g., interactions with time varying external electric or magnetic fields would add to the above classical energy expression time dependent terms discussed later in this text), the separations of variables techniques can be used to reduce the Schrödinger equation to a time-independent equation.

In such cases, H is not explicitly time dependent, so one can assume that $\Psi(q_j, t)$ is of the form

$$\Psi(q_j, t) = \Psi(q_j)F(t).$$

Substituting this 'ansatz' into the time-dependent Schrödinger equation gives

$$\Psi(q_j) i\hbar \frac{\partial F}{\partial t} = \mathbf{H}\Psi(q_j)F(t).$$

Dividing by $\Psi(q_j)F(t)$ then gives

$$F^{-1} \left(i\hbar \frac{\partial F}{\partial t} \right) = \Psi^{-1} (\mathbf{H}\Psi(q_j)).$$

Since $F(t)$ is only a function of time t , and $\Psi(q_j)$ is only a function of the spatial coordinates $\{q_j\}$, and because the left hand and right hand sides must be equal for all values of t and of $\{q_j\}$, both the left and right hand sides must equal a constant. If this constant is called E , the **two** equations that are embodied in this separated Schrödinger equation read as follows:

$$\begin{aligned} H\Psi(q_j) &= E\Psi(q_j), \\ i\hbar \frac{\partial F(t)}{\partial t} &= i\hbar \frac{dF(t)}{dt} = EF(t). \end{aligned} \tag{1.3.1}$$

Equation 1.3.1 is called the *time-independent Schrödinger Equation*; it is a so-called eigenvalue equation in which one is asked to find functions that yield a constant multiple of themselves when acted on by the Hamiltonian operator. Such functions are called eigenfunctions of \mathbf{H} and the corresponding constants are called eigenvalues of \mathbf{H} . For example, if \mathbf{H} were of the form

$$\frac{-\hbar^2}{2M} \frac{\partial^2}{\partial \phi^2} = H$$

then functions of the form $e^{(im\phi)}$ would be eigenfunctions because

$$\left(\frac{-\hbar^2}{2M} \frac{\partial^2}{\partial \phi^2} \right) e^{im\phi} = \left(\frac{m^2 \hbar^2}{2M} \right) e^{(im\phi)}$$

In this case, $\left(\frac{m^2 \hbar^2}{2M} \right)$ is the eigenvalue.

When the Schrödinger equation can be separated to generate a time-independent equation describing the spatial coordinate dependence of the wavefunction, the eigenvalue E must be returned to the equation determining $F(t)$ to find the time dependent part of the wavefunction. By solving

$$i\hbar \frac{dF(t)}{dt} = EF(t)$$

once E is known, one obtains

$$F(t) = e^{\frac{-iEt}{\hbar}}$$

and the full wavefunction can be written as

$$\Psi(q_j, t) = \Psi(q_j) e^{\frac{-iEt}{\hbar}}$$

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For the above example, the time dependence is expressed by

$$F(t) = e^{\left(\frac{-it}{\hbar} \frac{m^2 \hbar^2}{2M} \right)}$$

Having been introduced to the concepts of operators, wavefunctions, the Hamiltonian and its Schrödinger equation, it is important to now consider several examples of the applications of these concepts. The examples treated below were chosen to provide the learner with valuable experience in solving the Schrödinger equation; they were also chosen because the models they embody form the most elementary chemical models of electronic motions in conjugated molecules and in atoms, rotations of linear molecules, and vibrations of chemical bonds.

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