

## 2.1: Time-Evolution with a Time-Independent Hamiltonian

The time evolution of the state of a quantum system is described by the **time-dependent Schrödinger equation** (TDSE):

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) = \hat{H}(\vec{r}, t) \psi(\vec{r}, t) \quad (2.1.1)$$

$\hat{H}$  is the Hamiltonian operator which describes all interactions between particles and fields, and determines the state of the system in time and space.  $\hat{H}$  is the sum of the kinetic and potential energy. For one particle under the influence of a potential

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \hat{V}(\vec{r}, t) \quad (2.1.2)$$

The state of the system is expressed through the wavefunction  $\psi(\vec{r}, t)$ . The wavefunction is complex and cannot be observed itself, but through it we obtain the probability density

$$P = |\psi(\vec{r}, t)|^2, \quad (2.1.3)$$

which characterizes the spatial probability distribution for the particles described by  $\hat{H}$  at time  $t$ . Also, it is used to calculate the expectation value of an operator  $\hat{A}$

$$\langle \hat{A}(t) \rangle = \int \psi^*(\vec{r}, t) \hat{A} \psi(\vec{r}, t) d\vec{r} \quad (2.1.4)$$

$$= \langle \psi(t) | \hat{A} | \psi(t) \rangle \quad (2.1.5)$$

Physical observables **must be real**, and therefore will correspond to the expectation values of Hermitian operators ( $\hat{A} = \hat{A}^\dagger$ ).

Our first exposure to time-dependence in quantum mechanics is often for the specific case in which the Hamiltonian  $\hat{H}$  is assumed to be independent of time:  $\hat{H} = \hat{H}(\vec{r})$ . We then assume a solution with a form in which the spatial and temporal variables in the wavefunction are separable:

$$\psi(\vec{r}, t) = \varphi(\vec{r}) T(t) \quad (2.1.6)$$

$$i\hbar \frac{1}{T(t)} \frac{\partial}{\partial t} T(t) = \frac{\hat{H}(\vec{r}) \varphi(\vec{r})}{\varphi(\vec{r})} \quad (2.1.7)$$

Here the left-hand side is a function only of time, and the right-hand side is a function of space only ( $\vec{r}$ , or rather position and momentum). Equation 2.1.7 can only be satisfied if both sides are equal to the same constant,  $E$ . Taking the right-hand side we have

$$\frac{\hat{H}(\vec{r}) \varphi(\vec{r})}{\varphi(\vec{r})} = E \Rightarrow \hat{H}(\vec{r}) \varphi(\vec{r}) = E \varphi(\vec{r}) \quad (2.1.8)$$

This is the **Time-Independent Schrödinger Equation** (TISE), an eigenvalue equation, for which  $\varphi(\vec{r})$  are the eigenstates and  $E$  are the eigenvalues. Here we note that

$$\langle \hat{H} \rangle = \langle \psi | \hat{H} | \psi \rangle = E, \quad (2.1.9)$$

so  $\hat{H}$  is the operator corresponding to  $E$  and drawing on classical mechanics we associate  $\hat{H}$  with the expectation value of the energy of the system. Now taking the left-hand side of Equation 2.1.7 and integrating:

$$i\hbar \frac{1}{T(t)} \frac{\partial T}{\partial t} = E \quad (2.1.10)$$

$$\left( \frac{\partial}{\partial t} + \frac{iE}{\hbar} \right) T(t) = 0 \quad (2.1.11)$$

which has solutions like this:

$$T(t) = \exp(-iEt/\hbar) \quad (2.1.12)$$

So, in the case of a bound potential we will have a discrete set of eigenfunctions  $\varphi_n(\vec{r})$  with corresponding energy eigenvalues  $E_n$  from the TISE, and there are a set of corresponding solutions to the TDSE.

$$\psi_n(\vec{r}, t) = \varphi_n(\vec{r}) \underbrace{\exp(-iE_n t/\hbar)}_{\text{phase factor}} \quad (2.1.13)$$

### Phase Factor

For any complex number written in polar form (such as  $re^{i\theta}$ ), the phase factor is the complex exponential factor ( $e^{i\theta}$ ). The phase factor does not have any physical meaning, since the introduction of a phase factor does not change the expectation values of a Hermitian operator. That is

$$\langle \phi | A | \phi \rangle = \langle \phi | e^{-i\theta} A e^{i\theta} | \phi \rangle \quad (2.1.14)$$

Since the only time-dependence in  $\psi_n$  is a *phase factor*, the probability density for an eigenstate is *independent* of time:

$$P = |\psi_n(t)|^2 = \text{constant}. \quad (2.1.15)$$

Therefore, the eigenstates  $\varphi(\vec{r})$  do not change with time and are called **stationary states**.

However, more generally, a system may exist as a linear combination of eigenstates:

$$\psi(\vec{r}, t) = \sum_n c_n \psi_n(\vec{r}, t) \quad (2.1.16)$$

$$= \sum_n c_n e^{-iE_n t/\hbar} \varphi_n(\vec{r}) \quad (2.1.17)$$

where  $c_n$  are complex amplitudes, with

$$\sum_n |c_n|^2 = 1.$$

For such a case, the probability density will oscillate with time. As an example, consider two eigenstates

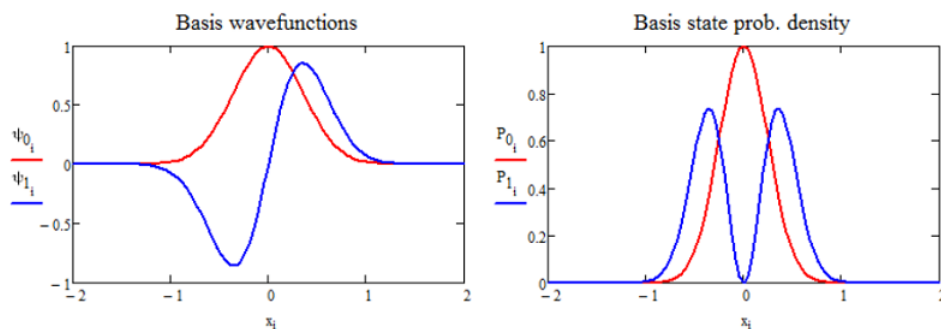
$$\begin{aligned} \psi(\vec{r}, t) &= \psi_1 + \psi_2 \\ &= c_1 \varphi_1 e^{-iE_1 t/\hbar} + c_2 \varphi_2 e^{-iE_2 t/\hbar} \end{aligned} \quad (2.1.18)$$

For this state the probability density oscillates in time as

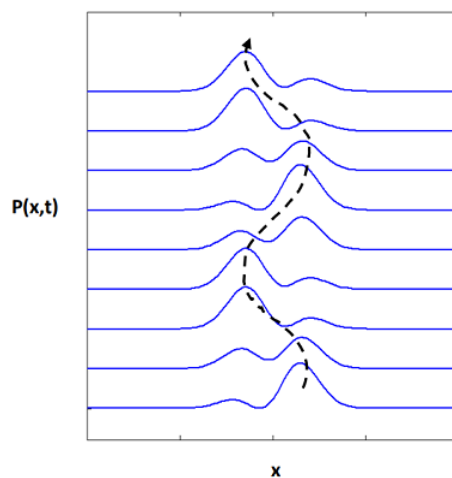
$$\begin{aligned} P(t) &= |\psi|^2 \\ &= |\psi_1 + \psi_2|^2 \\ &= |c_1 \varphi_1|^2 + |c_2 \varphi_2|^2 + c_1^* c_2 \varphi_1^* \varphi_2 e^{-i(E_2 - E_1)t/\hbar} + c_2^* c_1 \varphi_2^* \varphi_1 e^{+i(E_2 - E_1)t/\hbar} \\ &= |\psi_1|^2 + |\psi_2|^2 + 2 |\psi_1 \psi_2| \cos(\omega_2 - \omega_1)t \end{aligned} \quad (2.1.19)$$

where  $\omega_n = E_n/\hbar$ . We refer to this state of the system that gives rise to this time-dependent oscillation in probability density as a coherent superposition state, or coherence. More generally, the oscillation term in Equation 2.1.19 may also include a time-independent phase factor  $\phi$  that arises from the complex expansion coefficients.

As an example, consider the superposition of the ground and first excited states of the quantum harmonic oscillator. The basis wavefunctions,  $\psi_0(x)$  and  $\psi_1(x)$ , and their stationary probability densities  $P_i = \langle \psi_i(x) | \psi_i(x) \rangle$  are



If we create a superposition of these states with Equation 2.1.18 the time-dependent probability density oscillates, with  $\langle x(t) \rangle$  bearing similarity to the classical motion. (Here  $c_0 = 0.5$  and  $c_1 = 0.87$ .)



## Readings

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2. Nitzan, A., Chemical Dynamics in Condensed Phases. Oxford University Press: New York, 2006; Ch. 1.
3. Schatz, G. C.; Ratner, M. A., Quantum Mechanics in Chemistry. Dover Publications: Mineola, NY, 2002; Ch. 2.

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