

## TIME DEPENDENT SCHRÖDINGER EQUATION: TWO-STATE SYSTEMS

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 9.1.

We've seen that the general time-dependent solution of the Schrödinger equation with a time-independent potential is

$$(1) \quad \Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar}$$

where the  $c_n$  are constants determined by normalization.

In the special case where the system has only two states,  $\psi_a$  and  $\psi_b$ , we can write this as

$$(2) \quad \Psi(x,t) = c_a \psi_a e^{-iE_a t/\hbar} + c_b \psi_b e^{-iE_b t/\hbar}$$

Now suppose we add a time-dependent term  $H'(t)$  to the hamiltonian. The resulting wave function at any given time can still be expressed as a linear combination of  $\psi_a$  and  $\psi_b$ , since these two functions form a complete orthonormal set for the two-state system. The key point is that the parameters  $c_a$  and  $c_b$  may be different at different times; in other words, they are functions of time. That is

$$(3) \quad \Psi(x,t) = c_a(t) \psi_a e^{-iE_a t/\hbar} + c_b(t) \psi_b e^{-iE_b t/\hbar}$$

Note that  $c_a$  and  $c_b$  are still *not* functions of  $x$ ; the entire  $x$  dependence is contained in the time-independent functions  $\psi_a(x)$  and  $\psi_b(x)$ .

To find  $c_a$  and  $c_b$ , we require that 3 satisfy the full time-dependent Schrödinger equation

$$(4) \quad (H^0 + H') \Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

where  $H^0$  is the time-independent part of the hamiltonian, so that

$$(5) \quad H^0 \psi_i = E_i \psi_i$$

for  $i = a, b$ . Plugging in  $\Psi$  from 3, we get

$$(6) \quad (H^0 + H') \left[ c_a(t) \psi_a e^{-iE_a t/\hbar} + c_b(t) \psi_b e^{-iE_b t/\hbar} \right] = i\hbar \left[ \dot{c}_a(t) \psi_a e^{-iE_a t/\hbar} + \dot{c}_b(t) \psi_b e^{-iE_b t/\hbar} \right] + c_a(t) \psi_a E_a e^{-iE_a t/\hbar} + c_b(t) \psi_b E_b e^{-iE_b t/\hbar}$$

Using 5 we can cancel the terms on the LHS involving  $H^0$  with the last two terms on the RHS to get

$$(7) \quad c_a(t) H' \psi_a e^{-iE_a t/\hbar} + c_b(t) H' \psi_b e^{-iE_b t/\hbar} = i\hbar \left[ \dot{c}_a(t) \psi_a e^{-iE_a t/\hbar} + \dot{c}_b(t) \psi_b e^{-iE_b t/\hbar} \right]$$

Notice that the LHS implicitly assumes that  $H'$  (which depends on time) commutes with the  $c_i(t)$ . This is true provided  $H'$  contains no time derivatives, which is fine for pretty well all time-dependent potentials.

From here we can take the inner product of both sides with  $\psi_a$  or  $\psi_b$  and use the orthogonality of these two functions. We'll use the shorthand notation

$$(8) \quad H'_{ij} \equiv \langle \psi_i | H' | \psi_j \rangle$$

Taking the inner product with  $\psi_a$  gives

$$(9) \quad c_a H'_{aa} e^{-iE_a t/\hbar} + c_b H'_{ab} e^{-iE_b t/\hbar} = i\hbar \dot{c}_a e^{-iE_a t/\hbar}$$

$$(10) \quad \dot{c}_a = -\frac{i}{\hbar} \left[ c_a H'_{aa} + c_b H'_{ab} e^{-i(E_b - E_a)t/\hbar} \right]$$

Doing the same calculation with  $\psi_b$  gives

$$(11) \quad \dot{c}_b = -\frac{i}{\hbar} \left[ c_b H'_{bb} + c_a H'_{ba} e^{i(E_b - E_a)t/\hbar} \right]$$

This pair of coupled differential equations gives the complete solution to the time-dependent problem. In the special case where the diagonal elements of  $H'$  are zero, they reduce to

$$(12) \quad \dot{c}_a = -\frac{i}{\hbar} c_b H'_{ab} e^{-i(E_b - E_a)t/\hbar} \equiv -\frac{i}{\hbar} c_b H'_{ab} e^{-i\omega_0 t}$$

$$(13) \quad \dot{c}_b = -\frac{i}{\hbar} c_a H'_{ba} e^{i(E_b - E_a)t/\hbar} \equiv -\frac{i}{\hbar} c_a H'_{ba} e^{i\omega_0 t}$$

**Example.** We'll look at the hydrogen atom placed in a time-varying electric field  $\mathbf{E} = E(t)\hat{\mathbf{z}}$ , where  $E(t)$  is some arbitrary function of time. Looking only at the first two energy levels, we can get the exact spatial wave functions from the general formula:

$$(14) \quad \psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-r/na} \left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right) Y_l^m(\theta, \phi)$$

The ground state has  $n = 1$  and  $l = m = 0$ :

$$(15) \quad \psi_{100} = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

where  $a$  is the Bohr radius. The  $n = 2$  energy is four-fold degenerate, and has the four corresponding spatial wave functions:

$$(16) \quad \psi_{200} = \frac{\sqrt{2}}{16\sqrt{\pi a^3}} e^{-r/2a} \left(4 - \frac{2r}{a}\right)$$

$$(17) \quad \psi_{21\pm 1} = \mp \frac{1}{8\sqrt{\pi a^5}} r e^{-r/2a} \sin\theta e^{\pm i\phi}$$

$$(18) \quad \psi_{210} = \frac{\sqrt{2}}{8\sqrt{\pi a^5}} r e^{-r/2a} \cos\theta$$

The potential corresponding to the applied field is (where  $-e$  is the electron charge):

$$(19) \quad H' = -eE(t)z$$

$$(20) \quad = -eE(t)r\cos\theta$$

The matrix elements  $H'_{ij}$  can be calculated by direct integration, but notice that

$$(21) \quad \int_0^\pi \cos^p\theta \sin^q\theta d\theta = 0$$

provided  $p$  is odd ( $q$  can be any non-negative integer), since the cosine is odd over this interval while the sine is even. Since  $H'_{100,200}$  and  $H'_{100,21\pm 1}$  involve  $\theta$  integrals of this form (with  $p = 1$  in all cases and  $q = 1$  in the former case and  $q = 2$  in the latter case; remember to include the spherical

volume element factor of  $r^2 \sin \theta$ ), these matrix elements are all zero. Similarly, all diagonal matrix elements are zero, as  $p = 1$  for  $H'_{100,100}$ ,  $H'_{200,200}$  and  $H'_{21\pm 1,21\pm 1}$ , and  $p = 3$  for  $H'_{210,210}$ . Thus the only non-zero matrix element is

(22)

$$H'_{100,210} = -\frac{1}{\sqrt{\pi}a^{3/2}} \frac{\sqrt{2}}{8\sqrt{\pi}a^{5/2}} 2\pi eE \int_0^\infty r^4 e^{-r/a} e^{-r/2a} dr \int_0^\pi \cos^2 \theta \sin \theta d\theta$$

$$(23) \quad = -\frac{128\sqrt{2}}{243} aeE(t)$$

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