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

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar} \tag{0.1}$$

where the c_n are constants determined by normalization.

In the special case where the system has only two states, ψ_a and ψ_b, we can write this as

$$\Psi(x,t) = c_a \psi_a e^{-iE_a t/\hbar} + c_b \psi_b e^{-iE_b t/\hbar} \tag{0.2}$$

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 ψ_a and ψ_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

$$\Psi(x,t) = c_a(t)\,\psi_a e^{-iE_a t/\hbar} + c_b(t)\,\psi_b e^{-iE_b t/\hbar} \tag{0.3}$$

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 0.3 satisfy the full time-dependent Schrödinger equation

$$\left(H^0 + H'\right)\Psi = i\hbar\frac{\partial \Psi}{\partial t} \tag{0.4}$$

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

$$H^0\psi_i = E_i\psi_i \tag{0.5}$$

for $i = a, b$. Plugging in Ψ from 0.3, we get

(0.6)
$$\left(H^0 + H'\right)\left[c_a(t)\,\psi_a e^{-iE_a t/\hbar} + c_b(t)\,\psi_b e^{-iE_b t/\hbar}\right] = i\hbar\left[\dot{c}_a(t)\,\psi_a e^{-iE_a t/\hbar} + \dot{c}_b(t)\,\psi_b e^{-iE_b t/\hbar}\right] + c_a(t)\,\psi_a E_a e^{-iE_a t/\hbar} + c_b(t)\,\psi_b E_b e^{-iE_b t/\hbar}$$

Using 0.5 we can cancel the terms on the LHS involving H^0 with the last two terms on the RHS to get

(0.7)
$$c_a(t)\,H'\psi_a e^{-iE_a t/\hbar} + c_b(t)\,H'\psi_b e^{-iE_b t/\hbar} = i\hbar\left[\dot{c}_a(t)\,\psi_a e^{-iE_a t/\hbar} + \dot{c}_b(t)\,\psi_b e^{-iE_b t/\hbar}\right]$$

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 ψ_a or ψ_b and use the orthogonality of these two functions. We'll use the shorthand notation

$$H'_{ij} \equiv \langle \psi_i | H' | \psi_j \rangle \tag{0.8}$$

Taking the inner product with ψ_a gives

$$c_a H'_{aa} e^{-iE_a t/\hbar} + c_b H'_{ab} e^{-iE_b t/\hbar} = i\hbar \dot{c}_a e^{-iE_a t/\hbar} \tag{0.9}$$

$$\dot{c}_a = -\frac{i}{\hbar}\left[c_a H'_{aa} + c_b H'_{ab} e^{-i(E_b - E_a)t/\hbar}\right] \tag{0.10}$$

Doing the same calculation with ψ_b gives

$$\dot{c}_b = -\frac{i}{\hbar}\left[c_b H'_{bb} + c_a H'_{ba} e^{i(E_b - E_a)t/\hbar}\right] \tag{0.11}$$

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

$$\dot{c}_a = -\frac{i}{\hbar} c_b H'_{ab} e^{-i(E_b - E_a)t/\hbar} \equiv -\frac{i}{\hbar} c_b H'_{ab} e^{-i\omega_0 t} \tag{0.12}$$

$$\dot{c}_b = -\frac{i}{\hbar} c_a H'_{ba} e^{i(E_b - E_a)t/\hbar} \equiv -\frac{i}{\hbar} c_a H'_{ba} e^{i\omega_0 t} \tag{0.13}$$

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:

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}} e^{-r/na} \left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right) Y_l^m(\theta,\phi) \tag{0.14}$$

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

$$\psi_{100} = \frac{1}{\sqrt{\pi}a^{3/2}} e^{-r/a} \tag{0.15}$$

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

$$\psi_{200} = \frac{\sqrt{2}}{16\sqrt{\pi}a^{3/2}} e^{-r/2a}\left(4 - \frac{2}{a}r\right) \tag{0.16}$$

$$\psi_{21\pm1} = \mp\frac{1}{8\sqrt{\pi}a^{5/2}} re^{-r/2a}\sin\theta e^{\pm i\phi} \tag{0.17}$$

$$\psi_{210} = \frac{\sqrt{2}}{8\sqrt{\pi}a^{5/2}} re^{-r/2a}\cos\theta \tag{0.18}$$

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

$$H' = -eE(t)\,z \tag{0.19}$$

$$= -eE(t)\,r\cos\theta \tag{0.20}$$

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

$$\int_0^\pi \cos^p\theta \sin^q\theta\, d\theta = 0 \tag{0.21}$$

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 $H'_{100,21\pm1}$ involve θ 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 $H'_{21\pm1,21\pm1}$, and $p = 3$ for $H'_{210,210}$. Thus the only non-zero matrix element is

(0.22)
$$H'_{100,210} = -\frac{1}{\sqrt{\pi}a^{3/2}}\frac{\sqrt{2}}{8\sqrt{\pi}a^{5/2}}2\pi eE\int_0^\infty r^4 e^{-r/a}e^{-r/2a}dr\int_0^\pi \cos^2\theta\sin\theta d\theta$$

(0.23)
$$= -\frac{128\sqrt{2}}{243}aeE(t)$$

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