On the Time Evolution of Wavefunctions in Quantum Mechanics

C. David Sherrill
School of Chemistry and Biochemistry
Georgia Institute of Technology
October 1999

1   Introduction

The purpose of these notes is to help you appreciate the connection between eigenfunctions of the Hamiltonian and classical normal modes, and to help you understand the time propagator.

2   The Classical Coupled Mass Problem

Here we will review the results of the coupled mass problem, Example 1.8.6 from Shankar. This is an example from classical physics which nevertheless demonstrates some of the essential features of coupled degrees of freedom in quantum mechanical problems and a general approach for removing such coupling. The problem involves two objects of equal mass, connected to two different walls and also to each other by springs. Using $F = ma$ and Hooke's Law ($F = -kx$) for the springs, and denoting the displacements of the two masses as x_1 and x_2, it is straightforward to deduce equations for the acceleration (second derivative in time, $\ddot{x}_1$ and $\ddot{x}_2$):

$$\ddot{x}_1 = -\frac{2k}{m}x_1 + \frac{k}{m}x_2 \tag{1}$$

$$\ddot{x}_2 = \frac{k}{m}x_1 - \frac{2k}{m}x_2. \tag{2}$$

The goal of the problem is to solve these second-order differential equations to obtain the functions $x_1(t)$ and $x_2(t)$ describing the motion of the two masses at any given time. Since they are second-order differential equations, we need two initial conditions for each variable, i.e., $x_1(0), \dot{x}_1(0), x_2(0)$, and $\dot{x}_2(0)$.

Our two differential equations are clearly *coupled*, since $\ddot{x}_1$ depends not only on x_1, but also on x_2 (and likewise for $\ddot{x}_2$). This makes the equations difficult to solve! The solution was to write the differential equations in matrix form, and then diagonalize the matrix to obtain the eigenvectors and eigenvalues.

In matrix form, we have

$$\begin{bmatrix} \ddot{x}_1 \\ \ddot{x}_2 \end{bmatrix} = \begin{bmatrix} -2\gamma & \gamma \\ \gamma & -2\gamma \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix}, \tag{3}$$

where $\gamma = k/m$. Since this 2x2 matrix is real and symmetric, it must also be Hermitian, so we know that it has real eigenvalues, and that the eigenvectors will be linearly independent and can be made to form an orthonormal basis.

Equation 3 is a particular form of the more general equation (in Dirac notation)

$$|\ddot{x}(t)\rangle = \hat{\Omega}|x(t)\rangle \tag{4}$$

where we have picked a basis set which we will call $\{|1\rangle, |2\rangle\}$, where

$$|1\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \tag{5}$$

represents a unit displacement for coordinate x_1, and likewise

$$|2\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{6}$$

represents a unit displacement for coordinate x_2. Clearly any state of the system (x_1, x_2) can be written as a column vector

$$\begin{bmatrix} x_1 \\ x_2 \end{bmatrix} \tag{7}$$

(as in eq. 3), which can always be decomposed into our $\{|1\rangle, |2\rangle\}$ basis as

$$\begin{bmatrix} x_1 \\ x_2 \end{bmatrix} = x_1 \begin{bmatrix} 1 \\ 0 \end{bmatrix} + x_2 \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{8}$$

or

$$|x\rangle = x_1|1\rangle + x_2|2\rangle. \tag{9}$$

Hence, eq. 3 can be considered a representation of the more general eq. 4 in the $\{|1\rangle, |2\rangle\}$ basis.

If we assume the initial velocities are zero, then we should be able to predict $x_1(t)$ and $x_2(t)$ directly from $x_1(0)$ and $x_2(0)$. Thus, we seek a solution of the form

$$\begin{bmatrix} x_1(t) \\ x_2(t) \end{bmatrix} = \begin{bmatrix} G_{11}(t) & G_{12}(t) \\ G_{21}(t) & G_{22}(t) \end{bmatrix} \begin{bmatrix} x_1(0) \\ x_2(0) \end{bmatrix}, \tag{10}$$

where $\mathbf{G}(t)$ is a matrix, called the *propagator*, that lets us get motion at future times from the initial conditions. We will have to figure out what $\mathbf{G}(t)$ is.

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Again, the strategy is to diagonalize $\mathbf{\Omega}$. The point of diagonalizing $\mathbf{\Omega}$ is that, as you can see from eq. 3, the coupling between x_1 and x_2 *goes away* if $\mathbf{\Omega}$ becomes a diagonal matrix. You can easily verify that the eigenvectors and their corresponding eigenvalues, which we will label with Roman numerals I and II, are

$$\lambda_\text{I} = -\gamma, \quad |\text{I}\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix} \tag{11}$$

$$\lambda_\text{II} = -3\gamma, \quad |\text{II}\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix} \tag{12}$$

This new basis, the *eigenvector* basis, is just as legitimate as our original $\{|1\rangle, |2\rangle\}$ basis, and is in fact better in the sense that it diagonalizes $\mathbf{\Omega}$. So, instead of using the $\{|1\rangle, |2\rangle\}$ basis to obtain eq. 3 from eq. 4, we can use the $\{|\text{I}\rangle, |\text{II}\rangle\}$ basis to obtain

$$\begin{bmatrix} \ddot{x}_\text{I} \\ \ddot{x}_\text{II} \end{bmatrix} = \begin{bmatrix} \lambda_\text{I} & 0 \\ 0 & \lambda_\text{II} \end{bmatrix} \begin{bmatrix} x_\text{I} \\ x_\text{II} \end{bmatrix}, \tag{13}$$

so that now $\ddot{x}_\text{I}$ depends only on x_I, and $\ddot{x}_\text{II}$ depends only on x_II. The equations are uncoupled! Note that we are now expanding the solution $|x\rangle$ in the $\{|\text{I}\rangle, |\text{II}\rangle\}$ basis, so the components in this basis are now x_I and x_II instead of x_1 and x_2:

$$|x\rangle = x_\text{I}|\text{I}\rangle + \text{x}_\text{II}|\text{II}\rangle. \tag{14}$$

Of course it is possible to switch between the $\{|1\rangle, |2\rangle\}$ basis and the $\{|\text{I}\rangle, |\text{II}\rangle\}$ basis. If we define our basis set transformation matrix as that obtained by making each column one of the eigenvectors of $\mathbf{\Omega}$, we obtain

$$\mathbf{U} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}, \tag{15}$$

which is a unitary matrix (it has to be since $\mathbf{\Omega}$ is Hermitian). Vectors in the two basis sets are related by

$$\begin{bmatrix} x_1 \\ x_2 \end{bmatrix} = \mathbf{U} \begin{bmatrix} x_\text{I} \\ x_\text{II} \end{bmatrix}, \quad \begin{bmatrix} x_\text{I} \\ x_\text{II} \end{bmatrix} = \mathbf{U}^\dagger \begin{bmatrix} x_1 \\ x_2 \end{bmatrix}. \tag{16}$$

In this case, $\mathbf{U}$ is special because $\mathbf{U} = \mathbf{U}^\dagger$; this doesn't generally happen. You can verify that the $\mathbf{\Omega}$ matrix, when transformed into the $\{|\text{I}\rangle, |\text{II}\rangle\}$ basis via $\mathbf{U}^\dagger \mathbf{\Omega} \mathbf{U}$, becomes the diagonal matrix in equation 13.

The matrix equation 13 is of course equivalent to the two simple equations

$$\ddot{x}_\text{I} = -\gamma x_\text{I} \tag{17}$$
$$\ddot{x}_\text{II} = -3\gamma x_\text{II}, \tag{18}$$

and you can see that valid solutions (assuming that the initial velocities are zero) are

$$x_\mathrm{I}(t) = x_\mathrm{I}(0)cos(\omega_\mathrm{I}t) \tag{19}$$

$$x_\mathrm{II}(t) = x_\mathrm{II}(0)cos(\omega_\mathrm{II}t), \tag{20}$$

where we have defined

$$\omega_\mathrm{I} = \sqrt{\gamma} \tag{21}$$

$$\omega_\mathrm{II} = \sqrt{3\gamma}. \tag{22}$$

So, the $\{|\mathrm{I}\rangle, |\mathrm{II}\rangle\}$ basis is very special, since any motion of the system can be decomposed into two *decoupled* motions described by eigenvectors $|\mathrm{I}\rangle$ and $|\mathrm{II}\rangle$. In other words, if the system has its initial conditions as some multiple of $|\mathrm{I}\rangle$, it will never exhibit any motion of the type $|\mathrm{II}\rangle$ at later times, and vice-versa. In this context, the special vibrations described by $|\mathrm{I}\rangle$ and $|\mathrm{II}\rangle$ are called the *normal modes* of the system.

So, are we done? If we are content to work everything in the $\{|\mathrm{I}\rangle, |\mathrm{II}\rangle\}$ basis, yes. However, our original goal was to find the propagator $\mathbf{G}(t)$ (from eq. 10) in the original $\{|1\rangle, |2\rangle\}$ basis. But notice that we already have $\mathbf{G}(t)$ in the $\{|\mathrm{I}\rangle, |\mathrm{II}\rangle\}$ basis! We can simply rewrite equations 19 and 20 in matrix form as

$$\left[\begin{array}{c} x_\mathrm{I}(t) \\ x_\mathrm{II}(t) \end{array} \right] = \left[\begin{array}{cc} cos(\omega_\mathrm{I}t) & 0 \\ 0 & cos(\omega_\mathrm{II}t) \end{array} \right] \left[\begin{array}{c} x_\mathrm{I}(0) \\ x_\mathrm{II}(0) \end{array} \right]. \tag{23}$$

So, the propagator in the $\{|\mathrm{I}\rangle, |\mathrm{II}\rangle\}$ basis is just

$$\mathbf{G}(t)_{|\mathrm{I}\rangle, |\mathrm{II}\rangle} = \left[\begin{array}{cc} cos(\omega_\mathrm{I}t) & 0 \\ 0 & cos(\omega_\mathrm{II}t) \end{array} \right]. \tag{24}$$

To obtain $\mathbf{G}(t)$ in the original basis, we just have to apply the transformation

$$\mathbf{G}(t)_{|1\rangle, |2\rangle} = \mathbf{U}\mathbf{G}(t)_{|\mathrm{I}\rangle, |\mathrm{II}\rangle}\mathbf{U}^\dagger, \tag{25}$$

noting that this is the reverse transform from that needed to bring $\mathbf{\Omega}$ from the original to the eigenvector basis (so that $\mathbf{U}$ and $\mathbf{U}^\dagger$ swap). Working out $\mathbf{G}(t)_{|1\rangle, |2\rangle}$ was a problem in Problem Set II.

Finally, let us step back to the more general Dirac notation to point out that the general form of the solution is

$$|x(t)\rangle = \hat{G}(t)|x(0)\rangle, \tag{26}$$

and actual calculation just requires choosing a particular basis set and figuring out the components of $|x(t)\rangle$ and $|x(0)\rangle$ and the matrix elements of operator $\hat{G}(t)$ in that basis. Another representation of operator $\hat{G}(t)$ is clearly

$$\hat{G}(t) = |\mathrm{I}\rangle\langle\mathrm{I}|cos(\omega_\mathrm{I}t) + |\mathrm{II}\rangle\langle\mathrm{II}|cos(\omega_\mathrm{II}t), \tag{27}$$

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as you can check by evaluating the matrix elements in the $\{|\text{I}\rangle, |\text{II}\rangle\}$ basis to get eq. 24. Thus

$$
\begin{aligned}
|x(t)\rangle &= \hat{G}(t)|x(0)\rangle \\
&= |\text{I}\rangle\langle\text{I}|x(0)\rangle\cos(\omega_\text{I}t) + |\text{II}\rangle\langle\text{II}|x(0)\rangle\cos(\omega_\text{II}t)
\end{aligned}
\tag{28}
$$

2.1 Summary

A coupled system of differential equations was solved by writing the equations in matrix form, diagonalizing the matrix, and changing to the eigenvector basis which decoupled the equations and made them easily solvable. The propagator was easily obtained in the eigenvector basis. The problem is then solved either by (i) finding the components of the initial state in the eigenvector basis, and writing the solution in the eigenvector basis, or (ii) keeping the initial state in the original basis and instead transforming the propagator from the eigenvector basis into the original basis.

3 Decoupling of Equations in Quantum Mechanics

Recall that the time-dependent Schrödinger equation is

$$
i\hbar\frac{d\Psi(\mathbf{r},t)}{dt} = \hat{H}\Psi(\mathbf{r},t),
\tag{29}
$$

where $\mathbf{r}$ represents the set of all Cartesian coordinates of all particles in the system. If we assume that $\hat{H}$ is time-independent, and if we pretend that $\hat{H}$ is just a number, than we can be confident that the solution is just

$$
\Psi(\mathbf{r},t) = e^{-i\hat{H}t/\hbar}\Psi(\mathbf{r},0).
\tag{30}
$$

In fact, this remains true even though $\hat{H}$ is of course an operator, not just a number. So, the propagator in quantum mechanics is

$$
\hat{G}(t) = e^{-i\hat{H}t/\hbar}.
\tag{31}
$$

3.1 Basis Functions in Coordinate Space

Now imagine that we have a problem where the wavefunction can be expanded as a sum of only two basis functions (admittedly unlikely, but perhaps useful for a single electron spin problem):

$$
\Psi(\mathbf{r},t) = c_1(t)\Phi_1(\mathbf{r}) + c_2(t)\Phi_2(\mathbf{r}).
\tag{32}
$$

This leads to the time-dependent Schrödinger equation (where we will suppress variables $\mathbf{r}$ and t for convenience):

$$i\hbar \left(\dot{c}_1\Phi_1 + \dot{c}_2\Phi_2\right) = \hat{H}\left(c_1\Phi_1 + c_2\Phi_2\right). \tag{33}$$

How do we solve this equation? It's a *coupled* differential equation, similar to eq. 1 except that it's first-order instead of second order. Just as in the classical example, it's the coupling that makes it hard to solve! In the classical case, the answer to coupling was to get the eigenfunctions. What happens if we assume Φ_1 and Φ_2 to be eigenfunctions of $\hat{H}$? In that case,

$$\hat{H}\Phi_1 = E_1\Phi_1 \tag{34}$$
$$\hat{H}\Phi_2 = E_2\Phi_2 \tag{35}$$

and the time-dependent equation becomes

$$i\hbar \left(\dot{c}_1\Phi_1 + \dot{c}_2\Phi_2\right) = c_1 E_1\Phi_1 + c_2 E_2\Phi_2. \tag{36}$$

Furthermore, since the eigenvectors of a Hermitian operator are or can be made orthogonal, we can multiply by Φ_1^* and Φ_2^* and integrate over $d\mathbf{r}$ to obtain

$$i\hbar\dot{c}_1 = c_1 E_1 \tag{37}$$
$$i\hbar\dot{c}_2 = c_2 E_2 \tag{38}$$

which are simple first-order differential equations solved by

$$c_1(t) = c_1(0)e^{-iE_1 t/\hbar} \tag{39}$$
$$c_2(t) = c_2(0)e^{-iE_2 t/\hbar} \tag{40}$$

as you can verify by substituting and differentiating.

But what if our original wavefunction $\Psi(\mathbf{r}, t)$ is *not* given as a linear combination of eigenfunctions? A good strategy is to *re-write* it so that it is! In the coordinate representation (i.e., $\mathbf{r}$ space), we can get the coefficients $c_i(0)$ in an expansion over orthogonal eigenfunctions $\Phi_i(\mathbf{r})$ simply as

$$c_i(0) = \int \Phi_i^*(\mathbf{r})\Psi(\mathbf{r}, 0)d\mathbf{r}. \tag{41}$$

The other strategy would be to try to re-write the propagator in the original basis set. In the problems we do, we will usually use the first approach.

3.2 Matrix Version

We can use matrix notation to re-do the problem above. The time-dependent Schrödinger equation in the original $\{\Phi_1(\mathbf{r}), \Phi_2(\mathbf{r})\}$ basis becomes

$$i\hbar \begin{bmatrix} \dot{c}_1 \\ \dot{c}_2 \end{bmatrix} = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}. \tag{42}$$

Now, just as in eq. 3, we can see that if H was a diagonal matrix, then the equations for c_1 and c_2 would become decoupled. Again, we can make H diagonal by going to the special basis made of the eigenvectors of H. In this new basis, we will denote vector coefficients and matrix elements with tildes as a reminder that the basis set has changed, and we obtain:

$$i\hbar \begin{bmatrix} \dot{\tilde{c}}_1 \\ \dot{\tilde{c}}_2 \end{bmatrix} = \begin{bmatrix} \tilde{H}_{11} & 0 \\ 0 & \tilde{H}_{22} \end{bmatrix} \begin{bmatrix} \tilde{c}_1 \\ \tilde{c}_2 \end{bmatrix}. \tag{43}$$

Now remember that we've gone to the eigenvector basis (which we'll also denote with tildes to distinguish it from the original basis), so we know that

$$\hat{H}\tilde{\Phi}_1(\mathbf{r}) = E_1 \tilde{\Phi}_1(\mathbf{r}) \tag{44}$$
$$\hat{H}\tilde{\Phi}_2(\mathbf{r}) = E_2 \tilde{\Phi}_2(\mathbf{r}). \tag{45}$$

Thus we can further simplify the diagonal elements as

$$\tilde{H}_{11} = \int \tilde{\Phi}_1^*(\mathbf{r})\hat{H}\tilde{\Phi}_1(\mathbf{r})d\mathbf{r} \tag{46}$$
$$= E_1 \int \tilde{\Phi}_1^*(\mathbf{r})\tilde{\Phi}_1(\mathbf{r})d\mathbf{r}$$
$$= E_1$$

for normalized basis functions. Likewise of course $\tilde{H}_{22} = E_2$. Hence, we can expand our matrix equation 43 as

$$i\hbar\dot{\tilde{c}}_1 = \tilde{c}_1 E_1 \tag{47}$$
$$i\hbar\dot{\tilde{c}}_2 = \tilde{c}_2 E_2 \tag{48}$$

which is the same thing we got before when we assumed the given functions were orthonormal. The only difference is that here we emphasized the diagonalization of H rather than getting the eigenvectors, but of course it is the same process. These *decoupled* equations can be solved the same way as before to give

$$\tilde{c}_1(t) = \tilde{c}_1(0)e^{-iE_1 t/\hbar} \tag{49}$$
$$\tilde{c}_2(t) = \tilde{c}_2(0)e^{-iE_2 t/\hbar}, \tag{50}$$

which we could write back in matrix notation (still in the eigenvector or tilde basis) as

$$\begin{bmatrix} \tilde{c}_1(t) \\ \tilde{c}_2(t) \end{bmatrix} = \begin{bmatrix} e^{-iE_1 t/\hbar} & 0 \\ 0 & e^{-iE_2 t/\hbar} \end{bmatrix} \begin{bmatrix} \tilde{c}_1(0) \\ \tilde{c}_2(0) \end{bmatrix}. \tag{51}$$

We can identify the matrix as the propagator,

$$\tilde{\mathbf{G}}(t) = \begin{bmatrix} e^{-iE_1 t/\hbar} & 0 \\ 0 & e^{-iE_2 t/\hbar} \end{bmatrix} \tag{52}$$

in the eigenvector basis.

In the vector/matrix representation, we can go from our original to our tilde coefficients and back as

$$\begin{bmatrix} c_1(t) \\ c_2(t) \end{bmatrix} = \mathbf{U} \begin{bmatrix} \tilde{c}_1(t) \\ \tilde{c}_2(t) \end{bmatrix} \tag{53}$$

$$\begin{bmatrix} \tilde{c}_1(t) \\ \tilde{c}_2(t) \end{bmatrix} = \mathbf{U}^\dagger \begin{bmatrix} c_1(t) \\ c_2(t) \end{bmatrix}, \tag{54}$$

where $\mathbf{U}$ is the matrix made by making each column an eigenvector of $\hat{H}$ in the original basis. We could transform our propagator $\tilde{\mathbf{G}}(t)$ from the eigenvector basis to the original basis by

$$\mathbf{G}(t) = \mathbf{U}\tilde{\mathbf{G}}(t)\mathbf{U}^\dagger. \tag{55}$$

3.3   Dirac Notation Version

Let us do the same problem yet again in Dirac or Bracket notation. For this version, let's go ahead and assume that we expand our state function $|\Psi\rangle$ directly in terms of the Hamiltonian eigenvectors

$$|\Psi(t)\rangle = c_1(t)|\Phi_1\rangle + c_2(t)|\Phi_2\rangle. \tag{56}$$

When substituted into the time-dependent Schrödinger equation, this gives

$$\begin{aligned} i\hbar \left(\dot{c}_1(t)|\Phi_1\rangle + \dot{c}_2(t)|\Phi_2\rangle \right) &= \hat{H} \left(c_1(t)|\Phi_1\rangle + c_2(t)|\Phi_2\rangle \right) \\ &= E_1 c_1(t)|\Phi_1\rangle + E_2 c_2(t)|\Phi_2\rangle. \end{aligned} \tag{57}$$

Now multiply on the left by $\langle\Phi_1|$ and $\langle\Phi_2|$, respectively, and use $\langle\Phi_i|\Phi_j\rangle = \delta_{ij}$ to obtain

$$i\hbar\dot{c}_1(t) = E_1 c_1(t) \tag{58}$$

$$i\hbar\dot{c}_2(t) = E_2 c_2(t), \tag{59}$$

just as before, with solutions once again

$$c_1(t) = c_1(0)e^{-iE_1 t/\hbar} \tag{60}$$

$$c_2(t) = c_2(0)e^{-iE_2 t/\hbar}. \tag{61}$$

But what if we are given $|\Psi(0)\rangle$ in a form that looks different from that of eq. 56? Since the eigenvector basis must be complete (although it will usually have more than two basis vectors, as in this example!), we can always rewrite our state vector in this form, and the coefficients can always be computed as

$$c_i(0) = \langle\Phi_i|\Psi(0)\rangle. \tag{62}$$

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Note that in this subsection we aren't assuming anything about whether we are working in co-ordinate ($\mathbf{r}$) space or momentum ($\mathbf{p}$) space or some other space. However, if we were working in coordinate space, we could insert the resolution of the identity

$$\hat{I} = \int d\mathbf{r} |\mathbf{r}\rangle\langle\mathbf{r}| \tag{63}$$

to obtain

$$
\begin{aligned}
c_i(0) &= \int \langle\Phi_i|\mathbf{r}\rangle\langle\mathbf{r}|\Psi(0)\rangle d\mathbf{r} \\
&= \int \Phi_i^*(\mathbf{r})\Psi(\mathbf{r},0)d\mathbf{r},
\end{aligned} \tag{64}
$$

completely consistent with everything above. The propagator may be written as

$$\hat{G}(t) = |\Phi_1\rangle\langle\Phi_1|e^{-iE_1t/\hbar} + |\Phi_2\rangle\langle\Phi_2|e^{-iE_2t/\hbar} \tag{65}$$

again with $|\Phi_1\rangle$ and $|\Phi_2\rangle$ here representing eigenfunctions of $\hat{H}$ with eigenvalues E_1 and E_2, respectively. Note the similarity between this propagator and that from the classical example in eq. 27. The only real difference is that there, we chose to work with cosines as a phase factor, and here we are using the more general exponential. Evidently the frequency here is represented by $E_i/\hbar$. You can verify that in the eigenvector basis, this operator becomes $\tilde{\mathbf{G}}(t)$ from eq. 52 in the previous section. Hopefully you can also see that in the eigenvector basis this definition is equivalent to the more general form 31.