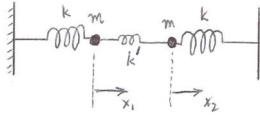# Coupled Oscillations in Diverse Phenomena
Part 2: The ammonia molecule as a quantum two-state system
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In the *Feynman Lectures on Physics*, Richard Feynman elegantly takes the reader through a set of quantum-mechanical two-state systems. One of them models the location of the nitrogen atom in the ammonia molecule NH_3 [5]. It's an important example, because those two states are at the heart of the ammonia maser, the 1953 precursor of the laser. The point to be made here emphasizes that this quantum two-state system (and Feynman's other two-state examples) is mathematically similar to the coupled mechanical oscillator problem. Let's examine the ammonia molecule problem along the lines of Feynman's approach. We keep in mind that a quantum state $|\psi\rangle$ contains complex numbers, so to get positive-definite probabilities, its square is $\psi^*\psi = |\psi|^2 = \langle\psi|\psi\rangle$, where ψ^* denotes the complex conjugate of ψ.

The architecture of the ammonia molecule features the three hydrogen atoms lying in a plane, with the nitrogen atom found on either side of the hydrogen-atom plane, as in Fig. 4.
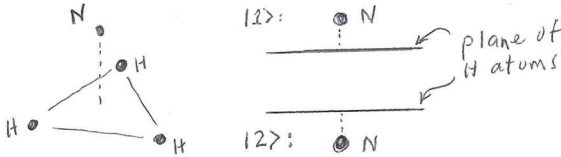
Figure 4. The structure of the ammonia molecule. The N atom can be on either side of the plane of hydrogen atoms. All figures by the author.

Let state $|1\rangle$ denote the molecule's state when the nitrogen atom is "above" the plane, and let $|2\rangle$ denote the state when the nitrogen lies "below" the plane. States $|1\rangle$ and $|2\rangle$ can be given the matrix representations of Eqs. (23a) and (23b), respectively. As a complete set of orthonormal vectors, $|1\rangle$ and $|2\rangle$ form a basis of any arbitrary state $|\psi\rangle$ that describes the location of the nitrogen atom relative to the plane of three hydrogens, so that

$$|\psi\rangle = \psi_1|1\rangle + \psi_2|2\rangle. \qquad (27)$$

The nitrogen molecule can jump across the plane of hydrogen atoms, from state $|1\rangle$ to state $|2\rangle$ or the reverse, or if in state $|1\rangle$ or $|2\rangle$ it may stay there. Let H be the

Hamiltonian for the nitrogen atom to either make a transition or remain in place. The probability amplitude for making the transition from state $|1\rangle$ to state $|2\rangle$ will be $\langle 2|H|1\rangle \equiv \beta$, where by symmetry $\langle 1|H|2\rangle = \beta$ as well; and let the probability amplitude for the nitrogen atom staying on one side of the plane of hydrogen atoms be $\langle 2|H|2\rangle = \langle 1|H|1\rangle \equiv \alpha$. The evolution of the nitrogen atom's behavior is described by the Schrödinger equation,

$$H|\psi\rangle = -\frac{\hbar}{i}\frac{\partial|\psi\rangle}{\partial t}, \qquad (28a)$$

or, with the matrices written out explicitly,

$$\begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = -\frac{\hbar}{i}\begin{pmatrix} \partial\psi_1/\partial t \\ \partial\psi_2/\partial t \end{pmatrix} \qquad (28b)$$

[compare to Eq. (10)], which splits into a pair of coupled equations:

$$\alpha\psi_1 + \beta\psi_2 = -\frac{\hbar}{i}\frac{\partial\psi_1}{\partial t} \qquad (28c)$$

and

$$\beta\psi_1 + \alpha\psi_2 = -\frac{\hbar}{i}\frac{\partial\psi_2}{\partial t}. \qquad (28d)$$

Other than the names of the variables and the order of the time derivative, Eqs. (28c) and (28d) describe *essentially the same system as the coupled oscillators of Eqs. (2).* Therefore, in following the same procedure (forming the sums and differences of ψ_1 and ψ_2, solving the problem for those combinations, and then inverting) and with the initial condition $\psi_1(0) = 1$ and $\psi_2(0) = 0$, we find

$$\psi_1(t) = e^{-i\alpha t/\hbar}cos\left(\frac{\beta t}{\hbar}\right) \qquad (29a)$$

$$\psi_2(t) = ie^{-i\alpha\ /\hbar}sin\left(\frac{\beta t}{\hbar}\right). \qquad (29b)$$

Consequently, the probabilities P_1 and P_2 of the nitrogen atom being in state $|1\rangle$ and state $|2\rangle$, respectively, are

$$P_1 = |\psi_1|^2 = \cos^2\left(\frac{\beta t}{\hbar}\right) \tag{30a}$$

$$P_2 = |\psi_2|^2 = \sin^2\left(\frac{\beta t}{\hbar}\right). \tag{30b}$$

Notice that $P_1 + P_2 = 1$ at all times, as required if the nitrogen atom is to remain part of the ammonia molecule. But it will be observed from Eqs. (30) that P_1 and P_2 are time dependent—ψ_1 and ψ_2 are not "stationary states." Figure 5 shows plots of $P_1(t)$ and $P_2(t)$ as functions of time. The probabilities oscillate with a period $T = \frac{\pi\hbar}{\beta}$.
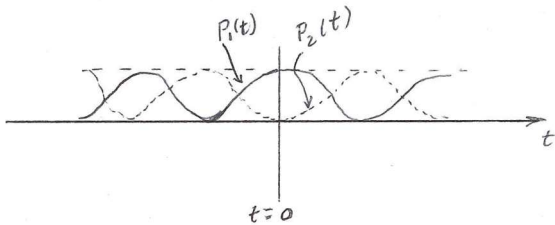
Figure 5. Illustration of the $P_1(t)$ and $P_2(t)$ states.

Figure 6 shows the same information in another way: "clouds" or "balloons" that contain the probabilities for the nitrogen atom being in state $|1\rangle$ or state $|2\rangle$ at different times.
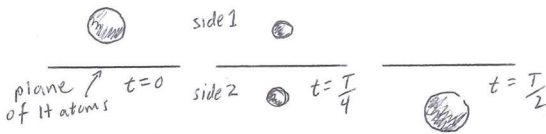
Figure 6. Illustration of how the probability of the nitrogen atom being above or below the plane of hydrogen atoms varies in time through one period. The shaded regions indicate a relatively high probability of locating the N atom.

At the risk of being repetitive, because the probability oscillates, the states ψ_1 and ψ_2 are not stationary states—i.e., not eigenstates, not normal modes of the nitrogen atom's motion in the NH$_3$ molecule. Let's find those eigenstates!

To find the eigenstates $|\psi_\omega\rangle$ of the nitrogen molecule in this system, we seek states with harmonic time dependence,

$$|\psi_\omega\rangle = \begin{pmatrix} A_1 \\ A_2 \end{pmatrix} e^{-i\omega t} \equiv |A\rangle e^{-\frac{iEt}{\hbar}} \tag{31}$$

(compare to Eq. (14), where

$$E = \hbar\omega, \tag{32}$$

and $|A\rangle$ is time independent; therefore $|\langle\psi_\omega|\psi_\omega\rangle|^2$ is time independent. The probability distributions for these states remain constant in time—analogous to how the normal-mode oscillations of the coupled oscillator remain steady in time, or how a single standing wave mode in musical acoustics does not change.

To proceed, insert the *ansatz* of Eq. (31) into the Schrödinger equation, Eq. (28a), to obtain

$$\begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}|A\rangle = E|A\rangle \tag{33a}$$

or

$$\begin{pmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{pmatrix}|A\rangle = |0\rangle. \tag{33b}$$

To obtain nontrivial solutions, set the determinant of the square matrix equal to zero, which gives

$$E = \alpha \pm \beta \equiv E_\pm . \tag{33c}$$

A radiative transition between these two eigenstates, with their energy difference $E_+ - E_- = 2\beta \sim 10^{-4}$ eV, produces photons in the microwave portion of the electromagnetic spectrum [5]. This energy gap is responsible for the population inversion in the ammonia maser.

Having found the eigenvalues, we turn to the eigenstates. We start with $E_+ = \alpha + \beta$. Upon inserting this into Eq. (33a), we find for its corresponding normalized eigenstate,

$$|\psi_+\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} e^{-i(\alpha+\beta)t/\hbar}. \tag{34a}$$

Similarly, for the eigenvalue $E_- = \alpha - \beta$, we find for its eigenstate

$$|\psi_-\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} -1 \\ 1 \end{pmatrix} e^{-i(\alpha-\beta)t/\hbar}. \tag{34b}$$

You can easily verify that these eigenstates are orthonormal and satisfy the completeness relation for all t:

$$|\psi_+\rangle\langle\psi_+| + |\psi_-\rangle\langle\psi_-| = \tilde{1}. \tag{35}$$

Notice (and this was the point of finding eigenstates) that the respective probabilities of finding the nitrogen atom in $|\psi_+\rangle$ or state $|\psi_-\rangle$ are constant in time:

$$P_+ = \left[\langle\psi_+|\psi_+\rangle\right]^2 = \frac{1}{2} \text{ and } P_- = \left[\langle\psi_-|\psi_-\rangle\right]^2 = \frac{1}{2}.$$

(The fact that P_+ and P_- happen to be the same merely reflects the symmetry of the nitrogen atom's placement above or below the plane of hydrogen atoms.) Thus the "clouds of probability" remain the same for the eigenstates for all times (Fig. 7); they are analogous to the electron orbitals in the hydrogen atom.
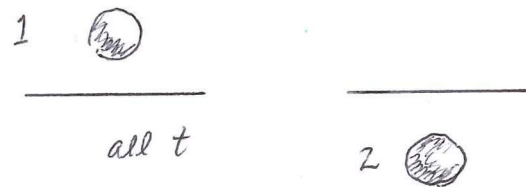
Figure 7. Shapes that enclose the probability of the nitrogen atom's whereabouts when it's in a stationary state.

Since the original $|1\rangle$, $|2\rangle$ vectors form a complete set, the eigenstates can be expressed as a superposition of them:

$$|\psi_+\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} e^{-i(\alpha+\beta)t/\hbar}$$

$$= \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)e^{-i(\alpha+\beta)t/\hbar}, \qquad (36a)$$

and

$$|\psi_-\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} -1 \\ 1 \end{pmatrix} e^{-i(\alpha+\beta)t/\hbar}$$

$$= \frac{1}{\sqrt{2}}(-|1\rangle + |2\rangle)e^{-i(\alpha-\beta)t/\hbar}. \qquad (36b)$$

If we think of $|1\rangle$ as the *x*-axis $\hat{\imath}$ and $|2\rangle$ as the *y*-axis $\hat{\jmath}$ basis vectors in a two-dimensional abstract "state space," then by Eqs. (36) the transformation from the $\{|1\rangle, |2\rangle\}$ basis to the $\{|\psi_+\rangle, |\psi_-\rangle\}$ basis corresponds to a clockwise rotation through 45° (Fig. 8).
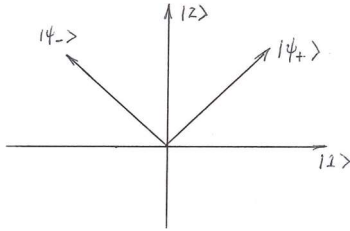
Figure 8. A change of basis as a rotation of axes.

The Hamiltonian matrix in the $\{|1\rangle, |2\rangle\}$ basis had nonzero off-diagonal terms. If we rewrite the Hamiltonian matrix in the eigenvector $\{|\psi_+\rangle, |\psi_-\rangle\}$ basis, then H becomes diagonal and the diagonal elements are the eigenvalues. Let's see how this feature emerges.

Any set $\{|n\rangle\}$ of orthonormal basis vectors (eigenvectors or otherwise) respects the completeness relation, for which

$$\tilde{1} = \sum_n |n\rangle\langle n|. \qquad (37)$$

Any vector $|\psi\rangle$ in the space can be expressed as a superposition of basis vectors. To carry this out, multiply the completeness relation from the right by $|\psi\rangle$:

$$|\psi\rangle = \sum_n |n\rangle\langle n|\psi\rangle$$

$$= \sum_n c_n |n\rangle \qquad (38)$$

where

$$c_n \equiv \langle n|\psi\rangle. \qquad (39)$$

The state vector $|\psi\rangle$ has now been projected onto the $\{|n\rangle\}$ basis set. Such a projection can also be done with the Hamiltonian matrix, as in Feynman's ammonia molecule problem. First, recall that in the notation for a matrix element such as H_{rc}, the first index *r* identifies the row and the second index *c* identifies the column in which the matrix element stands. Notice from the Hamiltonian matrix of Eq. (28b), expressed in the context of a $|1\rangle, |2\rangle$ basis, that

$$\langle 1|H|1\rangle = (1 \quad 0) \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \alpha = H_{11} \qquad (40a)$$

$$\langle 1|H|2\rangle = (1 \quad 0) \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \beta = H_{12} \qquad (40b)$$

and so on. More generally, for any basis vectors $|n\rangle$ and $|n'\rangle$ that belong to the same complete set,

$$H_{nn'} = \langle n|H|n'\rangle. \qquad (41)$$

So the matrix representation of the Hamiltonian in the $\{|\psi_+\rangle, |\psi_-\rangle\}$ basis is

$$\begin{pmatrix} \langle\psi_+|H|\psi_+\rangle & \langle\psi_+|H|\psi_-\rangle \\ \langle\psi_-|H|\psi_+\rangle & \langle\psi_-|H|\psi_-\rangle \end{pmatrix} \equiv \begin{pmatrix} H_{++} & H_{+-} \\ H_{-+} & H_{--} \end{pmatrix}. \qquad (42a)$$

Working out the four matrix elements gives a diagonal representation with the eigenvalues on the diagonal:

$$\begin{pmatrix} H_{++} & H_{+-} \\ H_{-+} & H_{--} \end{pmatrix} = \begin{pmatrix} \alpha + \beta & 0 \\ 0 & \alpha - \beta \end{pmatrix}. \qquad (42b)$$

In general, the transformation from a representation of a matrix M in one basis set $\{|n\rangle\}$ to its representation M' in another basis set $\{|\gamma\rangle\}$ is a "similarity transformation," which can be efficiently developed by inserting the unit matrix twice, in the form of the completeness relation:

$$M'_{\gamma\gamma'} = \langle \gamma|M|\gamma'\rangle$$

$$= \langle \gamma|\tilde{1}\, M\, \tilde{1}\,|\gamma'\rangle$$

$$= \langle \gamma|\sum_n |n\rangle\langle n|\, M\, \sum_{n'}|n'\rangle\langle n'|\gamma'\rangle$$

$$= \sum_{n,n'} \langle\gamma|n\rangle M_{nn'}\langle n'|\gamma'\rangle, \qquad (43a)$$

or, more succinctly, for the matrices themselves,

$$M' = \Lambda^\dagger M \Lambda, \qquad (43b)$$

where Λ denotes the matrix of transformation coefficients, $\Lambda_{n\gamma} = \langle n|\gamma\rangle$, and $\Lambda^\dagger$ denotes its Hermitian conjugate, the "adjoint" (the transpose and complex conjugate of Λ).

References
[5] Richard Feynman, Robert Leighton, and Matthew Sands, *The Feynman Lectures on Physics*, vol. III, chap. 9 (Reading, MA: Addison-Wesley, 1965).

Editor's note: This article was updated on Feb. 6, 2023, to correct formatting errors.