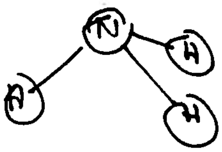
February 20

Two-Level Systems

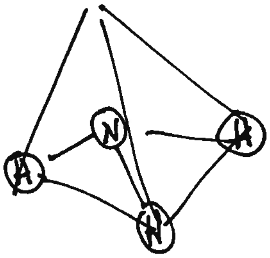
Real quantum mechanical system live in infinite-dimensional Hilbert spaces. However, very often, only a few directions in this space are important for the physical effect that we would like to study. In these cases, one can approximate the problem by choosing a finite basis of vectors that spans the relevant dimensions and considering only the finite-dimensional subspace spanned by these vectors. The very simple case arises very often in which only a two-dimensional space is important. In this lecture, I will describe two such system, one chosen specifically to illustrate the principle, and another that might surprise you.

The first example is the ammonia molecule. The physics of the ammonia molecule are described in a wonderful lecture in Volume III of the Feynman Lectures in Physics, from which much of this discussion is borrowed.

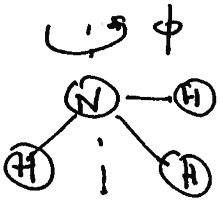
This molecule NH_3 has the form of a triangular pyramid



with a bond length of 1 Å and an angle between bonds of 108°. This is close to the expectation for a tetrahedron with the N at the center and the three H's at the three vertices of the base.

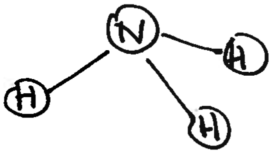


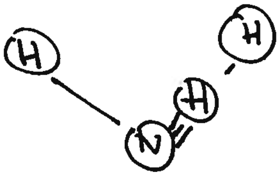
The ammonia molecule has many degrees of freedom, corresponding to fluctuations of directions and lengths of all of the bonds. The typical energy for exciting these degrees of freedom is eV. The molecule can also be rotated about its axis. The rotational states are described by wavefunctions of the angle ϕ



These wavefunctions are of the form $\psi(\phi) \sim e^{im\phi}$. States with $m \neq 0$ have an energy of excitation of the order of 0.01 eV. Finally, we find two states with $m = 0$ that are degenerate up to a very small effect.

There are actually two $m = 0$ states, one with the N above the plane of the H atoms, the other with the N below.





There is a quantum transition in which the N pushes through the plane of H's and moves from the top to the bottom or vice versa. To study this, we can concentrate on the two-dimensional space spanned by these two two states, which I will call

$$|\uparrow\rangle \quad \text{and} \quad |\downarrow\rangle$$

These states have equal expectation value of the Hamiltonian, by symmetry

$$\langle\uparrow|H|\uparrow\rangle = \langle\downarrow|H|\downarrow\rangle = E_0$$

The Hamiltonian must also have matrix elements between the two states. We can see this by noting that the equations of motion of these states have the form

$$i\frac{d}{dt}|\uparrow\rangle = E_0|\uparrow\rangle - \Delta|\downarrow\rangle$$

$$i\frac{d}{dt}|\downarrow\rangle = E_0|\downarrow\rangle - \Delta|\uparrow\rangle$$

These equations have the form of the Schrödinger equation

$$i\frac{d}{dt}|\psi(t)\rangle = H|\psi(t)\rangle$$

with

$$H = \begin{pmatrix} E_0 & -\Delta \\ -\Delta & E_0 \end{pmatrix}$$

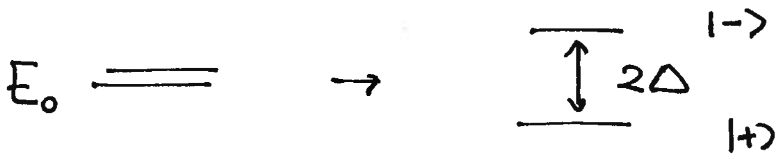
I have given the matrix element Δ a negative sign, but you can check that the physics would be the same if this sign were $+$.

It is easy to recognize the eigenvectors of this Hamiltonian. The eigenvectors and eigenvalues are

$$|+\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\rangle + |\downarrow\rangle\right) \qquad E_+ = E_0 - \Delta$$

$$|-\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\rangle - |\downarrow\rangle\right) \qquad E_- = E_0 + \Delta$$

The energy difference between these states is 2Δ.



The transition from one of these states to the other can be driven by an oscillating electric field with frequency

$$f = 23.79 \text{ GHz} \qquad \lambda = 1.26 \text{ cm}$$

corresponding to ($\hbar = 6.58 \times 10^{-16}$ eV-sec)

$$2\Delta = 2\pi\hbar f = 0.98 \times 10^{-4} \text{ eV}$$

The frequency difference $2\Delta/\hbar$ is similar to the beat frequency between two harmonic oscillators. If we start in the state $|\uparrow\rangle$,

$$|\uparrow\rangle = \frac{1}{\sqrt{2}}\left(|+\rangle + |-\rangle\right)$$

the time evolution of this state is

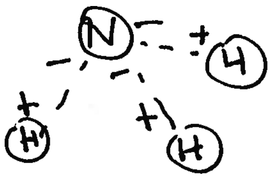
$$|\uparrow(t)\rangle = \frac{1}{\sqrt{2}}\left[|+\rangle e^{-i(E_0-\Delta)t/\hbar} + |-\rangle e^{-i(E_0+\Delta)t/\hbar}\right]$$

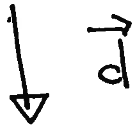
$$= e^{-iE_0t/\hbar}\left[|\uparrow\rangle \cos\frac{\Delta t}{\hbar} + i\,|\downarrow\rangle \sin\frac{\Delta t}{\hbar}\right]$$

The N atoms oscillates between the $|\uparrow\rangle$ and $|\downarrow\rangle$ positions. A state that is initially $|\uparrow\rangle$ comes back to $|\uparrow\rangle$—up to a phase, which is irrelevant—after a time

$$t = \frac{\pi\hbar}{\Delta} = 2\pi\frac{\hbar}{2\Delta}$$

Ammonia has an electric dipole moment. Electrons have a lower energy when they are close to the N atom, leading to a polarization





This means that ammonia molecules can be oriented by an electric field. Let $\vec{E} = E\hat{z}$ be the electric field. Then the presence of this electric field adds a term to the Hamiltonian

$$H = -\vec{E}\cdot\vec{d}$$

On the states $|\uparrow\rangle$ and $|\downarrow\rangle$,

$$H|\uparrow\rangle = +Ed \qquad H|\downarrow\rangle = -Ed$$

The total Hamiltonian is now

$$H = \begin{pmatrix} E_0 + Ed & -\Delta \\ -\Delta & E_0 - Ed \end{pmatrix}$$

It is not difficult to imagine how the eigenstates and eigenvalues vary as a function of E as E is varied from $-\infty$ to ∞. For E large and negative, the eigenvectors and eigenvalues are

$$|\psi_1\rangle \approx |\uparrow\rangle \quad E_1 \approx E_0 - |E|d$$

$$|\psi_2\rangle \approx |\downarrow\rangle \quad E_2 \approx E_0 + |E|d$$

For $E = 0$, we found above

$$|\psi_1\rangle = |+\rangle \qquad E_1 = E_0 - \Delta$$

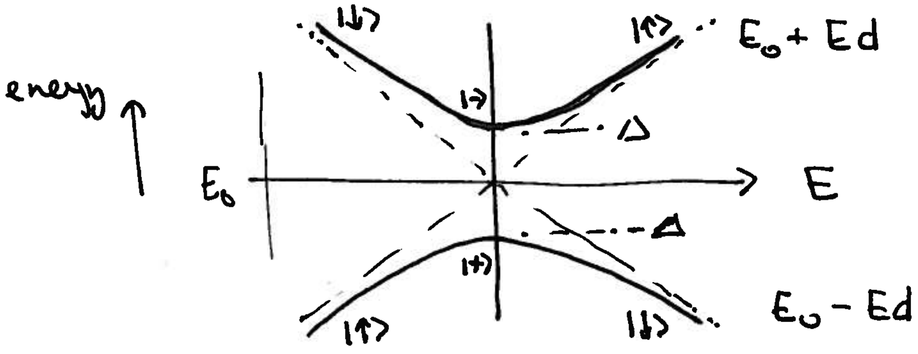
$$|\psi_2\rangle = |-\rangle \qquad E_2 = E_0 + \Delta$$

For E large and positive, we have

$$|\psi_1\rangle \approx |\downarrow\rangle \qquad E_1 \cong E_0 - Ed$$

$$|\psi_2\rangle \approx |\uparrow\rangle \qquad E_2 \cong E_0 + Ed$$

Joining these cases smoothly, we find the picture



In a previous lecture, I gave the exact eigenvalues of a 2 × 2 matrix. In this case, the formula gives

$$E_{1,2} = E_0 \pm \left[(Ed)^2 + \Delta^2 \right]^{\frac{1}{2}}$$

So the eigenvalues follow precisely the hyperbolas indicated in the figure.

Notice that the upper and lower energy levels approach each other but do not cross. This phenomenon of *level repulsion* is a general property of eigenvalue problems. Essentially, as two levels approach one another, they take advantage of any available off-diagonal terms to avoid crossing. Levels cross only when all of these off-diagonal terms are zero, for example, when the two states carry different values of conserved quantum numbers.

Consider, then, starting with an ammonia molecule in a large negative E field, in the state $|\uparrow\rangle$ that is the ground state in this situation. What happens if we change the value of E so that, at the end, it is large and positive? There are two different limits, and they lead to opposite results. On one hand, we can change the value of E very quickly, faster than the atomic dynamics can respond. The precise criterion is

$$\frac{\dot{E}}{E} \gg \frac{\Delta}{\hbar}$$

This is called the *sudden approximation.* In this case, we take the initial state $|\uparrow\rangle$ and expand it in eigenstates of the final Hamiltonian. If the final E is large and positive, we find

$$|\uparrow\rangle \longrightarrow |\uparrow\rangle \qquad E = E_0 + Ed$$

The opposite limit

$$\frac{\dot{E}}{E} \ll \frac{\Delta}{\hbar}$$

is called the *adiabatic approximation.* In this limit, E is changed through zero extremely slowly, and the atomic states have time to readjust at every step. In this case, it can be shown, each eigenstate of H follows the evolution of its energy level and does not make a transition to any other state. Then, in the adiabatic limit,

$$|\uparrow\rangle \rightarrow |\downarrow\rangle \qquad E = E_0 - \Delta d$$

Let's now turn to another example well described by a 2-state system, the simple molecule H_2^+. This is a system with one electron and two protons.

The interactions of electrons and nuclei in molecules can be approximated in the following way: The electrons and nuclei exchange momentum, and so

$$m_e v_e \approx m_p v_p$$

This implies that

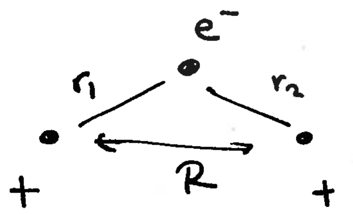
$$\frac{v_p}{v_e} \sim \frac{m_e}{m_p} \sim \frac{1}{2000}.$$

that is, the nuclei move very slowly compared to the electrons. It is then a good approximation to consider the nuclei as fixed, and solve the Schrödinger equation for the electrons in the fixed electrostatic field of the nuclei. If the electrons are in the ground state for on set of nuclear positions, the nuclei move adiabatically, and so the electrons remain in the ground state as the nuclei move to other positions. The energy of the electronic ground state then provides a potential that governs the motion of the nuclei. In fact, the quantum states of the heavy nuclei are well localized in the minima of this potential. This approximation, called the *Born-Oppenheimer approximation*, is the basis for calculations of the structure of molecules.

In the system H_2^+, we can start from a problem in which the two protons are separated by a distance R. The energy of the electron is an eigenvalue of the Schrödinger equation

$$E\psi = H\psi = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 R}$$

where r_1 and r_2 are the distances of the electron from the two protons



If the proton 2 is taken off to infinity, the ground state is the 1S state around the proton 1 and has an energy $E = -Ry$. If the proton 1 is taken off to infinity, the ground state is the 1S state around the proton 2. It makes sense, then, to approximate the ground state for any R as a linear combination of these two states, which I will call $|1\rangle$ and $|2\rangle$

By symmetry

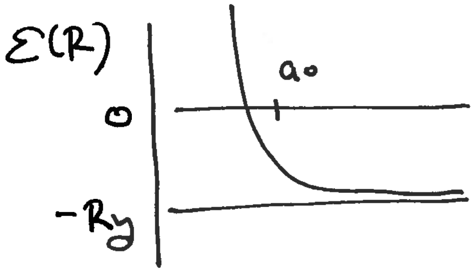
$$\langle 1|H|1\rangle = \langle 2|H|2\rangle$$

Actually, the states $|1\rangle$ and $|2\rangle$ are not quite orthogonal. We should orthogonalize them, in such a way that this equation remains true. This nicety will not affect the qualitative argument below.

The matrix element

$$\langle 1|H|1\rangle = \langle 2|H|2\rangle = \mathcal{E}(R)$$

has the following form as a function of R:

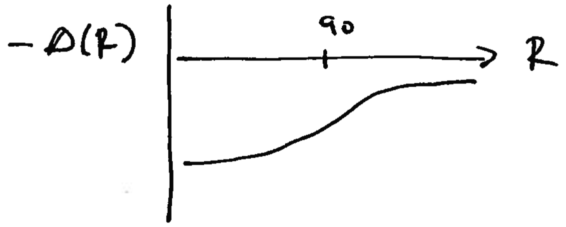


As $R \to \infty$, the value of $\mathcal{E}(R)$ goes to $(-Ry)$. For $R < a_0$, the Bohr radius, the proton 2 penetrates the electron wavefunction around the proton 1 and is repelled by that proton's positive charge.

There is another nonzero matrix element

$$\langle 1|H|2\rangle = \langle 2|H|1\rangle = -\Delta(R)$$

This is longer-ranged in R, with the form

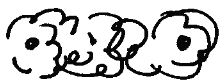


The matrix element turns out to be negative by explicit calculation, but the sign is not important for the effect that I will describe in a moment. The Hamiltonian of the electron in the two-state approximation is then

$$H = \begin{pmatrix} \varepsilon(R) & -\Delta(R) \\ -\Delta(R) & \varepsilon(R) \end{pmatrix}$$

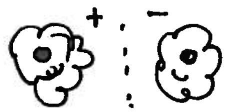
The eigenvectors and eigenvalues of this Hamiltonian are

$$|+\rangle = \frac{1}{\sqrt{2}}\left(|1\rangle + |2\rangle\right)$$



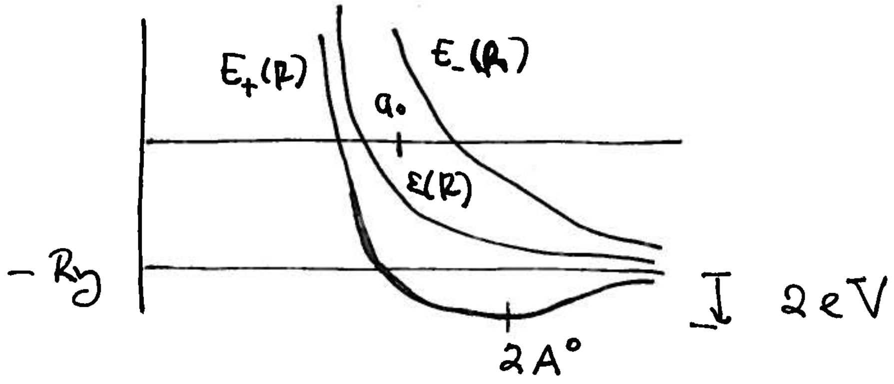
$$E_+ = \varepsilon(R) - \Delta(R)$$

$$|-\rangle = \frac{1}{\sqrt{2}}\left(|1\rangle - |2\rangle\right)$$



$$E_- = \varepsilon(R) + \Delta(R)$$

As a function of R, the energies of these states behave as

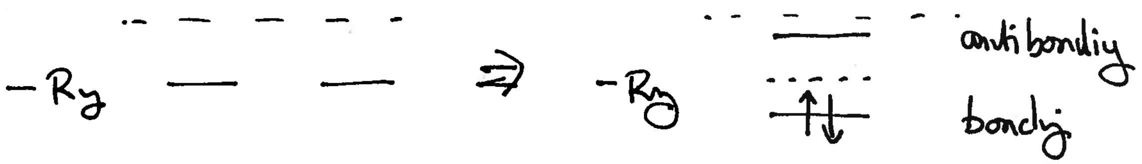


The energy $E_+(R)$ has a minimum as a function of R, at a value less than $(-Ry)$. A system of two protons and an electron with this separate has a lower energy than a system of a Hydrogen atom and a proton well separated from it. The minimum then describes a bound state of the two protons. This is exactly the H_2^+ molecule. The wavefunction $|+\rangle$ is called a *bonding orbital*. Conversely, the state $|-\rangle$, whose energy $E_-(R)$ is always higher than $\mathcal{E}(R)$, is called an *anti-bonding orbital*. Since

$$\frac{1}{2}(E_+ + E_-) = \mathcal{E}(R)$$

and $\mathcal{E}(R)$ is very flat as a function of R for $R > a_0$, it is easy for the lower eigenvalue $E_+(R)$ to drop below $(-Ry)$.

For the system of two protons and two electrons, there is a similar story. For the electrons, the lowest energy levels are the bonding and anti-bonding orbitals similar to those of the one-electron problem. The ground state is found by putting the two electrons, with opposite spins, into the bonding orbital.



This gives the H_2 molecule. This is a prototypical example of a chemical bond.

It is amazing that the phenomenon of chemical bonding, which is almost incomprehensible in classical physics, follows in such a simple way using the principles of quantum mechanics.