Quantum Analogs
Chapter 3
Student Manual

Broken Symmetry in the Spherical Resonator

and

Modeling a Molecule

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3. Broken symmetry in the spherical resonator and modeling a molecule

3.1 Lifting the degeneracy of states with different magnetic quantum numbers

Objective: In this series of experiments we will break the symmetry of the spherical cavity and study the resulting splitting of the resonance peaks. This is analogous to the splitting of quantum states.

Equipment Required:

TeachSpin Quantum Analog System: Controller, Hemispheres, Accessories
Computer with sound card installed and Quantum Analogs "SpectrumSLC.exe" running
Two adapter cables (BNC - 3.5 mm plug)
Two-Channel Oscilloscope

> **WARNING:** The BNC-to-3.5-mm adapter cables are provided as a convenient way to couple signals between the Controller and sound card. Unfortunately, they could also provide a way for excessive external voltage sources to damage a sound card. *It is the user's responsibility to ensure that these adapter cables are NOT used with signals greater than 5 Volts peak-to-peak*. The maximum peak-to-peak value for optimum performance of the Quantum Analogs system depends on your sound card and can vary from 500 mV to 2 V.

Setup:

First, set the *ATTENUATOR* knob on the Controller at 10 (out of 10) turns.

Attach a BNC splitter or "tee" to *SINE WAVE INPUT* on the Controller. Using an adaptor cable, connect the output of your computer sound card to one side of the splitter. Use a BNC cable to send the sound signal to Channel 1 of the oscilloscope. Plug the lead from the speaker on the lower hemisphere to *SPEAKER OUTPUT* on the Controller. The same sine wave now goes to both the speaker and Channel 1.

Use a BNC cable to connect the microphone output from the upper hemisphere to *MICROPHONE INPUT*. Connect *AC MONITOR* on the Controller to Channel 2 of the oscilloscope to display the sound signal received by the microphone. Trigger the oscilloscope on Channel 1.

**Important Note: You will need to adjust the magnitude of both the speaker and microphone signals to keep the microphone input to the computer from saturating.
Refer to the Appendix 2, titled 'Recognizing and Correcting Saturation', for instructions.**

Experiment:

Measure a spectrum in the spherical resonator including only the lower three resonances.

Now put the 3 mm spacer ring between the upper and lower hemisphere. Measure the spectrum again. What do you observe?

Measure the spectrum again using the 6 mm spacer ring, and using both rings (9 mm).

Analyze the data:

For the $l = 1$ resonance, you can now plot the frequency splitting as function of spacer ring thickness. What relationship do you find?

Background:

In a spherical resonator, each resonance with angular quantum number l is $(2l+1)$-fold degenerate. These states with quantum numbers $m = -l, \ldots, 0, \ldots, l$ all have the same resonance frequency. In the spherical resonator, we have seen that the quantization axis (z-axis) is determined by the position of the speaker. The only wavefunction that has a non-zero amplitude on the z-axis is the one with $m = 0$. This is the reason why the $m = 0$ resonance is exited in the sphere, exclusively.

When a spacer ring is introduced, the spherical symmetry is broken and the degeneracy of the eigenstates is lifted. The quantization axis (z-axis) is now determined by the symmetry axis of the resonator, which is the vertical axis. The speaker, which has a $\theta=45°$ position with respect to the symmetry axis, can now excite all states with different quantum numbers m. The sketches in Figure 3.1 will help you to visualize the change in the direction of the quantization axis.
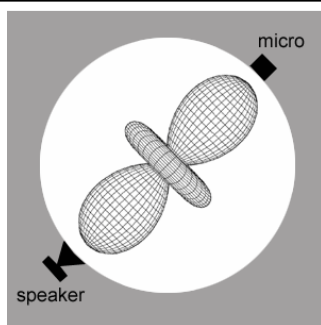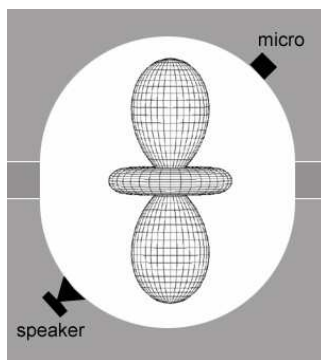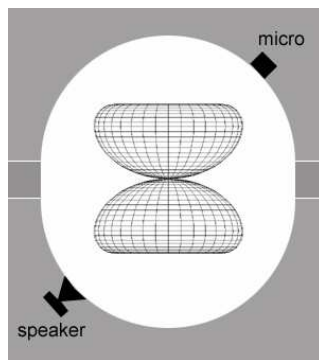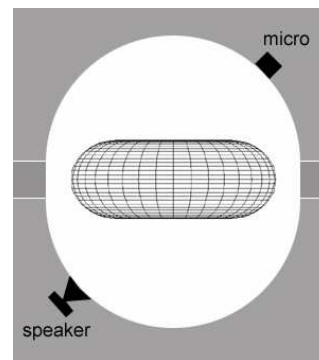

Fig. 3.1a: In the spherical resonator, the quantization axis is determined by the position of the speaker because it is the only part that breaks symmetry.

$m = 0$ $m = 1$ $m = 2$

Fig. 3.1b: In the resonator elongated by spacer rings, the quantization axis is given by the symmetry axis of the resonator. The degeneracy of the states with different m is lifted.

The degeneracy is not lifted completely because the states with positive and negative magnetic quantum number ±m are still degenerate. States with positive and negative m belong to waves in the resonator circulating around the quantization axis in right-handed and left-handed directions, respectively. Both of these waves are excited by the speaker and have the same amplitude for each m. A superposition of such two waves results in a standing wave with respect to the azimuthal angle φ.

$$e^{im\varphi} + e^{-im\varphi} = 2\cos(m\varphi) \tag{3.1}$$

In quantum chemistry, the superposition of the positive and negative versions of the magnetic quantum number m is used to form orbitals. Examples of the way these are labeled are: p_x, p_y, d_{xz}, d_{yz} for $m=1$ and d_{xy}, $d_{x^2-y^2}$ for $m=2$.

In the sense of perturbation theory, the eigenfunctions in broken symmetry are modified only slightly compared to the eigenfunctions of the spherical symmetric case, as long as the perturbation is small. We can therefore expect wavefunctions very similar to the spherical harmonics.

In the next experiments you can measure the azimuthal dependence of the wavefunctions and identify the magnetic quantum number of the peaks.

Experiment:

Using in turn the 3 mm, 6 mm and 9 mm spacer rings, acquire a high-resolution spectrum of the $l = 1$ resonance that resolves the two peaks attributable to $m = 0$ and $m = \pm 1$.

Experiment:

Now we will measure the amplitude as function of the azimuthal angle φ. We will then identify which m belongs to each peak. Click the left mouse button on top of a peak to choose this particular frequency. Then, open the window to measure the wavefunction > Windows > Measure Wave Function). Check the box labeled "Lifted degeneracy" to tell the program that the quantization axis is now vertical and that the angle α on the scale is equal to the azimuthal angle φ. In this mode the wavefunction is displayed in green.

Now you can measure the amplitude of the peak as function of azimuthal angle φ. Repeat the same measurement for the other peak. Use the oscilloscope to determine how changing the azimuth angle affects the sign of the microphone signal.

Alternatively, you can measure the amplitude by hand. Read the amplitude from the oscilloscope and the azimuthal angle $\varphi = \alpha$ from the scale.

Analyze the data:

Identify the magnetic quantum number for each of the peaks. Compare your results for the amplitude as function of φ with the theoretical prediction $A(\varphi) = \cos(m\varphi)$.

Experiment:

Choose the frequency of the $l = 1$ and $m = 0$ resonance and measure the phase of the microphone signal in the upper hemisphere at $\alpha = 180°$. Then, connect the cable to the microphone in the lower hemisphere and measure the phase again. Repeat the same experiment with the $m = 1$ resonance.

Experiment:

Measure a highly resolved spectrum with 3 mm, 6 mm and 9 mm spacer rings of the $l = 2$ resonance. It will split into three peaks with $m = 0$, $m = \pm 1$ and $m = \pm 2$.

Experiment:

For each of the three peaks, measure the amplitude as function of azimuthal angle φ and identify the magnetic quantum numbers.

Experiment:

You may measure the splitting of states with higher l, but the increasing overlapping of several peaks with different magnetic quantum number makes an identification of m more and more difficult.

One possible way to overcome this problem is to measure spectra for all angles φ and use the peak fitting procedure to determine the peak amplitudes. With this technique the overlapping of the peaks becomes irrelevant.

Another possibility is to measure at certain angles φ for which nodes in the wavefunction are expected for particular magnetic quantum numbers. If one of the peaks in the spectrum disappears at the nodes of a certain magnetic quantum number, its number has been identified.

3.2 Modeling a molecule

Objective: We will use a pair of spheres to create an analog of a hydrogen molecule.

Equipment needed:

TeachSpin Quantum Analogs System: Controller, 4 hemispheres, irises
Computer with sound card installed and Quantum Analogs "SpectrumSLC.exe" running
Two-Channel Oscilloscope
Two BNC – 3.5 mm plug adaptors

Setup:

Set a hemisphere with a hole on top of the hemisphere with the speaker. Through this hole, the sound in the lower sphere will couple to a second sphere. The strength of the coupling can be adjusted by choice of the iris diameter. Choose one of the irises and put it in place. (Iris diameters are 5 mm, 10 mm 15 mm or 20 mm.) Set the hole in the next hemisphere against the iris.   Use the hemisphere with the microphone to complete the upper sphere.
Put BNC splitters on both the *SINE WAVE INPUT* and the *AC-MONITOR* of the Controller box. Using a BNC to 3.5 mm jack converter, connect the output of the computer's sound card to one side of the BNC splitter on *SINE WAVE INPUT*. Connect the other side to Channel 1 of the oscilloscope. Connect the speaker cable from the lower hemisphere to *SPEAKER OUTPUT* on the Controller. (The sound card signal now goes to both the speaker and the 'scope.)

Use a BNC cable to connect the microphone in the top-hemisphere to *MICROPHONE INPUT*.   Use a BNC cable to send the microphone signal from one side of the splitter on *AC-MONITOR* to Channel 2 of the oscilloscope.   Use an adaptor cable to connect the other arm of the splitter on *AC-MONITOR* to the microphone line-in of your sound card.

Important Note: You will need to adjust the magnitude of both the speaker and microphone signals to keep the microphone input to the computer from saturating. Refer to the Appendix titled 'Recognizing and Correcting Saturation' for instructions.

Experiment:

Measure a spectrum in the "molecule" (two coupled spherical resonators) of the resonance at 2300 Hz. Repeat the measurement with the different irises. Compare with a measurement of this peak in the "atom" (spherical resonator).

Open questions:

Why does the peak split?

What is lifting the degeneracy?

Which quantum numbers can we use to label the peaks in the molecule?

What do the molecular orbitals look like?

Let's answer these questions step by step.

Experiment:

Measure a spectrum in the frequency range from 0 Hz to 1000 Hz first in the "atom" and then in the "molecule". Repeat the measurement with the other irises.

Analyze the data: Make a plot of the resonance-frequency as function of iris diameter.

Experiment:

Use one of the bigger irises and choose exactly the frequency of the resonance. This can be done by clicking the left mouse-button on the top of the peak. For the upper sphere, measure the phase of the microphone signal (*AC-MONITOR* connected to Channel 2 of the oscilloscope) with respect to the *SINE WAVE INPUT* signal (Channel 1 of the oscilloscope). Now connect the microphone in the lower sphere to the amplifier and repeat the measurement.

Question:

What is the phase difference between upper and lower sphere?

Experiment:

In the upper sphere, you can measure the azimuthal dependence of amplitude to identify the symmetry of the wavefunction.
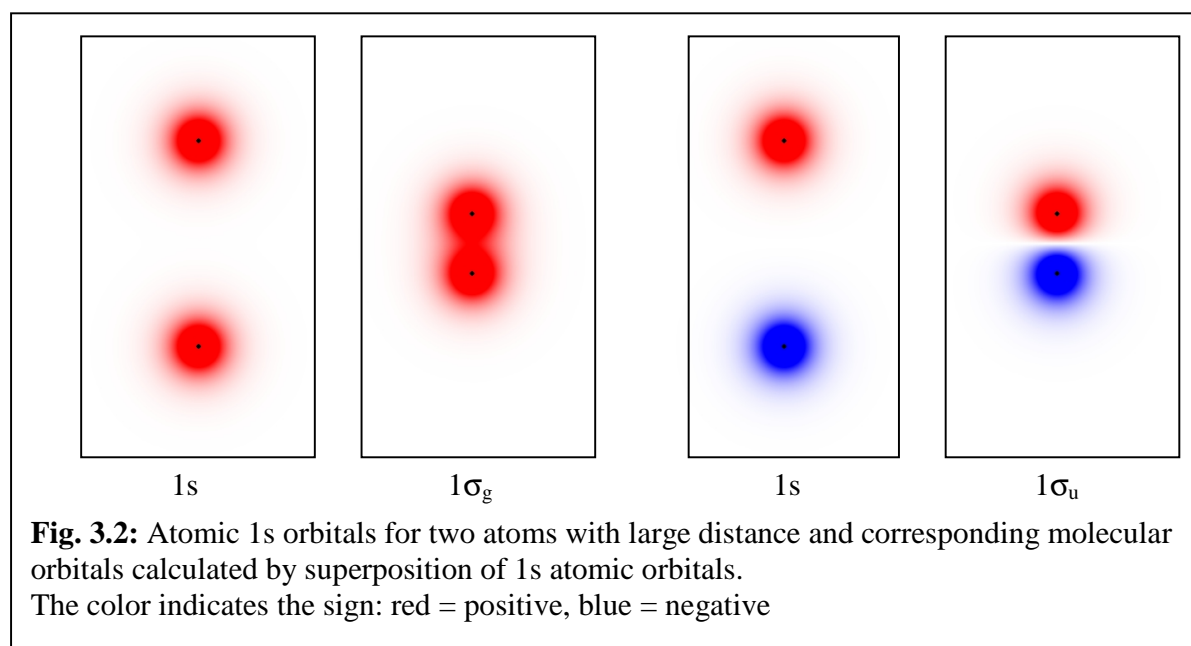:

Background:

The two, coupled spherical resonators model a diatomic molecule with two identical nuclei, a so-called homonuclear diatomic molecule. The simplest example of such a molecule is H_2^+. Since this molecule has only one single electron moving in the potential of two protons, it is an ideal model system to discuss quantum mechanical effects in molecules. Many of the observations can be transferred to molecules like H_2, O_2, N_2 and F_2.

Diatomic molecules have cylindrical symmetry with respect to the axis going through the nuclei. Due to this symmetry, we expect that m is a good quantum number for the molecule, just as it is in the atom. The quantum number l, however, cannot be used in molecules. In the sense of perturbation theory, we expect a continuous change from the atomic orbitals into the molecular orbitals as function of the nuclear distance. We will therefore label the molecular states additionally by the atomic states from which they are derived in square brackets (for example: $1\sigma_u[1s]$).

For a small coupling of the two atoms (a large inter-nuclear distance), a superposition of atomic orbitals is a fairly good approximation for the molecular orbitals. In general, the two atomic orbitals can be superimposed in two different ways to produce a molecular orbital: with the same sign or with different signs (phase shift 180°). Depending on the sign, the molecular orbital is labeled with an index: g for the German word gerade = even, when the signs are the same and u for the German word ungerade = odd, when the signs are different.

The quantum number m is labeled with Greek letters σ, π, and δ for $m = 0$, $m = 1$, and $m = 2$, respectively. This corresponds to the way the Latin letters s, p, d are used in the atom for the quantum number l. Additionally, a principal quantum number is used to number states with the same symmetry but with increasing energy. In this sense, the state $1\sigma_u[1s]$ describes a molecular orbital derived from two 1s atomic states that have been superimposed with different sign. It has the magnetic quantum number m = 0 and is the first state with this symmetry.

In the following figure, the molecular orbitals derived from 1s states are plotted.

1s $1\sigma_g$ 1s $1\sigma_u$

Fig. 3.2: Atomic 1s orbitals for two atoms with large distance and corresponding molecular orbitals calculated by superposition of 1s atomic orbitals.
The color indicates the sign: red = positive, blue = negative

Molecular orbitals with a high probability of finding the electron between the two nuclei are called bonding states, because they form a molecular bond. States that have a node between the nuclei, resulting in much lower electron density between the nuclei, are called anti-bonding. If they are occupied by electrons, it weakens the bond strength between two atoms. In the case shown in Fig. 3.2, as in most cases, the even state $1\sigma_g[1s]$ is bonding and the odd state $1\sigma_u[1s]$ is anti-bonding.

What is analogous, what is different?

In the acoustic analog, we have a situation very similar to that of the real molecule. The two, coupled spheres with same diameter correspond to the two identical nuclei that are coupled through the iris between them. The diameter of the iris determines the coupling strength, which corresponds to the internuclear distance of the real molecule. The symmetry is cylindrical, as it is in the real molecule. Therefore, we can use the same quantum numbers and labeling of states as in the real molecule. Due to different boundary conditions, and the absence of a potential, the eigenstates have a different order than in real molecules. The eigenstates can be identified experimentally by the "atomic" states from which they are derived by the quantum number m and by the phase of the wave function in the two spheres.

The eigenstate with a wave function that has no node at all (equal phase everywhere in space) has the frequency zero in the acoustic case. This is due to Neuman's boundary conditions that would result, for this case, in a constant amplitude of pressure everywhere. It cannot oscillate. In the case of a molecule this state is the $1\sigma_g[1s]$ state, the ground state of the H_2^+-molecule. It cannot be observed as resonance in the acoustic analog.

The state with lowest frequency in the acoustic analog is the $1\sigma_u[1s]$. It is derived from 1s states of the uncoupled "atoms", even though the 1s states of the uncoupled atoms cannot be observed because, for both, the frequency is zero. With increasing coupling strength, the frequency of this state increases, as you observed in the experiment above. Since the state is odd, the phase of the wave function has different sign in both spheres. You observed this on the oscilloscope when you measured the signal at the two different microphone locations in the two spheres. The state is a σ-state since the amplitude is constant as function of $\varphi = \alpha$ as you observed by rotating the top hemisphere. For higher m, the amplitude would show a dependence as $\cos(m\varphi)$.

π and δ orbitals

From atomic p orbitals, we derive molecular orbitals that can have magnetic quantum numbers m = 0 (σ) and $m = 1$ (π). Due to even and odd superposition, this results in four different molecular orbitals: σ_g , σ_u, π_g , π_u . In the case of atomic d-orbitals the number of derived molecular orbitals is six: σ_g , σ_u, π_g , π_u, δ_g , δ_u . The following figure shows the molecular orbitals along with the atomic orbitals they are derived from.
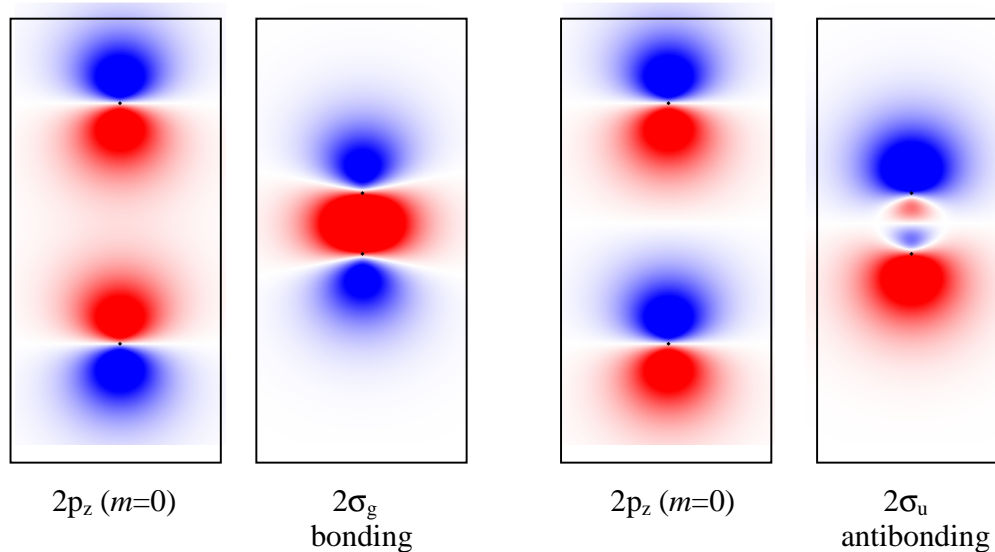
| $2p_z$ (*m*=0) | $2\sigma_g$ bonding | $2p_z$ (*m*=0) | $2\sigma_u$ antibonding |

Fig. 3.3a: Molecular σ-orbitals derived from the atomic 2p-orbital.

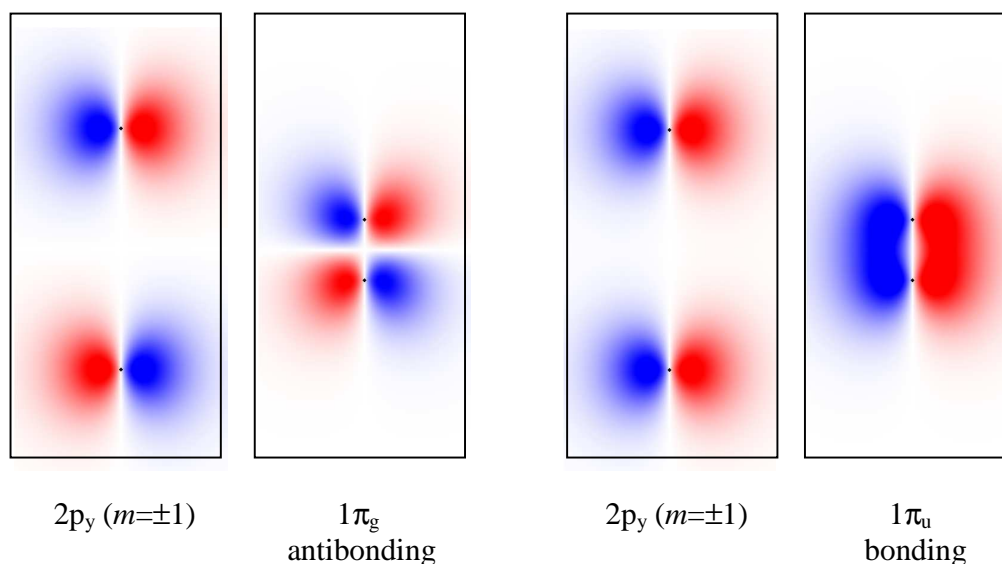| $2p_y$ (*m*=±1) | $1\pi_g$ antibonding | $2p_y$ (*m*=±1) | $1\pi_u$ bonding |

Fig. 3.3b: Molecular π-orbitals derived from the atomic 2p-orbital.

Experiment

Let us now investigate the molecular orbitals derived from the first atomic p-state that is observed at about 2300 Hz.

Measure a resonance spectrum in the "atom" for reference and then take a measurement in the "molecule". Use the 20 mm iris to produce the maximum splitting of the peaks.

Before measuring, press down firmly on top of the pile of hemispheres. Good contact is necessary to resolve peaks that are close to each other. You should scan slower than 50 ms/Hz.

Take spectra at different azimuthal angles.

Experiment

Now we want to identify the peaks in the spectra. In addition to the peak at about 2450 Hz there are *three peaks* around 2300 Hz, even though it looks like a double-peak structure.

You can measure the phase difference between the upper and lower spheres for the different peaks. Note that it is only in the $\alpha = 180°$ position that the microphone positions are equivalent for the upper and lower hemisphere. For all other α, you have to take the azimuthal dependence into account.

In the case of strongly overlapping peaks, it is difficult to measure the phase directly. Here you may observe how the amplitude develops as function of azimuth.