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Double Resonance Probes for Close Frequencies

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A new double resonance probe design for NMR experiments for systems with close resonance frequencies is introduced. The design is based on two coupled resonators and was extensively tested on magnetically aligned powders of several high temperature superconductors by performing double resonance experiments between the ^{65}Cu and ^{63}Cu isotopes as well as between transitions of different magnetic quantum number of the same spin. The probe's performance approaches that of a single resonance circuit and it has only 4 variable tuning/matching elements.

Key Words: **NMR; NQR; double resonance; hardware; probes.**

1. INTRODUCTION

Already in the early years of NMR, Pound (*1*) demonstrated the usefulness of double resonance (DR) techniques (on quadrupolar nuclei in solids). Since then numerous methods have been developed (for reviews see (*2–6*)).

Recently, we have introduced new double resonance techniques for resolution enhancement of quadrupolar nuclei (*7*) and showed their usefulness in the field of high temperature superconductors (*8*). These DR techniques involve transitions between neighboring Zeeman levels which are shifted by a strong quadrupolar interaction. For such experiments we needed a DR probe which is efficient for close frequencies. There are many other experiments which require a similar probe, e.g., spin echo double resonance (SEDOR) measurements between the two Cu isotopes in a variety of materials, or, between nuclei of different atoms which have similar resonance frequencies, e.g., Al and Na.

When both resonances of a DR probe have to be efficient, which basically means a high filling factor at both frequencies (*9*), designs with a single sample coil are superior to cross coil designs, in particular if the spatial variation of the radio frequency (RF) fields at both frequencies is important (e.g., for the Hartmann–Hahn condition). The concept of such designs is to build two resonant circuits which share the same sample coil and decouple both circuits by means of wave traps (which ideally represent a short at one frequency and an infinite impedance at the other frequency). Many variations of this design exist (*10, 11*), and problems are only caused by the available space (typically 6 variable impedances are needed), power handling, and spurious responses at higher frequencies (*12*). However, it is well known that such a probe design is not suitable for close frequencies since the finite bandwith of the traps prohibits easy tuning and matching.

We introduce a new concept for DR probe design which is based on coupled oscillators, an approach which is often employed in order to describe more involved coupled systems (e.g., coupled pendulums, chemical bonds). The coupling lifts the degeneracy of the two almost identical levels which acquire a frequency difference given by the strength of the coupling. The resulting two new normal modes are exploited in our probes. We discuss the basic principles of such probe design, show that they can be operated with the minimum set of variable impedances, are easily tuned and matched, and very suitable for close frequencies.

2. SIMPLE COUPLED CIRCUITS

Before we discuss three basic circuits with coupled oscillators we would like to address the mechanical analog of two coupled pendulums, Fig. 1.

The double pendulum has two normal modes of motion (symmetric and antisymmetric) where both pendulums move either in-phase or anti-phase. With the symmetry arguments shown in Fig. 1 we find the well known frequencies,

$$\omega_0^2 = \frac{g}{s}, \qquad \omega_+^2 = \frac{g}{s} + \frac{2K}{m}, \qquad [1]$$

where s denotes the length of each pendulum, K the spring constant, and m the mass of each pendulum. It is instructive for the discussion of the electric circuits to keep the properties of the coupled pendulums in mind. In particular, the choice of coupling for the two pendulums shown in Fig. 1 is responsible for the fact that one of the frequencies is the same as for the uncoupled case ω_0, whereas the second frequency ω_+ is shifted upwards.

Let us now consider some basic coupling schemes for two identical circuits, each consisting of a capacitor C and a parallel inductor L, i.e., with a resonance frequency

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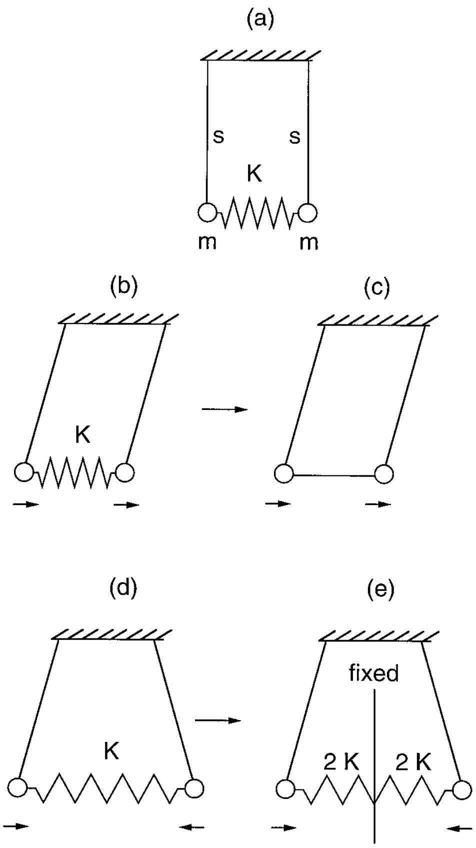

FIG. 1. (a) Two spring coupled identical pendulums. For in-phase motion (b) the spring K is not forced (c). For anti-phase motion (d) the center of the spring is at rest and K can be replaced by two springs with twice the stiffness, with the center fastened to a fixed wall (e).

$$\omega_0^2 = \frac{1}{LC}. \quad [2]$$

We start with the inductive coupling in Fig. 2a. If we denote the mutual inductance of both coils by M, then the circuit in Fig. 2a can be replaced by that in Fig. 2b. Now, for in-phase currents in both loops, Fig. 2c, no current flows through M and we can replace it with a ground connection. For anti-phase currents, Fig. 2d, twice the single loop current goes through M and we can replace M by two independent coils, each with inductance $2M$.

From Fig. 2 we find for the two modes the effective inductances $L' = L \pm M$, and the resonance frequencies,

$$\omega_-^2 = \frac{1}{(L+M)C}, \qquad \omega_+^2 = \frac{1}{(L-M)C}, \qquad \text{or}$$
$$\omega_\pm^2 = \omega_0^2 \frac{1}{1 \mp M/L}, \quad [3]$$

which are shifted downwards and upwards with respect to ω_0.

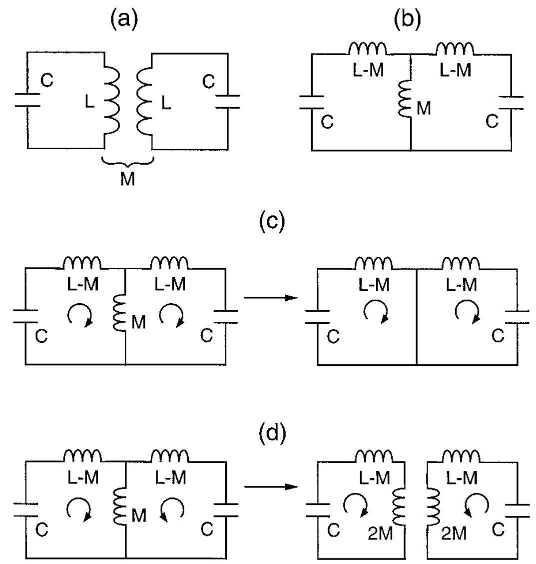

FIG. 2. (a) Two identical resonant circuits coupled by the mutual inductance M can be represented by the circuit (b). For in-phase currents (c) there is no current through M and we can replace it by a ground connection. For anti-phase currents (d) twice the current of a single loop flows through M and we can replace it by two independent inductances, each with $2M$.

Next we show in Fig. 3 a capacitively coupled circuit. With the symmetry arguments shown we conclude immediately for the resonance frequencies,

$$\omega_0^2 = \frac{1}{LC}, \qquad \omega_+^2 = \frac{C_c + 2C}{LCC_c}, \qquad \text{or} \qquad \omega_+^2 = \omega_0^2\left(1 + 2\frac{C}{C_c}\right). \quad [4]$$

We realize that the circuit in Fig. 3 corresponds to the pendulum of Fig. 1, in that the uncoupled frequency ω_0 is unchanged by the coupling and a higher frequency ω_+ appears.

As a last example we look at Fig. 4. This circuit follows from that in Fig. 3 by replacing the "T" capacitor network by

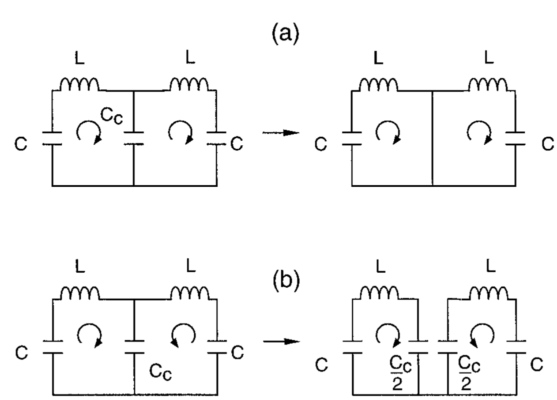

FIG. 3. Capacitor coupled circuit for (a) in-phase currents and (b) anti-phase currents.

a "Π" capacitor network. Again, from Fig. 4 we infer for the resonance frequencies

$$\omega_0^2 = \frac{1}{LC}, \qquad \omega_-^2 = \frac{1}{L(C + 2C_c)}, \qquad \text{or}$$

$$\omega_-^2 = \omega_0^2\left(\frac{1}{1 + 2C_c/C}\right). \qquad [5]$$

For this circuit the coupling introduces a second, lower frequency. (A mathematical description of the coupled systems shown in Figs. 1–3 can be found in Ref. (*13*).)

Of course, there are more possibilities in designing coupled circuits, e.g., by redistributing or dividing some of the lumped elements, or by adding additional L,C-combinations. The latter resembles methods for filter design, but has also been used in its extreme for the construction of an extremely broadband probe (*14*). While we were writing our manuscript Hu, Reimer, and Bell (*15*) have published a version of the two-coil design which is closely related to the circuit shown in Fig. 3.

3. OUR DOUBLE RESONANCE PROBE

If we want to use coupled circuits for our NMR probe we demand in addition to the mere frequency response a good filling factor, a homogeneous RF field, easy tuning, and easy adjustment of the driving impedance (matching). This leaves us with two questions: Which of the above circuits should one use for a double resonance probe? How should one match the circuit to the 50-Ω transmission line?

As to the first question, we abandoned the inductively coupled design of Fig. 2 since a reliable inductive coupling is problematic and it influences the RF homogeneity. Our decision between the two capacitively coupled circuits was based on our needs. Since we were predominantly interested in double resonance experiments between central and satellite transitions for quadrupolar nuclei, and we favored an easily adjustable lower frequency we chose the circuit in Fig. 4. Also, the coupling capacitor for the circuit in Fig. 4 is much smaller than that required for the circuit in Fig. 3. Therefore, it is easier to achieve a large tuning range with the setup of Fig. 4. In any case, we think it is very important

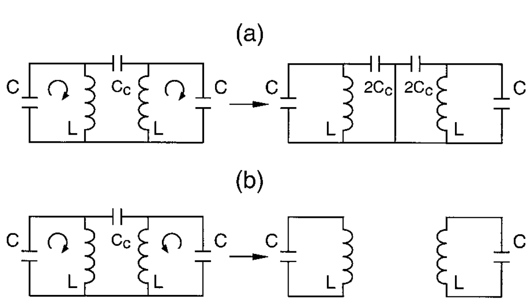

FIG. 4. Another capacitor coupled circuit for (a) in-phase currents and (b) anti-phase currents.

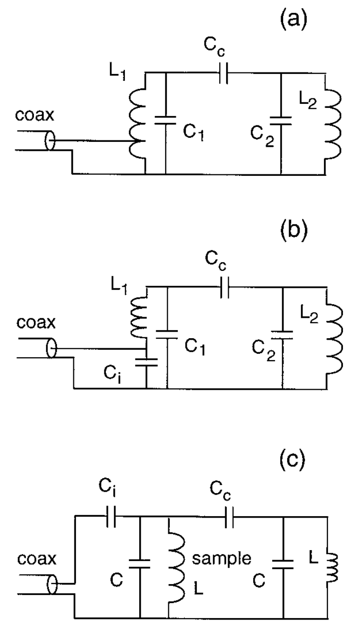

FIG. 5. Impedance matching for the circuit of Fig. 4. Inductive coupling (a) to one of the coils by means of voltage division provided by a tapped coil; capacitive voltage divider (b) with a large C_i; capacitive current divider (c) with a small C_i. For most of our experiments we used the circuit (c).

to use a circuit which leaves one frequency fixed. This way tuning and matching will be much easier.

As to the coupling of the circuit to the transmission line, many schemes are possible (capacitive or inductive at various parts of the circuit (*16*, *17*)). One has to remember, however, that the coupling to the two modes will depend on the symmetry, as well. For example, if one attempted to couple to the circuit in Fig. 4 by applying a voltage across C_c one would not excite the antisymmetric mode. We chose a design with a single connection from the 50-Ω system (single-point matching) since it enables us to use a single power-amplifier for both frequencies in the DR experiments.

In Fig. 5 we give some examples for single-point matching. For most of our experiments we have chosen the coupling circuit shown in Fig. 5c, therefore, we would like to discuss tuning and matching of this circuit in more detail.

For matching purposes we have to include losses in the system. For the frequency range of NMR one can in principle find capacitors such that all the losses in the above circuits are given by the resistive part of the impedance of the coil alone, typically represented by a series resistor r or a shunt resistor R to the coil. The quality factor of the coil is then given by $Q = \omega L/r = R/\omega L$ for low losses.

In the notation with a parallel resistor R, the input impedance of a simple parallel circuit shown in Fig. 6a can be written as

$$Z_0 = R\,\frac{1 + iQ(1 - \omega^2 LC)}{1 + Q^2(1 - \omega^2 LC)^2}. \qquad [6]$$

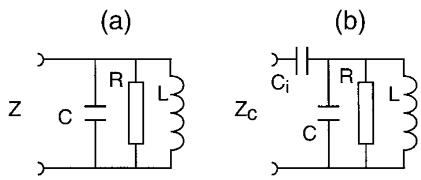

FIG. 6. Simple parallel circuit (a) and capacitively coupled circuit (b).

In order to match the circuit to the line, we add a matching capacitor C_i, cf. Fig. 6b, and obtain for the input impedance Z_c near resonance,

$$Z_c = \frac{1 + i2\epsilon Q}{\omega_-^2 C_i^2 R}, \qquad Z_c(\epsilon = 0) = \frac{L(C + C_i)}{C_i^2 R}, \qquad [7]$$

with

$$\epsilon = \frac{\omega - \omega_-}{\omega_-}, \qquad \omega_- = \frac{1}{\sqrt{L(C_i + C)}}, \qquad [8]$$

where ω_- is the new "resonant frequency" at which the impedance Z_c is purely resistive. It is somewhat smaller than the resonance frequency ω_0 of the simple parallel circuit.

As we derive in the Appendix, the single-point total input impedance Z_i for the coupled circuits in the arrangement of Fig. 5c is given by Eq. [A6],

$$Z_i = \frac{1}{i\omega C_i} + \frac{1}{2}(Z_0 + Z_-), \qquad [9]$$

where Z_0 and Z_- refer to the input impedance of a simple parallel circuit as in Eq. [6] with L, R, and the effective capacitances $C_0 = C$ and $C_- = C + 2C_c$ according to the replacement circuits shown in Fig. 4 for the two normal modes. Now, if we are close to one of the two well-separated normal mode frequencies, only the corresponding impedance will dominate, e.g., near the normal mode with ω_- the input capacitor C_i appears to be in series with $Z_-/2$ only. Equation [9] can then be interpreted as driving two simple parallel circuits, each with Z_-, in parallel through the coupling capacitor C_i. Therefore, near mode ω_0 and ω_- the input capacitor C_i appears to be in series with a single parallel circuit with $L/2$, $R/2$, C_0, and $L/2$, $R/2$, C_-, respectively. These considerations allow us to use Eq. [7] and Eq. [8] for an estimate of the matching frequency and the corresponding impedance. If we denote with $\omega_{\rm hf}$ and $\omega_{\rm lf}$ the matching frequencies near the two eigen frequencies ω_0 and ω_-, respectively, we find

$$\omega_{\rm hf} \approx \frac{1}{\sqrt{L(C + C_i/2)}}, \qquad Z_{\rm hf} \approx \frac{L(C + C_i/2)}{C_i^2 R/2} \qquad [10]$$

and

$$\omega_{\rm lf} \approx \frac{1}{\sqrt{L[C + 2C_c + C_i/2)]}}, \qquad Z_{\rm lf} \approx \frac{L(C + 2C_c + C_i/2)}{C_i^2 R/2}. \qquad [11]$$

These results seem to indicate that one cannot match the circuit at both frequencies to a fixed resistive impedance (50 Ω). However, a slight variation of one of the tuning capacitors C also changes the driving impedance for our chosen single point matching. For practical purposes, therefore, a detuning of the two oscillators with respect to each other gives us the missing degree of freedom for matching at two frequencies.

With regard to a mismatch in the Q's of both coils, we would like to mention that the losses of both coils appear in parallel. That restricts a gain in sensitivity by using a high-Q idling coil. At higher frequencies it might be desirable to replace this coil by another effective inductor (resonant transmission line). A mismatch in the Q's of both coils introduces a slight change in the relative RF amplitudes at either frequency, which is relatively unimportant.

The strategy for building our DR probe can be summarized as follows: First, one has to decide on the approximate position of ω_- and ω_0, i.e., ω_0 should be somewhat higher than the expected signal at the higher frequency. This gives us approximate values for L and C. Second, we choose C_c such that ω_- is placed somewhat above the expected lower frequency signal. The value of C_i is chosen to be somewhat less than C (similar to the setup for a single resonance probe).

Now we are ready to tune and match our DR probe. If one keeps the following basic rules in mind, one will find that tuning and matching are relatively easy with our probe design: (i) The frequencies of both simple parallel circuits, controlled by C and L, have to be very similar for the circuit to behave like coupled resonators. Otherwise one of the resonances will disappear. (ii) The coupling capacitor C_c changes predominantly ω_- (negligible effect on the input impedance at either frequency). (iii) Increasing the input capacitor C_i lowers the impedance at both frequencies, and vice versa (as for the simple circuit). (iv) If one increases (decreases) the resonance frequencies of both simple parallel circuits while obeying rule (i), both frequencies increase (decrease) rapidly, but the input impedances at both frequencies vary slowly. (v) Upon slightly detuning both parallel circuits, the impedance changes as $\omega_{\rm lf}$ and $\omega_{\rm hf}$ have different signs.

4. PROBE PERFORMANCE

The performance of our probe should be compared with a single capacitor coupled parallel resonance circuit which has an identical sample coil. As we already remarked earlier, the losses in the DR probe are caused by both coils. At first glance,

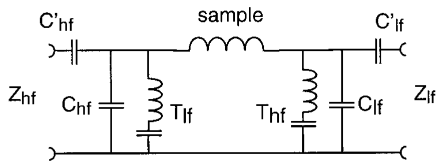

FIG. 7. Conventional circuit (so-called "single coil design") for a DR probe with an input for either frequency (hf, high frequency; lf, low frequency). T_{lf} and T_{hf} represent short circuits (traps) at one frequency and infinite impedance at the other frequency.

it may seem wasteful to use two such coils. However, if we filled both coils with sample, the performance of the probe would be almost that of a single resonance probe (maximum filling factor).

It is also interesting to compare this double resonance probe with the often met design, shown in Fig. 7, which is used if the resonances are far apart.

If we look into the circuit from the high frequency side, T_{lf} represents an infinite impedance and T_{hf} a short. Therefore, we effectively see a capacitively coupled parallel circuit. Similar arguments apply for looking into the low frequency side. We also realize that this so-called "single coil" design indeed has a second resonating coil (sometimes resonant lines) at each frequency, within the traps.

We can also view the circuit in Fig. 7 as two coupled resonators, each consisting of a trap and the nearest parallel capacitor. The sample coil then couples both resonators.

Our actual DR probes with the circuitry given in Fig. 5c were extensively used for studying ^{65,63}Cu resonances in aligned powders of several high temperature superconductors at 8.3 T (central transition frequencies of about 95 and 102 MHz) with quadrupolar frequencies of about 20 to 40 MHz, as well as, for performing ^{17}O–^{63}Cu double resonance on the same materials. For the newly developed double resonance methods between the transitions of a given isotope we refer to Refs. (*7, 8*).

We operated our probe from room temperature down to 10 K. Our main cylindrical coil was given by the sample geometry, and consisted of 12 turns of Cu wire with an inner diameter of 4 mm and a total length of about 1.5 cm. The space between the turns was equal to the wire diameter. No resistors were added. The inductance of the sample coil was about 0.15 μH. The second coil was wound on a threaded bolt of about 3 mm outer diameter so that by screwing the bolt in and out the inductance could be varied. This way we needed only 3 variable capacitors (Watkins-Johnson or Voltronics, 1–12 pF), namely C_i, C_c, and C in parallel with the sample coil, cf. Fig. 5c. The variable parallel capacitor C had an additional 5 pF in parallel and the fixed parallel capacitor C was 15 pF.

With this setup we achieved effective $\pi/2$ pulses of about 1 μs. As an example, at 300 K and for a power of 300 W our effective $\pi/2$ pulse duration was 1.5 μs for the ^{63}Cu central transition. This corresponds to an effective RF amplitude of $\nu'_{RF} = 167$ kHz. Taking into account the factor $(I + 1/2)$ for the amplification of the central transition effective RF amplitude, we obtain $\nu_{RF} = 83.5$ kHz, or with $\gamma = 11.285$ MHz/T, we find in units of the magnetic field $B_{RF} \approx 7.4$ mT. The measured Q was about 70 at 95 MHz.

With this setup we could tune and match our probe in the frequency range of about 75 MHz and 135 MHz without changing components.

4. CONCLUSION

We have demonstrated that a double resonance probe for close frequencies can easily be built with an very good overall performance. We have used the probe extensively for a variety of double resonance experiments on high temperature superconductors at variable temperatures. Our probe design can easily be retuned to form a single resonance probe, e.g., at a fixed temperature. Its special feature, that changes of the coupling capacitor only affect one of the frequencies but not the matching at either frequency, allowed us to measure lineshapes of broad resonances with frequency stepped spin echoes easily. We believe that many double resonance experiments for close frequencies will benefit from these or similar designs.

APPENDIX

In order to derive the single-point driving impedance and matching frequency of our circuit in Fig. 5c it is helpful to add a second coupling capacitor C_i to the right hand side, see Fig. A1a. Since this new circuit is physically symmetric about the center line, we can drive it with voltages which will excite either symmetric or antisymmetric response currents (Figs. A1b and A1c, respectively).

We define the impedances of the simple parallel circuits used for the replacement circuits in Fig. A1 by Z_0 and Z_-,

$$Z_0 = R\,\frac{1 + iQ(1 - \omega^2 LC)}{1 + Q^2(1 - \omega^2 LC)^2}, \qquad \text{[A1]}$$

$$Z_- = R\,\frac{1 + iQ(1 - \omega^2 L(C + 2C_c))}{1 + Q^2(1 - \omega^2 L(C + 2C_c))^2}. \qquad \text{[A2]}$$

With these definitions we find for the currents I_1 and I_2 in Figs. A1b, A1c,

$$I_1 = \frac{U_1}{Z_- + 1/(i\omega C_i)}, \qquad \text{[A3]}$$

$$I_2 = \frac{U_2}{Z_0 + 1/(i\omega C_i)}. \qquad \text{[A4]}$$

The currents and voltages (I_1, U_1) and (I_2, U_2) are both

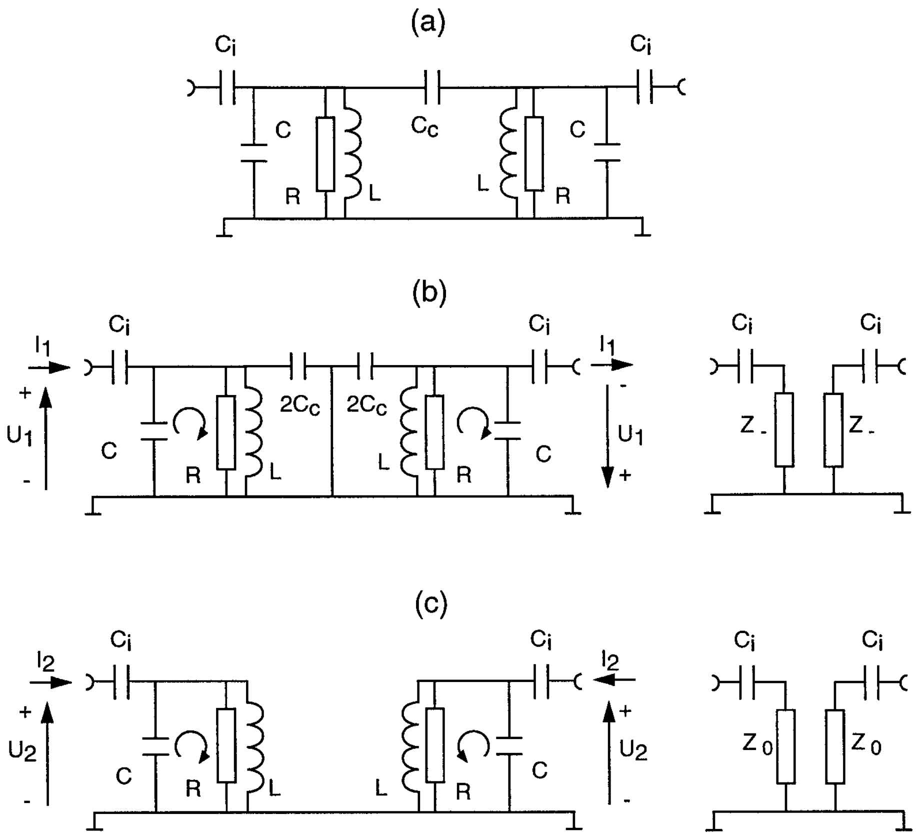

FIG. A1. (a) Capacitively coupled parallel circuits with losses and two capacitors C_i for driving purposes. (b), (c) The same circuit is driven in a manner to support the symmetric (b) and the antisymmetric (c) current mode shown in Fig. 4.

solutions of the circuit shown in Fig. A1a. Since the system is linear, their sums are also solutions. We can therefore create a situation in which we drive at the left hand side only by superposing the solutions so as to make the input current from the right be zero, i.e., by choosing $I_1 = I_2$. The total voltage $U = U_1 + U_2$ and current $I = I_1 + I_2$ are then given by

$$U = U_1\left(1 + \frac{1 + i\omega C_i Z_0}{1 + i\omega C_i Z_-}\right), \qquad I = U_1\left(\frac{2i\omega C_i}{1 + i\omega C_i Z_-}\right). \quad [A5]$$

From Eq. [A5] we calculate for the input impedance $Z_i = U/I$

$$Z_i = \frac{1}{i\omega C_i} + \frac{Z_- + Z_0}{2}. \quad [A6]$$

This is a general solution to the single-point driving impedance. The matching capacitor C_i appears in series with the mean impedance given by the two normal modes.

ACKNOWLEDGMENTS

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