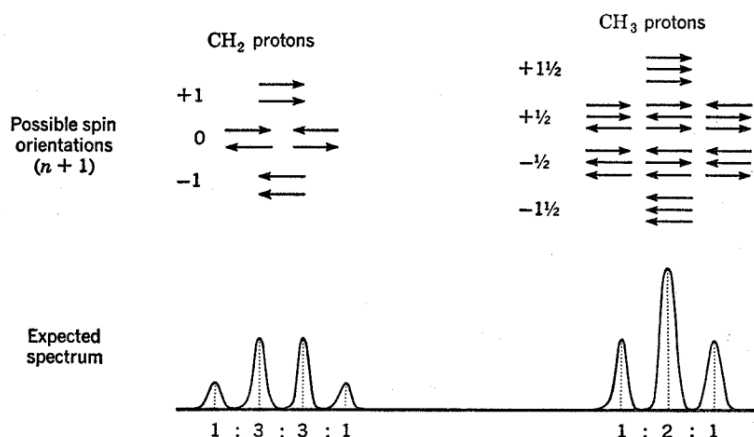


### 3.4: Spin-Spin Splitting in the Ethyl Group

The typical three-four line resonance pattern of the ethyl group arises because of spin-spin coupling between the methyl and methylene protons. It turns out that the coupling constant  $J$ , which represents the line spacings, is very nearly constant over a wide range of ethyl derivatives and amounts to about 1.6 milligauss or 7 cps.



**Fig. 3-5.** Possible orientations of nuclear spins of ethyl group protons and expected spin-spin splitting pattern.

Reference to Fig. 3-5 shows that the two methylene protons may have any one of four possible combinations of their magnetic quantum numbers. Thus, both magnetic quantum numbers may be the same with either a + or - sign for the total or they may be different two possible ways) and cancel each other's magnetic effect. The ethyl groups from molecule to molecule can then be classified into those in which the total spin of the methylene protons adds to +1, those in which they cancel each other, and those in which they add to -1. The methyl protons in ethyl groups whose methylene protons have a total spin of +1 will come into resonance when the magnetic field is increasing sooner than the others. When the methylene protons have a net spin of zero, they will have no effect on the resonance line position of the methyl, while if the net spin is -1, the line will come late by the same amount as the +1 combination came early. Consequently, there should be a total of three resonance lines for the methyl group because of the adjacent methylene protons. Since there are a total of four equally probable combinations of the methylene magnetic quantum numbers, one way to give +1, two ways to give zero, and one way to give -1, it will be expected that the three resonance lines will have signal-strength ratios of 1:2:1. Similar reasoning applied to the resonance absorption of the methylene protons in the presence of the methyl protons leads to prediction of a four-line spectrum with the signal strengths in the ratio 1:3:3:1. In the above analysis, the spins of a group of equivalent protons were taken to be independent (each with two possible orientations in the external field) and distributed statistically among the possible states as shown in Fig. 3-5. This procedure gives satisfactory predictions for many simple spin-spin splitting problems but fails in others. Chemically equivalent protons in a group like a methyl are actually coupled to one another to give, in effect, a larger magnet which in turn is coupled to the external field. Consequently, such protons are not to be expected to behave independently of one another in all situations. This point will be discussed further in Sec. 3-7.

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