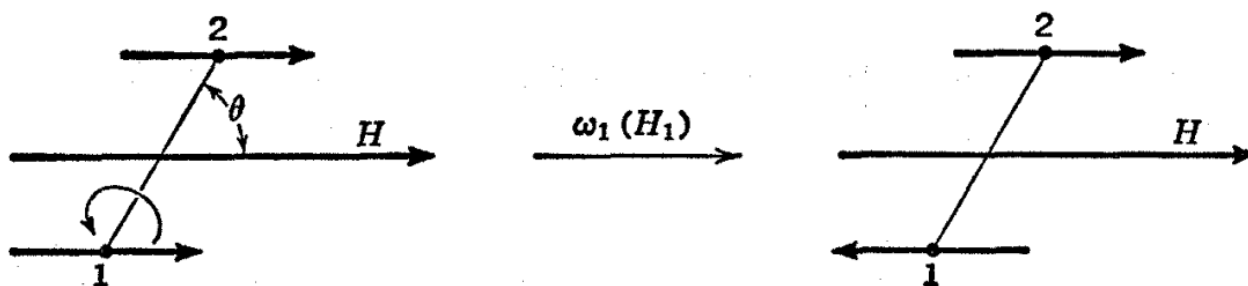
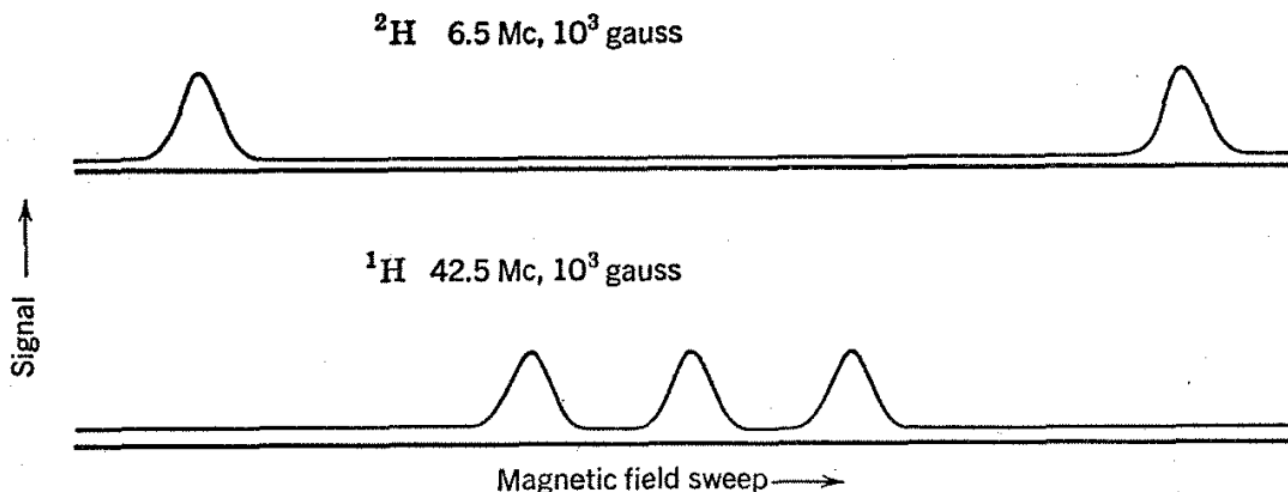


### 3.2: Spin-Spin Splitting in a Single Crystal



**Fig. 3-3.** A molecule of H-D in a hypothetical single crystal subjected to an applied magnetic field  $H$  and a suitable oscillator frequency  $\omega_1$  to cause nucleus 1 to absorb rf energy.

Consider a single crystal made up of H-D molecules, all of which are so oriented that the lines connecting the nuclei of the individual molecules make an angle  $\theta$  with an applied magnetic field (Fig. 3-3). Now consider nuclear resonance absorption by deuterium nuclei located at position 1. Each deuteron precesses in a field whose magnitude is determined partly by the applied field and partly by the degree of diamagnetic shielding produced by the bonding electrons. However, this is not the whole story, since each deuterium nucleus will be connected to a proton (at position 2) which can have either of the two possible magnetic quantum numbers,  $+1/2$  or  $-1/2$ . If the proton nuclear magnet is oriented in the direction of the magnetic field, then it will augment the field which is experienced by the adjacent deuteron and the total field at the deuteron will correspond to a higher precession frequency than if the proton had no nuclear moment. If the proton magnet is directed the other way, the field at the deuterium nucleus will be reduced from its nominal value. Therefore, the precession frequency of a given deuterium and the position of its resonance lines will depend on the magnetic quantum number of the proton to which it is bonded. In a large assemblage of H-D molecules, there will be almost precisely equal numbers of protons with the two possible spin quantum numbers, even in an intense applied field, unless the temperature is so low that thermal agitation cannot prevent an appreciable excess of the nuclei from being lined up with the applied field. Consequently, at ordinary temperatures, very nearly half of the H-D molecules will show a deuteron resonance at a lower field strength than would be the case if the proton moment were absent, while the other half of the molecules will have their deuterium resonance at a correspondingly higher field strength. The observed spectrum will then appear somewhat as in Fig. 3-4.



**Fig. 3-4.** Expected NMR spectrum for a single crystal of H-D molecules assuming negligible intermolecular magnetic interactions.

The proton resonance spectrum will be affected by the deuterons in an analogous way, except that, since the deuteron has  $I = 1$  and three possible magnetic quantum numbers (+1, 0, -1), the proton resonances will occur at three field strengths. Since the probability that a given deuteron will have any one of the magnetic quantum numbers is essentially one-third, the three lines will be of equal height. It can be shown theoretically that the interaction between the spins is such that the spacing of the deuteron and proton resonance lines depends on the ratios of the gyromagnetic ratios of the nuclei. A rough calculation for an H-D crystal with  $\theta = 90^\circ$  shows the predicted spacing of the deuteron resonances to be about 35 gauss, so that proton resonances would be separated by  $35 \times \gamma_D/\gamma_H$  or 5.3 gauss. This type of magnetic interaction between nuclei is usually called "spin-spin splitting." Since magnetic coupling between nuclei causes changes in precession frequencies depending on the magnitude of the nuclear moment but not the external field, it is clear that the magnitude of the splitting should be independent of the applied field.

Magnetic interaction among nuclei as postulated for the hypothetical crystal of H-D molecules is "direct dipole-dipole interaction" and leads to a line separation proportional to  $(3\cos^2\theta - 1)r^{-3}$  with  $\theta$  as defined earlier and  $r$  the distance between the nuclei. In crystals, besides the intramolecular nuclear interactions, one will expect also substantial intermolecular dipole-dipole interactions leading to additional splittings or broadening of the absorption lines (see earlier discussion, page 33).

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