Chemical Shift Calculation for AB Spectra

An AB spectrum usually exhibits the ‘roofing effect’ characteristic of higher order coupling systems. In such systems, you cannot think of each line representing a single transition of a nucleus as is possible with a first-order spectrum. Instead, the peaks of a higher-order spectrum should be thought of as a combination of all spins in the system.

Four lines are present in an AB system, and the coupling constant, $J$, is the same for each line:

$|J_{ab}| = (D_1 \square D_2) = (D_3 \square D_4)$

The line intensities ($i$) are no longer 1:1:1:1 as in an AX system, but are given by the ratios:

$i_2/i_1 = i_3/i_4 = (D_1 \square D_4) / (D_2 \square D_3)$

$\square_a$ and $\square_b$ are not exactly centered between lines 1 & 2 and 3 & 4. Instead, their chemical shifts are given by the centers of gravity for each doublet. This can be calculated using the following formulae:

$c =$ center of spectrum $= 0.5(D_2 + D_4) = 0.5(D_1 + D_3)$

$\square = (\square_a \square_b) = \sqrt{[(D_1 \square D_4)(D_2 \square D_3)]} = \sqrt{(2D)^2 - J^2}$

$\square_a = c + \square/2$, $\square_b = c - \square/2$