Splitting of Spectrum Lines for Perturbed Systems; EPR Analysis in Solutions

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Abstract — The real Hamiltonian representing all systems contains maybe a hundred kinds of perturbation Hamiltonian terms, each of which shows a system. In any system if we observe a spectrum line belong to a sample by the effect of any perturbation Hamiltonian, then, its previous system has a doubled degenerated energy levels respect to us, and the energy of the transition is obtained from the difference of the energy values of the levels. For the systems to which perturbations cause same effect in their upper and lower energy levels the effects of perturbation Hamiltonian terms can be thought individually if there is no degenerated transition in their previous systems. Since of the effect of the n.th perturbation term $H^{(n)}$ the splitting of the spectrum lines of a sample can be obtained by the equation of

$$W_n = 2[H_{mn}^{(n)} - H_{nn}^{(n)}].$$

Where $m$ and $n$ show two degenerated wave functions of the previous system $H^{(n-1)}$. If the Hamiltonian $H^{(n)}$ is diagonal, then, this equation is also valid for degenerate transitions in the previous system. EPR in solutions which has isotropic hyperfine splitting constants and diagonal perturbation Hamiltonian terms, was given as an easy example.

Keywords: Line Splitting, Perturbation, Hyperfine Splitting, EPR in solution.

1 Introduction

In any system, if we observe a transition or a spectrum line belong to a sample by the effect of a perturbation Hamiltonian term $H^{(1)}$, then, respect to us, these levels are degenerate in the previous system $H^{(0)}$. If we observe two spectrum lines in the system $H^{(2)}$, then, the system $H^{(1)}$ has two doubled degenerated energy levels respect to us. Therefore, the real Hamiltonian representing all the systems contains maybe a hundred kinds of the perturbation Hamiltonian terms and, has a wave function with a hundred term lengths.

In this study it has been shown the effect of any perturbation Hamiltonian term on the spectrum of a sample can easily be obtained by a deduced equation.
2 Results and Discussion

2.1 Perturbation Effect on a System

We can write the total Hamiltonian including all the systems as

\[ H = H^{(0)} + H^{(1)} + H^{(2)} + H^{(3)} + H^{(4)} + \ldots \quad (1) \]

and the total wave function as

\[ \Psi_i = \prod_j |\psi_i \rangle \quad i = 0, 1, 2, 3, \ldots; \quad j = 0, 1, 2, 3, \ldots \quad (2) \]

Where \( i \) shows the number of degenerated states in any beginning system (it can be any Hamiltonian term in the total Hamiltonian), and \( j \) is the number of degenerated states in the later system. Choosing \( H^{(0)} > H^{(1)} > H^{(2)} > H^{(3)} > H^{(4)} > \ldots \) gives easiness.

Let us consider the system \( H^{(0)} \) has only two energy levels, and it is perturbed by the perturbation Hamiltonian \( H^{(1)} \). So the Hamiltonian becomes

\[ H = H^{(0)} + H^{(1)} \]

Supposing that the two eigenfunctions of the system \( H^{(0)} \) are known, and chose them as \( \psi_m \) and \( \psi_n \). Thus, they correspond to the energies \( E_m \) and \( E_n \), respectively. So we can write

\[ H^{(0)} \psi_m = E^{(0)}_m \psi_m \quad \text{and} \quad H^{(0)} \psi_n = E^{(0)}_n \psi_n \]

and in the bases of \( \psi_m \) and \( \psi_n \), using made of orthonormality of the functions \( \delta_{mn} = \langle m | n \rangle \), the Hamiltonian secular determinant is

\[ \begin{vmatrix} H_{nn} - \varepsilon & H_{nn} \\ H_{nn} & H_{nn} - \varepsilon \end{vmatrix} = 0 \quad \text{and} \quad \begin{vmatrix} H^{(0)}_{mm} + H^{(1)}_{mm} - \varepsilon & H^{(1)}_{mm} \\ H^{(1)}_{mm} & H^{(0)}_{mm} + H^{(1)}_{mm} - \varepsilon \end{vmatrix} = 0 \]

[1]. In the special case of the perturbation for which \( H^{(1)}_{mn} = H^{(1)}_{nm} = 0 \), the diagonal elements are \( H^{(0)}_{mm} = E^{(0)}_m \), \( H^{(0)}_{nn} = E^{(0)}_n \) and \( H^{(1)}_{mm} = E^{(1)}_m \), \( H^{(1)}_{nn} = E^{(1)}_n \). Since of the orthogonality of the wave functions we can write

\[ \varepsilon_i = [H^{(0)}_{mm} + H^{(1)}_{mm}] = E^{(0)}_m + E^{(1)}_m \quad (3) \]

\[ -\varepsilon_i = [H^{(0)}_{nn} + H^{(1)}_{nn}] = E^{(0)}_n + E^{(1)}_n \quad (4) \]

If we add and subtract together (3) and (4) we get
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\[ 0 = [H_{nm}^{(0)} + H_{mn}^{(1)}] + [H_{nn}^{(0)} + H_{nn}^{(1)}] = [E_m^{(0)} + E_m^{(1)}] + [E_n^{(0)} + E_n^{(1)}] \]  

(5)

\[ 2\epsilon = [H_{mm}^{(0)} + H_{mm}^{(1)}] - [H_{mm}^{(0)} + H_{nn}^{(1)}] = [E_m^{(0)} + E_n^{(1)}] - [E_n^{(0)} + E_n^{(1)}] \]  

(6)

respectively. If we chose \( E_m^{(0)} = E_n^{(0)} = 0 \), then, \( \psi_m \) and \( \psi_n \) become two degenerated wave functions giving same energies, thus, (5) and (6) become

\[ 0 = E_m^{(1)} + E_n^{(1)} \]  

(7)

\[ 2\epsilon_1 = E_m^{(1)} - E_n^{(1)}. \]  

(8)

2.2 Splitting of Energy Levels; Transitions

The splitting of the energy levels of the system \( H^{(0)} \) perturbed by the Hamiltonian \( H^{(1)} \) is shown in Figure 1. We will call this new system as the system \( H^{(1)} \). Therefore, we can say the total of the energy values of the upper and lower levels is zero, and their splitting is \( 2\epsilon_1 \). If we observe this transition for any sample by a spectrometer, its energy will equal to \( 2\epsilon_1 \). It is important to note the spectrum line can occur with the transition from the upper level raised in energy to the lower level falled in energy by the Hamiltonian \( H^{(1)} \). If this system is perturbed by the another perturbation term \( H^{(2)} \) and we observe two spectrum lines we can write the following equations in the similar form thinking two transi- 

\[ 0 = [(E_m^{(1)} + E_n^{(2)}) - (E_m^{(1)} - E_n^{(2)})] + [(E_m^{(1)} - E_n^{(2)}) - (E_m^{(2)} + E_m^{(2)})] \]  

(9)

\[ 2\epsilon_2 = [(E_n^{(1)} + E_m^{(2)}) - (E_m^{(1)} - E_m^{(2)})] - [(E_n^{(1)} - E_n^{(2)}) - (E_m^{(1)} + E_m^{(2)})] \]  

(10)

respectively. Otherwise, the perturbation cannot increase the number of the lines observed. Therefore we can say that if any perturbation does not increase the number of the spectrum lines its effect cannot be understood from the spectrum because it gives the same lines at the same places like before perturbation.

The zero equality of (9) can be checked and (10) gives

\[ W_2 = 2\epsilon_2 = 2[E_m^{(2)} - E_n^{(2)}]. \]

This equation shows that the splitting of the lines occurred by the perturbation Hamiltonian term \( H^{(2)} \) can be obtained by using the two degenerate wave functions of the system \( H^{(0)} \), \( \psi_m \) and \( \psi_n \), so, we can write
\[ W_2 = 2\varepsilon_2 = 2\left[H_{mm}^{(2)} - H_{nn}^{(2)}\right] \]  
\hspace{2cm} (11)
2.4 EPR in Solution

We can give the electron paramagnetic resonance (EPR) in solutions which has isotropic hyperfine constants and diagonal perturbation Hamiltonian terms, as a marvellous example.

Let us consider a free radical with just two protons, which have the isotropic hyperfine couplings, being \( a_1 \) and \( a_2 \), respectively. The spin of the electron is aligned at random in the absence of a field. In the magnetic field \( H_0 \) (or in the system \( H^{(0)} \)) it will have preferred directions since the spin quantum number of the electron is \( \frac{1}{2} \). The two preferred directions are spin-up (\( \alpha_e \)) and spin-down (\( \beta_e \)), respectively. These levels are given in Figure 2. Therefore, in the system \( H^{(0)} \) these formed levels which are spin-down and spin-up are degenerate. Thus, we can write the degenerated wave functions of the free radical as \( |\Psi_m\rangle = |\alpha_e \alpha_1 \alpha_2\rangle \) and \( |\Psi_n\rangle = |\beta_e \alpha_1 \alpha_2\rangle \) by using the ket notation. Where \( \alpha_1 \) and \( \alpha_2 \) are used for the spins of the protons. Then \( H^{(1)} = g \beta H_0 S_z \) [3] and

\[
H^{(1)} |\Psi_m\rangle = \frac{1}{2} g \beta H_0 |\Psi_m\rangle \\
H^{(1)} |\Psi_n\rangle = -\frac{1}{2} g \beta H_0 |\Psi_n\rangle
\]

since \( S_z |\alpha_e\rangle = \frac{1}{2} |\alpha_e\rangle \) and \( S_z |\beta_e\rangle = -\frac{1}{2} |\beta_e\rangle \).

From these two equations, \( E_m^{(1)} = \frac{1}{2} g \beta H_0 \) and \( E_n^{(1)} = -\frac{1}{2} g \beta H_0 \). If we use (7) and (8) we get

\[
E_m^{(1)} + E_n^{(1)} = 0 \\
E_m^{(1)} - E_n^{(1)} = 2 a_1 = g \beta H_0,
\]

respectively, then, the transition energy becomes \( h \nu = g \beta H_0 \).

![Fig. 2: Electron spin levels in a magnetic field \( H_0 \)](image-url)
We can omit the term describing the interactions of the protons with the magnetic field $H_0 \left[ -g_N \beta_N H_0 (I_{z2} + I_{z1}) \right]$, because, as we said before, it does not increase the number of the observed lines in the spectrum since the transitions occur from the upper levels raised in energy to the lower levels falled in energy or vice versa and so, we obtain only the same spectrum lines at the same places as before. Therefore its effect cannot be understood from the spectrum.

If we think the interaction term of the electron with the first proton we can write $H^{(2)} = a_1 I_{z1} S_z$ since the spectrum shows two lines. By using (11) which shows the splitting of the lines as $W_2 = 2\alpha_2 = 2 \left[ H_{nm}^{(2)} - H_{nn}^{(2)} \right]$ we find

$$H_{mm}^{(2)} = \langle \psi_m | H^{(2)} | \psi_m \rangle = \langle a_1 \alpha_1 | a_1 \alpha_2 | a_1 I_{z1} S_z | a_1 \alpha_2 \alpha_2 \rangle = \frac{1}{4} a_1,$$

and in similar form,

![Fig. 3: a) Hyperfine energy levels and (b) transitions, for an electron interacting with two protons](image)

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\[ H_{nn}^{(2)} = \langle \Psi_n | H^{(2)} | \Psi_n \rangle = \langle \beta_1 \alpha_1 \alpha_2 | a_1 I_{12} S_z | \beta_1 \alpha_1 \alpha_2 \rangle = -\frac{1}{4} a_1 \]

since \( I_{12} | \alpha_1 \rangle = \frac{1}{2} | \alpha_1 \rangle \), \( \langle \Psi_m | \Psi_n \rangle = \delta_{mn} \) and \( \delta_{mn} = \begin{cases} 1 & m = n \\ 0 & m \neq n \end{cases} \).

Thus, \( W_2 \) becomes

\[ W_2 = 2 \epsilon_2 = 2 \left[ \frac{a_1}{4} - \left( -\frac{a_1}{4} \right) \right] = a_1. \]

If we think the interaction Hamiltonian of the electron with the second proton we write \( H(3) = a_2 I_{12} S_z \), and from (12) we get

\[ W_3 = 2 \epsilon_3 = 2 \left[ \frac{a_2}{4} - \left( -\frac{a_2}{4} \right) \right] = a_2. \]

Thus, the free radical will has the energy levels as shown in Figure 3a and the spectrum in Figure 3b (if we get \( a_1 > a_2 \)).

### 3. Conclusion

As a conclusion, in any system the effect of a perturbation Hamiltonian term in the total Hamiltonian including all the systems on the spectrum of a sample can individually be thought. Since of the effect of the n.th perturbation Hamiltonian term \( H^{(n)} \) the splitting of the spectrum lines can be obtained by the equation of \( W_n = 2 \epsilon_n = 2 \left[ H_{nn}^{(n)} - H_{nn}^{(n-1)} \right] \). If there is no degenerate transition in the previous system \( H^{(n-1)} \), and if \( H^{(n)} \) is diagonal, this equation is also valid for the degenerated transitions in the previous system \( H^{(n-1)} \).

### References


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