

Solution Problem Set 5: Spectral-Density Functions

The calculations and plots of the $T_{1,S}$ and the $T_{2,S}$ relaxation times are implemented in the completed Matlab scripts:

- `ex05_T1_1and2_solution.m`
- `ex05_T1_3_solution.m`
- `ex05_T2_1and2_solution.m`
- `ex05_T2_3_solution.m`
- `ex05_T2_4_solution.m`

Problem 1: T_1 Relaxation

1. Figure 1 shows a double logarithmic plot of $T_{1,S}$. One can clearly see, that the $T_{1,S}$ curve has a minimum that is roughly located at $\omega_S \tau_c = 1$. The location of the minimum can be understood by looking at the spectral density functions as a function of $\omega_S \tau_c$ as shown in Figure 2. The spectral density function at ω_S is largest and will dominate the behaviour of $T_{1,S}$. It has a maximum at $\omega_S \tau_c = 1$ and $T_{1,S}$ will therefore have a minimum for this correlation time. The additional features in Fig. 1 come from the minima of the spectral density functions at $\omega_S - \omega_I$ and $\omega_S + \omega_I$.

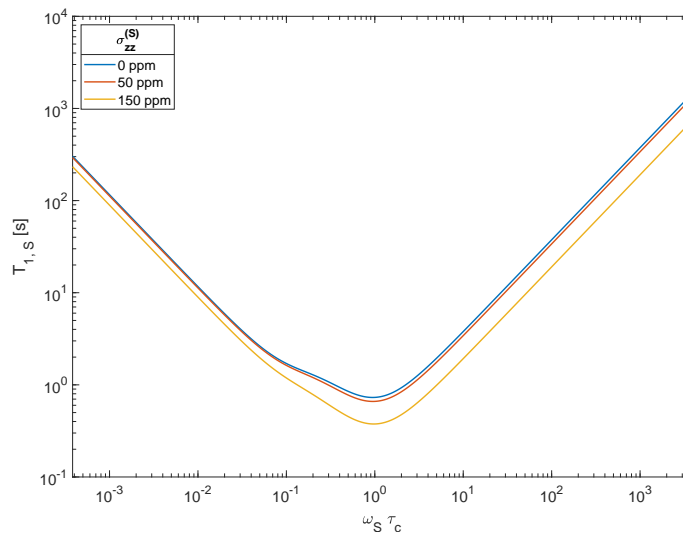


Figure 1: Double logarithmic plot of $T_{1,S}$ as a function of $\omega_S \tau_c$ for an ^{15}N – ^1H spin pair in a static magnetic field of 14.1 T and an internuclear distance of 1 Å. Chemical-shielding tensor values of 0, 50 and 150 ppm are shown.

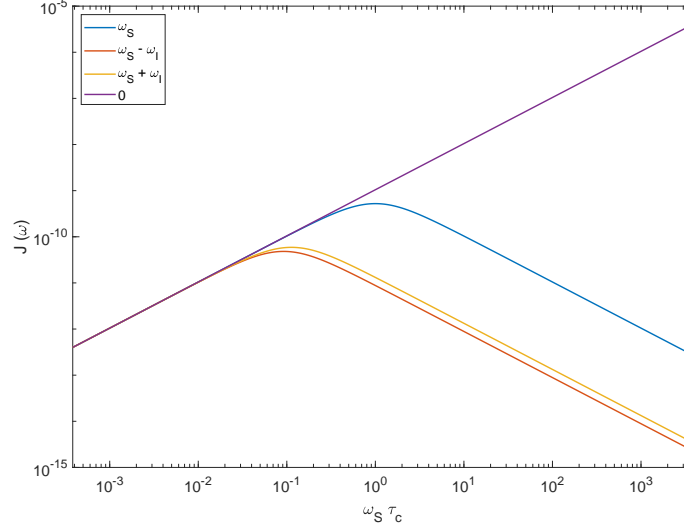


Figure 2: Double logarithmic plot of the spectral density function $J(\omega)$ for isotropic rotational tumbling as a function of the correlation time τ_c for different frequencies (ω_S , $\omega_S - \omega_I$, $\omega_S + \omega_I$ and 0). The spectral density function at ω_S has the largest value compared to $\omega_S - \omega_I$ and $\omega_S + \omega_I$ and will dominate the behaviour of $T_{1,S}$.

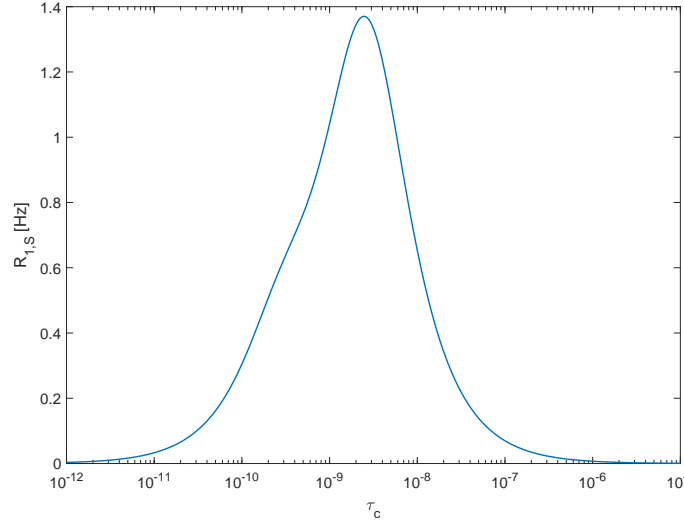


Figure 3: Semilogarithmic plot of the relaxation rate constant $R_{1,S} = \frac{1}{T_{1,S}}$ as a function of the correlation time τ_c .

Figure 3 shows a semilogarithmic plot of the relaxation rate constant $R_{1,S} = \frac{1}{T_{1,S}}$ as a function of the correlation time τ_c . Non-zero relaxation rate constants are obtained for correlation times between ca. 10^{-11} and 10^{-7} s.

2. As can be seen in Fig. 1, increasing the chemical-shielding tensor value will lead to additional relaxation that increases the rate constant $R_{1,S}$ and therefore decreases the $T_{1,S}$ time.
3. Figure 4 shows the dependence of the $T_{1,S}$ time on the static magnetic field for three different correlation times: $\tau_c = 10^{-12}$, 10^{-10} and 10^{-8} s assuming a chemical-shielding tensor value of $\sigma_{zz}^{(S)} = 0$ ppm. For correlation times of 10^{-12} and 10^{-10} s we

are always in the extreme narrowing limit ($\omega_S \tau_c < 1$) and the value of the spectral density function does not depend on the static magnetic field. For the correlation time of 10^{-8} s we observe a dependence of $T_{1,S}$ on B_0 since $\omega_S \tau_c > 1$.

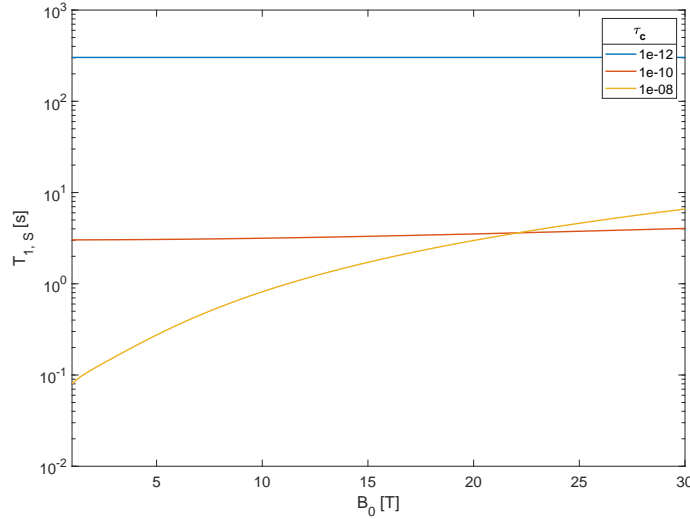


Figure 4: Semilogarithmic plot of $T_{1,S}$ as a function of the static magnetic field B_0 for correlation times of 10^{-12} , 10^{-10} and 10^{-8} .

4. A homonuclear spin pair with non-degenerate chemical shifts will essentially behave like a heteronuclear spin pair except for the fact that the two Larmor frequencies ω_S and ω_I are the same $\omega_S = \omega_I$. The spectral density function will therefore be sampled at frequencies 0, ω_S and $2\omega_S$. Due to the contribution of the spectral density function at a frequency of 0 (s. Fig. 2), the $T_{1,S}$ will not show a minimum as was seen for the heteronuclear case (s. Fig. 1) but will show a continuous decrease with longer correlation times.

Problem 2: T_2 Relaxation

1. Figure 5 shows a double-logarithmic plot of $T_{2,S}$ as a function $\omega_S \tau_c$ for chemical-shielding tensor values of 0, 50 and 150 ppm. One can clearly see, that the $T_{2,S}$ time decreases monotonically. This is due to the fact, that the equation for $T_{2,S}$ (s. Eq. (4) on the exercise sheet) contains the spectral density function at frequency 0 (s. Fig. 2) which dominates the behaviour at longer correlation times.
2. As was the case for $T_{1,S}$ (s. Fig. 1), increasing the chemical-shielding tensor value will increase the relaxation rate constant and, therefore, decrease the $T_{2,S}$. This is shown in Fig. 5.
3. The B_0 -field dependence of the $T_{2,S}$ relaxation is shown in Fig. 6 for correlation times of 10^{-12} , 10^{-10} and 10^{-8} . Only a very weak B_0 field dependence is observed, since the $T_{2,S}$ time is mainly determined by the $J(0)$ spectral density contribution for all three τ_c .

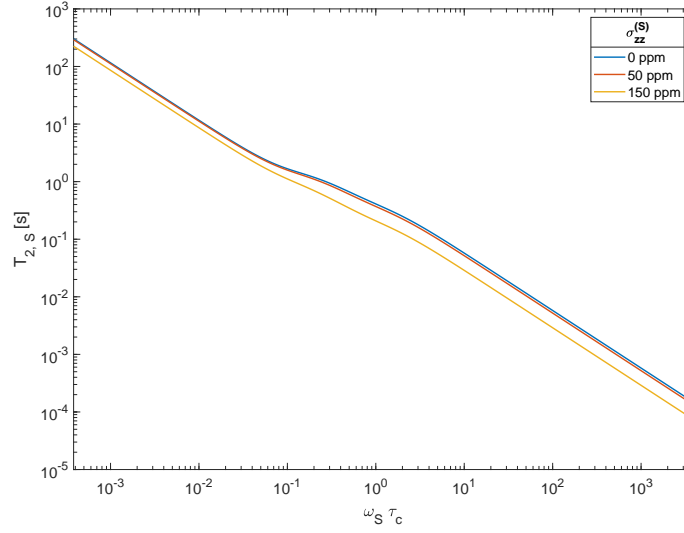


Figure 5: Double logarithmic plot of $T_{2,S}$ as a function of $\omega_S \tau_c$ for an ^{15}N – ^1H spin pair in a static magnetic field of 14.1 T and an internuclear distance of 1 Å. Chemical-shielding tensor values of 0, 50 and 150 ppm are shown.

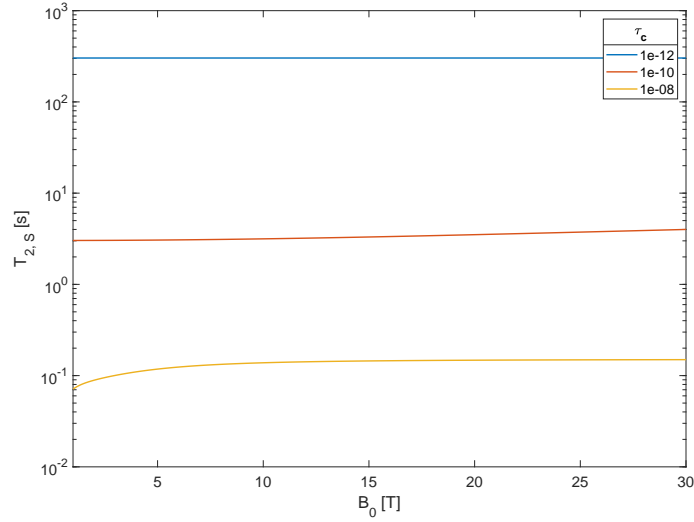


Figure 6: Semilogarithmic plot of $T_{2,S}$ as a function of the static magnetic field B_0 for correlation times of 10^{-12} , 10^{-10} and 10^{-8} .

4. The backcalculated correlation times vs the theoretical (input) correlation times are shown in Fig. 7. It can be seen, that Eq. (5) on the exercise sheet is only valid for large molecules with correlation times longer than about 1 ns. To obtain Eq. (5), we assume that only the spectral densities at frequency 0 and ω_S are relevant. It can be seen from Fig. 2, that this is reasonable for long correlation times and thus big molecules that tumble slowly. Using this assumption, we find

$$\frac{T_{1,S}}{T_{2,S}} = \frac{2J(0) + \frac{3}{2}J(\omega_S)}{3J(\omega_S)} = \frac{2}{3} \frac{J(0)}{J(\omega_S)} + \frac{1}{2} = \frac{2}{3} (1 + (\omega_S \tau_c)^2) + \frac{1}{2} \quad (1)$$

Solving this equation for τ_c yields Eq. (5) on the exercise sheet.

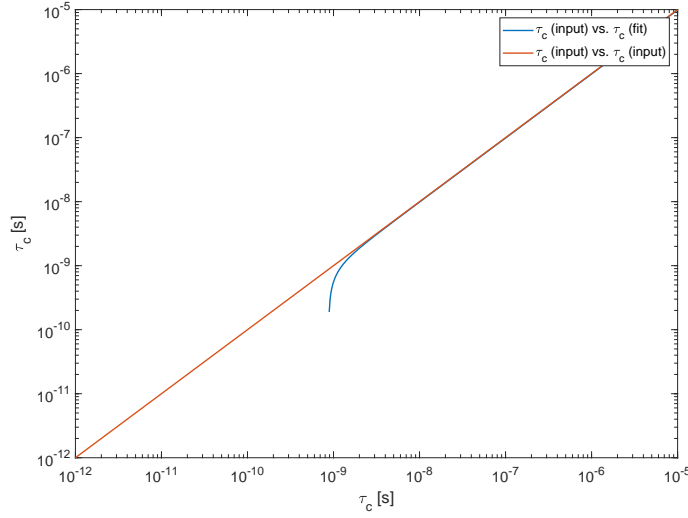


Figure 7: Double logarithmic plot of the backcalculated correlation time against the theoretical (input) correlation time.