REFINEMENT OF THE ROBERT-BONAMY FORMALISM: TAKING INTO ACCOUNT OF CONTRIBUTIONS FROM THE LINE COUPLING

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The Robert-Bonamy (RB) formalism [a] contains several approximations whose applicability has not been thoroughly justified. One of them is that lines of interest are well separated. When these authors develop the formalism, they have relied on this assumption twice. First, in calculating the spectral density F(ω), they have only considered the diagonal matrix elements of the resolvent operator. Due to this simplification, effects from the line mixing are ignored. Second, when they apply the linked cluster theorem to remove the cutoff, they have assumed that matrix elements of the operator exp(- iS_1 - S_2) can be replaced by the exponential of the matrix elements of - iS_1 - S_2. With this replacement, effects from the line coupling are also ignored. Although both these two simplifications are relied on the same approximation, their validity criterions are different and the latter is more stringent than the former. As a result, in many cases where the line mixing becomes negligible, significant effects from the line coupling have been completely missed. In the present study, we have developed a new method to evaluate the matrix elements of exp(- iS_1 - S_2) and have refined the RB formalism such that the line coupling can be well taking into account. Our numerical calculations of the half-widths for Raman Q lines of the N_2 - N_2 pair have demonstrated that effects from the line coupling are important. In comparison with values derived from the RB formalism, new calculated values for these lines are reduced significantly. A recent study on this system by Thibault et al. [b] has shown that in comparison with measurements and the most accurate close coupling calculations, results derived from the RB formalism are overestimated by a large amount. As a result, the refinement of the RB formalism goes in the right direction and these new calculated half-widths become closer to the "true" values.

[a] D. Robert and J. Bonamy, J. Phys.(Paris), **40**, 923 (1979).
[b] F. Thibault et al., J.Q.S.R.T **113**, 1887 (2012).