HOW TO CALCULATE SPIN-SPIN COUPLING AND SPIN-ROTATION COUPLING STRENGTHS AND THEIR UNCERTAINTIES FROM SPECTROSCOPIC DATA: APPLICATION TO THE $c(1^3\Sigma_g^+)$ STATE OF DIATOMIC LITHIUM

NIKESH S. DATTANI, *Department of Chemistry, Oxford University, Oxford, OX1 3QZ, UK*; XUAN LI, *Chemical Science Division, Lawrence Berkeley National Laboratory, Berkeley, 94720-8176, USA*.

Recent high-resolution (± 0.00002 cm^{-1}) photo-association spectroscopy (PAS) data of seven previously unexplored vibrational levels of the $1^3\Sigma_g^+$ state of Li_2 have allowed for the first ever experimental determination of the spin-spin (λ_v) and spin-rotation (γ_v) coupling constants in a diatomic lithium system[a]. For triplet states of diatomic molecules such as the $1^3\Sigma_g^+$ state of Li_2, the three spin-spin/spin-rotation resolved energies associated with a ro-vibrational state $|v, N\rangle$ were expressed explicity in terms of B_v, λ_v, and γ_v in 1929 by Kramer's first-order formulas[b] and then in 1937 by Schlapp's more refined formulas[c]. Given spectroscopic data, while it has never been difficult to extract λ_v and γ_v from Schlapp's formulas, it has been a challenge to reliably predict how accurate these extracted values are. This is for two reasons: (1) the lack of a rigorous method to estimate the uncertainty in B_v, (2) the non-linearity of Schlapp's coupled equations has meant that traditionally they have had to be solved numerically by Newton iterations which makes error propagation difficult. The former challenge has been this year solved by Le Roy with a modification of Hutson's perturbation theory of[d], and the latter problem has now been solved by symbolic computing software that solves Schlapp's coupled non-linear equations analytically for the first time since their introduction in 1937.

[a] M. Semczuk, X. Li, W. Gunton, M. Haw, N. Dattani, J. Witz, A. Mills, D. Jones, K. Madison, Physical Review A **87**, XX (2013)
[b] H. Kramers, Zeitschrift fur Physik 53, 422 (1929)
[c] R. Schlapp, Physical Review 51, 342 (1937)
[d] J. Hutson, J. Phys. B, **14**, 851 (1981)