FULL CI BENCHMARK POTENTIALS FOR THE $6e^-$ SYSTEM Li_2 WITH A CBS EXTRAPOLATION FROM aug-cc-pCV5Z AND aug-cc-pCV6Z BASIS SETS USING FCIQMC AND DMRG

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Being the simplest uncharged homonuclear dimer after H_2 that has a stable ground state, Li_2 is one of the most important benchmark systems for theory and experiment. In 1930, Delbrück used Li_2 to test his theory of homopolar binding, and it was used again and again as a prototype to test what have now become some of the most ubiquitous concepts in molecular physics (LCAO, SCF, MO, just to name a few). Experimentally, Roscoe and Schuster studied alkali dimers back in 1874. At the dawn of quantum mechanics, the emerging types of spectroscopic analyses we now use today, were tested on Li_2 in the labs of Wurm (1928), Harvey (1929), Lewis (1931), and many others, independently. Li_2 was at the centre of the development of PFOODR in the 80s, and PAS in the 90s; and Lithium Bose-Einstein condensates were announced only 1 month after the Nobel Prize winning BEC announcement in 1995. Even now in the 2010s, numerous experimental and theoretical studies on Li have tested QED up to the 7th power of the fine structure constant. Li_2 has also been of interest to sub-atomic physicists, as it was spectroscopic measurements on $^7Li_2$ that determined the spin of ^{7}Li to be 3/2 in 1931; and Li_2 has been proposed in 2014 as a candidate for the first "halo nucleonic molecule".

The lowest triplet state $a(1^3\Sigma_u^+)$ is an excellent benchmark system for all newly emerging *ab initio* techniques because it has only $6e^-$, its potential is only $334\,\mathrm{cm}^{-1}$ deep, it avoids harsh complications from spin-orbit coupling, and it is the deepest potential for which *all* predicted vibrational energy levels have been observed with $0.0001\,\mathrm{cm}^{-1}$ precision. However the current best *ab initio* potentials do not even yield all vibrational energy spacings correct to within $1\,\mathrm{cm}^{-1}$. This could be because the calculation was only done on a cc-pV5Z basis set, or because the QCISD(T,full) method that the authors used, only considered triple excitations while a full CI calculation should include up to hexuple excitations. CCSDTQPH calculations have never yet been reported for anything larger than a DZ basis set, and deterministic FCI calculations for $6e^-$ have not exceeded the level of TZ basis sets. With FCIQMC and DMRG we are able to calculate the potential with all levels of excitation included, and the hardware requirements for an aug-cc-pCV6Z basis set are modest. Energies for aug-cc-pCVQZ have already converged to the full CI limit within $0.3\,\mathrm{cm}^{-1}$, and 6Z potentials are underway.