State of the art for \textit{ab initio} vs empirical potentials for predicting 6e$^-$ excited state molecular energies: Application to Li$_2$ (\textit{b}, 1$^3\Pi_u$)

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We build the first analytic empirical potential for the most deeply bound Li$_2$ state: \textit{b} (1$^3\Pi_u$). Our potential is based on experimental energy transitions covering $v = 0 - 34$, and very high precision theoretical long-range constants. It provides high accuracy predictions up to $v = 100$ which pave the way for high-precision long-range measurements, and hopefully an eventual resolution of the age old discrepancy between experiment and theory for the Li(2$^2S$) + Li (2$^2P$) $C_3$ value. State of the art \textit{ab initio} calculations predict vibrational energy spacings that are all in at most 0.8 cm$^{-1}$ disagreement with the empirical potential.

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There is currently a rather large discrepancy between the best atomic 3e$^-$ \textit{ab initio} calculation \cite{1}, and the most current empirical value \cite{2, 3}, for the leading long-range Li(2$^2S$) $-$ Li(2$^2P$) interaction constant (C$_3$), despite the latter being the most precise experimentally determined oscillator strength for any system, by an order of magnitude \cite{3}. Li$_2$(\textit{b}, 1$^3\Pi_u$) is one of the molecular states that dissociates to Li(2$^2S$)+Li(2$^2P$), and therefore its long-range potential has this C$_3$ interaction constant. This “\textit{b}-state” is also the deepest Li$_2$ potential, and out of the five lowest Li$_2$ states, the \textit{b}-state is the only one for which an analytic empirical potential has never been made.

Since the highest 2000 cm$^{-1}$ worth of vibrational levels of the \textit{b}-state still have not been observed, and part of this region is now accessible by current ultra-high precision FA (photoassociation) technology \cite{2, 5}, an analytic potential would be very useful for making predictions to assist in observing the missing levels. The \textit{b}-state also mixes strongly with the A(1$^1\Sigma_u$)-state, which has by far the most precisely determined excited molecular state potential in all of chemistry, and therefore still has a rather large gap of missing data in the middle of its energy range \cite{2, 3}.

Finally, the b(1$^3\Pi_u$)-state has been a key doorway to the triplet manifold, and was directly involved in the measurements for a vast number of other triplet states such as 2$^3\Delta_g$ \cite{2, 6, 7}, 3$^3\Pi_g$ \cite{2}, 3$^3\Sigma_g^+$ \cite{2, 8, 9}, 2$^3\Sigma_g^+$ \cite{7, 10}, 2$^3\Pi_g$ \cite{7, 11, 12}, 1$^3\Delta_g$ \cite{8, 9, 11, 14, 13, 15}, and other undetermined $3\Lambda$ states \cite{15, 16}. Some of these more highly excited triplet states (namely 3$^3\Sigma_g^+$, 2$^3\Sigma_g^+$, 2$^3\Pi_g$, and 1$^3\Delta_g$) are so thoroughly covered by these spectroscopic measurements, that global empirical potentials can be built for them too. For this, an analytic potential for the \textit{b}-state would be used as a base.

In this work we will build analytic empirical potentials for the \textit{b}-states of all stable homonuclear isotopologues of Li$_2$. Previous work has shown that analytic empirical potentials for the c(1$^3\Sigma_g$)-state were able to predict energies correctly to about 1 cm$^{-1}$, in the middle of a gap of > 5000 cm$^{-1}$ where data were unavailable \cite{3, 17}, and this was much better agreement than was obtained with the most sophisticated Li$_2$ \textit{ab initio} calculations of the time \cite{18}.

It was recently shown that the best ground-state rotationless \textit{ab initio} potentials for the 5e$^-$ molecules BeH, BeD, and BeT, were able to predict vibrational energy spacings to within 1 cm$^{-1}$ for all measured energy levels except one. The \textit{b}-state of Li$_2$ might be expected to be more challenging \textit{ab initio} because it (1) is an excited state, (2) has one more e$^-$, and (3) involves many more vibrational energies. We will therefore compare our analytic empirical potentials for the \textit{b}-state of $\text{^6}^6\text{Li}_2$ and $\text{^7}^7\text{Li}_2$ with the most state-of-the-art \textit{ab initio} calculations, which were published recently in \cite{19}.

Table I summarizes all experiments we could find which provided information on rovibrational levels of the \textit{b}-state. Unfortunately attempts to recover the data from \cite{3, 15, 20, 22} were unsuccessful, but we were still able to include all data from the other experiments in our study. Furthermore, it is noted that the \textit{b}-state was also involved in various other studies \cite{6, 8, 22, 24} but these just made use of rovibrational levels that were already determined in the studies listed in Table I in order to access levels of other electronic states.

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Ital and the "non-adiabatic" rotational g-factor. For homonuclear diatomics it is given by [31–33]:

\[ \Delta V_{\alpha}(r) = \langle T_{\text{nuc},\alpha} \rangle + \Delta_2 V_{\alpha}(r) \]

\[ \langle T_{\text{nuc},\alpha} \rangle \equiv Q_{\alpha}(r) + P_{\alpha}(R) + S_{\alpha}(R) \]

\[ Q_{\alpha}(r) \equiv -\frac{\hbar^2}{2\mu_{\alpha}} \left( \frac{\partial^2}{\partial r^2} \right)_{\alpha} \]

\[ P_{\alpha}(r) \equiv \frac{\hbar^2}{2\mu_{\alpha}} \left( L_x^2 + L_y^2 \right)_{\alpha} \]

The ∆V_{\alpha}(r) correction can be approximated by the expectation value of the nuclear kinetic energy operator in the molecular electronic wavefunction basis (\( T_{\text{nuc},\alpha} \)). For homonuclear diatomics it is given by [31, 33]:

\[ \Delta V_{\alpha}(r) = \langle T_{\text{nuc},\alpha} \rangle + \Delta_2 V_{\alpha}(r) \]

\[ \langle T_{\text{nuc},\alpha} \rangle \equiv Q_{\alpha}(r) + P_{\alpha}(R) + S_{\alpha}(R) \]

\[ Q_{\alpha}(r) \equiv -\frac{\hbar^2}{2\mu_{\alpha}} \left( \frac{\partial^2}{\partial r^2} \right)_{\alpha} \]

\[ P_{\alpha}(r) \equiv \frac{\hbar^2}{2\mu_{\alpha}} \left( L_x^2 + L_y^2 \right)_{\alpha} \]
\[ S_\alpha(r) \equiv -\frac{\hbar^2}{8\mu_\alpha} \left( \sum_i \nabla_i^2 + \sum_{i \neq j} \nabla_i \nabla_j \right)_\alpha \]
\[ = \frac{m_e}{4\mu_\alpha} (T_{e,\alpha}) - \frac{\hbar^2}{8\mu_\alpha} \sum_{i \neq j} \nabla_i \nabla_j \]
\[ = -\frac{m_e}{4\mu_\alpha} (V_{BO}(r) + r \frac{\partial}{\partial r} V_{BO}(r)) \]
\[ \equiv -\frac{\hbar^2}{8\mu_\alpha} \sum_{i \neq j} \nabla_i \nabla_j \]
\[ \equiv -\frac{m_e}{4\mu_\alpha} (V_{BO}(r) + r \frac{\partial}{\partial r} V_{BO}(r)) + \Delta S_\alpha(r) \]

where \( \alpha \) represents the internuclear axis, \( L_x \) and \( L_y \) are then projections of the total electronic orbital angular momentum, \( i, j \) represent indices for individual electrons of the molecule, and the first term of \( S_\alpha(r) \) has been expressed in terms of the average electronic kinetic energy \( \langle T_{e,\alpha} \rangle \) and then re-expressed in terms of \( V_{BO}(r) \) using the virial theorem \[31, 32\]. We can define a long-range term \( P_{LR,\alpha}(r) \) by evaluating \( P_\alpha(r) \) in the long-range Heitler-London basis, where electron overlap is zero. \( P_\alpha(r) \) is then expressed as \( P_{LR,\alpha}(r) \) plus a correction \( \Delta P_\alpha(r) \) \[31\]:

\[ P_\alpha(r) \equiv P_{LR,\alpha}(r) + \Delta P_\alpha(r) \]
\[ P_{LR,\alpha}(r) = \frac{\hbar^2}{2\mu_\alpha r^2} \sum_k l_k (l_k + 1), \]

where \( l_k \) represents the orbital angular momentum of the electrons in constituent atom \( k \) of the molecule. Herein we restrict our attention to the \( b \)-state of \( Li_2 \) which dissociates into \( Li(S) + Li(P) \):

\[ P_{LR,\alpha}(r) = \frac{\hbar^2}{2\mu_\alpha r^2} (l_s (l_s + 1) + l_p (l_p + 1)) \]
\[ = \frac{2\hbar^2}{\mu_\alpha r^2}, \text{ since } (l_s = 0, l_p = 1). \]

While we know that in the long-range limit, \( Q_\alpha(r) \) will become a constant \[31\], \( \Delta P_\alpha(r) \) will be zero, and \( \Delta S_\alpha(r) \) will be small \[31\], no other information about these terms is known. Therefore, we may re-write the diagonal Born-Oppenheimer correction (DBOC) in terms of what we know, and then represent these parts that we don’t know, by model functions \( \tilde{S}_k(r) \) for each constituent atom \( k \) of the molecule:

\[ \Delta V_\alpha(r) = \frac{\hbar^2}{\mu_\alpha r^2} \left( \frac{m_e}{4\mu_\alpha} \left( V_{BO}(r) + r \frac{\partial}{\partial r} V_{BO}(r) \right) + \Delta S_\alpha(r) + \Delta P_\alpha(r) + Q_\alpha(r) + \Delta_2 V_\alpha(r) \right) \]

II. EMPIRICAL POTENTIAL AND BORN-Oppenheimer BREAKDOWN (BOB) CORRECTIONS

We now wish to determine empirical functions for \( V_{BO}(r), S(r), \) and \( \tilde{R}(r) \) that accurately reproduce all measured energies when using the Hamiltonian of Eq. 1.

There is a gap of more than 2000 cm\(^{-1}\) (> 60 THz) in experimental information between the highest observed level of \( Li_2 (b, 1^3\Pi_g) \), and its dissociation energy. This means that when building an empirical potential that aims to be relevant in the large data gap, it is very important to take great care in ensuring the potential behaves physically correctly in the extrapolation region. In 2011 the MLR (Morse/long-range) model was used in a fit to build empirical potentials from spectroscopic data for the \( c (1^3\Sigma_g^+) \) -states of \( ^6\Sigma Li_2 \) and \( ^7\Sigma Li_2 \), where there was a gap of more than 5000 cm\(^{-1}\) between data near the bottom of the potential, and data at the very top \[17\]. In 2013 spectroscopic measurements were made in the very middle of this gap \[3\], and it was found that the vibrational energies predicted by the MLR potential from \[17\] were correct to within about 1 cm\(^{-1}\). The present case for the \( b \)-state is in some sense more interesting because there is no data at the top helping to anchor the potential with the right shape near dissociation.
However, as for the c-state, the MLR model is still expected to be able to represent the physics in the long-range region faithfully since the correct theoretical long-range is built into the model. Having this long-range physics accurately built into the model is almost as helpful as having data in the long-range region, as was the case of the c-state. MLR-type empirical potentials have now successfully described spectroscopic data for many diatomic \[2,8,10,17,43,53\] and polyatomic \[43,54,66\] systems. Therefore, we will proceed to use the MLR model to describe \( V_{BO}(r) \).

The MLR model is defined by

\[
V_{\text{MLR}}(r) \equiv D_e \left( 1 - \frac{u(r)}{u(r_e)} e^{-\beta(r) y_{\text{ref}}(r)} \right)^2, \tag{19}
\]

where \( D_e \) is the dissociation energy, \( r_e \) is the equilibrium internuclear distance, and the polynomial \( \beta(r) \) is

\[
\beta(r) \equiv \beta_\infty y_{\text{ref}}(r) + \left( 1 - y_{\text{ref}}(r) \right) \sum_{i=0}^{N_B} \beta_i \left( y_{\text{ref}}(r) \right)^i, \tag{20}
\]

with

\[
\beta_\infty \equiv \lim_{r \to \infty} \beta(r) = \ln \left( \frac{2 D_e}{u(r_e)} \right). \tag{21}
\]

Equations (19) and (20) also depend on the radial variable

\[
y_{\text{ref}}(r) = \frac{r^n - r_{\text{ref}}^n}{r^n + r_{\text{ref}}^n}, \tag{22}
\]

where the reference distance \( r_{\text{ref}} \) is simply the equilibrium distance \( r_e \) in most cases, but can be adjusted to optimize the fit to equation (19).

It is well known \[2,17\] that for large \( r \) we have

\[
V(r) \simeq D_e - u(r) + \cdots, \tag{23}
\]

therefore the long-range behavior of the potential is defined by \( u(r) \), and the short to mid-range behavior is defined by \( \beta(r) \). In the \( b \) \((1^3\Pi_u)\) state, a spin-orbit interaction emerges at large internuclear distances, which splits the potential into four components. Therefore, different potentials \( V^\Omega_u(r) \) can be defined to have the same \( \beta(r) \) defining the short-range behavior where there is no significant splitting, and to have four different \( u^\Omega_u,\Omega_u(r) \) defining the long-range where the splitting occurs.

For large \( r \) where the spin-orbit interaction becomes strong, it is dangerous to label the spin angular momentum \( S \) and orbital angular momentum \( \Lambda \) separately, as in the molecular term symbol \( 2S+1\Lambda \). Instead, these two momenta are combined into a total electronic angular momentum \( \Omega \). For \( ^3\Pi_u, S = 1 \) and \( \Lambda = 1 \), so there are states with four possible symmetries in the \( \Omega \) representation: \( 0^+_u, 0^+_u, 1_u, \) and \( 2_u \). Each of these four states has a slightly different behavior at large internuclear distances,
due to coupling with states that have the same symmetry in the $\Omega$ representation, but different symmetry in the $\Lambda$ representation. This coupling has been described in [61] and has been used for building appropriate analytic empirical potentials for the $A(1^1\Sigma^+_u)$ [2, 3] and $c(1^1\Sigma^+_u)$ [3, 17] states of Li$_2$. The long-range function $u(r)$ is defined separately for each spin-orbit state:

$$u(r) = \begin{cases} u^{b,0^+_u}(r), & 0^+_u \\ u^{b,0^-_u}(r), & 0^-_u \\ u^{b,1^-_u}(r), & 1^-_u \\ u^{b,2^-_u}(r), & 2^-_u. \end{cases} \quad (24)$$

Each of these functions is an eigenvalue of a matrix $u^{0^+_u}$ for each $\Omega_u$ state. These matrices are given in the subsections below, in terms of the (positive) spin-orbit splitting energy $\Delta E$, and neglecting exchange interaction terms.

A. The $0^+_u$ states

In addition to the $b(3^3\Pi_u)$ state, the other $\Lambda$ state that can give rise to $0^+_u$ symmetry is the $A(1^1\Sigma^+_u)$ state [62]. The interstate coupling is therefore given by the $2 \times 2$ matrix [61]:

$$u^{0^+_u}(r) = \begin{pmatrix} \frac{1}{3} \sum_{m=3,6,8,9,10,11,...} C_m^A \left(1^1\Sigma^+_u\right) \begin{pmatrix} a^0_0 \end{pmatrix}_{\pi m}^2 +\frac{2}{3}C_m^A \left(1^1\Sigma^+_u\right) \begin{pmatrix} a^0_0 \end{pmatrix}_{\pi m}^2 \\ \frac{\sqrt{3}}{3} \sum_{m=3,6,8,9,10,11,...} C_m^A \left(1^1\Sigma^+_u\right) \begin{pmatrix} a^0_0 \end{pmatrix}_{\pi m}^2 \Delta E + \frac{2}{3} \sum_{m=3,6,8,9,10,11,...} C_m^A \left(1^1\Sigma^+_u\right) \begin{pmatrix} a^0_0 \end{pmatrix}_{\pi m}^2 \end{pmatrix} \\ \frac{\sqrt{3}}{3} \sum_{m=3,6,8,9,10,11,...} C_m^A \left(1^1\Sigma^+_u\right) \begin{pmatrix} a^0_0 \end{pmatrix}_{\pi m}^2 \Delta E + \frac{2}{3} \sum_{m=3,6,8,9,10,11,...} C_m^A \left(1^1\Sigma^+_u\right) \begin{pmatrix} a^0_0 \end{pmatrix}_{\pi m}^2 \end{pmatrix} \end{pmatrix}, \quad (25)$$

where the lower energy eigenvalue $u^{A,0^+_u}(r)$ comes from $A(1^1\Sigma^+_u)$ and approaches the dissociation limit of Li$(2^2S_{1/2}) +$ Li $(2^2P_{3/2})$, and the higher energy eigenvalue $u^{b,0^+_u}(r)$ comes from $b(1^3\Pi_u)$ and approaches the dissociation limit of Li$(2^2S_{1/2}) +$ Li $(2^2P_{3/2})$ [62].

B. The $0^-_u$ states

The interstate coupling is therefore given by the $2 \times 2$ matrix [61]:

$$u^{0^-_u}(r) = \begin{pmatrix} \frac{1}{3} \sum_{m=3,6,8,9,10,11,...} C_m^A \left(1^3\Sigma^+_u\right) \begin{pmatrix} a^0_0 \end{pmatrix}_{\pi m}^2 +\frac{2}{3}C_m^A \left(1^3\Sigma^+_u\right) \begin{pmatrix} a^0_0 \end{pmatrix}_{\pi m}^2 \\ \frac{\sqrt{3}}{3} \sum_{m=3,6,8,9,10,11,...} C_m^A \left(1^3\Sigma^+_u\right) \begin{pmatrix} a^0_0 \end{pmatrix}_{\pi m}^2 \Delta E + \frac{2}{3} \sum_{m=3,6,8,9,10,11,...} C_m^A \left(1^3\Sigma^+_u\right) \begin{pmatrix} a^0_0 \end{pmatrix}_{\pi m}^2 \end{pmatrix} \\ \frac{\sqrt{3}}{3} \sum_{m=3,6,8,9,10,11,...} C_m^A \left(1^3\Sigma^+_u\right) \begin{pmatrix} a^0_0 \end{pmatrix}_{\pi m}^2 \Delta E + \frac{2}{3} \sum_{m=3,6,8,9,10,11,...} C_m^A \left(1^3\Sigma^+_u\right) \begin{pmatrix} a^0_0 \end{pmatrix}_{\pi m}^2 \end{pmatrix} \end{pmatrix}, \quad (26)$$

where the lower energy eigenvalue comes from $b \left(1^3\Pi_u\right)$ and approaches the dissociation limit of Li$(2^2S_{1/2}) +$ Li $(2^2P_{1/2})$, and the higher energy eigenvalue comes from $2a \left(3^3\Sigma^+_u\right)$ and approaches the dissociation limit of Li$(2^2S_{1/2}) +$ Li $(2^2P_{3/2})$ [62].

C. The $1_u$ states

In addition to the $b(1^3\Pi_u)$ state, the other $\Lambda$ states that can give rise to $1_u$ symmetry are the $2a \left(2^3\Sigma^+_u\right)$ state and the $B \left(1^1\Pi_u\right)$ state [62]. The interstate coupling is therefore given by the $3 \times 3$ matrix [61]:

$$u^{1_u}(r) = \begin{pmatrix} a^0_0 \\ a^0_0 \\ a^0_0 \end{pmatrix} \quad (27)$$
where the lowest energy eigenvalue comes from \( b(1^3\Pi_u) \) and approaches the dissociation limit of \( \text{Li}(^2S_{1/2}) + \text{Li}(^2P_{1/2}) \), and the middle and highest energy eigenvalues come from \( B(1^3\Pi_u) \) and \( 2a(2^3\Sigma_u^+) \) respectively and both approach the dissociation limit of \( \text{Li}(^2S_{1/2}) + \text{Li}(^2P_{3/2}) \) \cite{62}.

**D. The \( 2_u \) state**

The \( 2_u \) state approaching the dissociation limit of \( 2S + 2P \) is alone in its symmetry, and approaches \( \text{Li}(^2S_{1/2}) + \text{Li}(^2P_{3/2}) \) \cite{62}. It has the long-range function \cite{1}:

\[
\begin{align*}
\Delta E &= -\sum_{m=3,6,8,10,11,\ldots} \frac{C_m b(1^3\Pi_u)}{r^m} \\
&= -\left( \Delta E - \frac{C_3 b(1^3\Pi_u)}{r^3} - \frac{C_6 b(3^3\Pi_u)}{r^6} - \frac{C_8 b(1^3\Pi_u + 1/2)}{r^8} - \frac{C_9 b(1^3\Pi_u + 1/2)}{r^9} - \frac{C_{10} b(3^3\Pi_u)}{r^{10}} - \frac{C_{11} b(3^3\Pi_u)}{r^{11}} \right)
\end{align*}
\]  

**E. All four \( \Omega_u \) states combined**

One can imagine an experiment which obtains spectroscopic measurements for all of the four \( \Omega_u \) states, and fits to all of this data simultaneously by using the appropriate eigenvalues of the \( 8 \times 8 \) matrix below:

\[
\begin{pmatrix}
  \mathbf{u}^0_u \\
  \mathbf{u}^0_u \\
  \mathbf{u}^1_u \\
  \mathbf{u}^2_u \\
\end{pmatrix}
\]

\[
\begin{pmatrix}
  \mathbf{u}^0_u \\
  \mathbf{u}^0_u \\
  \mathbf{u}^1_u \\
  \mathbf{u}^2_u \\
\end{pmatrix}
\]

\[
\begin{pmatrix}
  \mathbf{u}^0_u \\
  \mathbf{u}^0_u \\
  \mathbf{u}^1_u \\
  \mathbf{u}^2_u \\
\end{pmatrix}
\]

\[
\begin{pmatrix}
  \mathbf{u}^0_u \\
  \mathbf{u}^0_u \\
  \mathbf{u}^1_u \\
  \mathbf{u}^2_u \\
\end{pmatrix}
\]

\[
\begin{pmatrix}
  \mathbf{u}^0_u \\
  \mathbf{u}^0_u \\
  \mathbf{u}^1_u \\
  \mathbf{u}^2_u \\
\end{pmatrix}
\]

However, Fig. 1 shows the data region, and Fig. 2 shows that the spin-orbit splitting does not seem to become apparent until well past this region. Since the measurements that have been done on the \( b \)-state thus far are far away from the effect of the spin-orbit splitting, we choose to use the simplest spin-orbit long-range function: \( u^{b,2_u}(r) \).

**F. Quadratic corrections and damping functions**

Since the leading term not shown in Eq. 23 is \( \frac{u(r)^2}{4\Delta_e} \), the contribution of the \( C_3 \) terms to the long-range form of the potential, will interfere with the desired \( C_6 \) and \( C_8 \) terms, and all \( C_9 \) and \( C_{11} \) terms will therefore have spurious contributions from the cross-terms formed by the products of the \( C_3 \) terms with the \( C_6 \) and \( C_8 \) terms respectively. We fix this in the same way as was done for \( C_6 \) and \( C_9 \) in \cite{2, 3, 5, 17, 64}, by applying a transformation to all \( C_6 \), \( C_9 \), and this time also \( C_{11} \) terms:

\[
\begin{align*}
C_6 &\to C_6 + \frac{C_3^2}{4\Delta_e}, \\
C_9 &\to C_9 + \frac{C_3 C_6}{2\Delta_e}, \\
C_{11} &\to C_{11} + \frac{C_3 C_8}{2\Delta_e}.
\end{align*}
\]

where the transformation in Eq. 33 has to be made first due to Eq. 33’s dependence on \( C_6 \).

Additionally, The long-range formulas in terms of \( C_m \) constants in the above sub-sections were derived under the assumption that two free atoms are interacting with each other, and there is no overlap of the electrons’ wavefunctions as in a bound molecule. To take into account the effect of electron overlap, we use the damping function form from \cite{45}.
Figure 2. In the long-range region, the splitting of the \( b (1^3\Pi_a) \) state into four spin-orbit components becomes increasingly obvious. This is well beyond the region where data is available, so our empirical potential fits to a model with the simplest long-range potential energy function (the \( 2_u \) state, since there are no other \( 2_u \) states that are nearby in energy, see Eqs. \[20, 52\]). The fine-structure splitting of 0.33532461313 \( \text{cm}^{-1} \) comes from measurements in \[63\].

\[
\begin{align*}
\Delta E (^6\text{Li}) &= 0.33532461313 \text{cm}^{-1} \\
{^6}\text{Li}(2^2S_{1/2}) + {^6}\text{Li}(2^2P_{3/2}) \\
{^6}\text{Li}(2^2S_{1/2}) + {^6}\text{Li}(2^2P_{1/2})
\end{align*}
\]

\[
\begin{align*}
\text{Li}_2 (b, 1^3\Pi_u) \\
0^-_u \quad 0^+_u \quad 2_u \\
1_u
\end{align*}
\]

\[
\text{Internuclear distance} \text{ Å}
\]

\[
C_m \rightarrow C_m D_m^{(s)} (r) = \left( 1 - e^{-\left( \frac{b(s)_{\text{fit}} - b(s)_{\text{AB}})}{\sqrt{m}} \right)^{m+s}} \right) m
\]

\[
D_m^{(s)} (r) &= \left( 1 - e^{-\left( \frac{b(s)_{\text{fit}} - b(s)_{\text{AB}})}{\sqrt{m}} \right)^{m+s}} \right)^{m+s}
\]

where for interacting atoms A and B, \( \rho \equiv \rho_{AB} = \frac{2\rho_A \rho_B}{\rho_A \rho_B} \), in which \( \rho_A \equiv \left( \frac{I^X}{I^H} \right)^{1/2} \) is defined in terms of the ionization potentials of atom X, denoted (I\( ^X \)), and hydrogen(I\( ^H \)). We use \( s = -1 \), which as shown in \[43\], means that the MLR potential in Eq. \[19\] has the physically desired behavior \( V \propto \frac{1}{r^2} \) in the limit as \( r \rightarrow 0 \). For \( s = -1 \), the system independent parameters take the values \( b^{(-1)} = 3.30 \), and \( c^{(-1)} = 0.423 \) \[13\].

**G. Long-range constants**

In previous studies of the \( A (1^1\Sigma_u^+) \) state \[3, 65\] and \( c (1^3\Sigma_u^+) \) state \[3, 17\], it was found that the most precise theoretical values of \( C_3 \) known at those times \[66, 67\] did not fit as well with the measurements of the high-lying vibrational levels near the dissociation, as the values of \( C_3 \) obtained by setting it as a free parameter determined by a least-squares fit to the data.

However, for the \( b (1^3\Pi_u) \)-state, no measurements of such high-lying vibrational levels have been made, so such an “empirical fit” to \( C_3 \) is impossible, and we will have to use the most precise theoretical value known.

For \(^7^7\text{Li}_2\) this is the value from \[66\] and for \(^6^6\text{Li}_2\) this is an unpublished value from Tang calculated in 2015 \[68\]. These values are listed in Table II along with the theoretical values for the higher-order \( C_m \) constants used in our analysis (it has not yet been possible to fit these higher-order \( m > 3 \) constants to spectroscopic data in any direct-potential-fit analysis, so they are held fixed). For \( m > 8 \), no finite-mass corrections have been calculated yet.

**H. Dissociation energy \( \mathcal{D}_e \)**

At the time of carrying out our analysis, the best experimental value for \( \mathcal{D}_e \) of which we were aware, was the 1983 value from \[20\]: \( 12145 \pm 200 \text{ cm}^{-1} \). In a recent study on BeH \[54\], the gap between the highest observed level and the dissociation asymptote was \( \sim 1000 \text{ cm}^{-1} \), and the fitted value of \( \mathcal{D}_e \) varied by about \( 400 \text{ cm}^{-1} \) as parameters such as \( r_{\text{ref}}, p, \) and \( q \) were changed. For the present case of the \( b \)-state of \( \text{Li}_2 \), the data region stops more than \( 4000 \text{ cm}^{-1} \) below the dissociation asymptote, so we do not expect to be able to determine \( \mathcal{D}_e \) any more precisely than the 1983 experimental value. However, we still tried, by letting \( \mathcal{D}_e \) be a free parameter, and we indeed found that the fitted values varied by more than \( 400 \text{ cm}^{-1} \). Therefore, it might make sense to use experimental value from \[20\] which was claimed to be within \( 400 \text{ cm}^{-1} \).
Table II. The best currently available long-range constants and their sources (in Hartree atomic units). $^{\infty}$Li$_2$ represents a Li$_2$ molecule where both nuclei have infinite mass, since finite mass corrections have not yet been calculated for $C_m$ coefficients with $m \geq 3$.

|                | $A\left(1^1\Sigma_u^+\right)$ | $B\left(1^1\Pi_u\right)$ | $b\left(1^3\Pi_u\right)$ |
|----------------|-------------------------------|---------------------------|---------------------------|
|                | $^{6.6}$Li$_2$ | $^{7.7}$Li$_2$ | $^{6.6}$Li$_2$ | $^{7.7}$Li$_2$ | $^{6.6}$Li$_2$ | $^{7.7}$Li$_2$ | $^{6.6}$Li$_2$ | $^{7.7}$Li$_2$ | Ref. |
| $C_0$          | 11.0009 [ES]   | 11.0007 [ES]   | -11.0009 [ES]  | -11.0007 [ES]  | -5.5005 [ES]  | -5.5004 [ES]  | 5.5005 [ES]  | 5.5004 [ES]  | -  |
| $C_9$          | 2076.19(7)     | 2076.08(7)     | 2076.19(7)     | 2076.08(7)     | 1407.29(2)     | 1407.15(5)     | 1407.20(2)     | 1407.15(5)     | E0 |
| $C_{10}$       | 274137(6)      | 274128(5)      | 991105(4)      | 991075(6)      | 48566.9(4)     | 48566.4(2)     | 103053(1)     | 103052(1)     | E0 |
| $C_{11}$       | -5.930 x 10$^7$ | -1.211 x 10$^8$ | -5.032 x 10$^8$ | -9.924 x 10$^7$ | 2.65 x 10$^7$ | 2.65 x 10$^7$ | - |

Figure 3. Various $(N_\beta)^{v_{\text{fit}}}$ models with the same quality of fit are in agreement with each other, until large values of $r$ at which the $N_\beta = 7$ model dips significantly below the red curve representing the theoretical long-range behavior. This dip was obvious in the $-r^3V(r)$ vs $1/r^3$ plots for all models mentioned in the text except for the three $N_\beta = 11$ cases shown. The inset shows $-r^3V(r)$ for the four mentioned models, subtracted from the red theoretical curve. All models match the theory for very large $r$ (small $1/r^3$), but the cases with higher $p$ and/or $q$ match the theory for a much larger range of $r$. Each green circle represents an outer classical turning point of the $ab\ initio$ potential. In the inset, the $ab\ initio$ values lie too high above 0 to be seen.

Because we systematically checked the $ab\ initio$ $D_e$ values for all electronic Li$_2$ states calculated in [19], and found that they were at most 68 cm$^{-1}$ different from the best experimental value, even when the experimental values were known to as high of a precision as 0.0023 cm$^{-1}$ (see Table III). Furthermore, the $ab\ initio$ value for the $b$-state was within the 400 cm$^{-1}$ confidence interval given by the 1983 experimental value [20] discussed in the previous paragraph. Therefore, we decided to fix our $D_e$ value at the $ab\ initio$ value of 12166 cm$^{-1}$ and to only allow the other parameters be free parameters for the remainder of the fitting analysis.

After the completion of this work, we discovered that a much less known paper co-authored by one of the same authors from [20], reported a more precise $D_e$ value of (12180.6 $\pm$ 0.6) cm$^{-1}$ just over 4 years afterwards [21], but it is not clear in the paper how this value, nor its uncertainty is obtained. Particularly, it is not clear whether this is a purely empirical value, or if it also uses the $ab\ initio$ potential which is part of the subject of the paper.
Table III. Dissociation energies $\mathcal{D}_e$ in cm$^{-1}$ of various electronic states of Li$_2$. “obs - calc” denotes the $ab\ initio$ value subtracted from the empirical value. Numbers in parenthesis indicate the experimental uncertainty in the last digit(s) shown. Where possible, $^{6/7}\text{Li}_2$ values were used for the empirical values. When empirical values for the $\mathcal{D}_e$ of $^{6/7}\text{Li}_2$ were not available, the empirical value for $^{7/8}\text{Li}_2$ is given. All $ab\ initio$ values are for $^{8}\text{Li}_2$ which is a hypothetical Li$_2$ molecule with infinite mass.

\[
\begin{array}{cccc}
2S + 2S & X(1^1\Sigma_g^+) & a(1^3\Sigma_u^+) \\
\text{\textit{ab initio}} [19] & 8466. & 334. \\
\text{empirical} & 8516.7800(23) & 333.7795(62) \ [5] \\
\text{obs - calc} & 31. & 0. \\
\end{array}
\]

\[
\begin{array}{cccc}
2S + 2P & A(1^1\Sigma_u^+) & B(1^3\Pi_u) & 2X(2^1\Sigma_u^+) & C(1^3\Pi_u) & b(1^3\Pi_u) & c(1^3\Sigma_u^+) \\
\text{\textit{ab initio}} [19] & 9356. & 2930. & 3289. & 1426. & 12166. & \text{12145.(200)} \\
\text{empirical} & 9353.1795(28) & 2984.444(110) & 3318.66(30) & 1422.5(3) & 7092.4926(86) \ [5] \\
\text{obs - calc} & -3. & 54. & -3. & -21. & -21. \\
\end{array}
\]

\[
\begin{array}{cccc}
2S + 3S & 3X(3^1\Sigma_u^+) \ (1\text{st min.}) & 2A(1^3\Sigma_u^+) \ (1\text{st min.}) & 2A(1^3\Sigma_u^+) \ (2\text{nd min.}) \\
\text{\textit{ab initio}} [19] & 8290. & 5608. & 5389. \\
\text{empirical} & 8317.75,76 & 5615.77,78 & 5321.77,78 \\
\text{obs - calc} & 27. & 7. & -68. \\
\end{array}
\]

\[
\begin{array}{cccc}
2S + 3P & 4X(4^1\Sigma_u^+) \ (1\text{st min.}) & 2B(2^1\Pi_u) & 2C(2^1\Pi_u) & D(1^1\Delta_g) & 2d(2^3\Pi_g) \\
\text{\textit{ab initio}} [19] & 8380. & 6481. & 7773. & 9592. & 8505. \\
\text{empirical} & 8349.79 & 6455.80 & 7773.7(3) & 9579.81 & 8484.80 \\
\text{obs - calc} & -31. & -26. & 1. & -13. & -21. \\
\end{array}
\]

\section{I. Choice of model parameters}

Using the Hamiltonian of Eq. 1 we fit the parameters of Eq. 19 to the 1234 data, with the involved energy levels of the upper states $2^3\Pi_u$ and $1^3\Delta_g$ treated as free parameters. All fits to the data were done using the freely available program DPotFit2.0 [82]. Starting parameters for the fits to Eq. 19 were found by fitting to an RKR potential using the freely available program betafit 2.1 [83]. The RKR potential was made using the program RRR1.20 [64] using the Dunham coefficients found in Table IV of [12].

The quality of a fit was determined by the dimensionless root-mean-square-deviation ($\bar{dd}$) which scales each deviation between an energy predicted by the model ($E_{\text{calc}}$) and the corresponding measurement ($E_{\text{obs}}$), by the uncertainty of the measurement ($u_{\text{obs}}$), for all N$_{\text{data}}$ measurements:

$$
\bar{dd} = \sqrt{\frac{1}{N_{\text{data}}} \sum_{i=1}^{N_{\text{data}}} \left( \frac{E_{\text{calc}}(i) - E_{\text{obs}}(i)}{u_{\text{obs}}(i)} \right)^2}.
$$

In previous studies of the $A(1^1\Sigma_u^+)$ state [65] and $c(1^3\Sigma_u^+)\ state [3]$, it was determined that there was no benefit in including long-range terms beyond $C_9$, because the data for the high-lying rovibrational energies began to deviate from the theoretical long-range potential energy curve at distances shorter than the distance where $C_9$ began to give a noticeable effect on the long-range function $u_{LR}(r)$ (see Fig. 6 of [3] for example).

However, for the b-state, no data exists in the long-range region, so it might make more sense to include more $C_m$ terms in $u_{LR}(r)$ in order to anchor the potential somewhat appropriately in the $>2500$ cm$^{-1}$ gap at the top of the potential well where no data exists to guide the potential. Nevertheless, we first followed the $A-$ and $c-$state studies and only used up to $C_9$. We found an excellent fit with $\bar{dd} = 0.95$ with only $N_3 = 7$, $p = 6$, $q = 2$. However, the long-range behavior of this potential was in vast disagreement with the long-range behavior expected by theory (see Fig. 3). This is because with $(p, q) = (6, 2)$, the long-range form of the potential described in Eq. 23 does not “turn on” until too high a value of $r$ (a larger value of $r$ is needed for $y_p^{\text{ref}}(r)$ and $y_q^{\text{ref}}(r)$ to become sufficiently close to their limiting values of 1).

We can often encourage the the long-range form to “turn on” earlier by increasing $p$ and/or $q$, which often comes with the expense of requiring a higher polynomial degree $N_3$ to recover the same $\bar{dd}$. We explored models with $p \in \{6, 7, 8, 9\}$ and $q \in \{2, 3\}$, including the $C_9$ term in $u_{LR}$ for $p \geq 7$, $C_{10}$ for $p \geq 8$, and $C_{11}$ for $p = 9$. Ideally we would always use as many $C_m$ constants as are known, but as explained in [3, 17], the value of $p$ in Eqs. 19 and 20 need to satisfy $p > m_{\text{last}} - m_{\text{first}}$ where...
\(m_{\text{last}}\) and \(m_{\text{first}}\) represent respectively the last and first \(C_n\) terms included in \(u_{1L}(r)\). We also note that \(C_{12}\) for the \(\text{Li}(2^2S) + \text{Li}(2^2P)\) asymptote is not available, as far as we know.

We found that if \(p < 9\) and/or \(q < 3\), the long-range behavior does not turn on until about \(r = 32\) Å (in the very best cases), while the \(m\)-dependent Le Roy radius \(\dd<\) calculated from the radial expectation values found in \([\text{I}1]\) suggests that the long-range behavior should turn on before \(r = 10\) Å. With \((p,q) = (9,3)\), we found a fit with \(N_\beta = 11\) and \(\dd> = 0.94\), where the long-range behavior turns on at about \(r = 20\) Å (see Fig [3]). Increasing \(q\) to 4 would likely turn the long-range behavior on at closer to the \(m\)-dependent Le Roy radius, but no \((p,q) = (9,4)\) fits with \(N_\beta \leq 11\) had a \(\dd< < 1\) and we needed to push to \(N_\beta \geq 13\) in order to match the \(\dd<\) of the best \((p,q,N_\beta) = (9,3,11)\) fits. Using such a high-degree polynomial, when the data only required \(N_\beta = 7\) for a good fit, can be dangerous in terms of the potential’s extrapolation in the regions neither constrained by data nor built-in \(C_n\) constants. In this respect, we also tried \((p,q) = (9,3)\) fits with \(N_\beta = 10\) for various \(r_{\text{ref}}\) values, but no such fit had a \(\dd< < 1\).

\[\text{J. Born-Oppenheimer breakdown (BOB) corrections}\]

With our best MLR model: \(\text{MLR}^{r=9}_{p,q}(N_3) = \text{MLR}^{3,3}_{3,3}(11)\), we attempted to add adiabatic \(\langle S(r)\rangle\), from Eq. [17] and non-adiabatic \(\langle R(r)\rangle\), from Eq. [18] BOB corrections with the same model functions as used in previous studies of \(\text{Li}_2\) since these models were improved in 2009 \([2,3,5,82]\). It was surprising that despite there being 599 \(^6\text{Li}_2\) data (with \(v_{\text{max}} = 9\), \(N_{\text{max}} = 46\)) and 696 \(^7\text{Li}_2\) data (with \(v_{\text{max}} = 27\), \(N_{\text{max}} = 27\)), adding BOB correction functions did not improve the fit. Even when fitting to 3 adiabatic BOB parameters and 3 non-adiabatic BOB parameters, the \(\dd<\) went down by less than 1%. This is unexpected when there is just as much data for each isotopologue, and there is such a big difference in the highest \(v\) and \(N\) levels observed for each isotopologue.

Nevertheless, it seems that the isotopologue shifts due to the kinetic energy term in the Hamiltonian, and due to the mass-dependent BOB corrections incorporated from Eqs. [9] and [14] are the only significant sources of energy difference between \(^6\text{Li}_2\) and \(^7\text{Li}_2\) for the \(b\)-state (within our data’s precision). This may also explain why the \(\text{ab initio}\) potentials \([19]\) calculated assuming an infinite molecular mass managed to predict both the \(^6\text{Li}_2\) and \(^7\text{Li}_2\) energies so fabulously (see discussion in Section [III] and Table IV), while the \(\text{ab initio}\) BOB correction functions for the not much lighter molecule BeH, were so crucial in matching the ro-vibrational energies predicted from the \(\text{ab initio}\) and empirical potentials \([5,4,59]\). Therefore, the final potential that we recommend, which is the same for both \(^6\text{Li}_2\) and \(^7\text{Li}_2\) in the \(b\)-state except for the small mass-dependent contributions coming from the kinetic energy and the un-colored terms in Eq. [10] does not contain any empirically fitted \(\tilde{S}(r)\) and \(\tilde{R}(r)\) BOB correction functions.

\[\text{K. Sequential rounding and re-fitting (SRR)\]}

Observing the predicted values for \(r_e\) yielded by 139 different fits which had \(\dd< < 0.957\) (within 1.5% of the optimal fit, which had \(\dd< = 0.942\), we see that no fit predicted an \(r_e\) outside the range \((2.589825 < r_e < 2.589871)\) Å, regardless of the values of \((p,q,r_{\text{ref}},N_\beta)\), though the more extreme predictions of \(r_e\) within this range corresponded to fits with \(N_\beta \leq 9\). Based on this observation, we recommend the value \(r_e = (2.589848 \pm 0.0000023)\) Å, which is the average of these upper and lower bounds, with the uncertainty being the distance from the average to either bound.

We then re-fitted the potential to the data, but with \(r_e\) fixed at 2.589848 Å, once with the DPlotFit setting \(\text{IROUND} = -1\) and once with \(\text{IROUND} = +1\) in order to implement the SRR procedure described in \([88]\) and in the DPlotFit manual \([82]\). Neither of these cases affected the 3-digit value \(\dd< = 0.942\). The \(\text{IROUND} = -1\) fit ended up with 2 more total digits than when \(\text{IROUND} = +1\) was used, but had a lower \(\dd<\) in the 4th digit, and has the more elegant feature that the number of digits in \(\beta\) decreases monotonically with increasing \(i\). Therefore, we recommend the potential with \(\text{IROUND} = -1\), whose parameters are listed in Table IV.

\[\text{L. Vibrational energy spacings of the recommended Li}_2(6^2\Sigma^+_b) potential, and comparison to best ab initio potential\]}

Very recently, a review paper on the 5e\(^-\) systems BeH, BeD, and BeT \([54]\) revealed that the state of the art \(\text{ab initio}\) potentials \([52]\) (which used MR-ACPF/aug-cc-pCV7Z(i)), a further estimate of electron correlation effects beyond the approximations of MR-ACPF, second-order DKH scalar relativistic corrections, and mass-dependent BOB corrections), predicted vibrational energy spacings with up to at most 1.8 cm\(^{-1}\) discrepancy with the state of the art empirical potential in the region for which vibrational energies had been measured. The \(\text{ab initio}\) potential also predicted the existence of one more vibrational level than the empirical potential, in the cases of BeH and BeD. This was all for the ground electronic state \(X(1^2\Sigma^+)_b\), so it is of interest to see how well the most state-of-the-art \(\text{ab initio}\) potential for the \(6e^-\) \(\text{Li}_2\) excited state \(b(1^3\Pi_u)\) will be.

A Fock space MRCC method based on the (2,0) sector of the Fock space, called FS-CCSD(2,0) \([89]\), was recently implemented and used to calculate potential energy curves for many excited states of \(\text{Li}_2\) \([19]\) with the
ANO-RCC basis set [90]. While in principle possible, DKH and BOB corrections have not been made in any Li2 \textit{ab initio} calculations to date. However, fortunately we found in Section III that the addition of $S(r)$ or $R(r)$ functions did not significantly improve the fit to the data, meaning that Born-Oppenheimer breakdown beyond the effects included in Eqs. (3) and (4) do not seem to have a big effect in this particular state of Li2, at least in the data region. Said another way, the \textit{ab initio} Born-Oppenheimer potential is expected to give good predictions of the energies of $^{6,6}$Li2 and $^{7,7}$Li2, with mass-dependent differences accounted for only by the Hamiltonian’s kinetic energy operator, as was the case with the empirical MLR potential.

Using the \textit{ab initio} Born-Oppenheimer potential provided to us by the authors of 15, and the MLR potential described by Table IV, we used LEVEL to calculate the vibrational energies of both the $^{6,6}$Li2 and $^{7,7}$Li2 isotopologues. We found that the highest levels had outer classical turning points of several thousand Angstroms, and therefore we found it useful to use the recently developed mapping which allows the radial mesh to extend to $r = \infty$ when numerically solving the Schroedinger equation 91, 92, which is also implemented in LEVEL. With this method we were able to find up to $v = 91$ for $^{6,6}$Li2 and $v = 98$ for $^{7,7}$Li2, however, when we calculated the scattering wavefunction, the number of nodes indicated that the highest bound vibrational levels should be $v = 92$ and $v = 100$ respectively. Impressively, these results were identical whether we used the \textit{ab initio} potential, or the MLR potential.

We used Le Roy-Bernstein theory to predict these missing levels for each isotopologue: For a $C_2v/r^3$ potential, the powers $E_v^{(r^3)}$ of the binding energies should be linear in $v$ [93]. We used the slope calculated from $v = 90$ and 91 for $^{6,6}$Li2, and the slope calculated from $v = 97$ and 98, for predicting the energies of $v = 92$ and $v = 99$ levels respectively. We then used the last two points again to calculate a new slope for predicting the energies of $v = 100$. Interestingly, both the \textit{ab initio} potential, and the MLR potential predict the existence of a $^{6,6}$Li2 level bound by $< 8 \times 10^{-8}$ cm$^{-1}$ (< 3 kHz) and a $^{7,7}$Li2 level bound by $< 2 \times 10^{-10}$ cm$^{-1}$ (< 6 Hz). Using $C_3^6Li/v^3$ and $C_3^7Li/v^3$ we get that the outer classical turning points for the least bound levels of each isotopologue are predicted to be at least 13 000 Å and 120 000 Å respectively.

These vibrational energies were then used to calculate the zero point energies (ZPEs) and vibrational energy spacings $\omega_i$, which are presented in the table below, along with the discrepancy between the \textit{ab initio} and empirical potentials. We have compared the vibrational energies (since these are important for photoassociation experiments) and the vibrational spacings (since these are important for experiments involving energy transitions). For both $^{6,6}$Li2 and $^{7,7}$Li2, the discrepancy for the vibrational energies is less than 12 cm$^{-1}$. The agreement for the vibrational spacings is much better than for the case of BeH discussed in the beginning of this subsection. The largest discrepancy for a $^{6,6}$Li2 vibrational spacing is < 0.8 cm$^{-1}$ and for $^{7,7}$Li2 cm$^{-1}$ is < 0.6 cm$^{-1}$.

### III. CONCLUSION

The motivation for this work was to build a potential that could predict high-accuracy vibrational energies for $^{6,6}$Li2(b) in the accessible energy range of the recently built high-precision experimental setup which has so far been very successful for photoassociation spectroscopy of $c (1^3Σ^+_g)$ 3 and $A (1^1Σ^+_u)$-states 2. A similar photoassociation apparatus has recently also been setup by Kai Dieckmann’s group to measure energy levels of ultracold $^{6,6}$Li2 electronic states dissociating to the 2Σ +3P asymptote 94. The best \textit{ab initio} vs empirical potential comparison for Li2 in the literature 18, predicted vibrational levels with a discrepancy of up to 2.04 cm$^{-1}$ for the $a (1^3Σ^+_u)$, which would have simply not been good enough for finding the levels in this type of experiment. The spectroscopic features in this type of experiment are typically around 0.000 2 cm$^{-1}$; and covering 2 cm$^{-1}$ with one-minute measurements and a 0.000 2 cm$^{-1}$ step size would take about 7 days.

However, the empirical MLR potential of 17 for the c-state predicted energies were accurate enough to cut the experiment’s duration to under 2 days, since the first level in the laser’s range turned out to be predicted correctly to within 0.525 cm$^{-1}$, despite this energy being right in the middle of a 5000 cm$^{-1}$ gap in available experimental data to guide the empirical potential. In our table comparing the \textit{ab initio} and empirical MLR energies for the b-state we see that the vibrational energies predicted by the \textit{ab initio} potential are sometimes in > 10 cm$^{-1}$ disagreement with the empirical values in the region where the energies have in fact been measured. However, the \textit{ab initio} seems to predict all vibrational energy spacings correctly within less than 1 cm$^{-1}$ which is much better than the result in the current best ground state 5e− BeH study 54, 87.
The reason we are interested in measuring more levels of the b-state with high-precision, is because it is surprising that the best ab initio calculation of the first Li(2S) – Li(2P) interaction term (C3) is still in vast disagreement with the empirically fitted values from the studies of the A-state \[2, 2\] and c-state \[2, 17\], despite lithium only having 3c⁻, and this C3 value having significance for atomic clocks \[3\]. Lithium is also expected to play a major role in polarizability metrology, since polarizability ratios can be measured much more precisely than individual polarizabilities \[92\], and Li is the preferred choice for the standard in the denominator of such a ratio \[90\]. But this discrepancy in C3 limits the accuracy of a potential Li-based standard for polarizabilities \[3\]. Consolingly, in this study we have found that the b-state is predicted to have levels bound by \( < 8 \times 10^{-8} \) cm\(^{-1}\) (< 3 kHz) which would imply an outer classical turning point of > 13,000 \( \AA \), which is larger than any case in our awareness. Since the less bound the level measured, the more precisely C3 can be determined from a fit, these extremely weakly bound energies are promising for resolving the discrepancy. While the technology to measure these extremely weakly bound energies may still be years away, many of the very high vibrational levels predicted in our analysis are indeed accessible with today’s photoassociation technology.

The least bound levels for the A-state which have been measured have binding energies of \( E_v = 8 \) cm\(^{-1}\), \( E_v = 8 \) cm\(^{-1}\), and \( E_v = 97 \) cm\(^{-1}\) for \( ^6\text{Li}^2\), \( ^6\text{Li}^2\) and \( ^7\text{Li}^2\) respectively, and the least-squares fit to the data gave a C3 value with a 95% confidence limit uncertainty of about \( \pm 8 \) cm\(^{-1}\)/\( \AA^3 \) \[3\], which is currently the most precise experimentally determined oscillator strength for any system, by an order of magnitude \[3\]. The ab initio and empirical MLR potentials for the b-state compared in this work, both give predictions that are in great agreement for energy levels that are several orders of magnitude less deeply bound than the least deeply bound A-state measurements, making it therefore possible to obtain an empirical C3 value far more precise than in \[3\]. Hopefully, this would resolve the age-old discrepancy between experiment and theory for this C3 value, which was first measured experimentally by Loomis and Nusbaum in 1931 \[97\].

Empirical potentials have recently been built for the b- and A-states of \( ^{7}\text{Li}_2 \) in 2009 \[96\] and again in 2013 \[98\], \( ^{7}\text{Li}_2 \), \( ^{7}\text{Li}_2 \) in 2010 \[100\], and \( ^{7}\text{Li}_2 \) in 2011 \[101\] and \( ^{7}\text{Li}_2 \) in 2015 \[103\], however, this is to our knowledge, the first empirical potential built for the \( ^6\text{Li}_2 \) state of Li2.

Table IV. Comparison of the binding energies, denoted \( G(v_i) \): zero-point energies (ZPE); and vibrational energy spacings, denoted \( \omega_i \equiv G(v_{i+1}) - G(v_i) \); for \( ^6\text{Li}_2 \) and \( ^7\text{Li}_2 \). The last column is the difference between the two columns directly prior. Discrepancies of \( \geq 0.5 \) cm\(^{-1}\) are marked by one star (two stars if it was for vibrational level within the data range). Lines with blue font are for unobserved levels, lines with bold green font are for unobserved levels which are accessible by the UBC lab. All energies were calculated by the program LEVEL 8.2 with atomic masses and \( \text{ROSE} = 0.1 \text{R}^2 1, \text{ILR} = 3, \text{MC} = 6, \) and \( \text{CHW} = 3 \). All numbers were converged with respect to the radial mesh parameters, to at least to the number of digits shown.

| \( v \) | 2015 Empirical | 2014 Empirical |
|------|----------------|----------------|
| \( [\text{Present work}] \) | \( E_v(2015) - E_v(2014) \) | \( \omega(2015) - \omega(2014) \) |
| \( \omega \) | \( \omega \) | \( \omega \) |
| \( \text{LiCs in 2009} \) | \( \text{LiCs in 2013} \) | \( \text{LiCs in 2014} \) |
81 \(-1.61050129\) \(-1.68134448\) \(7.1 \times 10^{-2}\) 
82 \(-1.17975971\) \(-1.2344662\) \(5.5 \times 10^{-2}\) 
83 \(-0.84966509\) \(-0.89120346\) \(4.2 \times 10^{-2}\) 
84 \(-0.69043025\) \(-0.69141251\) \(3.1 \times 10^{-2}\) 
85 \(-0.41533866\) \(-0.43807249\) \(3.3 \times 10^{-2}\) 
86 \(-0.28043783\) \(-0.29697717\) \(3.3 \times 10^{-2}\) 
87 \(-0.18419163\) \(-0.19566591\) \(2.1 \times 10^{-2}\) 
88 \(-0.11718257\) \(-0.12503825\) \(7.9 \times 10^{-3}\) 
89 \(-0.07183187\) \(-0.07751583\) \(5.2 \times 10^{-3}\) 
90 \(-0.04214098\) \(-0.04548936\) \(4.4 \times 10^{-3}\) 
91 \(-0.0245378\) \(-0.02551255\) \(1.8 \times 10^{-3}\) 
92 \(-0.0123887\) \(-0.01344075\) \(1.3 \times 10^{-3}\) 
93 \(-0.0058916\) \(-0.00654915\) \(6.6 \times 10^{-4}\) 
94 \(-0.00255567\) \(-0.00288656\) \(3.3 \times 10^{-4}\) 
95 \(-0.00096382\) \(-0.00111272\) \(1.5 \times 10^{-4}\) 
96 \(-0.00029784\) \(-0.00035508\) \(5.7 \times 10^{-5}\) 
97 \(-0.00006752\) \(-0.00008843\) \(1.7 \times 10^{-5}\) 
98 \(-0.00000869\) \(-0.00001212\) \(3.4 \times 10^{-6}\) 
99 \(-0.00000023\) \(-0.00000043\) \(2.1 \times 10^{-7}\) 
100 \(-0.00000004\) \(-0.00000001\) \(1.2 \times 10^{-10}\)
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