Long-range three-body atom-diatom potential for doublet Li$_3$

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An accurate long-range \textit{ab initio} potential energy surface has been calculated for the ground state $^2A'$ lithium trimer in the frozen diatom approximation using all electron RCCSD(T). The \textit{ab initio} energies are corrected for basis set superposition error and extrapolated to the complete basis limit. Molecular van der Waals dispersion coefficients and three-body dispersion damping terms for the atom-diatom dissociation limit are presented from a linear least squares fit and shown to be an essentially exact representation of the \textit{ab initio} surface at large range.

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I. INTRODUCTION

Progress in the field of ultracold molecules has been rapidly growing for the past decade, as many atomic and molecular research groups have turned towards the study of either production or dynamics of ultracold diatomic molecules. The success behind the study of ultracold molecular formation lies in the use of photoassociation and Feshbach resonances (see Jones et al.\textsuperscript{1} and Köhler et al.\textsuperscript{2} for recent reviews). Using a combination of photoassociation and STIRAP\textsuperscript{3} (stimulated Raman adiabatic passage) the formation of vibrational ground state KRb\textsuperscript{4,5} and Cs\textsubscript{2}\textsuperscript{6} molecules have been reported. With this prospect of ground vibrational diatoms in mind we focus our study to the interaction effects of a colliding lithium atom with that of a \( v = 0 \) singlet lithium diatom. Knowledge of both the long- and short-range\textsuperscript{7} interaction potential can be used to calculate inelastic three body rates\textsuperscript{8} as well as investigate Efimov collisions\textsuperscript{9}.

The assumption of a vibrational ground state diatom greatly simplifies the physics of the interaction, however the complexity of calculating long-range interactions for even the \( v = 0 \) range of motion of the diatom is significant. Given this we work within the frozen diatom approximation, which entails freezing the diatom at the calculated equilibrium bond length for the entire potential energy surface, which is analogous to vibrationally averaging the diatom over the course of the collision. The long-range interaction is not strongly effected by this approximation due to the small linear changes seen in the diatomic polarizability as the diatom undergoes small oscillations. Here then the polarizability averaged over the vibrational motion is just the polarizability evaluated at \( r_e \). The validity of the rigid rotor approximation for short atom-diatom collisional distances was found to be good for distances greater than 10Å.

We structure this work into the following three parts, first is the discussion of the \textit{ab initio} calculations. Here we discuss the methodology involved in choosing the appropriate basis set which provides both the optimal values for the spectroscopic constants as well as the best atomic static polarizability. Further improvement to the interaction energy is shown to come from accounting for basis set superposition error through a counterpoise correction\textsuperscript{10} and from extrapolating the counterpoise corrected energies to the complete basis limit. Next we present a summary of the long-range van der Waals interaction for the tri-atomic dissociation limit. An account of the many-body terms arising from third and fourth order Rayleigh-
Schrödinger perturbation theory that contribute to the three-atom $C_6$ and $C_8$ van der Waals coefficients is given. Finally we present the long-range analytic van der Waals atom-diatom interaction energy of Cvitaš et al.\textsuperscript{11} and our fitted non-additive van der Waals coefficients.

II. AB INITIO CALCULATION

The long-range potential energy surface for the $^2A'$ Li$_3$ state has been calculated within a frozen diatom approximation for collisional angles near the $C_{2v}$ geometry, which corresponds to a lithium diatom in the $X^1\Sigma^+_g$ state colliding with a single $^2S$ state lithium atom. The long-range potential energy surface was calculated for atom-diatom distances ranging from 10Å to 100Å, a region we consider to be both outside of any consideration of charge overlap yet still well within the very-long-range limit where the retarded potential starts contributing. The collisional angle sampling of $\theta = 60$, 70, 80 and 90 degrees (where $\theta = 90^\circ$ corresponds to $C_{2v}$ geometry in Jacobi $R, r, \theta$ coordinates) is both sufficient for an accurate fit and consistent with our previous work on the near equilibrium geometry potential energy surface.\textsuperscript{7} All electronic energy calculations in this work were done correlating all electrons using spin restricted coupled cluster theory with singles, doubles and iterative triples (RCCSD(T)) as implemented in the MOLPRO 2008.1\textsuperscript{14} suite of \textit{ab initio} programs.

Cold scattering calculations require exceptionally accurate interaction potentials in order to properly predict cross-sections and scattering lengths. To provide this accuracy we apply a series of corrections to the RCCSD(T) energy which account for deficiencies within the basis set. Additionally we correlate all electrons in the RCCSD(T) energy so as to account for the core-core and core-valence (CV) contributions. The inclusion of CV correlation energy has been shown to account for roughly 0.002Å for multiple bonds and several hundred cm$^{-1}$ to atomization energies.\textsuperscript{15} To properly correlate all electrons within an \textit{ab initio} calculation necessitates the use of a CV consistent basis set.\textsuperscript{15,16} We have examined the use of the four and five zeta cc-pVnZ basis sets from Feller\textsuperscript{17} and the CV consistent CVnZ basis sets of Iron \textit{et al.}\textsuperscript{16} In Table II is a comparison between calculated spectroscopic constants from the above basis sets and the experimental values, it can be seen that the five zeta basis sets provide a marked improvement in terms of both $r_e$ and $D_e$. The calculated polarizability is also used as a benchmark calculation in addition to $r_e$ and $D_e$. The accuracy of which is a strong indicator of the accuracy of the atomic static polarizability is a strong indicator of
the accuracy of long-range molecular dispersion interactions.

The first improvement to the trimer potential energy surface was to calculate the basis set superposition error (BSSE) through a counterpoise calculation. The interaction energy of the trimer is then

$$E_{\text{int}} = E_{\text{trimer}} - E_{\text{atom}}^{12} - E_{\text{atom}}^{13} - E_{\text{atom}}^{23}$$

(1)

where $E_{\text{atom}}^{ij}$ is the energy of the resulting atom when atoms $i$ and $j$ within the trimer are replaced with dummy centers. Accounting for BSSE the CVQZ basis provides a correction of 5.27 cm$^{-1}$ and the CV5Z basis has a correction of 1.05 cm$^{-1}$. Across the total long-range surface the total BSSE correction varies no more than 1%, finally converging to a constant value at interaction regions greater than 20Å. This suggests that the majority of the BSSE corresponds to the diatom and not the atom-diatom interaction itself. Still this counterpoise correction does not fully account for all of the dissociation energy of the Li$_2$ diatom. We further improve upon the accuracy of the potential energy surface by extrapolating the counterpoise corrected energies to the complete basis set (CBS) limit. We use the CBS limit extrapolation formulation of Helgaker et al.

$$E_n = E_\infty + \frac{a}{n^3}.$$  

(2)

This extrapolation scheme was applied to the CVQZ and CV5Z counterpoise corrected interaction energies for the final potential energy surface calculation.

We calculate the static polarizability for the ground state lithium atom and singlet lithium diatom with the static field method by calculating the RCCSD(T) energies in the presence of an electric dipole field (given here as $E(F)$). The static polarizability is given by the finite field gradient

$$\alpha_{ii} = \frac{5E(0)/2 - 8E(F)/3 + E(2F)/6}{F^2}$$

(3)

and reported in Table [II]. The dispersion energy between two monomers at long-range (no charge overlap) can be expressed as

$$u_{\text{disp}} \simeq \frac{3V\alpha_1\alpha_2}{2R^6},$$

(4)

where $\alpha_i$ is the static polarizability for the $i$th monomer and $V$ is a characteristic excitation energy of the molecule. Due to the important contribution of the long-range tail of the electron wave function to the molecular polarizability, the effects of adding diffuse functions
can be significant. In the calculation of the polarizability discussed above, a set of even tempered diffuse functions were added to the CVnZ basis sets and found to contribute little to the extrapolated polarizability. A further test on the effect of adding diffuse functions was performed by evaluating a CBS extrapolated single point energy calculation at 10Å with the even tempered diffuse functions discussed above. The results showed that in the CBS limit the difference between the standard and augmented CVnZ basis sets amounts to less than half a wavenumber.

Because the long-range interaction depends explicitly upon the monomer static polarizability, it is clear from the reported atomic static polarizability in Table II that the CVnZ basis sets are the optimal. The variation in theoretically reported parallel and perpendicular polarizabilities for the lithium diatom (see Deiglmayr et al\textsuperscript{22} for a review of alkali diatomic static polarizabilities) do not offer a significant constraint on the chosen basis set. Our final recommended calculations make use of the counterpoise correction with the extrapolation to the CBS limit as discussed above. We expect that our calculated diatomic long-range interactions will be suitably accurate given the precision of the calculated spectroscopic values and static atomic polarizability.

III. LONG-RANGE VAN DER WAALS POTENTIAL

We now examine the trimer potential energy surface at the three atom dissociation limit, which is expanded analytically in terms of the two-body dispersion interactions with the addition of a purely three-body interaction potential. The three-body contribution to the interaction energy is well known to be strong for Li\textsubscript{3}, for both the doublet\textsuperscript{27} and quartet\textsuperscript{23} state. Thus it is important to accurately include such effects in any model of the long-range interaction. By using perturbation theory to examine this expansion it is possible to express the generalized dispersion coefficients in terms of known diatom and triatomic constants. Our goal in this section is to overview the essential theory of three-body atomic interactions, which can then be specialized to the case of atom-diatom interactions within the frozen diatom approximation previously discussed.

The tri-atomic dissociation interaction potential can be described in terms of the diatomic
van der Waals interaction potential $V_d(r_{ij})$ and non-additive many-body potential $V_3(r)$ as

$$V(r) = \sum_{i>j} V_d(r_{ij}) + V_3(r), \quad (5)$$

where $r = (r_{12}, r_{13}, r_{23})$ are the three internuclear vectors. Long-range dispersion interaction potentials (excluding retardation and orbital overlap effects) between two S-state atoms are described using the multipole expansion

$$V_d(r_{ij}) = -C_6 r_{ij}^{-6} - C_8 r_{ij}^{-8} + O(r_{ij}^{-10}), \quad (6)$$

where the $C_6$ and $C_8$ coefficients are respectively the dipole-dipole, quadrupole-quadrupole and dipole-octopole expansions of the inter-atomic electrostatic Hamiltonian $V_{ij}$. To obtain the leading terms of the non-additive potential $V_3(r)$ in Eq. 5, the analogous expansion method used for the diatom van der Waals interaction can be used. Here, Rayleigh-Schrödinger (RS) perturbation theory is applied to the total inter-atomic interaction Hamiltonian $H_{\text{int}} = H_{\text{tot}} - H_A - H_B - H_C$, where $H_x$ is the atomic Hamiltonian for the $x$'th atomic, then expanded by multipole moments. The desired contributions to the non-additive potential $V_3(r)$ arise from the first many-body terms in third order RS perturbation theory.

The bipolar expansion of the many-body terms from third order RS perturbation theory leads to a summation of purely geometric factors with interaction constants dependent on the atomic species,$^{24,25}$

$$V_3^{(3)} = \sum_{l_1l_2l_3} W_{l_1l_2l_3}(r)Z_{l_1l_2l_3}. \quad (7)$$

The interaction constant can be expressed with the Casimir-Polder integral of the dynamic $2^l$ polarizabilities$^{26}$ over complex frequencies

$$Z_{l_1l_2l_3} = \frac{1}{\pi} \int_0^\infty \alpha^{l_1}(i\omega)\alpha^{l_2}(i\omega)\alpha^{l_3}(i\omega)d\omega. \quad (8)$$

With the dynamic polarizability defined as$^{27}$

$$\alpha^l(\omega) = \sum_n \frac{f^{(l)}_{n0}}{E_n^2 - \omega^2} \quad (9)$$

and the $2^l$ oscillator strength defined as

$$f^{(l)}_{n0} = \frac{8\pi}{2l+1} E_n |\langle 0 | \sum_i r_i'^l Y_{lm}(\hat{r}_i) |n \rangle|^2, \quad (10)$$
the sum over \( i \) goes over all the electrons in the given atom and \( E_n \) is again the excitation energy for state \( n \). The geometric factors \( W_{l_1l_2l_3}(r) \) have been reported by a number of authors\(^{11,24-26} \) and will not be reproduced here. The first term in the third order expansion can be identified as the well known Axilrod-Teller-Muto triple-dipole\(^{28} \) term. Additionally, it has been identified that the quadruple dipole term \( Z_{1111} \), from fourth order perturbation theory, has a contribution to the van der Waals dispersion coefficients of consideration here. This term has no exact expression in terms of the dynamic polarizabilities\(^{11} \), but it can be approximated using a Drude oscillator model in the case of three \( S \) state atoms. Using the corresponding Drude oscillator approximation for the \( C_6 \) van der Waals dispersion coefficient, the \( Z_{1111} \) term can be approximated as\(^{29} \)

\[
Z_{1111} = 10Z_{11}^2/(3C_6). \tag{11}
\]

Using the values \( C_6 = 1393.39 \) and \( Z_{11} = v_{abc}/3 = 56865 \) from Yan \textit{et al.}\(^{27} \), this provides the approximate value \( Z_{1111} = 7735638 \) a.u. for the quadrupole dipole term.

In the other asymptotic limit of the trimer where the system dissociates to a diatom and separated atom, the van der Waals type interaction can again be expressed as a series of multipole terms of the diatomic and atomic polarizabilities. Using the Jacobi coordinates \( R, r, \) and \( \theta \) to describe the atom-diatom system, where \( r \) is the diatomic internuclear distance, \( R \) is the diatomic center of mass to colliding atom distance and \( \theta \) is the angle between \( r \) and \( R \), for the asymptotic limit of \( R \gg r \) the interaction potential in the absence of damping and exchange is\(^{21} \)

\[
V(R, r, \theta) = D_e - C_6(r, \theta)R^{-6} - C_8(r, \theta)R^{-8} + O(R^{-10}) \tag{12}
\]

Where \( D_e \) is the interaction energy of the diatom, and the dispersion coefficients are defined in terms of Legendre polynomials as

\[
C_6(r, \theta) = C_6^0(r) + C_6^2(r)P_2(\cos \theta), \tag{13}
\]

\[
C_8(r, \theta) = C_8^0(r) + C_8^2(r)P_2(\cos \theta) + C_8^4(r)P_4(\cos \theta) \tag{14}
\]

To obtain the analytic form for the atom-diatom van der Waals coefficients in terms of the tri-atomic terms, we transform the internuclear \( r_{ij} \) coordinates to Jacobi coordinates.
through the transformations

\begin{align*}
  r_{12} &= r, \quad (16) \\
  r_{23} &= (R^2 + \frac{r^2}{4} + R r \cos \theta)^{1/2}, \quad (17) \\
  r_{31} &= (R^2 + \frac{r^2}{4} - R r \cos \theta)^{1/2} \quad (18)
\end{align*}

in the limit of \( R \gg r \).

The contributions to \( C_6(r, \theta) \) and \( C_8(r, \theta) \) can be found by transforming the \( W_{i_1 i_2 i_3}(r) \) and \( r_{ij}^{-n} \) coefficients and then expanding in a power series with respect to \( r/R \). This expansion has been completed by Cvitaš \textit{et al.}\(^{11}\) for the contributions to \( C_6(r, \theta) \) and \( C_8(r, \theta) \). The resulting terms included in these van der Waals coefficients are

\begin{align*}
  C_6^0(r) &= 2C_6 + 12Z_{111}r^{-6} + O(r^{-8}), \quad (19) \\
  C_6^2(r) &= 6Z_{111}r^{-3} + 6Z_{111}r^{-6} + O(r^{-8}), \quad (20) \\
  C_8^0(r) &= 2C_8 + \frac{5}{2}C_6r^2 - \frac{3}{2}Z_{111}r^{-1} + \\
  &\quad \frac{33}{2}Z_{111}r^{-4} + O(r^{-6}), \quad (21) \\
  C_8^2(r) &= 8C_6r^2 + \frac{6}{7}Z_{111}r^{-1} + \frac{120}{7}Z_{112}r^{-3} + \\
  &\quad \frac{402}{7}Z_{111}r^{-4} + O(r^{-6}) \quad (22)
\end{align*}

and

\begin{align*}
  C_8^4(r) &= \frac{36}{7}Z_{111}r^{-1} - \frac{120}{7}Z_{112}r^{-3} + \frac{144}{7}Z_{111}r^{-4} + \\
  &\quad (40Z_{113} - 30Z_{122})r^{-5} + O(r^{-6}). \quad (23)
\end{align*}

In the atom-diatom dissociation limit the effects of charge overlap damping in the \( r \) dependent terms of Eqs. 19-23 cannot be neglected. The standard method of accounting for charge overlap is the inclusion of a damping coefficient \( f_n(r_{ij}) \) for each \( r_{ij}^{-n} \) contribution. Recent reports\(^{11,30}\) have made use of the popular Tang and Toennies\(^{31}\) dispersion damping functions

\[ f_n(r_{ij}) = 1 - e^{-br_{ij}} \sum_{k=0}^{n} \frac{(br_{ij})^k}{k!}. \quad (24) \]

In this work we chose to follow Rérat and Bussery-Honvault\(^{32}\)’s implementation of the Tang and Toennies damping functions, where each anisotropic contribution in terms of \( r \) has the
following mapping
\[ r^{-n} \rightarrow f_n(r)r^{-n}. \] (25)

Working within the frozen diatom approximation the charge overlap damping can be simply modeled as a constant fitting parameter, \( F_n \), evaluated at the diatomic equilibrium bond length. Inserting the fitting parameter into Eqs. [19,23] provides the following

\[
C_6^0(r_e) = 2C_6 + 12Z_{1111}F_6r_e^{-6} + O(r^{-8}), \tag{26}
\]

\[
C_6^2(r_e) = 6Z_{111}F_3r_e^{-3} + 6Z_{1111}F_6r_e^{-6} + O(r^{-8}), \tag{27}
\]

\[
C_8^0(r_e) = 2C_8 + \frac{5}{2}C_6F_2r_e^2 - \frac{3}{2}Z_{111}F_1r_e^{-1} + \frac{33}{2}Z_{1111}F_4r_e^{-4} + O(r^{-6}), \tag{28}
\]

\[
C_8^2(r_e) = 8C_6F_2r_e^2 + \frac{6}{7}Z_{111}F_1r_e^{-1} + \frac{120}{7}Z_{112}F_3r_e^{-3} + \frac{402}{7}Z_{1111}F_4r_e^{-4} + O(r^{-6}), \tag{29}
\]

and

\[
C_8^4(r_e) = \frac{36}{7}Z_{111}F_1r_e^{-1} - \frac{120}{7}Z_{112}F_3r_e^{-3} + \frac{144}{7}Z_{1111}F_4r_e^{-4} + (40Z_{113} - 30Z_{122})F_5r_e^{-5} + O(r^{-6}). \tag{30}
\]

As evaluated in Eqs. [26,30], the fitting parameter \( F_n \) no longer directly correspond to the Tang and Toennies damping function as has been noted.\textsuperscript{11}

We have performed a linear least squares fit of Eq. [12] with the definitions given by Eqs. [13,14] to obtain the van der Waals coefficients given in Table III. We have also fitted Eq. [12] with the definitions given in Eqs. [19,23]. We use the diatom \( C_6 = 1393.39 \) and \( C_8 = 8342 \) dispersion coefficients as well as the \( Z_{111} = v_{abc}/3 = 56865 \) triple dipole term from Yan et al.\textsuperscript{27} and the \( Z_{112} = 581000 \), \( Z_{113} = 1.7 \times 10^7 \) and \( Z_{122} = 6.41 \times 10^6 \) from Patil and Tang.\textsuperscript{32}

Fitting to these values we obtain the same dispersion coefficients as above due to the nature of the least squares fit, with the values for the damping parameters given in Table III. Plotted in Fig. \textsuperscript{1} is a comparison of the \textit{ab initio} surface and the fitted van der Waals potential. As can be seen the fit is very accurate, which is confirmed by the RMS surface fitting error of \( 10^{-3} \) cm\(^{-1}\). This analytical long-range expansion can be used in conjunction with our previous work\textsuperscript{7} on the ground state surface of \( ^2A' \) Li\(_3\) to evaluate scattering properties of the Li+Li\(_2\) rigid rotor system. The results of which we leave to future work.
IV. CONCLUSIONS

We have calculated \textit{ab initio} an accurate long-range \(^2A'\) Li\(_3\) surface for the dissociation to the Li \([^2S]+\) Li\(_2\) \([X^1\Sigma^+_g]\). The lithium diatom was taken to be rigid rotor with the bond length constrained to \(r = r_e\), the calculated equilibrium bond length in table I. The surface was calculated at the RCCSD(T) level of theory, correlating all electrons. To accurately describe the CV interaction, the CVQZ and CV5Z basis sets of Iron \textit{et al}.\(^{16}\) were used; the final counterpoise corrected interaction energies were then extrapolated to the CBS limit. At this level of theory, the atomic and diatomic dipole polarizabilities are shown to be in good agreement with published experimental and theoretical results, which is an important component to long-range interactions. Using the expansion for the atom-diatom many body van der Waals potential (Eq. 12 and 13) we calculate the non-additive interaction coefficients by fitting to the calculated \textit{ab initio} surface. The resulting repulsive contribution of the three-body interaction to the total interaction energy is found to be up to 33\% of the total energy. The fitted van der Waals coefficients were found to be consistent with the existing literature on the related \(^4A'\) state.\(^{11,30}\)

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basis & $r_e$ Å & $D_0$ cm$^{-1}$ & $D_e$ cm$^{-1}$ \\ 
Exp. & 2.673$^a$ & 8434.58$^a$ & 8516.78$^b$ \\
Extrapolated & 2.674 & 8510.926 & \\
CV5Z & 2.674 & 8310.85 & 8487.402 & \\
CVQZ & 2.676 & 8288.66 & 8465.005 & \\
cc-pV5Z & 2.680 & 8319.12 & 8470.085 & \\
cc-pVqZ & 2.685 & 8270.86 & 8445.741 & \\

$^a$ reference$^{33}$  
$^b$ reference$^{34}$

TABLE I. Spectroscopic constants for the ground state singlet lithium diatom calculated using four and five zeta correlation consistent basis sets with counterpoise.

| basis | Li $[^{2}\text{S}]$ | Li$_2$ $[X^1\Sigma_g^+]$ |
|-------|-----------------|-----------------|
|       | $\alpha a_0^3$ | $\alpha_{\perp} a_0^3$ | $\alpha_{\parallel} a_0^3$ |
| Extrapolated | 164.1 | 165.6 | 296.1 |
| CV5Z | 164.2 | 165.1 | 296.7 |
| CVQZ | 164.3 | 164.6 | 297.2 |
| cc-pV5Z | 165.6 | 166.4 | 299.6 |
| cc-pVqZ | 166.7 | 166.4 | 300.8 |
| Theory | 164.111$^a$ | 164.4$^b$ | 162.4$^a$ | 305.2$^a$ |
| Experiment | 164.2(1.0)$^c$ |

$^a$ reference$^{27}$  
$^b$ reference$^{22}$  
$^c$ reference$^{35}$

TABLE II. Calculated finite field static polarizabilities for the ground state lithium atom and singlet lithium diatom evaluated at the RCCSD(T)/CV5Z equilibrium bond length.
\[ C^0_0(\text{r}_e) = 1604 \quad F_1 = -0.2823 \]
\[ C^2_6(\text{r}_e) = 120 \quad F_2 = 0.1602 \]
\[ C^0_6(\text{r}_e) = 221646 \quad F_3 = 0.0399 \]
\[ C^2_8(\text{r}_e) = 173870 \quad F_4 = 0.0167 \]
\[ C^4_8(\text{r}_e) = 27104 \quad F_5 = 0.0075 \]
\[ F_6 = -0.0047 \]

**TABLE III.** Fitted van der Waals coefficients in a.u. for the Li+Li$_2$ ridged rotor system.

**FIG. 1.** Comparison of the *ab initio* surface (points) and fitted van der Waals potential (solid lines) for the Li [2S]+ Li$_2$ [X$^1\Sigma^+_g$] interaction. The Li$_2$ bond length is held at the calculated equilibrium bond length $r_e$. 