

## Potential-energy curve for the $a^3\Sigma_u^+$ state of a lithium dimer with Slater-type orbitals

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We report state-of-the-art *ab initio* calculations of the potential energy curve for the  $a^3\Sigma_u^+$  state of the lithium dimer, conducted to achieve spectroscopic accuracy ( $<1\text{ cm}^{-1}$ ) without any prior adjustment to fit the corresponding experimental data. The nonrelativistic clamped-nuclei component of the interaction energy is calculated with a composite method involving a six-electron coupled cluster and full configuration interaction theories combined with basis sets of Slater-type orbitals ranging in quality from double to sextuple zeta. We additionally include both the leading-order relativistic and adiabatic corrections, and find both of these effects to be non-negligible within the present accuracy standards. The potential energy curve developed by us allowed us to calculate molecular parameters ( $D_e$ ,  $D_0$ ,  $\omega_e$ , etc.) for this system, as well as the corresponding vibrational energy levels, with an error of only about  $0.2\text{--}0.4\text{ cm}^{-1}$ . We also report an *ab initio* value for the scattering length of two  $^2S$  lithium atoms.

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### I. INTRODUCTION

The lithium dimer is one of the simplest (bound) homonuclear many-electron molecules. Therefore, it has attracted significant attention in recent years, with many experimental [1–33] and theoretical [34–40] works devoted entirely to its observation and description. However, singlet electronic states of  $\text{Li}_2$  were the main subjects of the studies; Refs. [41–49] provide a good overview on this topic.

In contrast, the triplet electronic states of the lithium dimer were observed for the first time only relatively recently. Experimental studies of the triplet states of  $\text{Li}_2$  are difficult because transitions from the ground  $X^1\Sigma_g^+$  state are dipole forbidden. Moreover, the spin-orbit coupling in lithium is very weak. This impasse has been broken by improvements in experimental techniques such as perturbation-facilitated optical-optical double resonance (PFOODR) [9,10,19,20]. Xie and Field [9,10] were the first to access the triplet state  $a^3\Sigma_u^+$  and determine the relevant spectroscopic constants. They started with the (bound) ground state  $X^1\Sigma_g^+$  and excited into the mixed  $A^1\Sigma_u^+ - b^3\Pi_u$  manifold. A subsequent fluorescence led to the final  $a^3\Sigma_u^+$  state. Later, Martin *et al.* [23,43], Linton *et al.* [12,13], and others [17] determined accurate vibrational and rotational constants for this state by using high-resolution Fourier transform spectroscopy. These data were further revised by Zemke and Stwalley [50] reporting more bound vibrational levels than initially claimed. Abraham *et al.* [51] performed photoassociation of ultracold lithium atoms, allowing one to determine precise positions of the highest vibrational levels. Finally, Linton *et al.* [24] determined spectroscopic constants for the  $a^3\Sigma_u^+$  state to an accuracy of only a small fraction of  $\text{cm}^{-1}$ . This progress was accompanied by a number of works where semiempirical potentials were

developed to reproduce the experimental spectra (see, for example, Refs. [52–55] and references therein).

Observation of the Bose-Einstein condensate of lithium atoms [51,56,57] sparked a renewed interest in the  $a^3\Sigma_u^+$  electronic state, also in analogous diatomic molecules composed of heavier alkali metals [58]. The reason is the relation between the stability of the Bose-Einstein condensate of spin-polarized atoms and the scattering length ( $a$ ) of these atoms. This quantity can be calculated from first principles having an accurate potential energy curve (PEC) for the  $a^3\Sigma_u^+$  state. Unfortunately, the scattering length is very sensitive to tiny details of the PEC, especially in the asymptotic region. This can be illustrated by an approximate formula [59],  $a^2 \approx \frac{\hbar^2}{m|E_b|}$ , relating the scattering length  $a$  to the binding energy of the highest occupied vibrational level,  $E_b$  ( $m$  is the atomic mass). One can see that even a relatively small change in the well depth of the PEC can shift the value of  $E_b$  significantly and thus impact the calculated scattering length dramatically. This makes accurate *ab initio* determination of  $a$  very challenging, and it has been achieved thus far only for the smallest systems. Quite recently, the lithium atom and dimer have been also the subject of research in the context of quantum information theory [60–63].

The triplet  $a^3\Sigma_u^+$  state of the lithium dimer is weakly bound with a PEC well depth of about  $334\text{ cm}^{-1}$  and a minimum around  $4.2\text{ \AA}$  [54]. Despite that, it accommodates as many as ten vibrational levels. To get a broader picture, let us present a short survey of theoretical results available in the literature for this state.

The first works devoted to various electronic states of  $\text{Li}_2$  employed effective core potentials (with one valence electron) and optional core polarization corrections. The papers of Konowalow and co-workers [64–68], Müller and Mayer [69], Schmidt-Mink *et al.* [70], and several others [71], are prime examples of this approach. The biggest advantage of the core potentials is that the remaining effective

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two-electron system can be treated with relative ease. As a result, many excited states of different spatial and spin symmetries can be studied simultaneously, as best illustrated by recent papers of Jasik *et al.* [72–74]. Unfortunately, the accuracy of this effective approach is somewhat limited, with errors reaching several percent for some quantities. To reduce this error a more elaborate first-principles method must be used. This has recently been achieved by Musiał and Kucharski [75] by using a sophisticated all-electron coupled cluster approach. The error has been reduced by an order of magnitude compared with the previous works; at the same time, more than thirty electronic states were characterized.

In this paper we present a state-of-the-art *ab initio* PEC for the  $a^3\Sigma_u^+$  state of the lithium dimer. We combine high-level quantum chemical methods with large one-electron basis sets composed of Slater-type orbitals (STOs) [76,77] to reach saturation of the calculated values. We employ techniques for calculation of the two-center matrix elements over STOs reported recently [78–82]. Moreover, we evaluate corrections arising from several minor physical effects, e.g., adiabatic or relativistic. We also calculate various spectroscopic parameters, such as dissociation energy, vibrational energy levels, etc., and compare them with the latest experimental data. We would like to emphasize that all calculations reported here utilize only rigorous *ab initio* methods. In other words, the results were obtained with no prior reference to the empirical data.

Atomic units are used throughout the paper unless explicitly stated otherwise. We adopt the following conversion factors and fundamental constants:  $1a_0 = 0.529\,177\text{ \AA}$  (Bohr radius),  $1\text{ u} = 1822.888$  (unified atomic mass unit),  $1\text{ H} = 219\,474.63\text{ cm}^{-1}$  (Hartree),  $\alpha = 1/137.035\,999$  (the fine structure constant). These values are in line with the recent recommendations by the Committee on Data for Science and Technology (CODATA) [83]. We also adopt a convention that the interaction energy is positive whenever the underlying interaction is attractive.

## II. ELECTRONIC STRUCTURE CALCULATIONS

### A. Basis sets

In accurate *ab initio* calculations employing basis sets of any kind it is of utmost importance to generate a systematic sequence of basis sets guaranteeing that the results converge to the exact answer. This allows for reliable extrapolation towards the complete basis set (CBS) limit and (partly) overcomes the slow convergence of the correlation energy with the basis set size. Unfortunately, we are not aware of any openly available Slater-type basis sets which would satisfy the present accuracy requirements. There are many papers devoted to optimization of the STOs' basis sets in the literature [84–89]. However, they are either very old and concentrated mainly on atomic properties or aimed at the density functional theory calculations where the basis set requirements are different. As a result, the first step of this work is optimization of Slater-type basis sets fulfilling the high accuracy standards of the present study.

TABLE I. Composition of the STOs basis sets wtcc- $l$  and da-wtcc- $l$  for the lithium atom;  $l$  is the largest angular momentum included (see the main text for details).

$l$	Atomic	Diffuse
1	5s1p	2s1p
2	6s2p1d	2s2p1d
3	7s3p2d1f	2s2p2d1f
4	8s4p3d2f1g	2s2p2d2f1g
5	9s5p4d3f2g1h	2s2p2d2f2g1h
6	10s6p5d4f3g2h1i	2s2p2d2f2g2h1i

All basis sets used in this paper are composed of canonical STOs [76,77]

$$\chi_{lm}(\mathbf{r}; \zeta) = \frac{(2\zeta)^{n+1/2}}{\sqrt{(2n)!}} r^l e^{-\zeta r} Y_{lm}(\theta, \phi), \quad (1)$$

where  $\zeta > 0$  is a free nonlinear parameter and  $Y_{lm}$  are the spherical harmonics in the Condon-Shortley phase convention. By the term ‘‘canonical STOs’’ we mean that the power of  $r$  is equal to the angular momentum  $l$ .

To optimize the nonlinear parameters, we employ the well-tempering scheme [90–92]: exponents for a given angular momentum  $l$  are written as

$$\zeta_{lk} = \alpha_l \beta_l^{k+\gamma_l k^2} \quad \text{with } k = 0, 1, 2, \dots \quad (2)$$

where  $\alpha_l$ ,  $\beta_l$ , and  $\gamma_l$  are the actual parameters which have to be determined variationally. Well tempering (or related schemes) not only reduces the computational costs of the optimization, but also alleviates the linear dependency problems and helps to avoid troublesome local minima. The latter merit is particularly advantageous in maintaining the consistency of the basis sets sequence. At the same time, the flexibility of Eq. (2) is usually surprisingly good. Brute-force optimizations typically give only marginally better results, especially when a large number of functions are included.

When deciding on the composition of the STOs basis sets we follow the correlation-consistency principle, first proposed by Dunning [93]. The smallest basis set considered here has the composition 5s1p and is systematically expanded, reoptimizing the nonlinear parameters at each step. This gives a sequence of basis sets denoted shortly wtcc- $l$  (well-tempered correlation-consistent) where  $l$  is the largest angular momentum included. A detailed composition of these basis sets is given in Table I. To find the optimal values of the well-tempering parameters for each  $l$  we minimized the total CISD (configuration interaction with single and double substitutions) energy of the lithium atom with all electrons active.

Basis sets designed to reproduce the atomic energies may not be equally satisfactory in a molecular environment. This is especially true for weakly bound systems where the tails of the electronic density are important for the bonding phenomena. To ensure that the basis sets developed here are truly universal we supplemented them with two sets of diffuse functions; see Table I. The exponents of these functions were varied freely to maximize the static dipole polarizability of the lithium atom evaluated at the coupled Hartree-Fock level of theory. The

TABLE II. Total energy ( $E_{\text{total}}$ ) and the correlation energy ( $E_{\text{corr}}$ ) of the lithium atom calculated at the FCI level of theory by using the STOs basis sets da-wtcc- $l$ . All values are given in atomic units.

$l$	$E_{\text{corr}}$	$E_{\text{total}}$
2	-0.041 842	-7.474 511
3	-0.043 749	-7.476 454
4	-0.044 532	-7.477 239
5	-0.044 862	-7.477 569
6	-0.045 056	-7.477 763
$\infty$	-0.045 386	-7.478 093
Ref. [95]	-0.045 353	-7.478 060

modified (augmented) basis sets are denoted da-wtcc- $l$  where “da” stands for doubly augmented.

Finally, in this work we are concerned with the calculation of the relativistic corrections, which have somewhat specific basis set requirements. To eliminate possible sources of error we created a special sequence of basis sets denoted (da-)wtcc- $l$ + $s$ . These basis sets share the polarization and/or augmented functions with the standard (da-)wtcc- $l$ , but all  $s$  functions were replaced with a universal set of twelve  $1s$  orbitals obtained by minimizing the Hartree-Fock energy of the lithium atom. Detailed compositions of all basis sets used in this work (including values of the nonlinear parameters) are given in the Supplemental Material [94].

As a benchmark of these basis sets we compared our atomic results with the reference values available in the literature. For the lithium atom a very accurate value of the clamped-nucleus nonrelativistic energy is available [95] from the three-body Hylleraas calculations,  $E_{\text{total}} = -7.478\,060\,323\,904\,1(^{+10}_{-50})$ . This value is virtually exact for the present purposes. For comparison, we calculated Hartree-Fock and full configuration interaction (FCI) correlation energies in the da-wtcc- $l$  basis sets; see Table II.

The Hartree-Fock energy converges at an exponential rate. Indeed, by comparing the results from the largest two basis sets we see that the energy difference is less than  $1\ \mu\text{H}$ . Therefore, we simply take the value from the largest basis set,  $E_{\text{HF}} = -7.432\,707(1)$ , and conservatively assume that the error is at most  $1\ \mu\text{H}$ . Extrapolation of the HF energies by using the exponential formula barely changed the results. On the other hand, the correlation energy converges at a much slower rate and we apply the conventional three-point extrapolation [96]

$$E = a + \frac{b}{l^3} + \frac{c}{l^5}, \quad (3)$$

where the constants  $a$ ,  $b$ ,  $c$  are obtained by fitting. In Table II we present results obtained with the basis sets  $l = 2-6$  and the values obtained by the extrapolation. Note that our final number for the total energy of the lithium atom differs by only about  $34\ \mu\text{H}$  ( $\approx 7\ \text{cm}^{-1}$ ) from the aforementioned reference value.

### B. Born-Oppenheimer potential

The lithium dimer is a two-center six-electron molecule. For such a system the FCI method, which gives the exact

TABLE III. Nonrelativistic contributions to the interaction energy of the lithium dimer calculated with the da-wtcc- $l$  basis sets;  $E_{\text{int}}^{\text{HF}}$  and  $E_{\text{int}}^{\text{ccsd}(t)}$  denote the interaction energy obtained at Hartree-Fock and CCSD(T) levels of theory, respectively. The abbreviations  $\Delta E_{\text{int}}^{\text{ccsd}t}$  and  $\Delta E_{\text{int}}^{\text{fci}}$  stand for the post-CCSD(T) corrections; see Eqs. (5) and (6). Counterpoise correction was applied to remove the basis set superposition error. All values are given in  $\text{cm}^{-1}$ .

$l$	$E_{\text{int}}^{\text{HF}}$	$E_{\text{int}}^{\text{ccsd}(t)}$	$\Delta E_{\text{int}}^{\text{ccsd}t}$	$\Delta E_{\text{int}}^{\text{fci}}$
$R = 7.75$				
2	-359.46	276.40	1.45	0.15
3	-345.15	322.50	2.2 8	
4	-344.14	328.30	2.29	
5	-344.05	329.21		
6	-344.10	329.51		
$\infty$	$-344.05 \pm 0.01$	$330.09 \pm 0.29$	$2.30 \pm 0.12$	$0.18 \pm 0.05$
$R = 12.5$				
2	-9.64	73.79	0.22	0.05
3	-9.51	85.83	0.30	
4	-9.46	87.05	0.30	
5	-9.45	87.26		
6	-9.44	87.74		
$\infty$	$-9.42 \pm 0.01$	$87.96 \pm 0.11$	$0.30 \pm 0.02$	$0.06 \pm 0.02$

solution of the Schrödinger equation in the CBS limit, cannot be applied. Therefore, in the present work we rely on a composite method which is based mostly on the coupled cluster (CC) theory [97,98].

Within the Born-Oppenheimer (BO) approximation, the interaction energy of the lithium dimer for each internuclear distance is defined as

$$-E_{\text{int}}^{\text{X}} = E_{\text{X}}(\text{Li}_2) - 2E_{\text{X}}(\text{Li}), \quad (4)$$

where  $E_{\text{X}}(\text{Li}_2)$  is the energy of the molecule in the  $a^3\Sigma_u^+$  state,  $E_{\text{X}}(\text{Li})$  is the ground-state energy of the atom, and the superscript X denotes the level of theory. The negative sign in front of the above formula is a convention. Unless explicitly stated otherwise, the counterpoise correction [99] is used in computation of the interaction energies in order to eliminate the basis set superposition error. In this approach the energy of the atom is calculated in the basis set of the molecule and thus the quantity  $E_{\text{X}}(\text{Li})$  is different for each internuclear separation. Our protocol for obtaining accurate Born-Oppenheimer interaction energies is as follows.

First, we evaluate the BO interaction energies by using the Hartree-Fock and coupled cluster with single, double, and perturbative triple excitations (CCSD(T)) [100] methods (all electrons active). The values obtained are abbreviated  $E_{\text{int}}^{\text{HF}}$  and  $E_{\text{int}}^{\text{ccsd}(t)}$ , respectively. At these levels of theory the complete sequence of basis sets,  $l = 2-6$ , can be used. The Hartree-Fock and correlation contributions are extrapolated separately; the exponential formula is used for the HF component and the formula (3) is applied for the remainder. In Table III we present results of this procedure for two interatomic distances: 7.75 and 12.5 a.u. The former value is near the minimum of PEC while the latter lies close to the dissociation limit.

Interestingly, there is a small inconsistency in the Hartree-Fock values: the interaction energy calculated with the  $l = 6$  basis set is a tiny bit smaller than that with  $l = 5$ . To overcome this problem we extrapolate the HF limit from the  $l = 3, 4, 5$  basis sets, omitting the  $l = 6$  value. Due to comparatively fast convergence of the HF energies towards the CBS limit, the error introduced by this approximation is minor for all inter-electronic distances. More importantly, this artifact is absent in the correlated contribution and thus not of a major concern. In the estimation of the extrapolation errors we adopt a fairly conservative approach. Unless explicitly stated otherwise, we assume that the uncertainty is equal to half the difference between the extrapolated result and the corresponding value in the largest basis set.

To bring the accuracy down to the sub- $\text{cm}^{-1}$  regime we need to consider some minor corrections beyond the CCSD(T) model. They naturally split into two contributions. The first is the full triples correction, being defined as a difference between the interaction energies obtained with the CCSDT [101] and CCSD(T) methods:

$$\Delta E_{\text{int}}^{\text{ccsdT}} = E_{\text{int}}^{\text{ccsdT}} - E_{\text{int}}^{\text{ccsd(t)}}. \quad (5)$$

The second correction accounts for excitations higher than triple and is calculated as a difference between the FCI and CCSDT interaction energies:

$$\Delta E_{\text{int}}^{\text{fci}} = E_{\text{int}}^{\text{fci}} - E_{\text{int}}^{\text{ccsdT}} \quad (6)$$

The post-CCSD(T) corrections are especially computationally intensive. In fact, we were able to calculate  $\Delta E_{\text{int}}^{\text{ccsdT}}$  in basis sets only up to  $l = 4$ . Even more disappointingly, the FCI correction is feasible only in the smallest basis set considered here,  $l = 2$ . These restrictions eliminate the possibility of a reliable extrapolation.

To estimate the CBS limits of the post-CCSD(T) corrections we invoke a different strategy. Let us assume that the rate of convergence of the interaction energy with respect to the basis set size is the same at the CCSD(T) level and for the post-CCSD(T) corrections. Because a reliable limit of the CCSD(T) interaction energy is known, approximate CBS limits of the  $\Delta E_{\text{int}}^{\text{ccsdT}}$  and  $\Delta E_{\text{int}}^{\text{fci}}$  corrections can now be obtained by a simple scaling. The scaling parameter is chosen so that the interaction energy calculated with a given finite basis set at the CCSD(T) level matches the extrapolated value.

Clearly, the scaling procedure is not as reliable as extrapolation, the latter having firm theoretical underpinnings. We assume that this procedure gives an accuracy of 5% for  $\Delta E_{\text{int}}^{\text{ccsdT}}$  and 25% for  $\Delta E_{\text{int}}^{\text{fci}}$ . The results of the scaling are given in Table III. The final theoretical error is computed by summing squares of the uncertainties in the individual components and taking the square root. For example, at the internuclear distance  $R = 7.75$  this gives  $332.57 \pm 0.32 \text{ cm}^{-1}$  for the total BO interaction energy.

### C. Relativistic effects

For light systems, such as the lithium dimer, the leading-order relativistic corrections (quadratic in the fine structure constant,  $\alpha$ ) can be calculated perturbatively. Here we adopt

the approach based on the one-electron part of the Breit-Pauli Hamiltonian [102],

$$E^{(2)} = \langle P_4 \rangle + \langle D_1 \rangle, \quad (7)$$

$$\langle P_4 \rangle = -\frac{\alpha^2}{8} \left\langle \sum_i \nabla_i^4 \right\rangle, \quad (8)$$

$$\langle D_1 \rangle = \frac{\pi}{2} \alpha^2 \sum_a Z_a \left\langle \sum_i \delta(\mathbf{r}_{ia}) \right\rangle, \quad (9)$$

where  $i$  and  $a$  denote electrons and nuclei, respectively. The notation  $\langle \hat{O} \rangle$  stands for the expectation value of an operator  $\hat{O}$  on the nonrelativistic clamped-nuclei wave function. For brevity, the consecutive terms in the above equation are called the mass-velocity  $\langle P_4 \rangle$  and the one-electron Darwin  $\langle D_1 \rangle$  corrections. Some authors [103] use the name ‘‘Cowan-Griffin correction’’ for the sum of  $\langle P_4 \rangle$  and  $\langle D_1 \rangle$ .

Note that in the above formulation we neglected the two-electron relativistic corrections (Breit and two-electron Darwin contributions). For light systems they are usually at least by an order of magnitude smaller [104] than the one-electron corrections given by Eqs. (8) and (9). As demonstrated further in the text, the one-electron relativistic effects contribute only a fraction of  $\text{cm}^{-1}$  to the total interaction energy of  $\text{Li}_2$ . Therefore, we estimate that the two-electron effects are of the order of a few hundreds of  $\text{cm}^{-1}$ , and thus entirely negligible in comparison with other sources of error. An additional approximation adopted in this work is the neglect of spin-spin and spin-orbit interactions. The former term is very small ( $\approx 0.01 \text{ cm}^{-1}$  for all points of the potential energy curve) as confirmed by the recent work of Minaev [105], and vanishes quickly with the internuclear distance. The spin-orbit interaction is identically zero in the first-order perturbation theory since we are considering a molecular  $\Sigma$  state.

The one-electron relativistic corrections were calculated analytically on the top of the CCSD(T) wave function. Contractions with the appropriate density matrices were accomplished by using a code written especially for this task. Because the CCSD(T) method performs very well for the interaction energies, we neglect the higher-order mixed relativistic-correlation contributions and apply no post-CCSD(T) corrections. Example results of the calculations are given in Table IV, where, for consistency, we consider the same two interatomic distances as in the preceding section. To speed up the calculations, we evaluated the one-electron relativistic corrections in the basis sets up to  $l = 5$  only.

From Table IV one can see that the mass-velocity and one-electron Darwin corrections converge very quickly with respect to the basis set size. The results in the two largest basis sets are barely distinguishable. Therefore, it is not necessary to extrapolate the values of  $\langle P_4 \rangle$  and  $\langle D_1 \rangle$ . The final result is simply the value obtained with the largest basis set and the error is estimated to be less than 5% of the absolute value.

### D. Other corrections

Since the goal of the present paper is to reach the spectroscopic accuracy, we have to include some further corrections to the potential energy curve originating from the QED and adiabatic effects. Starting with the former, the most

TABLE IV. Relativistic corrections to the interaction of the lithium dimer energy calculated with the da-wtcc- $l$  basis sets. The corrections  $\langle P_4 \rangle$  and  $\langle D_1 \rangle$  are defined by Eqs. (8) and (9), respectively. The last column provides the sum of the values from the preceding two. All values are given in  $\text{cm}^{-1}$ .

$l$	$\langle P_4 \rangle$	$\langle D_1 \rangle$	Total Cowan-Griffin
$R = 7.75$			
2	-0.85	0.63	-0.22
3	-0.91	0.67	-0.24
4	-0.91	0.67	-0.24
5	-0.91	0.67	-0.24
$R = 12.5$			
2	-0.11	0.08	-0.03
3	-0.13	0.09	-0.04
4	-0.13	0.09	-0.04
5	-0.14	0.10	-0.04

convenient framework to describe the QED effects in light systems is the so-called nonrelativistic QED (NRQED) theory [106,107]. In the NRQED the energy of the system is expanded in powers of the fine-structure constant. The quadratic terms correspond to the aforementioned Breit-Pauli Hamiltonian and the  $\alpha^3$  and  $\alpha^3 \ln \alpha$  corrections are the leading-order (pure) QED effects,  $E^{(3)}$ . Explicit expressions for the latter are known [108,109], but their computation for many-electron systems is still a considerable challenge. In the present work we adopt the following approximation to the  $\alpha^3$  and  $\alpha^3 \ln \alpha$  corrections:

$$E^{(3)} \approx \frac{8\alpha}{3\pi} \left( \frac{19}{30} - 2 \ln \alpha - \ln k_0^{\text{Li}} \right) \langle D_1 \rangle, \quad (10)$$

where  $\ln k_0$  is the Bethe logarithm [102,110] and  $\langle D_1 \rangle$  is the same as in Eq. (9). This is essentially the dominant one-electron component of the complete  $\alpha^3$  QED correction (the one-electron Lamb shift). For the Bethe logarithm we adopt the atomic value,  $\ln k_0^{\text{Li}} = 5.178\,17(3)$  [111]. This is a reasonable approximation because this quantity is usually weakly dependent on the molecular geometry [112,113]. For reasons similar as in the case of the relativistic corrections, in Eq. (10) we neglected two-electron contributions, i.e., two-electron Lamb shift and the Araki-Sucher correction. We assume that the approximations introduced in (10) result in a relative error smaller than 50%.

Finally, let us consider the finite nuclear mass effects. The leading-order correction to the PEC due to the nuclear motion is the so-called diagonal Born-Oppenheimer correction (DBOC or the adiabatic correction for short). It is given by the formula [114,115]

$$E_{\text{DBOC}} = \frac{1}{2} \sum_a \frac{1}{M_a} \langle \nabla_a \Psi_0 | \nabla_a \Psi_0 \rangle, \quad (11)$$

where  $a$  runs over all nuclei of the system and  $M_a$  denote the nuclear masses. Unfortunately, calculation of the DBOC with the basis set of STOs is not developed yet and we must resort to the Gaussian-type orbitals (GTOs) in the present paper. We have used the all-electron CCSD method to calculate the adiabatic correction [116] with the augmented quadruple-zeta

basis set developed by Prascher *et al.* [117]. The post-CCSD corrections and basis set incompleteness errors are neglected in this case. We assume that this introduces an error of at most 25%.

### E. Computational details

For the record, in this section we would like to provide some additional technical details concerning the electronic structure calculations described above. The basis set optimizations were carried out by using a program written especially for this purpose. It is interfaced with the GAMESS package [118,119] which carries out the necessary CISD calculations. To optimize the well-tempering parameters we employed the pseudo-Newton-Rhaphson method with the Broyden-Fletcher-Goldfarb-Shanno (BFGS) update of the approximate Hessian matrix [120] and numerically evaluated gradient (two-point finite difference). The optimizations were stopped when the energy difference between two consecutive cycles fell below 10 nH.

All subsequent electronic structure calculations were carried out with help of the ACESII program package [121]. The only exception is the FCI method where the GAMESS package was used and calculation of the adiabatic correction where we employed the CFOUR program [122]. In all coupled cluster computations we employed the restricted open-shell (RO) reference wave function. Inclusion of the relativistic corrections requires expectation values of several operators specified in the preceding sections. Matrix elements of these operators were calculated directly in the STOs basis sets. Coupled cluster density matrices were extracted from the ACESII package by proper manipulation of the CC gradients code logic.

To evaluate the complete potential energy curve we repeated the procedures described in the preceding sections on a grid of internuclear distances. For the nonrelativistic calculations we used the following grid: from  $R = 5.5$  to  $R = 9.0$  the step is  $R = 0.25$ ; from  $R = 9.0$  to  $R = 14.0$  it is  $R = 0.5$ ; from  $R = 14.0$  to  $R = 25.0$  it is  $R = 1.0$ ; and finally above  $R = 25.0$  the step is  $R = 2.5$  up to  $R = 40.0$  (all values are given in multiples of the Bohr radius). Additionally, we evaluated a single point at  $R = 7.882$  which is close to the actual minimum of the potential energy curve. This gives a grand total of 43 points spaced from  $R = 5.5$  to  $R = 40.0$ . For the relativistic corrections the grid was slightly smaller, ending at  $R = 30.0$ . This is mostly due to large cancellations occurring at large  $R$  making the calculated values less reliable.

## III. ANALYTIC FITS OF THE POTENTIALS

### A. General method

In order to generate results directly comparable with the experimental values, the raw *ab initio* data points must be fitted with a suitable functional form to give a smooth function of the internuclear distance,  $R$ . For all contributions to the interaction energy described in the previous sections we adopt the following generic formula:

$$V(R) = \sum_{k=1}^{N_e} e^{-\alpha_k R} \sum_{n=0}^{N_p} c_{nk} R^n - \sum_{n=3}^{N_a} \frac{C_{2n}}{R^{2n}} f_{2n}(\eta R), \quad (12)$$

where  $N_e$ ,  $N_p$ , and  $N_a$  control the expansion length,  $\alpha_k$  and  $\eta$  are (nonlinear) parameters of the fit,  $c_{nk}$  are linear parameters, and  $f_{2n}(\eta R)$  is the Tang-Toennies damping function [123]

$$f_{2n}(x) = 1 - e^{-x} \sum_{k=0}^{2n} \frac{x^k}{k!}. \quad (13)$$

The asymptotic coefficients,  $C_{2n}$ , in Eq. (12) are either taken from more accurate theoretical calculations or fitted (discussed further). Note that we found it unnecessary to include the repulsive Coulomb wall (the unified atoms limit,  $Z^2/R$ ) in the potential formula (12).

The nonlinear and linear parameters in Eq. (12) are chosen to minimize weighted error of the fit. At each point of the grid we are given the values of the potential,  $V_k^{\text{comp}}$ , and the corresponding errors,  $\delta V_k^{\text{comp}}$ . The target function  $\Delta$  for the optimization is chosen as

$$\Delta^2 = \frac{1}{N_g} \sum_{k=1}^{N_g} \left[ \frac{V_k^{\text{comp}} - V(R_k)}{\delta V_k^{\text{comp}}} \right]^2, \quad (14)$$

where  $V(R_k)$  is the value of the fitting function evaluated at a given grid point. We optimize the nonlinear parameters by using the Powell procedure [124]. The optimization is stopped when the target function varies by less than  $10^{-5} \text{ cm}^{-1}$  between several consecutive iterations. The raw *ab initio* data ( $V_k^{\text{comp}}$ ,  $\delta V_k^{\text{comp}}$ ) for all components of the PEC are given in the Supplemental Material [94]. A simple *Mathematica* program [125] implementing all the fits discussed here can be obtained from the authors upon request.

### B. Nonrelativistic potentials

An important issue in the generation of the analytic potentials is to assure that the long-range tail of PEC is correct. Therefore, we prefer to use the asymptotic constants calculated with more accurate theoretical methods (whenever available) rather than relying solely on fitting to match the data points. Fortunately, reliable values of the first three nonrelativistic asymptotic constants ( $C_6$ ,  $C_8$ ,  $C_{10}$ ) were given by Yan *et al.* [126] These values were obtained from variational wave functions in Hylleraas basis sets and are all accurate to better than one part per thousand. For the higher asymptotic constants ( $C_{2n}$  with  $n > 5$ ) the data in the literature are not as abundant. Remarkably, Patil *et al.* [127] report values of the asymptotic constants up to  $n = 12$ . Their values are progressively less reliable with increasing  $n$ . For example, we find that the error in  $C_6$  is only about 0.3% compared with the work of Yan *et al.* [126] but rises to almost 2% for  $C_{10}$ . Therefore, we adopt the values of  $C_{12}$ ,  $C_{14}$ , and  $C_{16}$  from Ref. [127] and neglect the higher-order inverse powers of  $R$  in Eq. (12). We checked that the inclusion of terms beyond  $C_{16}$  changes the results only marginally. The same is true for the asymptotic terms such as  $C_{11}/R^{11}$  (resulting from higher-order perturbation theory) which can be safely neglected at this point.

Concerning the adiabatic correction, the corresponding asymptotic constants are not available for lithium. Despite explicit expressions for these coefficients are available in the literature [128], their calculation is complicated and has been achieved only for one- and two-electron systems thus far. Therefore, we have no other option but to obtain the

TABLE V. Optimized parameters of the fit (12) for the Born-Oppenheimer potential [ $V^{\text{BO}}(R)$ ] and for the adiabatic correction [ $V^{\text{ad}}(R)$ ] (without dividing by the mass term). All values are given in the atomic units. The symbol  $X[\pm n]$  stands for  $X \times 10^{\pm n}$ . Not all digits reported are significant.

Parameter	$V^{\text{BO}}(R)$	$V^{\text{ad}}(R)$
$\alpha_1$	+1.27 983[+00]	+1.87 631[+00]
$\alpha_2$	+2.29 122[−01]	+3.24 019[−01]
$\eta$	+1.02 337[+00]	+5.84 617[−01]
$c_{01}$	+1.28 843[+02]	−8.45 797[+00]
$c_{11}$	−9.02 013[+01]	+4.52 239[+00]
$c_{21}$	+2.67 910[+01]	−8.14 315[−01]
$c_{31}$	−3.42 393[+00]	+5.01 342[−02]
$c_{41}$	+2.07 665[−01]	— <sup>b</sup>
$c_{02}$	+2.11 421[−03]	+1.95 248[−06]
$c_{12}$	−2.40 579[−04]	−5.40 041[−08]
$c_{22}$	+1.05 528[−05]	−1.43 211[−08]
$c_{32}$	−2.07 608[−07]	+4.64 261[−10]
$c_{42}$	+1.54 659[−09]	— <sup>b</sup>
$C_6$	+1.39 339[+03] <sup>a</sup>	+1.47 084[+00]
$C_8$	+8.34 258[+04] <sup>a</sup>	−1.18 756[+03]
$C_{10}$	+7.37 210[+06] <sup>a</sup>	+4.05 449[+05]
$C_{12}$	+9.03 000[+08] <sup>a</sup>	— <sup>b</sup>
$C_{14}$	+1.48 000[+11] <sup>a</sup>	— <sup>b</sup>
$C_{16}$	+3.09 000[+13] <sup>a</sup>	— <sup>b</sup>

<sup>a</sup>Taken from Refs. [126] and [127].

<sup>b</sup>Not included in the fit.

asymptotic constants  $C_{2n}^{\text{ad}}$  by fitting. We find that inclusion of the first three coefficients is sufficient to provide a reasonable accuracy.

Overall, the fitting function (12) with  $N_e = 2$ ,  $N_p = 3$  or 4, and  $N_a \leq 8$  provides a satisfactory representation of the raw *ab initio* data, both for the Born-Oppenheimer results [ $V^{\text{BO}}(R)$ ,  $N_p = 4$ ,  $N_a = 8$ ] and for the adiabatic correction [ $V^{\text{ad}}(R)$ ,  $N_p = 3$ ,  $N_a = 5$ ]. Both fits contain ten linear and three nonlinear parameters, which is a modest amount compared to about 40 points of the raw *ab initio* data. The fitting errors are by an order of magnitude smaller than the estimated uncertainty of the corresponding theoretical calculations. Only one or two points are exceptional in this respect, but the error is still well within the acceptable range. Optimized parameters of the Born-Oppenheimer and adiabatic potentials are given in Table V. Note that the adiabatic correction fitting error is larger than for the BO potential (cf. Table VII) but this mostly due to increased relative errors  $\delta V_k^{\text{comp}}$  and smaller number of fitting parameters.

### C. Relativistic effects

Analytic potentials corresponding to the one-electron relativistic effects were obtained in a similar fashion as for the adiabatic correction. The mass-velocity [Eq. (8)] and one-electron Darwin [Eq. (9)] terms were separately represented in the form given by Eq. (12) with  $N_e = 2$ ,  $N_p = 3$ ,  $N_a = 5$ . The optimized parameters are given in Table VI. For convenience, in both cases we have included the factor of  $\alpha^2$  into the coefficients.

TABLE VI. Optimized parameters of the fit (12) for the one-electron relativistic corrections: mass-velocity [ $V^{P4}(R)$ ] and one-electron Darwin [ $V^{D1}(R)$ ]; see Eqs. (8) and (9), respectively, for the definitions. All values are given in atomic units. The symbol  $X[\pm n]$  stands for  $X \times 10^{\pm n}$ .

Parameter	$V^{P4}(R)$	$V^{D1}(R)$
$\alpha_1$	+1.3284[+00]	+1.3624[+00]
$\alpha_2$	+4.9227[-01]	+5.2275[-01]
$\eta$	+3.2767[-01]	+3.7855[-01]
$c_{01}$	-1.2702[-01]	+1.4557[-01]
$c_{11}$	+8.8288[-02]	-9.7541[-02]
$c_{21}$	-2.1025[-02]	+2.2358[-02]
$c_{31}$	+1.9023[-03]	-1.9527[-03]
$c_{02}$	-1.4425[-03]	+1.3737[-03]
$c_{12}$	+2.6974[-04]	-2.5064[-04]
$c_{22}$	-1.4610[-05]	+1.3126[-05]
$c_{32}$	+2.8967[-07]	-2.5278[-07]
$C_6$	-2.2228[+00]	+1.5773[+00]
$C_8$	-8.9706[+01]	+7.3228[+01]
$C_{10}$	-1.9637[+04]	+1.0532[+05]

Note that the last asymptotic constant ( $C_{10}$ ) in both fits optimized to a surprisingly large value. We believe that this result should be treated cautiously. While the first two asymptotic coefficients are reasonably stable with respect to various modifications of the fitting formula, the last one depends significantly on the adopted parametrization. In order to stabilize this quantity one would need to include more asymptotic terms, but, because of the risk of overparametrization, we decided not to do it. Therefore, the obtained values of  $C_{10}$  should not be used as a reference for other methods. The same conclusion is probably valid for the fit of the adiabatic correction described in the previous section.

The accuracies of the fitting functions for are summarized in Table VII. More detailed data are given in Supplemental Material [94]. This includes explicit listing of the raw *ab initio* values at each point and the corresponding errors.

#### IV. SPECTROSCOPIC DATA

In order to generate the spectroscopic data we add up all components of the PEC described above (BO, adiabatic, relativistic, and QED). The final PEC is illustrated in Fig. 1. Based on the complete curve we calculate the relevant molecular parameters. The total binding energy (i.e., the well depth,  $D_e$ ) and the equilibrium internuclear distance ( $R_e$ ) are obtained

TABLE VII. Root-mean-square deviations (in  $\text{cm}^{-1}$ ) and maximum absolute deviations (percentage-wise) of the fitted values from the raw data points. The symbol  $X[\pm n]$  stands for  $X \times 10^{\pm n}$ .

	rms error	max error (%)
$V^{\text{BO}}(R)$	1.8[-01]	3.0[-01]
$V^{\text{D1}}(R)$	3.6[-05]	6.7[-02]
$V^{\text{P4}}(R)$	8.1[-05]	6.1[-02]
$V^{\text{ad}}(R)$	6.0[-03]	4.7[+00]

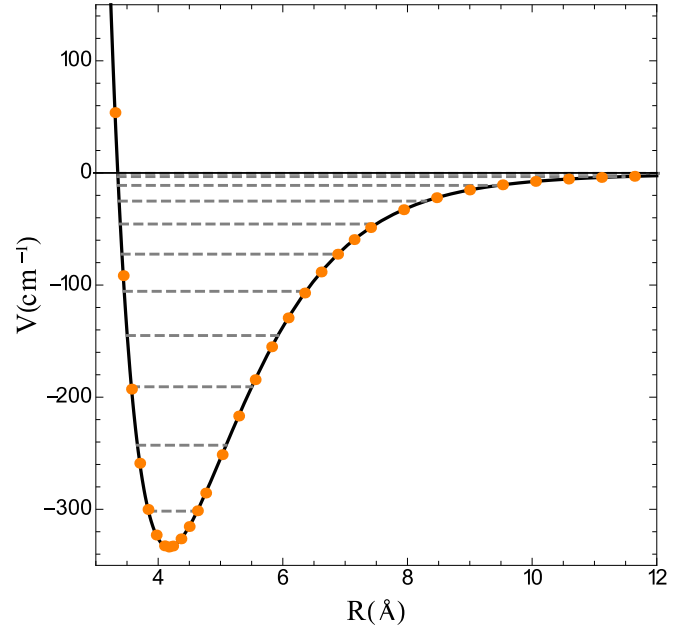


FIG. 1. Complete potential energy curve for the for the  $a^3\Sigma_u^+$  state of  ${}^{7,7}\text{Li}_2$  (solid black line); orange dots are the actual *ab initio* data points. The horizontal dashed lines are energies of the  $J = 0$  vibrational levels. The horizontal black solid line denotes the onset of continuum.

by finding the minimum of the fitted PEC. The harmonic vibrational frequency is defined as

$$\omega_e^2 = \frac{1}{\mu} \left( \frac{\partial^2 V}{\partial R^2} \right) \Big|_{R_e}, \quad (15)$$

in atomic units, where  $\mu$  is the reduced mass of an isotopomer. We consider two stable isotopes of lithium ( ${}^6\text{Li}$  and  ${}^7\text{Li}$ ) with atomic masses equal to

$$m({}^6\text{Li}) = 6.015\,123\, \text{u}, \quad (16)$$

$$m({}^7\text{Li}) = 7.016\,005\, \text{u}, \quad (17)$$

according to the recent compilation [129].

In order to find the rovibrational wavefunctions ( $\Psi_{v,J}$ ) and energies ( $E_{v,J}$ ) we solve the nuclear (radial) Schrödinger equation within the adiabatic approximation

$$\left[ -\frac{1}{2\mu} \frac{d^2}{dR^2} + D_e + V(R) + \frac{J(J+1)}{2\mu R^2} - E_{v,J} \right] \Psi_{v,J}(R) = 0, \quad (18)$$

where  $J$  is the rotational quantum number. Note that we have added the well depth ( $D_e$ ) to the left-hand side of Eq. (18). This makes all  $E_{v,J}$  positive by convention and their values grow with increasing values of  $v$  and  $J$ . Further, in the paper we are mostly concerned with the lowest rotational state ( $J = 0$ ) and thus adopt the notation  $E_v := E_{v,0}$ . Finally, the dissociation energy is defined as a sum of the interaction energy and the zero-point vibrational energy,  $D_0 = D_e + E_{v=0}$ .

In Table VIII we report the calculated *ab initio* values of the molecular parameters ( $D_e$ ,  $R_e$ ,  $D_0$ ,  $\omega_e$ ) for both isotopomers of the lithium dimer. The error of  $D_e$  was estimated by interpolating the theoretical errors at several neighboring grid points.

TABLE VIII. Molecular parameters of the  $a^3\Sigma_u^+$  state of  ${}^{6,6}\text{Li}_2$  and  ${}^{7,7}\text{Li}_2$ . See the main text for precise definitions of the listed quantities. All values are given in  $\text{cm}^{-1}$ , apart from  $R_e$  which are given in ångströms, Å.

	$D_e$	$R_e$	$D_0$	$\omega_e$
		${}^{6,6}\text{Li}_2$		
This work	333.68(30)	4.1688	299.13	71.05
Ref. [54]	333.778(8)	4.170038(30)		70.65 <sup>a</sup>
		${}^{7,7}\text{Li}_2$		
This work	333.69(30)	4.1687	301.61	65.78
Ref. [54]	333.758(7)	4.17005(3)		65.42 <sup>a</sup>
Ref. [24]	333.69(10)	4.173	301.829(15)	

<sup>a</sup>Not reported originally in Ref. [54]; extracted by taking the second derivative of the final potential.

Let us compare our results with the most recent experimental values of Linton *et al.* [24] and with a very reliable 17-parameter Morse–long-range potential of Dattani and Le Roy [54]. The agreement with these values is remarkably good. For example, our  $D_e$  for the isotopomer  ${}^{7,7}\text{Li}_2$  differs from the results of Refs. [24] and [54] by only 0.01 and 0.07  $\text{cm}^{-1}$ , respectively, while our estimated error is about 0.3  $\text{cm}^{-1}$  at the bottom of the well. The same conclusion is valid for the dissociation energy,  $D_0$ . This suggest that our error estimations are indeed quite conservative, at least in the regions close to the minimum of the potential. A similarly good agreement is found for the remaining molecular parameters.

The radial nuclear Schrödinger equation (18) was solved with help of the discrete variable representation (DVR) method [130]. The obtained vibrational energy levels ( $J = 0$ ) are listed in Table IX and compared with the experimental values of Linton *et al.* [24]. Additionally, we calculate the classical turning points ( $R^\nu$ ) defined as solutions of the

TABLE IX. Vibrational energy levels ( $J = 0$ ) for the  $a^3\Sigma_u^+$  state of  ${}^{7,7}\text{Li}_2$ . The vibrational energies ( $E_\nu$ ) are given in  $\text{cm}^{-1}$ , and the classical turning points ( $R_{\min}^\nu, R_{\max}^\nu$ ) in ångströms, Å. The minimum of PEC corresponds to the zero energy. The last two rows are the maximum and root-mean-square errors with respect to the experimental data [24].

	This work			Ref. [24]		
$\nu$	$E_\nu$	$R_{\min}^\nu$	$R_{\max}^\nu$	$E_\nu$	$R_{\min}^\nu$	$R_{\max}^\nu$
0	32.06	3.844	4.627	31.857	3.846	4.630
1	90.83	3.668	5.090	90.453	3.668	5.092
2	142.94	3.570	5.502	142.523	3.571	5.503
3	188.65	3.504	5.920	188.240	3.505	5.922
4	228.07	3.455	6.371	227.679	3.458	6.373
5	261.24	3.419	6.882	260.837	3.422	6.885
6	288.11	3.392	7.496	287.665	3.395	7.501
7	308.55	3.373	8.293	308.098	3.377	8.297
8	322.55	3.361	9.453	322.155	3.365	9.441
9	330.39	3.354	11.476	330.170	3.358	11.392
10	333.32	3.352	16.478	333.269	3.356	16.052
$\delta_{\max}$	0.45	0.004	0.424			
$\delta_{\text{rms}}$	0.34	0.003	0.130			

following implicit equations:

$$D_e + V(R^\nu) = E_\nu. \quad (19)$$

For each  $\nu$  we have two solutions of Eq. (19), denoted  $R_{\min}^\nu$  and  $R_{\max}^\nu$ , and both of them are listed in Table IX.

One can see an excellent agreement between the theoretical and experimental vibrational energy levels in Table IX. The maximum absolute deviation is found for  $\nu = 7$  and amounts to about 0.4  $\text{cm}^{-1}$ . On average, the deviation is of the order of 0.3  $\text{cm}^{-1}$ . Let us point out that resolution of the spectroscopic data of Linton *et al.* is about 0.1  $\text{cm}^{-1}$ , so that the actual error of our calculations can be even smaller. Moreover, our *ab initio* values are more accurate than reported recently by Lau *et al.* [55] based on a semiempirical model potential. Their data exhibits the maximum  $E_\nu$  deviation of about 1.5  $\text{cm}^{-1}$  if they use the accurate  $\omega_e$  in the potential. By relaxing the value of  $\omega_e$  by about 1% the accuracy improves to about 0.5  $\text{cm}^{-1}$  on the average, but this may be due to a fruitful cancellation of errors. In fact, our results support the semiempirical value of  $\omega_e$ . Let us also point out that our potential reproduces the binding energy of the last vibrational level with surprising accuracy. While the experimentally derived value is  $12.47 \pm 0.04$  GHz [51], the PEC developed in this work gives 10.5 GHz.

Let us now turn our attention to the theoretical description of the Li-Li scattering process. The main goal is to evaluate the  $s$ -wave scattering length ( $a$ ) for two lithium atoms in the ground state from the first-principles PEC developed in this work. This can be accomplished by solving the radial Schrödinger equation (18) with  $J = 0$  at zero energy [131]. It is well known that for large  $R$  the solutions  $\Psi_{E=0}(R)$  behave asymptotically as a linear function [132,133]

$$\Psi_{E=0}(R) \rightarrow C(R - a) + \dots, \quad (20)$$

where  $a$  is the desired scattering length. Very sophisticated methods for numerical calculation of  $a$  were presented [134–138], but our case is not particularly technically challenging and we adopt the following simplistic procedure. First, we propagate the radial Schrödinger equation at zero energy up to very large  $R$  ( $\approx 10^5$ ). The initial conditions are  $\Psi_{E=0}(R_0) = 0$ , where  $R_0$  is deep within the repulsive wall, and an arbitrary value of the derivative at  $R_0$ . Next, we continue the asymptotic straight line (20) to the point where it crosses the  $r$  axis. By the virtue of Eq. (20) this point corresponds to the value of  $a$ .

The  $s$ -wave scattering length for the  ${}^{7,7}\text{Li}_2$  isotopomer calculated from the PEC developed in this work is  $-9.2$  a.u. This is by a factor of 3 too small compared with the experimental result of Abraham *et al.* [51] who report  $-27.3 \pm 0.8$  a.u. Despite this deviation being large, we note that the sign of the scattering length calculated by us is correct. This is sufficient to predict the stability of the corresponding Bose-Einstein condensate [139,140]. Moreover, the rough magnitude of the scattering length is also correct, which makes it useful for other predictions [141,142]. To predict  $a$  with the accuracy of a few percent the errors in PEC must be reduced probably by an order of magnitude. We believe that this is possible in the foreseeable future.



## V. CONCLUSIONS

In this paper we have developed an *ab initio* potential energy curve for the  $a^3\Sigma_u^+$  state of the lithium dimer. To bring the accuracy down to the sub- $\text{cm}^{-1}$  regime, we have employed state-of-the-art techniques of the electronic structure theory. In particular, large (double to sextuple zeta) one-electron basis sets composed of Slater-type orbitals have been developed specifically for the present purposes. The Born-Oppenheimer potential has been calculated by using a composite scheme utilizing high-order coupled cluster and full CI methods. Moreover, we have included several minor corrections to account for the the adiabatic, relativistic, and QED effects.

The computed *ab initio* data points have been fitted with theoretically motivated analytic functions. When available, we employed van der Waals asymptotic constants  $C_n$  obtained from the most accurate theoretical methods. By solving the nuclear Schrödinger equation we have obtained the molecular parameters ( $D_e$ ,  $D_0$ ,  $\omega_e$ , etc.) for this system, as well as the corresponding vibrational energy levels, which are directly comparable with the experimental data. For example, the bond dissociation energy determined by us ( $D_0 = 301.61 \text{ cm}^{-1}$ ) differs by only about  $0.2 \text{ cm}^{-1}$  from the empirical values reported by Linton *et al.* [24] We have also reproduced all eleven bound vibrational levels with an accuracy of  $0.2\text{--}0.4 \text{ cm}^{-1}$ . In

particular, the position of the last vibrational level has been predicted to within 2 GHz, or 15% of the experimental value. Crucially, all these results have been obtained without prior adjustment to match the empirical values.

The data presented in this paper are probably the most accurate *ab initio* results available for this system in the literature thus far. Moreover, this paper constitutes a proof that Slater-type orbitals can now be used routinely in calculations for diatomic systems with large basis sets (up to several hundred functions) and are capable of providing spectroscopically accurate results.

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