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Relation between properties of long-range diatomic bound states

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Long-range states of diatomic molecules have average values of internuclear separations $\langle R\rangle$ at least one order of magnitude larger than the equilibrium value of R. For example, the helium dimer $^4He_2$ has a single bound state with $\langle R\rangle$ of about 50 Å. We show that the properties of these states, such as $\langle R\rangle$, the dissociation energy, or the s-wave scattering length, can be related by simple, yet very accurate, formulas if a potential-energy curve is known. By examining a range of *ab initio* and empirical helium dimer potentials as well as scaling these potentials, we found that the formulas remain accurate, even if very approximate potentials were used. In addition to $^4He_2$, we present results for $^9Be_2$, $^{20}Ne_2$, and KRb.

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I. INTRODUCTION

The highest rovibrational states of diatomic molecules play a fundamental role in cold-atom scattering as their properties, such as dissociation energies D_0 and average values of internuclear separations $\langle R\rangle$ are closely related to the s-wave scattering lengths a, which fully determine low-energy behavior of such systems including creations of Bose-Einstein condensates and degenerate Fermi gases. In the first approximation, $D_0 = (\hbar^2/2\mu)(1/a)^2$ and $\langle R\rangle = a/2$, where μ is the reduced mass of the dimer [1,2]. As shown below, for $^4He_2$ this approximation gives about 10% errors. The knowledge of more accurate relations is of significant practical interest (see, e.g., Refs. [3–6]) as it allows one to predict these properties if only one of them is known and to estimate relative accuracies if more than one quantity is known. Gao [5] has shown that one way of deriving a more accurate relation between D_0 and a can be based on the angular momentum-insensitive quantum defect theory, whereas other relations have been derived from the semiclassical approach [4]. However, since these theories are approximate, alternative approaches are still needed. The aim of the present paper is to show that a simple, yet accurate, method can be developed utilizing potential-energy curves of diatoms, even very approximate ones. For $^4He_2$, the resulting relations were fitted by low-degree rational polynomials, which may be useful in the interpretation of future experiments and in discussions of the Efimov states of the helium trimer [7–11].

We test the proposed approach mainly on the helium dimer since, for this system, a nearly exact interaction potential is available [12]. We will refer to this potential as PCKLJS (Przybytek-Cencek-Komasa-Lach-Jeziorski-Szalewicz). The $^4He_2$ very weakly bound state is of significant interest by itself with its *ab initio* predicted dissociation energy $D_0 = 1.62 \pm 0.03$ milliKelvin (mK) and the average internuclear distance $\langle R\rangle = 47.1 \pm 0.5$ angstrom (Å) [12]. The separation $\langle R\rangle$ is the only property of the helium dimer bound state that has been measured. The best experimental value is 52 ± 4 Å, obtained by Grisenti *et al.* in 2000 [13]. The measurements of $\langle R\rangle$ are very difficult, and one may recall that the previous best experimental result of Luo *et al.* [14] was 62 ± 10 Å. The helium dimer also exhibits other fairly unusual and interesting properties, such as an ultra-long-range energy transfer by interatomic Coulombic decay [15–22] and quantum reflections [23].

Grisenti *et al.* [13] also published "experimental" values of $D_0 = 1.1^{+0.3}_{-0.2}$ mK and of $a = 104^{+8}_{-18}$ Å. These values are often compared to the theoretical ones (see, e.g., Refs. [9,10]) and are used to evaluate the accuracy of the potentials. In most cases, the discrepancies are much larger for D_0 and a than for $\langle R\rangle$. This can be seen, for example, by comparing to the values from Ref. [12] quoted above and to $a = 90.42 \pm 0.92$ Å also computed in Ref. [12]. The actual reason for this behavior is that D_0 and a were not measured in any way but were simply calculated [13] from the value of $\langle R\rangle$ using the relations given below. The upper error bars for the former quantity and the lower ones for the latter were increased as indicated by the results from the Tang-Toennies-Yiu (TTY) theoretical He_2 potential of Ref. [24]. Much better estimates of what should be the values of D_0 and a, corresponding to the experimental $\langle R\rangle$ were recently obtained in Ref. [25] by adding to the potential of Ref. [12] such a percentage of its estimated error that the new potential exactly gives the experimental $\langle R\rangle$. This procedure gave $D_0 = 1.30^{+0.25}_{-0.19}$ mK and $a = 100.2^{+8.0}_{-7.9}$ Å, substantially closer to and nearly consistent with the *ab initio* results. One may conclude that, if D_0 and a were actually measured, these values would be, at least, nearly consistent with the theoretical ones similarly as in the case of $\langle R\rangle$.

II. COMPARISONS OF He_2 LITERATURE POTENTIALS

In order to show that the predictions of the method proposed by us do not depend on the accuracy of the potential used, we have selected a subset of He_2 potentials developed in the past 30 years, which vary dramatically in accuracy. The predictions of these potentials for D_0, $\langle R\rangle$, and a are listed in Table I. Until the 1990s, helium dimer potentials were fitted to experimental

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TABLE I. Comparison of the average bond lengths $\langle R\rangle$, dissociation energies D_0, and s-wave scattering lengths a, from literature and computed in this paper. In the lower part, values from the selected scaled potentials are given with the target value in bold. Numbers in parentheses are the predictions from our fits of Eqs. (2) and (3), corresponding to a given $\langle R\rangle$.

Potential	Calculation	D_0 (mK)	$\langle R\rangle$ (Å)	a (Å)	f
HFDHE2 [26]	Reference [27]	0.830 (0.830)	64.21	89.30 (124.59)	
HFDHE2 [26]	This paper	0.835 (0.835)	64.02	124.30 (124.21)	
HFD-B [28]	Reference [10]	1.685 (1.685)	46.18	88.50 (88.58)	
LM2M2 [29,30]	Reference [10]	1.303 (1.303)	52.00	100.23 (100.20)	
LM2M1 [29,30]	Reference [27]	1.209 (1.209)	53.85	101.10 (103.90)	
LM2M1 [29,30]	This paper	1.209 (1.209)	53.85	103.89 (103.90)	
LM-2[a] [29]	This paper	1.140 (1.140)	55.34	106.90 (106.87)	
HFD-ID [30,31]	Reference [27]	0.402 (0.402)	91.50	177.40 (109.20)	
HFD-ID [30,31]	This paper	1.090 (1.091)	56.50	109.24 (109.19)	
TTY [24]	Reference [10]	1.310 (1.309)	51.89	100.01 (99.98)	
HFD-B3-FCI1 [32,33]	This paper	1.594 (1.594)	47.38	91.00 (90.98)	
HFD-B3-FCI1[b] [32,33]	Reference [34]	1.417 (1.405)	50.22	96.27 (96.65)	
HFD-B3-FCI1[b] [32,33]	This paper	1.448 (1.448)	49.52	95.30 (95.26)	
SAPT96[b] [35,36]	Reference [34]	1.712 (1.712)	45.84	87.92 (87.90)	
HM [37]	This paper	1.722 (1.722)	45.72	85.55 (85.53)	
HM[b] [37]	This paper	1.551 (1.551)	47.98	92.21 (92.17)	
CCSAPT07[b] [38]	Reference [38]	1.56 (1.563)	47.8	91.8 (91.81)	
HBV [39]	This paper	1.813 (1.813)	44.65	85.55 (85.53)	
HBV[b] [39]	This paper	1.637 (1.636)	46.81	89.87 (89.87)	
PCKLJS [12]	Reference [12]	1.615 $\pm$ 0.034	47.09 $\pm$ 0.46	90.42 $\pm$ 0.92	
Scaled LM-2[a]		1.615 (1.615)	**47.09**	90.43 (90.40)	1.004 613
Scaled HBV		1.615 (1.615)	**47.09**	90.43 (90.40)	0.998 29
Scaled HBV[b]		1.615 (1.615)	**47.09**	90.43 (90.40)	0.999 809
Scaled-D_0 PCKLJS		**1.100**	56.27	108.73	0.994 985
Scaled-$\langle R\rangle$ PCKLJS		1.303	**52.00**	100.20	0.997 079
Scaled-a PCKLJS		1.206	53.90	**104.00**	0.996 102
Grisenti *et al.* [13]		$1.1^{+0.3}_{-0.2}$	52 ± 4 [c]	104^{+8}_{-18}	
Cencek *et al.* [25]		$1.30^{+0.25}_{-0.19}$	52 ± 4	$100.2^{+8.0}_{-7.9}$	

[a] Potential fitted in this paper (see Table IV in the Appendix).

[b] Including the retardation correction for all R.

[c] Measured in Ref. [13].

data, mainly thermophysical and scattering measurements, and the best known such potentials were HFDHE2 [26] and HFD-B [28]. The empirical potentials obtained in this way reproduced measured quantities much better than the theoretical potentials of that time. However, since no spectroscopic data—providing most accurate input to such fittings—are available for the helium dimer, many empirical fits utilized some theoretical information, in particular, about the asymptotics and the repulsive wall of the potential. In 1989, Liu and McLean [29] computed an *ab initio* interaction potential denoted as LM-2. In 1991, Aziz and Slaman [30] constructed an analytic representation of LM-2, called by them LM2M1, by modifying an empirical potential in such a way that its values were within the error bars of LM-2. This restriction was then lifted, and the parameters of LM2M1 were tuned [30] to recover experimental data as closely as possible. The resulting empirical potential dubbed LM2M2 provided the best predictions of the measurements at that time. Since LM2M2 was only a minor modification of LM-2 and the computed interaction energies were a part of the fit data set, this potential can also be called a "tuned" or "morphed" *ab initio* potential. LM2M2 was the last widely recognized empirical potential for the helium dimer. The HFD-ID potential, taken from Table II of Ref. [30], is a fit to unpublished *ab initio* interaction energies computed by Vos *et al.* [31] using an approach applied earlier by Vos *et al.* in Ref. [40]. Since Aziz and Slaman found HFD-ID to be slightly inferior to LM2M1, it was not pursued further.

Starting from the mid-1990s, purely *ab initio* potentials have provided the best predictions. The HFD-B3-FCI1 potential of van Mourik and van Lenthe [32] and the SAPT96 potential of Williams *et al.* [35] and Korona *et al.* [36] were shown by Aziz and collaborators to reproduce experiments still better than LM2M2 [33,34]. Let us also mention that the SAPT96 potential from Refs. [35,36] (based on calculations using symmetry-adapted perturbation theory [41,42]) is often wrongly attributed to Janzen and Aziz [34], whereas, these authors only used SAPT96, under the names SAPT1 and SAPT2—depending on how the retardation correction was

TABLE II. Fit parameters of Eqs. (2) and (3).

A_0	$2.981\,6185 \times 10^{3}$	A_1	$9.468\,7166$
B_0	$1.747\,7753$	B_1	$0.361\,5444 \times 10^{-2}$
B_2	$-0.402\,8595 \times 10^{-4}$	B_3	$0.166\,7976 \times 10^{-6}$

applied, in calculations of properties of helium. Another popular *ab initio* potential of that time named TTY was computed by Tang *et al.* [24]. This trend continued, and the current most accurate potential for helium is the PCKLJS potential [12] with the Born-Oppenheimer part from Refs. [38,43,44]. This potential reproduces thermophysical data with uncertainties several times smaller than experimental uncertainties and is used by the thermophysics community to calibrate instruments and to develop new metrology standards [25]. Two other recent *ab initio* potentials are the one fitted by Hurly and Mehl (HM) [37] to a weighted average of several *ab initio* calculations and that of Hellmann *et al.* [39], denoted by HBV.

The data in Table I show enormous progress in the accuracy of predictions. Very surprisingly, and probably completely accidentally, the TTY potential gives values almost identical to those produced by LM2M2. It is interesting to compare the LM-2, LM2M1, and LM2M2 fits. In this sequence, the amount of empirical information is gradually increased, and the predictions are gradually improved. Also, one can see that the LM-2 predictions are slightly better than those of HFD-ID. The predictions of the purely empirical HFD-B potential are significantly better than those of the discussed older *ab initio*-based potentials, in fact, in excellent agreement with those of PCKLJS. This shows that, until the early 1990s, the empirical potentials were more accurate than *ab initio* or tuned *ab initio* ones. The pure *ab initio* potentials of the 1990s are, however, getting close to the accuracy of HFD-B: In particular, SAPT96 is in almost perfect agreement with HFD-B. The three potentials of recent years: HM, CCSAPT07, and HBV are more accurate than HFD-B, and HBV is within the error bounds of PCKLJS. The predictions of the CCSAPT07 and HM potentials are nearly identical since the latter potential utilized a number of virtually the same *ab initio* interaction energies as used in CCSAPT07. All the potentials giving such disparate predictions will be shown below to reproduce the PCKLJS values of D_0, $\langle R\rangle$, and a upon a very simple scaling.

III. SCALED POTENTIALS

In order to better understand the relations among D_0, $\langle R\rangle$, and a, we tuned various potentials in such a way that a given value of *one* of these quantities is recovered exactly. Accordingly, we have used only one tuning parameter in the potential. After some experimentation, we have found that the simplest possible procedure, scaling of the whole potential by a constant,

$$V^{\mathrm{sc}}(R) = f\,V(R) \tag{1}$$

worked the best. Scaled results for the LM-2 [29], HBV [39], and PCKLJS [12] potentials are shown in Table I. In the first two cases, the potentials were scaled to recover the values of $\langle R\rangle$ given by PCKLJS. As one can see, the scaled values of D_0 (a) agree to better than 0.001 mK (within 0.01 Å) with the values computed from the PCKLJS potential, a virtually perfect agreement. This agreement should be contrasted with up to 0.48 mK (16.5 Å) discrepancies between the prediction of PCKLJS and the original potentials. In the PCKLJS case, we scaled this potential to recover the values from Ref. [13]. It is very interesting that scaling on $\langle R\rangle = 52.00$ Å produces the values of D_0 and a identical to those obtained by quite a different procedure in Ref. [25]. As expected, scaling on the values of D_0 or a from Ref. [13] gives poor values of the predicted quantities.

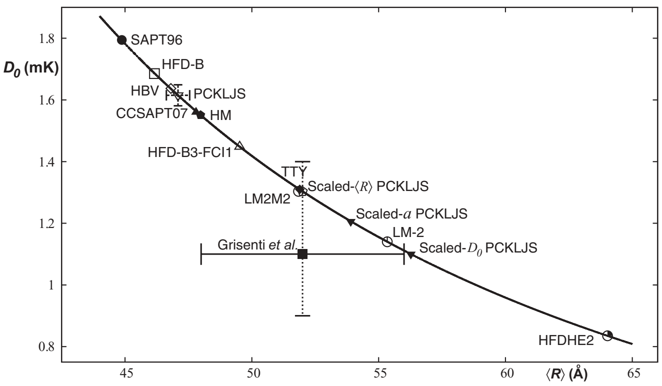

FIG. 1. ^{4}He$_2$ dissociation energies versus average bond lengths.

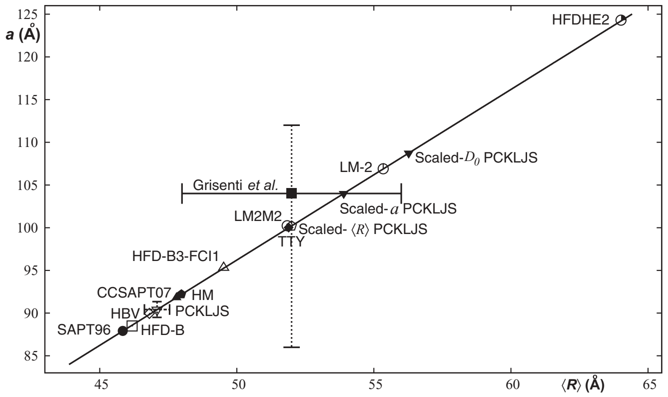

FIG. 2. ^{4}He$_2$ scattering lengths versus average bond lengths.

The observed relations among D_0, $\langle R\rangle$, and a show that these three quantities are strongly correlated. Therefore,

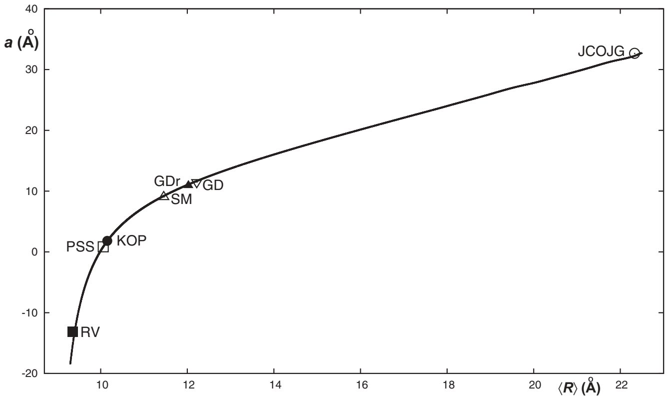

FIG. 3. ^{9}Be$_2$ scattering length versus average bond length of the highest rotationless state. The curve was obtained by scaling the potential from Ref. [45] [point PSS (Patkowski-Spirko-Szalewicz) corresponds to $f = 1$]. The remaining points were obtained using the potentials from references: Røeggen and Veseth (RV) [46]; Koput (KOP) [47]; Stärk and Meyer (SM) [48]; Gdanitz (GD) and GD corrected for relativistic effects (GDr) [49]; and Jamieson-Cheung-Ouerdane-Jeung-Geum (JCOJG) [50].

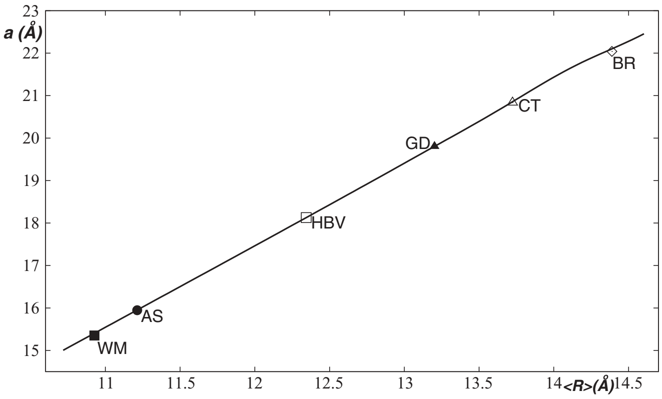

FIG. 4. $^{20}Ne_2$ scattering length versus average bond length of the highest rotationless state. The curve was obtained by scaling the HBV potential from Ref. [51] (point HBV corresponds to $f = 1$). The remaining points were obtained using the potentials from references: Wüst and Merkt (WM) [52]; Aziz and Slaman (AS) [53]; Cybulski and Toczylowski (CT) [54]; GD [55]; and Bytautas and Ruedenberg (BR) with aug-cc-pV6Z basis set [56].

we have developed simple formulas relating pairs of these quantities, which may be handy in future investigations of ^{4}He. In particular, we found that D_0 and a can be represented as the following functions of $\langle R\rangle$ (any other quantity can be taken as the independent variable):

$$D_0 = A_0[1 + A_1/\langle R\rangle]/\langle R\rangle^2, \tag{2}$$

$$a = B_0\langle R\rangle[1 + B_1\langle R\rangle + B_2\langle R\rangle^2 + B_3\langle R\rangle^3], \tag{3}$$

where D_0 is in mK whereas $\langle R\rangle$ and a are in Å. The linear parameters were least-squares fitted to a suitable set of pairs $(D_0,\langle R\rangle)$ or $(a,\langle R\rangle)$ generated by scaling the PCKLJS potential by the factor f ranging from 0.987 to 1.005. The values of the parameters are given in Table II.

The values predicted by Eqs. (2) and (3) are listed in parentheses in Table I. As one can see, these simple formulas work amazingly well for all of the potentials, despite the fact that only the PCKLJS potential was used to derive them. In virtually all cases, nearly four significant digits are predicted exactly. The literature values computed with the HFD-B3-FCI1 potential are the only exception, but our calculations with the same potential show that this is only due to a limited accuracy of the calculations of Ref. [34]. The functions of Eqs. (2) and (3) are plotted in Figs. 1 and 2, respectively. The values computed with various potentials are also plotted as symbols. The figures show the excellent agreement already discussed above as all the points lay almost exactly on the lines given by Eqs. (2) and (3). The figures show very clearly that the dependence of D_0 and a on $\langle R\rangle$ is very generic, independent of the details of the potentials.

To check if our approach is applicable to other diatoms, we performed similar calculations for $^9Be_2$, $^{20}Ne_2$, and KRb. For the two former systems, a large number of published potentials are available so that we could prepare figures analogous to those for $^4He_2$. As can be seen in Figs. 3 and 4, the behavior is the same as observed for $^4He_2$, i.e., all the values computed from vastly different literature potentials lie on the curve computed from best literature potentials scaled according to Eq. (1). For $^9Be_2$, the dependence becomes nonlinear for small $\langle R\rangle$ since such values correspond to probing the region where the potential becomes quickly deeper due to the onset of chemical interactions. For KRb, a model for ultracold gases, we present our results in Table III. Here, just two potentials are available: a fairly accurate empirical one fitted to spectroscopic data [57] and a much less accurate *ab initio* one [58], both independent of atomic masses. We computed D_0's for all combinations of isotopes from the former potential and then used the latter one scaled to reproduce these D_0's to compute a's. The agreement with experimental scattering lengths is excellent: only 4 out of 36 predicted values are (slightly) outside experimental error bars.

IV. SUMMARY

In conclusion, we have shown that parameters characterizing the highest bound state of a diatomic molecule and low-energy scattering of the atoms involved can be found with high precision if one of these parameters is accurately measured. One needs to know a potential-energy curve for the dimer, but even low-accuracy curves give high-accuracy predictions after being scaled to reproduce the measured quantity. This strong correlation indicates that the properties of the dimers in the investigated energy range are mainly sensitive to the values of the potential in the same range. Since all potentials produce virtually identical vertical walls at small R, the scaling that recovers accurate D_0 must produce a very accurate potential

TABLE III. Experimental and predicted scattering lengths (in units of a_0) for the $a^3\Sigma^+$ electronic state of KRb.

Isotopes	Expt.[a]	Reference [57][b]	Reference [58][c]	$^{39}K\,^{85}Rb$[d]	$^{39}K\,^{87}Rb$[d]	$^{40}K\,^{85}Rb$[d]	$^{40}K\,^{87}Rb$[d]	$^{41}K\,^{85}Rb$[d]	$^{41}K\,^{87}Rb$[d]
$^{39}K\,^{85}Rb$	63.0 ± 0.5	63.9	63.2	63.2	63.3	63.4	63.5	63.6	63.6
$^{39}K\,^{87}Rb$	35.9 ± 0.7	35.9	36.0	36.0	36.1	36.2	36.4	36.5	36.5
$^{40}K\,^{85}Rb$	− 28.4 ± 1.6	− 28.6	− 28.4	− 28.5	− 28.3	− 28.0	− 27.7	− 27.4	− 27.3
$^{40}K\,^{87}Rb$	− 215 ± 10	− 215.6	− 215.0	− 216.3	− 215.3	− 213.0	− 211.3	− 209.6	− 208.8
$^{41}K\,^{85}Rb$	348 ± 10	349.8	350.1	348.8	349.8	352.0	353.8	355.5	356.3
$^{41}K\,^{87}Rb$	163.7 ± 1.6	164.4	164.6	164.4	164.6	165.0	165.2	165.5	165.7

[a] Reference [59].

[b] Calculated from an empirical potential fitted to dimer spectra.

[c] Calculated from an *ab initio* potential tuned to exactly reproduce the experimental scattering length of $^{40}K\,^{87}Rb$.

[d] Calculated in this paper by scaling the purely *ab initio* potential of Ref. [58] to reproduce the binding energies of the highest rotationless bound states of the indicated isotopes computed from the empirical potential of Ref. [57].

near the outer turning point. Since this potential is in this region, well approximated by C_6/R^6, it is also accurate for all larger R's. Our results can be compared with approximate semiclassical relations. As already discussed, the simplest such relations [1–3] are too approximate. However, more sophisticated relations of this type have been published more recently. For example, formulas (2) and (32) in Ref. [4] allow one to calculate a quantity κ, which gives $D_0 = \hbar^2\kappa^2/2\mu$ from the knowledge of a and of C_6. This formula, applied to He$_2$, gives only a 0.25% error, but fails completely for Be$_2$.

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APPENDIX

TABLE IV. The parameters (all in atomic units) of the LM-2 *ab initio* potential.[a]

a	2.517 3059	P_0	− 65.277 1699
b	2.334 5579	Q_0	72.294 7935
c	0.024 2266	Q_1	− 9.269 2253
η	1.790 7966		

[a] The coefficients C_n were fixed at their reference Born-Oppenheimer values from Ref. [60]: $C_6 = 1.460\,977\,837\,725$, $C_8 = 14.117\,857\,37$, and $C_{10} = 183.691\,075$.

As there is no analytic representation for the LM-2 *ab initio* calculations of Ref. [29] available in the literature (as described earlier, LM2M1 is not a true fit of LM-2 data), we have fitted it using the following functional form, similar to that used for the PCKLJS potential of Ref. [12]:

$$V(R) = e^{-aR-cR^2}P_0 + e^{-bR}(Q_0 + Q_1 R) - \sum_{n=6,8,10} f_n(\eta R)C_n/R^n, \qquad \text{(A1)}$$

where $f_n(x)$ is the Tang-Toennies damping function,

$$f_n(x) = 1 - e^{-x}\sum_{k=0}^{n} x^k/k! \qquad \text{(A2)}$$

The fit was constrained by fixing the long-range asymptotic coefficients C_n at their reference values taken from Ref. [60]. The parameters of the fit are given in Table IV.

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