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Accurate calculation of the scattering length for the cooling of hydrogen atoms by lithium atoms

F.X. Gadéa[1,a], T. Leininger[1], and A.S. Dickinson[2]

[1] Laboratoire de Physique Quantique[b], IRSAMC, université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 4, France
[2] Department of Physics, The University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK

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Abstract. An improved *ab initio* calculation has been performed for the potential for the LiH a $^3\Sigma^+$ state, using two very large basis sets. The Basis Set Superposition Error (BSSE) correction has been determined for both basis sets and the non-Born-Oppenheimer correction estimated to be negligible. The best potential is approximately 10% deeper than the previous estimate. Vibrational energies and scattering lengths have been calculated for ^{6,7}LiH(D) with both potentials, with and without the BSSE correction, and also with an estimated potential expected to bracket the true potential. The ^{7}LiH scattering length is estimated to be $(45 \pm 4)a_0$ and hence the low-energy cross-section in the best a $^3\Sigma^+$ potential is about half that calculated previously. Enhanced cooling by ^{7}Li of trapped H atoms remains feasible.

PACS. 34.20.Cf Interatomic potentials and forces – 34.50.-s Scattering of atoms and molecules

1 Introduction

In order to assist the achievement of Bose-Einstein condensation of atomic hydrogen it has been proposed recently to use enhanced cooling by a cloud of ultracold lithium atoms [1]. Magnetically trapped hydrogen and lithium atoms are predominantly in low-field seeker pure stretched-spin states and hence the Li–H collisions take place in the lowest triplet state of the lithium hydride molecule, that denoted a $^3\Sigma^+$. Because of the ultralow temperatures of relevance for Bose-Einstein condensation in hydrogen, ≈ 50 μK [2], the efficiency of this cooling process depends crucially on the scattering length in the a $^3\Sigma^+$ state of LiH. This quantity has been calculated by Côté *et al.* [1] to be much larger than the corresponding value for H–H scattering, thus allowing for an enhanced cooling. However, the well of the LiH a $^3\Sigma^+$ state arises mainly from the dispersion interaction and hence is very shallow (about 4 cm^{-1}). Indeed all the earlier calculations for this state [3] found it to be purely repulsive. As the well supports just one vibrational state for ^{7}LiH with a binding energy 0.3% of the well depth, the scattering length is very sensitive to the potential.

A challenging accuracy, on the borderline of the best current *ab initio* calculations, is thus necessary here. In addition, small effects such as Basis Set Superposition Error (BSSE) and non-Born-Oppenheimer corrections, which can be important when the potential curve is required with an accuracy of well below a wavenumber, were not considered in the previous estimate [1]. Moreover, the 1.45% corrections to the *ab initio* curve employed in reference [1] rely on a comparison with the experimentally derived IPA (Inverted Perturbation Approach) values [3] for the $X^1\Sigma^+$ potential calculated similarly. This potential, however is strongly affected by the ionic state (Li$^+$ + H$^-$): for example the calculated dissociation energy depends crucially on the H electron affinity [4] yielded by the basis set employed, while the triplet state is unaffected by the ionic state. Hence different physical effects govern the two potentials and the extrapolation of the correction from the singlet around its equilibrium geometry to the triplet at large internuclear distance is not well founded.

In this paper, an improved estimate of the scattering length and hence of the cooling efficiency is performed using a more accurate *ab initio* potential. In the next section the new *ab initio* calculations are presented, followed by a discussion of the corrections to this Born-Oppenheimer evaluation. The binding energy and scattering-length results follow and we end with a discussion and conclusions.

2 Born-Oppenheimer calculations

Two basis sets have been used in the present *ab initio* calculation of the LiH a $^3\Sigma^+$ state. The MOLPRO package [5] has been employed and only all-electron calculations have been performed. The first basis set corresponds to that used [6] for the previous estimate [1], although since we have detected an error in the first contraction coefficient of the H basis set given in Table 1 of reference [6], we have used these exponents without contraction for H.

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[a] e-mail: `gadea@irsamc.ups-tlse.fr`

[b] UMR 5626 du CNRS

Table 1. Atomic energies for $\mathrm{H}, \mathrm{H}^-, \mathrm{Li}, \mathrm{Li}^+$ and Li^- using the HB and YD basis sets described in the text, with various levels of calculations: HF corresponds to Hartree Fock, fci to full CI and *ccsd*(t) to coupled cluster approaches.

	HB (E_h)	error (cm^{-1})	YD (E_h)	error (cm^{-1})	exact (E_h)
H (1s)	−0.49999603	0.9	−0.49970822	64.0	−0.5
H (2s)	−0.12499270	1.2	−0.12465223	76.3	−0.125
H^- fci	−0.52764511	15.6	−0.52677260	207.1	-0.527716^a
Li (2s) HF	−7.43270542	14.0	−7.43257147	44.0	-7.43277^b
Li (2s) *ccsd*(t)	−7.47752019	121.0	−7.47295981	1122.0	-7.47807^b
Li (2s) fci			−7.47296479	1120.0	-7.47807^b
Li (2p) *ccsd*(t)	−7.40960436	122.0			-7.41016^b
Li^+ fci	−7.27940143	116.0	−7.27500357	1081.0	-7.27993^c
Li^- *ccsd*(t)	−7.50016010	136.0	−7.49556302	1145.0	-7.50078^d

^{a}Using the recommended H electron affinity [7], ^{b}Reference [8], ^{c}using (b) for the Li energy and the experimental IP 43 487 cm^{-1} [9], ^{d}using (b) for the Li energy and the recommended Li $EA = 0.6180$ eV [7].

We have also checked that using correct contraction coefficients or no contraction leads to almost identical results both for the H atom and for the molecule. This basis set will be labelled YD hereafter. It contains 12s (the first contracted on 4s primitives), 10p, 6d and 3f functions for Li and 6s, 4p and 2d uncontracted functions for H. This can be considered as a large basis set expected to yield results of spectroscopic accuracy.

To go beyond the YD basis we have considerably extended the basis set for Li and used a huge one for H. This new basis set contains only uncontracted Gaussian functions: 24s, 17p, 13d, 6f and 2g for Li, along with 20s, 11p, 7d, 4f and 2g for H. It will be labelled HB hereafter. The calculated energies for the various atomic species are reported in Table 1, together with the exact results in the sense of a complete basis set. It is noteworthy that the differences from the exact values have decreased by at least a factor of ten on replacing the YD basis by the HB basis.

With the YD basis set we could perform a full CI calculation for Li and compare it to the coupled cluster *ccsd*(t) approach [10] that we will adopt for the molecule. These two energies differ by only 1.1 cm^{-1}, showing that the core-valence correlation energy is almost completely taken into account by the *ccsd*(t) approach within the basis set limitation. It can also be noticed that the alternative CI approach adopted in reference [6] remains 59 cm^{-1} above the full CI result, although the authors considered it as a full CI-quality calculation. The errors for the energy spacings in Li and its ions have also been significantly reduced: 1, 5 and 14 cm^{-1} for the 2s–2p transition energy, the ionisation potential and the electron affinity, respectively, compared to 23, 41 and 24 cm^{-1}, respectively using the YD basis. For H, the electron-affinity error, calculated at the full CI level, decreases from 143.1 cm^{-1} using YD to 14.8 cm^{-1} using HB.

For the molecule, we have performed *ab initio* calculations at the *ccsd*(t) level for these two basis sets in order to see the evolution of the scattering length when improving the basis set. The *ccsd*(t) approach presents the important advantage of being size consistent, a quality required here because of the tiny well. Moreover, since the lowest triplet state admits a single determinantal configuration even at dissociation, the damped divergence which may arise when the bond breaks [11] is totally absent here at all distances. We have checked that the *ccsd*(t) molecular energy matches at large distance ($1\,000a_0$) the *ccsd*(t) separated-atom limit within less than 10^{-10} Hartree.

The potential curves, $V(R)$ at internuclear separation R are illustrated in Figure 1 for separations $10a_0 \leq R \leq 25a_0$. For separations beyond $20a_0$ the potential is well described by the long-range approximation, discussed below. The better estimate of the potential (that using HB) leads to a deeper well than with YD. Because, as discussed above, we have improved the calculation of the correlation energy, the present potential using YD is also slightly deeper ($\approx 0.05 \times 10^{-5} E_\mathrm{h}$) than that employed previously [1]. Thus, the main effect of improving the basis set and the level for the treatment of the correlation energy has been to deepen the well and to shift the repulsive wall. More deeply bound vibrational levels can be expected and thus a decrease in the scattering length can be anticipated since the current estimate, $65a_0$, is well in excess of the characteristic value, approximately $10a_0$, for this interaction [1,12]. A decrease in the scattering length from deeper potentials is also expected following the analysis of Jamieson and Dalgarno [13].

To attempt to estimate the possible uncertainty in our HB result we have introduced a third potential, denoted LB, which at each separation lies as far below the HB result as that does below the YD value. This potential is also shown in Figure 1. For this estimate the corrected potentials, including allowance for BSSE (see below), have been used since no BSSE is expected for a complete basis set.

3 Corrections

Exploiting the size consistency of the *ccsd*(t) approach, we could perform accurate and confident estimates of Basis Set Superposition Errors (BSSE), computing for both basis sets at varying distances the energy of each atom in the presence of the companion atomic basis set. In the

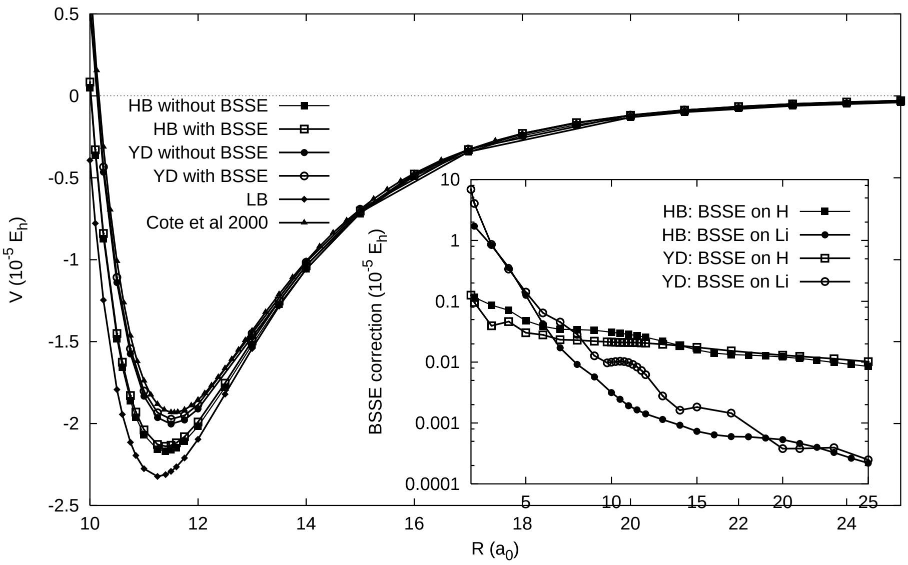

Fig. 1. *Ab initio* Born-Oppenheimer potential energy curve for the a $^3\Sigma$ state of LiH computed at the *ccsd*(*t*) level using the HB and YD basis sets. Also shown are the extrapolated potential denoted LB and that employed by Côté *et al.* [1]. The inset shows the BSSE error on both atoms with both basis sets.

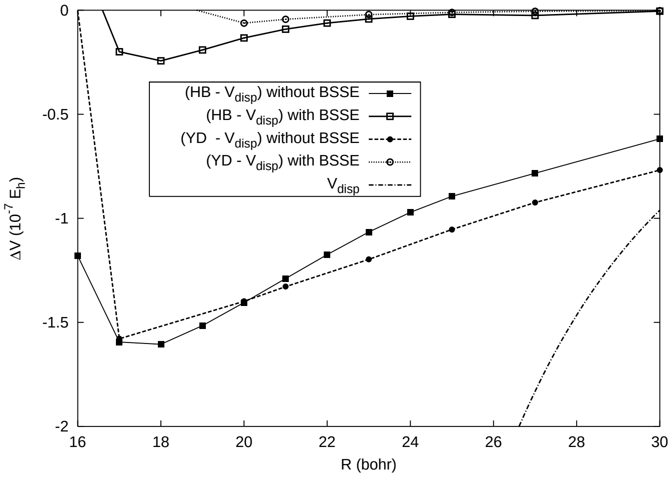

Fig. 2. Differences ΔV between the *ab initio* results and the long-range dispersion interaction, equation (1). The dispersion interaction is also plotted to indicate the magnitudes involved.

range of interest here, BSSE is quite small (≈ 0.06 cm^{-1}) for both basis sets, remaining larger for H than for Li, notwithstanding the atomic errors being in the reverse order. However, at short distances the error increases, see Figure 1. Improving significantly the basis set decreases BSSE only for Li, quite surprisingly, although this highlights the different deficiencies in the two atomic basis sets. For Li mainly functions helping estimate the correlation energy are missing and the H basis set gives only marginal improvements to that, although the addition of high angular momentum functions does bring a small but systematic improvement for $R \gtrsim 5a_0$. For H it is the inability of Gaussian functions to reproduce the slater function and the cusp at origin which dominates the error and, curiously, with the huge basis set on H there can be more BSSE than with the smaller one, probably because of the added diffuse functions on Li.

For our current application, BSSE remains a minor effect: at $R = 11.5a_0$, for example, it amounts only to 0.063 cm^{-1} with HB and to 0.064 cm^{-1} with YD. As is clear from Figure 1, BSSE increases as R decreases, presenting weak undulations which are probably related to the various nodal patterns in the basis sets. Although the influence of BSSE on the shape of the potential is quite limited here, effects of comparable magnitude (about 1.4%) were discussed previously [1] and shown to lead to differences of about 7.5% for the triplet scattering length [1].

For large values of R we follow Côté *et al.* [1] in using the dispersion interaction

$$V_{\mathrm{disp}}(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}}\,. \qquad (1)$$

We have employed the C_6 value from Côté *et al.* (66.544 a.u.) and the value of C_8 (3 003 a.u.) from Bussery *et al.* [14]. Their value for C_{10} is 148 509 a.u. Using these values, where the exchange interaction can be neglected, the changes from the results for $V_{\mathrm{disp}}(R)$ obtained by Côté *et al.* with a 10% different value for C_8 and ignoring C_{10} are negligible. From Figure 2 it can also be seen that taking BSSE into account improves significantly the agreement with $V_{\mathrm{disp}}(R)$. In the calculations of scattering lengths and binding energies described below we have employed the *ab initio* points for $R \leq 20a_0$. We have then used $V(20)$ to determine an effective value of C_{10} to give a continuous fit to the dispersion interaction and employed equation (1) with this effective C_{10} for larger R values. The values of C_{10} for the potentials corrected for BSSE were typically twice the values from [14], while for the potentials without correction the C_{10} values were typically ten times larger.

Since non-Born-Oppenheimer interactions will also influence the interatomic potential we have estimated their effect. It has been shown recently [15] that for the ground state of LiH ($X^1\Sigma^+$), which presents a broad avoided crossing between the ionic ($\mathrm{Li}^+\mathrm{H}^-$) and the neutral ($\mathrm{Li}(2s)\mathrm{H}(1s)$) configurations, the intrastate adiabatic correction dominates over the effect of the interstate nonadiabatic couplings. For the a state there is no avoided

Table 2. Binding energy, E_0 (cm^{-1}) and scattering length, a (a_0) for isotopomers of LiH using the various potentials. For YD and HB the results in parentheses are those obtained when ignoring BSSE.

		^{7}LiH	^{6}LiH	^{7}LiD	^{6}LiD
Côté *et al.* [1]	E_0	0.0146	0.0102	0.342	0.312
	a	65^{+5}_{-5}	71^{+6}_{-5}	22^{+1}_{-1}	23^{+1}_{-1}
YD	E_0	0.0310 (0.0435)	0.0251 (0.0365)	0.379 (0.413)	0.348 (0.382)
	a	61.1 (53.7)	66.9 (57.8)	22.0 (21.5)	22.9 (22.3)
HB	E_0	0.0541 (0.0687)	0.0461 (0.0597)	0.463 (0.498)	0.429 (0.463)
	a	49.3 (45.2)	52.7 (47.9)	20.7 (20.3)	21.4 (21.0)
LB	E_0	0.0858	0.0754	0.562	0.524
	a	41.2	43.3	19.4	20.0

crossing and the nearest $^3\Sigma^+$ electronic state lies quite high in energy, thus the preponderance of the adiabatic correction should be even greater. For a diatomic molecule the virial theorem allows for an easy estimate of that part of the adiabatic correction involving $\partial^2/\partial R^2$ which modifies the electronic kinetic energy. This correction can be written as [16]

$$\Delta E = -\frac{1}{2(M_A+M_B)}\left(E + R\frac{\mathrm{d}E}{\mathrm{d}R}\right), \tag{2}$$

M_A and M_B being the atomic masses, in units of the electron mass. In principle E should be the electronic energy only, discarding the nuclear repulsion, but since for a Coulombic potential the two terms cancel, E can be taken as the usual total energy. For the $X^1\Sigma^+$ ground state of LiH, the total adiabatic correction has been computed [17] and it has been verified that this virial-based contribution gives about 60% of the whole [18], allowing thus for reasonable estimates. Although the value of ΔE appears relatively large (about 60 cm^{-1}), its variation with R in the range of interest here is extremely small, only about 5×10^{-4} cm^{-1}. This correction has thus been discarded in comparison to BSSE.

Tabulated values of the HB and YD potentials, with and without the BSSE correction, can be obtained from the authors.

4 Dynamics calculations

The behaviour of the scattering length, a, is closely related to the binding energy of the highest vibrational level in the same potential. Hence we start by determining the binding energies, E_0 of the vibrational levels of the five potentials described above for the four isotopomers ^{7}LiH, ^{7}LiD, ^{6}LiH and ^{6}LiD. The LEVEL code of LeRoy [19] has been employed, with the extrapolation of the potentials to large values of R described above. For extrapolation to smaller values of R than $1.8a_0$, the smallest R value for which *ab initio* points were calculated, the procedures in LEVEL were employed. Our results for the rotationless $v = 0$ state are compared in Table 2 with those obtained by Côté *et al.* [1]. The larger binding energies obtained here are consistent with the slightly deeper potentials discussed above. The binding energies of the very weakly bound ^{6}LiH and ^{7}LiH states are particularly sensitive to small changes in the potential, recalling that the vibrational level of Côté *et al.* [1] for ^{6}LiH was bound by $\approx 0.3\%$ of the dissociation energy. The LiD potentials are sufficiently strongly bound to support one rotationally excited level, thus opening up in principle the possibility of observing a purely rotational transition at 9.19 GHz for ^{7}LiD.

The scattering length has been determined by fitting to the standard result in terms of the scattering length and effective range, r_e at collision energies in the nanoHartree region. We also checked our phase shifts δ using the identity

$$\tan\delta = \frac{2\mu}{\hbar^2 k}\int_0^\infty \sin(kR)\,V(R)\,y(R)\,\mathrm{d}R \tag{3}$$

where μ denotes the reduced mass, k the wavenumber and y the regular solution of the radial Schrödinger equation with normalization

$$\mathrm{Lim}_{R\to\infty} y(R) = \sin(kR) + \tan\delta\cos(kR).$$

Results for a obtained from the asymptotic form directly and using equation (3) typically agreed to at least five significant figures. Our results are compared with those of Côté *et al.* [1] in Table 2. Plotting the behaviour of the integral appearing in equation (3) as the upper limit is increased it is clear that there is considerable cancellation between contributions from the repulsive and attractive parts of the potential. The larger binding energies with the potentials considered here are reflected in the smaller scattering lengths, resulting for ^{7}LiH in the limiting low-energy cross-section $\sigma \approx 30\,000a_0^2$, just over half that obtained previously [1]. However this still yields a rate coefficient about 550 times larger than the corresponding value for triplet H + H scattering [1].

Semiclassical approximation

While semiclassical methods are expected to be less reliable for systems supporting just one vibrational level, nevertheless it is of interest to assess the accuracy of such methods in a very unfavourable case. It has been shown [12,20] that for a potential falling off as R^{-6} the semiclassical approximations to the scattering length, a^{SC} and the effective range, $r_{\mathrm{e}}^{\mathrm{SC}}$ are given by:

$$a^{\mathrm{SC}} = \bar{a}[1 - \tan(\Phi - \pi/8)] \tag{4}$$

where

$$\bar{a} = \sqrt{2\gamma}\,\Gamma(3/4)/\Gamma(1/4)$$
$$\Phi = \frac{1}{\hbar}\int_{R_0}^{\infty} \sqrt{-2\mu V(R)}\,\mathrm{d}R, \quad \gamma = \sqrt{2\mu C_6}/\hbar$$

μ being the reduced mass, $V(R_0) = 0$ and

$$r_{\mathrm{e}}^{\mathrm{SC}} = \frac{\bar{a}}{3}\left[\frac{\Gamma(1/4)}{\Gamma(3/4)}\right]^2 \left[1 - 2\frac{\bar{a}}{a^{\mathrm{SC}}} + 2\left(\frac{\bar{a}}{a^{\mathrm{SC}}}\right)^2\right]. \tag{5}$$

For ^{7}LiH $\bar{a} = 10.28a_0$ and, taking the case of the HB potential, without correction for BSSE, $\Phi = 0.6926\pi$, yielding $a^{\mathrm{SC}} = 57.9a_0$, differing by 17% from the numerical result $49.3a_0$. The corresponding value for $r_{\mathrm{e}}^{\mathrm{SC}}$ is $21.2a_0$, or $20.1a_0$ using the numerical value of a in equation (5), differing by 6% and 1% respectively from the numerical value of $19.95a_0$. Considering the sensitivity of a^{SC} to Φ for the values arising here, the success of the semiclassical estimate is certainly encouraging. We note that the value of Φ in equation (4) consistent with the numerical value of a is 0.7070π, differing by just 2% from the semiclassical value.

In principle a semiclassical estimate can also be employed for the near-dissociation bound levels. However the corresponding quantization condition for a potential falling off as R^{-6} [21] is:

$$\Phi'(\epsilon) = (v + 1/2 + \phi)\pi$$

where $\Phi'(\epsilon)$ is the phase integral at energy ϵ, analogous to the zero-energy Φ above. Here ϕ is zero well below dissociation and 1/8 at dissociation, leading to considerable uncertainty in this case.

5 Conclusions

Enlarging considerably the LiH basis set from that employed previously [1] has led to a deepening of the well and to a reduction in the scattering lengths, a for H + Li scattering with parallel spins and consequently in the cooling efficiency. Any additional improvement to the basis set is expected to reduce further the value of a. As the resulting changes in the potential are believed to be unlikely to exceed the change to the LB potential, the calculated result for a (HB) can be considered as an upper bound with the LB result as a lower bound. Our recommended scattering length values are then: 45 ± 4, 48 ± 5, 20 ± 1 and 21 ± 1 for ^{7}LiH, ^{6}LiH, ^{7}LiD and ^{6}LiD, respectively. Semiclassical estimates show the scattering length to be within 20% of the numerical value and the effective range within 6%. Although the LiH scattering lengths are substantially smaller than the previous estimate, their large magnitude compared to that for H–H collisions still predicts an efficiency about 500 times larger for hydrogen cooling by lithium atoms than by hydrogen atoms. The main conclusion that lithium seeding can assist achievement of Bose-Einstein condensation for hydrogen remains.

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