# Interaction potentials of LiH, NaH, KH, RbH, and CsH

N. Geum

Department of Chemistry, Dankook University, Cheonan 330-714, South Korea

G.-H. Jeung

Laboratoire Aimé Cotton, Bâtiment 505, Université de Paris Sud, 91405 Orsay, France

A. Derevianko

Department of Physics, University of Nevada, Reno, Nevada 89557

R. Côté<sup>a)</sup>

Department of Physics, University of Connecticut, Storrs, Connecticut 06269-3046

A. Dalgarno

Institute for Theoretical Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts 02138

(Received 9 January 2001; accepted 5 June 2001)

Quantum-mechanical calculations of the potential energy curves of the singlet and triplet states of LiH, NaH, KH, RbH, and CsH formed by the approach of ground state alkali-metal atoms and hydrogen atoms are presented. Precise values are determined for the coefficients of the van der Waals interaction and estimates are made of the contribution of the exchange interaction at large distances. Together with empirical data, they are used to assess and improve the accuracy of the *ab initio* potentials. © *2001 American Institute of Physics*. [DOI: 10.1063/1.1388044]

# **I. INTRODUCTION**

Recent progress in trapping of cold atoms and photoassociation spectroscopy in ultracold samples<sup>1,2</sup> have allowed the determination of diatomic interaction potentials with high precision. Accurate interaction potentials, particularly at large separations, are needed in calculations of the scattering of atoms at ultralow energies.<sup>1</sup> Collisions at ultracold temperatures are major factors in determining the behavior of trapped atoms and the formation of Bose-Einstein condensates.<sup>3</sup> For example, evaporative cooling (used to reach ultralow temperatures) depends on the thermalization rate coefficient which is determined by the cross sections for elastic collisions of the atoms. The scattering lengths, which give the ultralow energy scattering cross sections, also dictate many properties of Bose-Einstein condensates, such as their stability, size, and excitation modes.<sup>3,4</sup> Mixtures of the alkali metal atoms with hydrogen atoms may be effective in enhancing the cooling efficiency.<sup>5</sup> We present here ab initio calculations of the potential energy curves of the singlet and triplet states of LiH, NaH, KH, RbH, and CsH formed by the approach of ground state alkali-metal atoms and hydrogen atoms. The result for LiH has been presented graphically.<sup>5,6</sup> For NaH and KH, the effective core potential combined with the core polarization potential has been used to calculate a large number of electronic states.<sup>7</sup> As this method has a semiempirical character, we performed new calculations using ab initio all-electron methods for NaH, KH, RbH, and CsH which are presented in this work.

We attempt here to use an analysis of the atom interac-

tions at large separations to assess and improve the accuracy of the *ab initio* potentials.

#### II. AB INITIO CALCULATIONS

Ab initio calculations using a large scale configuration interaction method<sup>6</sup> have been carried out of the potential energy curves of the lowest  ${}^{1}\Sigma$  and  ${}^{3}\Sigma$  states of the alkali metal hydrides LiH, NaH, KH, RbH, and CsH at internuclear distances from  $0.3a_{0}$  to  $25a_{0}$  or  $30a_{0}$ .

The calculations employed products of atomic basis functions represented by primitive Gaussian functions optimized to describe the lowest electronic states of the various allowed symmetries as in the LiH case.<sup>5,6</sup> For atomic hydrogen seven orbitals with exponents 19.79, 2.945, 0.7209, 0.2301, 0.08552, 0.031, and 0.0098, three p orbitals withexponents 1.4, 0.34, and 0.093 and two d orbitals with exponents 1.2 and 0.25 without contraction were adopted. This basis set yields a binding energy that is 0.008 eV less than the exact nonrelativistic value of 0.5 a.u. and an electron affinity of 0.740 eV compared to the accurate value of 0.756 eV.<sup>8</sup> For lithium we used 15s, 10p, 6d, and 3f primitive Gaussian functions,<sup>6</sup> for Na 18s, 12p, 7d, and 3f, for K 18s, 14p, and 8d, for Rb 19s15p10d, and for Cs 20s15p10d, all without contraction. The atomic Hartree-Fock calculation using these bases gave total energies close to the corresponding numerical values.<sup>9</sup>

Optimal molecular orbitals were constructed from multiconfiguration self-consistent field calculations with two active sigma orbitals, and multireference configurationinteraction calculations<sup>6</sup> were carried out which included all possible single and double excitations. For LiH, all four electrons were represented explicitly in the construction. For

5984

<sup>&</sup>lt;sup>a)</sup>Electronic mail: rcote@phys.uconn.edu

NaH, KH, RbH, and CsH, the valence-core correlation was included by augmenting the full valence configurations with single core excitations.

The MOLCAS program<sup>10</sup> was used for the molecular configuration-interaction calculations. The calculated binding energies and the resulting interaction potentials are available electronically.<sup>11</sup>

At large distances the interaction potentials have the form

$$V(^{1}\Sigma^{+}|R) = V^{\text{disp}}(R) + V^{\text{exch}}_{S}(R), \qquad (1)$$

$$V(^{3}\Sigma^{+}|R) = V^{\text{disp}}(R) + V^{\text{exch}}_{T}(R), \qquad (2)$$

where the dispersion interaction may be represented by a power series expansion in the inverse of the internuclear distance

$$V^{\text{disp}}(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} + \cdots,$$
(3)

and the exchange terms  $V_S^{\text{exch}}$  and  $V_T^{\text{exch}}$  are exponentially decreasing functions of R whose form we consider in Sec. IV.

### **III. DISPERSION FORCES**

The van der Waals coefficients  $C_6$  and  $C_8$  in Eq. (3) may be determined to high accuracy by writing them in the forms

$$C_6 = \frac{3}{\pi} \int_0^\infty \alpha_{\rm H}^d(i\omega) \,\alpha_{\rm A}^d(i\omega) d\omega, \tag{4}$$

and

$$C_8 = \frac{15}{2\pi} \int_0^\infty (\alpha_{\rm H}^d(i\omega)\alpha_{\rm A}^q(i\omega) + \alpha_{\rm A}^d(i\omega)\alpha_{\rm H}^q(i\omega))d\omega, \quad (5)$$

where  $\alpha^{d}(i\omega)$  and  $\alpha^{q}(i\omega)$  are the dynamic dipole and quadrupole polarizabilities of the hydrogen and alkali metal atoms evaluated at imaginary frequencies  $i\omega$ . The dipole polarizabilities of Na, K, Rb, and Cs have been calculated to within an uncertainty of less than 0.5% or better by manybody perturbation theory.<sup>12</sup> We obtain  $C_6 = 73.83(9)$  a.u. for NaH, 111.2(2) a.u. for KH, 124.3(3) a.u. for RbH, and 149.7(2) a.u. for CsH. The value for LiH is 66.544 a.u.<sup>5</sup>

To determine  $C_8$  for Na we extended many-body techniques<sup>12</sup> to calculate the dynamic quadrupole polarizability. The dynamic quadrupole polarizability can be written as a sum of quadrupole transition matrix elements divided by energy denominators. The major contribution arises for Na from the  $3S_{1/2}-3D_I$  transitions. We used an *ab initio* relativistic coupled-cluster method which included single and double excitations<sup>13</sup> and we obtained  $\langle 3S_{1/2} \| Q \| 3D_{5/2} \rangle$ = 24.31 a.u. and  $\langle 3S_{1/2} \| Q \| 3D_{3/2} \rangle$  = 19.85 a.u. for the reduced matrix elements of the quadrupole operator Q. We combined these values with experimental energy differences and added their contributions to  $\alpha^{q}(i\omega)$  to those of the higher discrete and continuum valence states computed in the Dirac-Hartree-Fock approximation. The resulting static quadrupole polarizability for Na is  $\alpha^{q}(0) = 1922$  a.u., which should be an improvement over the nonrelativistic model potential values  $\alpha^q = 1878$  a.u. of Marinescu, Sadeghpour, and Dalgarno<sup>14</sup> and  $\alpha^q = 1807$  a.u. of Patil and Tang.<sup>15</sup>

For NaH, we obtain  $C_8 = 4059$  a.u. within a probable uncertainty of 2% whereas Patil and Tang<sup>15</sup> obtained  $C_8 = 3856$  a.u., which is smaller by 5%. For KH, RbH, and CsH we adopted the  $R^{-8}$  coefficients of Patil and Tang.<sup>15</sup>

Estimates of the higher order coefficients beyond  $R^{-8}$  arising from second-order perturbation theory have also been presented by Patil and Tang<sup>15</sup> and we used them here in our calculations of the dispersion forces. Contributions from higher orders of perturbation theory were neglected.

Examination of the *ab initio* calculations of the singlet and triplet potentials<sup>11</sup> shows that exchange forces become negligible for  $R > 18a_0$  and only the dispersion contributions remain. At such large distances the interaction energies are small but a limited comparison can be made.

For LiH, the *ab initio* calculations are consistent with an asymptotic form of about  $-73/R^6$  a.u., some 10% larger than the correct values. In absolute terms, the numerical accuracy of the individual values is high. Thus at  $R=27a_0$  the expansion (3) yields an interaction energy of  $-2.0 \times 10^{-7}$  a.u. compared to the *ab initio* value of  $-1.8 \times 10^{-7}$  a.u.

There is some loss of accuracy for the heavier alkali metal hydrides due presumably to the increase in superposition error associated with the requirement of larger basis sets for a multielectron system. For NaH, the asymptotic form of the dispersion energy is about  $-100/R^6$  whereas the correct form is  $-73.8/R^6$ . Bearing in mind that the interaction potentials obtained in the molecular configuration interaction calculation is the result of subtracting one large quantity from another, the numerical accuracy of individual points is again high. At  $R = 27a_0$ , the series (3) yields an interaction energy of  $-2.1 \times 10^{-7}$  a.u. and the *ab initio* value is  $-2.7 \times 10^{-7}$  a.u.

For KH, the *ab initio* calculations overestimate the long range dispersion forces by a factor of about 2. The leading term of the dispersion energy derived from the *ab initio* values is about  $-200/R^6$  a.u. whereas the correct value is  $-111.2/R^6$  a.u. At  $R=20a_0$ , the *ab initio* value is  $-6.3 \times 10^{-7}$  a.u. and the predicted value is  $-4.2 \times 10^{-7}$  a.u.

The results for RbH and CsH are similar to those for KH, the *ab initio* calculations yielding dispersion energies that are too large by factors of about 2. Our calculated values of  $C_6$  for RbH and CsH are, respectively, 124.3 and 149.7 a.u. to within an estimated error of 0.2%. At  $R = 20a_0$  the *ab initio* value for RbH is  $-3.0 \times 10^{-6}$  a.u. compared to the predicted  $-2.3 \times 10^{-6}$  a.u., and for CsH the *ab initio* dispersion energy is  $-3.9 \times 10^{-6}$  a.u. and the predicted value is  $-3.0 \times 10^{-6}$  a.u.

The discrepancy between predicted and *ab initio* values illustrates the great difficulty that conventional methods have in predicting quantitatively the long-range form of interaction potentials. The achievement of an absolute accuracy of  $10^{-7}$  a.u. for the lighter hydrides and a few times  $10^{-6}$  a.u. for the heavier indicates that the *ab initio* calculations presented here are very successful.

# **IV. EXCHANGE INTERACTIONS**

We attempt here to assess the accuracy of the exchange interaction, which distinguishes the singlet and triplet potentials. For a pair of like atoms,  $V_S^{\text{exch}}(R) = -V_T^{\text{exch}}(R)$  asymptotically and *ab initio* values of the exchange energies can be obtained by subtracting the *ab initio* singlet and triplet potentials. For like atoms, a formula given by Smirnov and Chibisov<sup>16</sup> provides a reliable representation of the exchange forces at large distances. Their representation assumes that the exchange energy arises from the interaction of the valence electrons in the region on the internuclear axis midway between the nuclei. In the case where the ionization potentials are quite different, the exchange interactions are determined more by the valence electron distribution near the atom with the higher ionization potential. The assumption leads to the approximate formula

$$V_T^{\text{exch}}(R) - V_S^{\text{exch}}(R) = F(\kappa) |\Phi(R)|^2, \qquad (6)$$

where  $\Phi(R)$  is the valence electron wave function at *R* and  $\kappa$  is an imaginary momentum given in a.u. in terms of the ionization potential  $\alpha^2/2$  of the alkali metal atom by<sup>17</sup>

$$\kappa^2 = -\alpha^2 + \frac{2}{R}.\tag{7}$$

The valence electron wave function can be represented asymptotically as

$$\Phi(r) \approx \frac{A}{\sqrt{4\pi}} r^{1/\alpha - 1} e^{-\alpha r}.$$
(8)

In the calculations we used experimental ionization energies and factors A from Ref. 18. The function  $F(\kappa)$  depends only on the scattering of slow electrons by atomic hydrogen in the singlet and triplet states and does not depend on the alkali metal atom. We assume that  $F(\kappa)$  is a constant and attempt to determine it from the *ab initio* calculations of the potentials. If we subtract  $V({}^{3}\Sigma|R)$  from  $V({}^{1}\Sigma|R)$  we eliminate asymptotically the dispersion forces. The resulting interaction energies vary over many orders of magnitude and for  $R > 10a_0$  they are consistent with the exponential variation with R given by  $|\Phi(R)|^2$ . The best overall choice of the external constant F that reproduces the exchange interactions for the five hydrides appears to be 180 a.u. In Table I we compare the *ab initio* values with the values given by

$$V_T^{\text{exch}}(R) - V_S^{\text{exch}}(R) \approx 180 |\Phi(R)|^2.$$
 (9)

The *ab initio* calculations capture the rapid variation of the exchange energy with *R*, even at very large *R* where extreme cancellation is occurring. At  $R = 15a_0$ , the possible numerical uncertainty in the *ab initio* interaction energies is of the order of  $10^{-8}$  a.u.

### **V. DISCUSSION AND CONCLUSIONS**

At small values of R, empirical data on the  ${}^{1}\Sigma^{+}$  potentials are available.<sup>19</sup> The case of LiH has been discussed earlier,<sup>5,20</sup> and the potential curves are shown in Fig. 1. The *ab initio* data for NaH are compared with RKR (Rydberg-Klein-Rees) data in Fig. 2. For the  $X^{1}\Sigma^{+}$  state the predicted

TABLE I. Comparison of the *ab initio* exchange splitting between  $a^{3}\Sigma^{+}$  and  $X^{1}\Sigma^{+}$  potentials with the predictions based on Eq. (9). Here,  $\Delta V \equiv V(^{3}\Sigma^{+}|R) - V(^{1}\Sigma^{+}|R)$ . All quantities are in atomic units and notation x[y] stands for  $x \times 10^{y}$ .

D						
(bohr)	10.0	12.5	15.0	17.5	20.0	
LiH						
$\Delta V$	4.37[-4]	2.65[-5]	1.52[-6]	8.63[-8]	1.00[-8]	
$180 \Phi(R) ^2$	4.87[-4]	2.72[-5]	1.45[-6]	7.45[-8]	3.75[-9]	
		Nal	H			
$\Delta V$	6.38[-4]	4.19[-5]	2.65[-6]	1.33[-7]	1.00[-8]	
$180 \Phi(R) ^2$	6.92[-4]	4.23[-5]	2.46[-6]	1.38[-7]	7.55[-9]	
1/11						
		Kr	1			
$\Delta V$	2.06[-3]	1.65[-4]	1.32[-5]	1.01[-6]	7.00[-8]	
$180 \Phi(R) ^2$	2.21[-3]	1.85[-4]	1.46[-5]	1.10[-6]	7.99[-8]	
РЬН						
ΔV	3 21[-3]	202[-4]	180[-5]	266[-6]	1.60[-7]	
$\Delta V$	3.21[-3]	2.92[-4]	1.60[-5]	2.00[-0]	1.00[-7]	
$180 \Phi(R) ^2$	2.91[-3]	2.61[-4]	2.19[-5]	1.76[-6]	1.37[-7]	
CsH						
$\Delta V$	6.82[-3]	6.36[-4]	6.04[-5]	5.84[-6]	5.60[-7]	
$180 \Phi(R) ^2$	4.61[-3]	4.68[-4]	4.43[-5]	3.99[-6]	3.47[-7]	

well depth  $D_e$  is 15 638.3 cm<sup>-1</sup> and the predicted equilibrium separation is  $R_e = 3.578a_0$ . Stwalley *et al.*<sup>19</sup> recommended the empirical values  $D_e = 15\,900 \,\mathrm{cm}^{-1}$  and  $R_e = 3.5659a_0$ . RKR data are available only for the eight lowest vibrational levels.<sup>21</sup> Over a limited range of *R* they indicate a potential that is uniformly deeper by 1.6% than the theoretical curve. The triplet state has a shallow well with a depth of 4.1 cm<sup>-1</sup> at an equilibrium distance of  $12a_0$  and it supports one vibrational level.

We carried out a similar analysis for KH. The *ab initio* singlet potential has a dissociation energy  $D_e$  of 14 803 cm<sup>-1</sup> and an equilibrium distance  $R_e = 4.22a_0$ . Empirical RKR data are available for all the 24 bound vibrational levels that are supported by the potential. They yield  $D_e = 14772.7 \pm 0.6$  cm<sup>-1</sup> and  $R_e = 4.2332a_0$ .<sup>22</sup> The *ab initio* well depth of the  $a^{3}\Sigma^{+}$  state is 3.8 cm<sup>-1</sup> and the equilibrium separation is  $R_e = 13.2a_0$ . It supports one vibrational level. A comparison



FIG. 1. LiH. *Ab initio* potentials and comparison with the RKR data (+) from Ref. 20. Solid and long-dashed lines represent *ab initio*  $X^{1}\Sigma^{+}$  and  $a^{3}\Sigma^{+}$  potential curves, respectively (see also Ref. 5 for a detailed discussion).

Downloaded 04 Jul 2011 to 134.197.31.110. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights\_and\_permissions



FIG. 2. NaH. *Ab initio* potentials and comparison with the RKR data (+) from Ref. 21. Solid and long-dashed lines represent *ab initio*  $X^{1}\Sigma^{+}$  and  $a^{3}\Sigma^{+}$  potential curves, respectively.

of *ab initio* results for the  $X^{1}\Sigma^{+}$  state and the energies derived from the RKR analysis is given in Fig. 3. The *ab initio* calculations underestimate the singlet binding energies by about 0.2%.

For RbH RKR data are available for the lowest 11 vibrational levels of the  $X^{1}\Sigma^{+}$  state.<sup>23</sup> A comparison with the RKR data is presented in Fig. 4. The *ab initio* dissociation energy  $D_e = 14301 \text{ cm}^{-1}$  is 2.0% smaller than the recommended value  $D_e = 14580 \pm 600 \text{ cm}^{-1}$ .<sup>19</sup> The predicted equilibrium separation is  $4.5a_0$  and the experimental value is  $4.4726a_0$ . The well depth of the  $a^{3}\Sigma^{+}$  state is 2.7 cm<sup>-1</sup> with the equilibrium separation  $R_e = 14a_0$ . Only one vibrational level is supported by this well.

For the  $X^{1}\Sigma^{+}$  state of CsH the calculated dissociation energy  $D_{e} = 14\,805.9\,\mathrm{cm}^{-1}$  is in excellent agreement with the recommended value  $14\,792.2\,\mathrm{cm}^{-1}$ .<sup>19</sup> The calculated equilibrium separation is  $4.8a_{0}$  compared to the measured  $4.7135a_{0}$ . Figure 5 shows that the calculated values lie below the semiempirical data for internuclear distances beyond the equilibrium separation. For example at  $R = 8a_{0}$  the *ab initio* result is 13% lower than the semiempirical value. The *ab initio*  $a^{3}\Sigma^{+}$  potential has a well depth  $D_{e} = 2.4\,\mathrm{cm}^{-1}$  and  $R_{e} = 15a_{0}$  and again supports one vibrational level.



FIG. 4. RbH. *Ab initio* potentials and comparison with the RKR data of Ref. 23. See the caption of Fig. 2 for an explanation of the labels.

Subsequent to the review of Stwalley *et al.*,<sup>19</sup> *ab initio* calculations of the potential curves of the lowest  $X^{1}\Sigma^{+}$  states of KH and RbH have been carried out by Garcia, Caballol, and Malrieu.<sup>24</sup> They obtain for KH a variational estimate of 15 491 cm<sup>-1</sup> for  $D_{e}$  and of 4.36 $a_{0}$  for  $R_{e}$  and for RbH 14 200 cm<sup>-1</sup> and 3.39 $a_{0}$ . The values for RbH are in fair agreement with our calculations but there are substantial differences for KH.

Based on the *ab initio* potentials, RKR data, and dispersion coefficients we constructed the hybrid potentials. For the  $X^{1}\Sigma^{+}$  states the RKR data were augmented with the uniformly scaled *ab initio* values, and in the region  $20a_{0} < R < 30a_{0}$  we smoothly merged the scaled *ab initio* potentials into the theoretical dispersion interactions. Using these constructed singlet potentials, we assembled the triplet potentials as

$$V(a^{3}\Sigma^{+}|R) = V(X^{1}\Sigma^{+}|R) + 180|\Phi(R)|^{2}$$
(10)

for  $R > 25a_0$ . In the region  $20a_0 < R < 25a_0$  this potential was combined with the *ab initio* data to provide a continuous transition to the *ab initio* potential at smaller internuclear separations.

A comparison of the *ab initio* and the constructed potentials (interpolated when necessary) is given in Table II for a number of internuclear distances. The complete tables are available in electronic form.<sup>11</sup> We believe these potentials



FIG. 3. KH. *Ab initio* potentials and comparison with the RKR data of Ref. 22. See the caption of Fig. 2 for an explanation of the labels.



FIG. 5. CsH. *Ab initio* potentials and comparison with the RKR data of Ref. 25. See the caption of Fig. 2 for an explanation of the labels.

Downloaded 04 Jul 2011 to 134.197.31.110. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights\_and\_permissions

TABLE II. Comparison of hybrid and ab initio potentials.

D	$V(X^{-1})$ (10 <sup>-3</sup> 1	$V(X^{1}\Sigma^{+} R)$ (10 <sup>-3</sup> hartree)		$\frac{V(a^{3}\Sigma^{+} R)}{(10^{-3} \text{ hartree})}$		
(bohr)	Hybrid	Ab initio	Hybrid	Ab initio		
		LiH				
5.0	-46.34928	-45.60992	6.716 54	6.716 54		
7.5	-6.05766	-5.88594	0.737 80	0.737 80		
10.0	-0.44801	-0.42979	0.007 14	0.007 14		
12.5	-0.04493	$-0.043\ 10$	-0.016 63	-0.016 63		
15.0	$-0.008\ 80$	-0.00844	-0.00692	-0.00692		
17.5	-0.00295	-0.00283	-0.00274	-0.00274		
20.0	-0.00126	-0.00121	$-0.001\ 20$	$-0.001\ 20$		
25.0	-0.00030	-0.00032	-0.00029	$-0.000\ 32$		
30.0	$-0.000\ 10$	$-0.000\ 10$	$-0.000\ 10$	$-0.000\ 11$		
		NaH				
5.0	-48.13187	-47.46891	8.028 91	8.028 91		
7.5	-7.92694	-7.80256	0.935 84	0.935 84		
10.0	-0.62214	-0.61238	0.025 90	0.025 90		
12.5	-0.06072	-0.05977	$-0.017\ 84$	$-0.017\ 84$		
15.0	-0.01086	-0.01069	-0.00804	-0.00804		
17.5	-0.00345	$-0.003\ 40$	-0.00326	-0.00326		
20.0	-0.00156	-0.00154	-0.00153	-0.00153		
25.0	-0.00037	-0.00040	-0.00037	-0.00040		
30.0	$-0.000\ 11$	$-0.000\ 15$	$-0.000\ 11$	$-0.000\ 15$		
		KH				
5.0	-60.04424	-59.72203	9.395 32	9.395 32		
7.5	-18.50058	-18.00672	1.563 01	1.563 01		
10.0	-1.99776	-1.92298	0.133 44	0.133 44		
12.5	-0.18088	-0.18025	-0.01523	-0.015 23		
15.0	-0.02733	-0.02556	-0.01240	-0.01240		
17.5	$-0.007\ 13$	-0.00667	$-0.005\ 67$	$-0.005\ 67$		
20.0	-0.003 16	-0.00296	-0.002 89	-0.00289		
25.0	-0.00068	-0.00079	-0.00069	-0.00079		
30.0	-0.00017	-0.000 39	-0.000 17	-0.000 39		
		RbH				
5.0	-62.877 56	- 62.005 62	10.482 75	10.482 75		
7.5	-23.182 51	-23.088 61	1.863 25	1.863 25		
10.0	-3.00798	- 2.995 81	0.21170	0.211 70		
12.5	-0.29769	-0.296 49	-0.004 11	-0.004 11		
15.0	-0.02917	-0.029 05	-0.01104	-0.011 04		
17.5	-0.00867	-0.008 64	-0.005 98	- 0.005 98		
20.0	-0.003 07	-0.003 06	-0.00290	- 0.002 90		
25.0	-0.000 /6	-0.000 95	-0.000 /6	- 0.000 98		
30.0	-0.000 19	-0.000 45	-0.000 19	-0.000 45		
5.0	66 212 28	CsH	11 027 95	11 027 95		
5.0	- 00.312 28	- 00.892 83	2 210 82	2 210 82		
10.0	- 29.200 /3	- 52.255 /8	2.219 83	2.219 83		
10.0	-5.00250 -0.53445	-0.602.42	0.211 /0	0.211 /0		
12.3	-0.061.21	-0.02542	-0.012.39	-0.012.39		
17.5	-0.00131	-0.071.32	-0.01112	-0.01112 -0.00709		
20.0	-0.003.50	-0.0012.93	-0.007.08	- 0.007.08		
25.0	-0.000.85	-0.004.19	- 0 000 83	-0.005.05		
30.0	-0.00023	-0.00042	-0.000.03	-0.00142		
20.0	0.000 25	0.000 12	5.000 25	5.000 42		

will enable accurate predictions to be made of the scattering of the alkali metal atoms by hydrogen atoms.<sup>5</sup> This method should be applicable to other systems, in particular to the interaction of Rydberg atoms.

#### ACKNOWLEDGMENTS

The authors would like to thank Vasili Kharchenko for useful discussions. The work of A. Da. and A. De. was supported by the Chemical Sciences, Geosciences and Biosciences Division of the Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy. G.-H.J. was partly supported by the Centre National de la Recherche Scientifique (C.N.R.S.) and R.C. by National Science Foundation Grant No. PHY-9970757.

- <sup>1</sup>V. S. Bagnato, S. Zilio, and P. S. Julienne, Rev. Mod. Phys. 71, 1 (1999).
- <sup>2</sup>R. Côté, A. Dalgarno, Y. Sun, and R. G. Hulet, Phys. Rev. Lett. **74**, 3581 (1995).
- <sup>3</sup>F. Dalfovo, S. Giorgini, L. P. Pitaevskii, and S. Stringari, Rev. Mod. Phys. **71**, 463 (1999).
- <sup>4</sup>E. Timmermans, R. Côté, and I. Simbotin, J. Phys. B 33, 4157 (2000).
- <sup>5</sup>R. Côté, M. J. Jamieson, Z.-C. Yan, N. Geum, G.-H. Jeung, and A. Dalgarno, Phys. Rev. Lett. **84**, 2806 (2000); A. Derevienko, R. Côté, A. Dalgarno, and G.-H. Jeung, Phys. Rev. A **64**, 011404(R) (2001).
- <sup>6</sup>A. Yiannopoulou, G.-H. Jeung, S. J. Park, H. S. Lee, and Y. S. Lee, Phys. Rev. A **59**, 1178 (1999).
- <sup>7</sup>H. S. Lee, Y. S. Lee, and G.-H. Jeung, Chem. Phys. Lett. **325**, 46 (2000).
- <sup>8</sup>C. L. Peckeris, Phys. Rev. **126**, 1470 (1962).
- <sup>9</sup>C. Froese-Fischer, *The Hartree–Fock Method for Atoms* (Wiley, New York, 1977).
- <sup>10</sup>K. Andersson, M. R. A. Blomberg, M. P. Fülscher *et al.*, MOLCAS, Version 4, 1997, Lund University, Sweden.
- <sup>11</sup> See EPAPS Document No. E-JCPSA6-115-311132 for tables of the *ab initio* singlet and triplet potential curves of LiH, NaH, KH, RbH, and CsH. This document may be retrieved via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.
- <sup>12</sup> A. Derevianko, W. R. Johnson, M. S. Safronova, and J. F. Babb, Phys. Rev. Lett. 82, 3589 (1999).
- <sup>13</sup> M. S. Safronova, A. Derevianko, and W. R. Johnson, Phys. Rev. A 58, 1016 (1998).
- <sup>14</sup> M. Marinescu, H. Sadeghpour, and A. Dalgarno, Phys. Rev. A 49, 982 (1994).
- <sup>15</sup>S. H. Patil and K. T. Tang, J. Chem. Phys. **106**, 2298 (1997).
- <sup>16</sup>B. M. Smirnov and M. I. Chibisov, Zh. Eksp. Teor. Fiz. **48**, 939 (1965) [Sov. Phys. JETP **21**, 624 (1965)].
- <sup>17</sup> B. M. Smirnov, Zh. Eksp. Teor. Fiz. **51**, 466 (1966) [Sov. Phys. JETP **24**, 314 (1967)].
- <sup>18</sup>M. Marinescu and A. Dalgarno, Z. Phys. D: At., Mol. Clusters **36**, 239 (1996).
- <sup>19</sup> W. Stwalley, W. Zemke, and S. C. Yang, J. Phys. Chem. Ref. Data **20**, 153 (1991).
- <sup>20</sup> Y. C. Chan, D. R. Harding, W. C. Stwalley, and C. R. Vidal, J. Chem. Phys. **85**, 2436 (1986); W. C. Stwalley and W. T. Zemke, J. Phys. Chem. Ref. Data **22**, 87 (1993).
- <sup>21</sup>A. Maki and W. Olson, J. Chem. Phys. **90**, 6887 (1989).
- <sup>22</sup>K. Hussein, C. Effantin, J. D'Incan, J. Verges, and R. F. Barrow, Chem. Phys. Lett. **124**, 105 (1986).
- <sup>23</sup> H. Kato, Y. Toyosaka, and T. Suzuki, Bull. Chem. Soc. Jpn. 58, 562 (1985).
- <sup>24</sup> V. Garcia, R. Caballol, and J. Malrieu, J. Chem. Phys. **109**, 504 (1998).
- <sup>25</sup>C. Crepin, J. Verges, and C. Amiot, Chem. Phys. Lett. **112**, 10 (1984).