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# Potential-Energy Curves of the Excited States of Alkali Hydride Molecules

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The potential-energy curves of the excited states of NaH and KH have been obtained by the Rydberg-Klein-Rees method as described by Singh and Jain. The simple-harmonic curves and ionic curves for LiH, NaH, KH, and RbH have also been calculated. It has been found that the potential-energy curves mostly agree with Mulliken's findings as to the anomalous behavior of the excited states of alkali hydrides.

## INTRODUCTION

THE excited states of alkali hydrides are of considerable interest because in their case the successive vibrational quanta,  $\Delta G_{v+1/2}$ , increase, at first, with increasing vibrational quantum number, and the rotational constant  $\alpha_e$  is negative in the region of the first few vibrational levels. Mulliken<sup>1</sup> has attributed these facts to the unusual shape of their potential-energy curves. According to him the two low states of an alkali hydride molecule arise from an interaction between the two  $^1\Sigma^+$  states, one homopolar and derived from unexcited neutral atoms and the other ionic and derived from  $M^+$  and  $H^-$ , where  $M$  is an alkali atom. Rosenbaum<sup>2</sup> and Almy and Beiler<sup>3</sup> have indicated that the excited state of an alkali hydride most probably dissociates into  $M(^2P)$  and  $H(^2S)$  atoms rather than into ions, hence it would be necessary to assume a second similar interaction between the  $^1\Sigma^+$  state derived from  $M(^2P)$  and  $H(^2S)$  atoms and the  $^1\Sigma^+$  state derived from  $M^+$  and  $H^-$  ions. In view of this, it has been considered worthwhile to obtain the potential-energy curves of the excited states of alkali hydrides and to determine their positions with respect to the ionic curves. The potential-energy curves of the excited states of LiH and RbH molecules, obtained by the Rydberg-Klein-Rees method, have been reported by Singh and Jain.<sup>4</sup> We have calculated the potential-energy curves of the excited states of NaH and KH by the same method. The ionic curves for all the four molecules have also been obtained. Further, Mulliken<sup>1</sup> has indicated that both the limbs of the potential-energy curves are expected to rise faster than the corresponding limbs of the simple-harmonic curves in the neighborhood of the equilibrium internuclear distance, owing to their  $\omega_e x_e$  values being negative. Therefore, for comparison, we have obtained the simple-harmonic curves as well.

## RYDBERG-KLEIN-REES-METHOD

The semiclassical method of Rydberg and Klein is the only one available for constructing the potential-energy curves of diatomic molecules, using band spectroscopic data. Rees<sup>5</sup> has given analytical expressions for the quantities  $f$  and  $g$  involved therein. For the electronic states whose vibrational terms can be represented by quadratics in  $(v+\frac{1}{2})$ , his expressions take the following simple form.

$$f = (\delta\pi^2\mu c/h)^{-1/2} Z, \quad (1)$$

$$g = (2\pi^2\mu c/h)^{1/2} \{ (2\alpha_e/\omega_e x_e) U^{1/2} + [2B_e - (\alpha_e\omega_e/\omega_e x_e)] Z \}, \quad (2)$$

where  $Z = (\omega_e x_e)^{-1/2} \ln \left[ \frac{\omega_e - 2\omega_e x_e(v+\frac{1}{2})}{\omega_e - 2(\omega_e x_e)^{1/2} U^{1/2}} \right]$ , and

$U = G(v)$ , the term value for the vibrational level in question.

The other symbols have their usual meaning.

For an electronic state whose vibrational terms cannot be represented by a single quadratic in  $(v+\frac{1}{2})$ , Rees has suggested two methods. One method consists of retaining the cubic term in the expression for  $G(v)$ , and the other one, of introducing artificial discontinuities in the law of force. The expressions obtained in the former case are quite cumbersome. Therefore, for dealing with such cases, Vanderslice *et al.*<sup>6</sup> have adopted the method of introducing an artificial discontinuity in the law of force at each vibrational level and determining the values of  $\omega_i$  and  $(\omega x)_i$  appropriate to the interval between any two vibrational levels by the least-squares method. Thus they have extended Rees's expressions to the following form<sup>7</sup>

$$f = (8\pi^2\mu c/h)^{-1/2} \sum_{i=1}^n (\omega x)_i^{-1/2} \ln W_i, \quad (3)$$

$$g = (2\pi^2\mu c/h)^{1/2} \sum_{i=1}^n \{ 2\alpha_i (\omega x)_i^{-1/2} [(U_n - U_{i-1})^{1/2} - (U_n - U_i)^{1/2}] + (\omega x)_i^{-1/2} [2B_i - \alpha_i (\omega x)_i^{-1/2} \omega_i] \ln W_i \}, \quad (4)$$

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<sup>1</sup> R. S. Mulliken, *Phys. Rev.* **50**, 1028 (1936).

<sup>2</sup> E. J. Rosenbaum, *J. Chem. Phys.* **6**, 16 (1938).

<sup>3</sup> G. M. Almy and A. C. Beiler, *Phys. Rev.* **61**, 476 (1942).

<sup>4</sup> N. L. Singh and D. C. Jain, *Proc. Phys. Soc. (London)* **79**, 753 (1962).

<sup>5</sup> A. L. G. Rees, *Proc. Phys. Soc. (London)* **59**, 998 (1947).

<sup>6</sup> J. T. Vanderslice, E. A. Mason, W. G. Maisch, and E. R. Lippincott, *J. Mol. Spectry.* **3**, 17 (1959).

<sup>7</sup> J. T. Vanderslice, E. A. Mason, W. G. Maisch, and E. R. Lippincott, *J. Chem. Phys.* **33**, 614 (1960).

TABLE I. Molecular constants of the excited ( $A\ ^1\Sigma^+$ ) states of alkali hydrides.

Molecule \ Constant	$\omega_e$	$\omega_e x_e$	$\omega_e y_e$	$B_e$	$\alpha_e$	$\gamma_e$	$r_e$ (Å)
LiH	240.0	-22.99	-1.5494	2.828	-0.0573	-0.0107	2.6010
NaH	312.9	-4.66	-0.1341	1.710	-0.0899	-0.0095	3.1682
KH	251.9	-4.06	-0.1675	1.318	-0.0349	-0.0030	3.6393
RbH	244.6	-4.07	-0.1592	1.231	-0.0209	-0.0020	3.7077

where

$$W_i = \left\{ \frac{[\omega_i^2 - 4(\omega x)_i U_i]^{\frac{1}{2}} - 2(\omega x)_i^{\frac{1}{2}}(U_n - U_i)^{\frac{1}{2}}}{[\omega_i^2 - 4(\omega x)_i U_{i-1}]^{\frac{1}{2}} - 2(\omega x)_i^{\frac{1}{2}}(U_n - U_{i-1})^{\frac{1}{2}}} \right\}.$$

Singh and Jain<sup>8</sup> have pointed out that the value of  $f$  at any vibrational level depends upon the nature of the Klein's function in its immediate neighborhood only, and thus they have obtained the following expression for  $f$ .

$$f = (8\pi^2\mu c/h)^{-\frac{1}{2}} Z_i, \quad (5)$$

TABLE II. The potential-energy curve of the  $A\ ^1\Sigma^+$  state of the NaH molecule.

$v$	$G(v)$ (cm <sup>-1</sup> )	$r_{\min}$ (Å)	$r_{\max}$ (Å)
0	158	2.841	3.506
1	479	2.607	3.746
2	809	2.452	3.905
3	1147	2.337	4.040
4	1490	2.248	4.166
5	1840	2.175	4.282
6	2194	2.114	4.391
7	2551	2.062	4.498
8	2910	2.015	4.602
9	3271	1.972	4.704
10	3631	1.934	4.803
11	3990	1.896	4.900
12	4348	1.856	4.993
13	4702	1.815	5.085
14	5055	1.785	5.182
15	5403	1.755	5.281
16	5747	1.725	5.379
17	6087	1.695	5.478
18	6421	1.680	5.590
19	6751	1.665	5.703
20	7074	1.650	5.816

where

$$Z_i = (\omega x)_i^{-\frac{1}{2}} \ln \left[ \frac{\omega_i - 2(\omega x)_i(v + \frac{1}{2})}{\omega_i - 2(\omega x)_i^{\frac{1}{2}} U_i^{\frac{1}{2}}} \right].$$

As a check on this, we have performed calculations for the  $A\ ^3\Pi_g$  state of  $C_2$  and  $C\ ^3\Pi_u$  state of  $N_2$  by using Eq. (3) and have found that in the sum on the right-hand side of Eq. (3) the contributions of all the terms except the one for  $i=n$  is negligible, within limits of errors introduced owing to the approximations involved. This is further supported by the fact that the values of  $f$  obtained by using Eqs. (3) and (5) agree quite well.<sup>7,8,9</sup>

Again, by defining the Klein's function as the sum of a number of terms, each one corresponding to the interval between the successive vibrational levels and characterized by the values of  $\omega_i$  and  $(\omega x)_i$  appropriate to the interval, Singh and Jain<sup>8</sup> have obtained the following expression for  $g$ .

$$g = \left( \frac{2\pi^2\mu c}{h} \right)^{\frac{1}{2}} \sum_{i=1}^n \left\{ 2\alpha_i (\omega x)_i^{-1} (U_i^{\frac{1}{2}} - U_{i-1}^{\frac{1}{2}}) + \left[ 2B_i - \frac{\alpha_i \omega_i}{(\omega x)_i} \right] (Z_i - Z_{i-1}) \right\}. \quad (6)$$

The corresponding expressions for the excited states of alkali hydrides whose  $\omega_e x_e$  values are negative, are

$$f = (8\pi^2\mu c/h)^{-\frac{1}{2}} Z_i', \quad (7)$$

$$g = (2\pi^2\mu c/h)^{\frac{1}{2}} \sum_{i=1}^n \left\{ \left[ 2B_i + \frac{\alpha_i \omega_i}{(-\omega x)_i} \right] (Z_i' - Z_{i-1}') - 2\alpha_i (-\omega x)_i^{-1} (U_i^{\frac{1}{2}} - U_{i-1}^{\frac{1}{2}}) \right\}, \quad (8)$$

where  $Z_i' = (-\omega x)_i^{-\frac{1}{2}} \arccos$

$$\times \left\{ \omega_i / [\omega_i + 2(-\omega x)_i(v + \frac{1}{2})] \right\}.$$

The potential-energy curves of the excited states of LiH and RbH obtained by using Eqs. (7) and (8) have been found to satisfy the quantization condition quite well,<sup>4</sup> which indicates that the approximations made in deducing the above expressions do not entail much error in the potential-energy curves. Therefore

<sup>8</sup> N. L. Singh and D. C. Jain, Proc. Phys. Soc. (London) **79**, 274 (1962).

<sup>9</sup> N. L. Singh and D. C. Jain, Can. J. Phys. **40**, 520 (1962).

we have used them for calculating the potential-energy curves of the excited states of NaH and KH. The  $r_{\max}$  and  $r_{\min}$  values for  $B^3\Sigma_u^+$  state of  $\text{Br}^{79}\text{Br}^{81}$  reported by Singh and Jain<sup>8</sup> differ from those of Rees<sup>5</sup> by about 0.5%. This is the order of maximum error one should expect in the present results as well.

### COMPUTATIONAL PROCEDURE AND RESULTS

The molecular constants of the excited states of alkali hydrides depend upon the number of vibrational

TABLE III. The potential-energy curve of the  $A^1\Sigma^+$  state of the KH molecule.

$v$	$G(v)$ ( $\text{cm}^{-1}$ )	$r_{\min}$ ( $\text{\AA}$ )	$r_{\max}$ ( $\text{\AA}$ )
0	127	3.239	3.973
1	387	2.992	4.248
2	653	2.832	4.437
3	924	2.712	4.595
4	1201	2.616	4.733
5	1485	2.539	4.860
6	1773	2.476	4.980
7	2064	2.419	5.099
8	2356	2.369	5.213
9	2649	2.322	5.324
10	2942	2.279	5.433
11	3235	2.237	5.539
12	3527	2.194	5.642
13	3817	2.151	5.740
14	4104	2.100	5.828
15	4389	2.005	5.871
16	4671	1.990	5.996
17	4950	2.012	6.158
18	5225	2.024	6.307
19	5495	2.032	6.454
20	5761	2.030	6.593
21	6022	2.028	6.733
22	6279	2.027	6.878
23	6529	2.034	7.032
24	6773	2.051	7.196

levels considered.<sup>3,10</sup> In view of such a discrepancy, Almy and Beiler<sup>3</sup> have suggested the method of graphical extrapolation of a plot of  $\Delta G'$  and that of  $B_v'$  for obtaining  $\omega_e'$  and  $B_e'$ , respectively. Singh and Jain<sup>4</sup> have adopted the method of extrapolation of  $\Delta G'$  against  $(v' + \frac{1}{2})$  by the least-squares method for obtaining the values of  $\omega_e$  and  $\omega_e x_e$  for the excited states of LiH and RbH. We have used the same method for calculating

<sup>10</sup> F. H. Crawford and T. Jorgensen, Phys. Rev. **47**, 932 (1935).

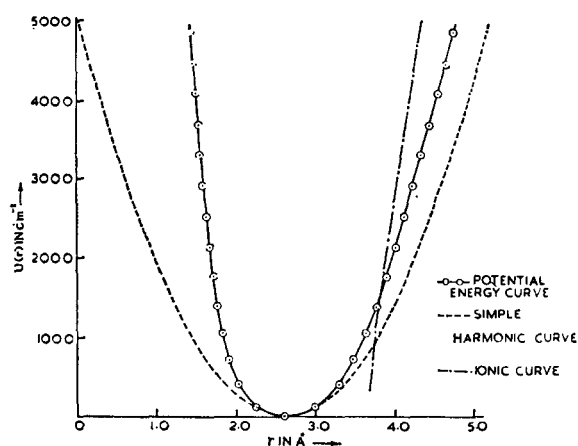


FIG. 1. The potential-energy curve of the  $A^1\Sigma^+$  state of the LiH molecule.

the vibrational constants of the excited states of NaH and KH and have used the first three observed  $\Delta G_{v'+\frac{1}{2}}$  values in each case. Similarly, by least-squaring the first three observed  $B_v'$  values against  $(v' + \frac{1}{2})$ , we have obtained the rotational constants for the excited states of the four alkali hydrides. The experimental data of Crawford and Jorgensen<sup>10</sup> and of Gaydon and Pearse<sup>11</sup> have been used for LiH and RbH, respectively. For NaH, the experimental data of Pankhurst<sup>12</sup> have

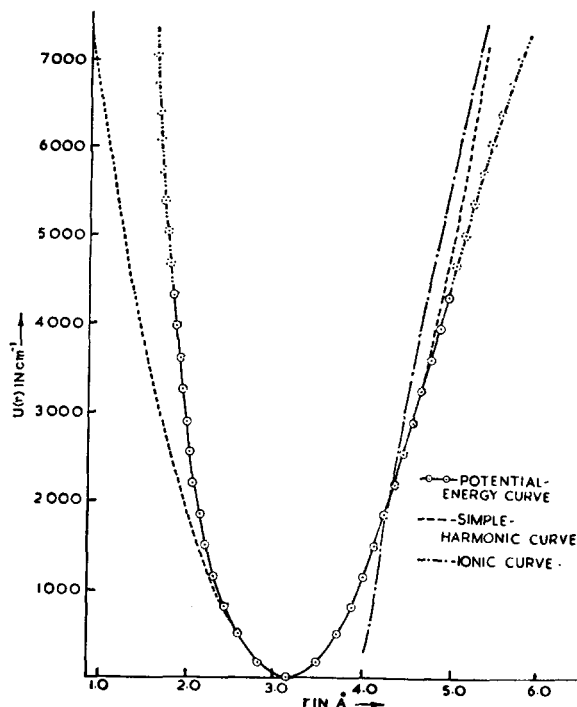


FIG. 2. The potential-energy curve of the  $A^1\Sigma^+$  state of the NaH molecule.

<sup>11</sup> A. G. Gaydon and R. W. B. Pearse, Proc. Roy. Soc. (London) **A173**, 28 (1939).

<sup>12</sup> R. C. Pankhurst, Proc. Phys. Soc. (London) **62**, 191 (1949).

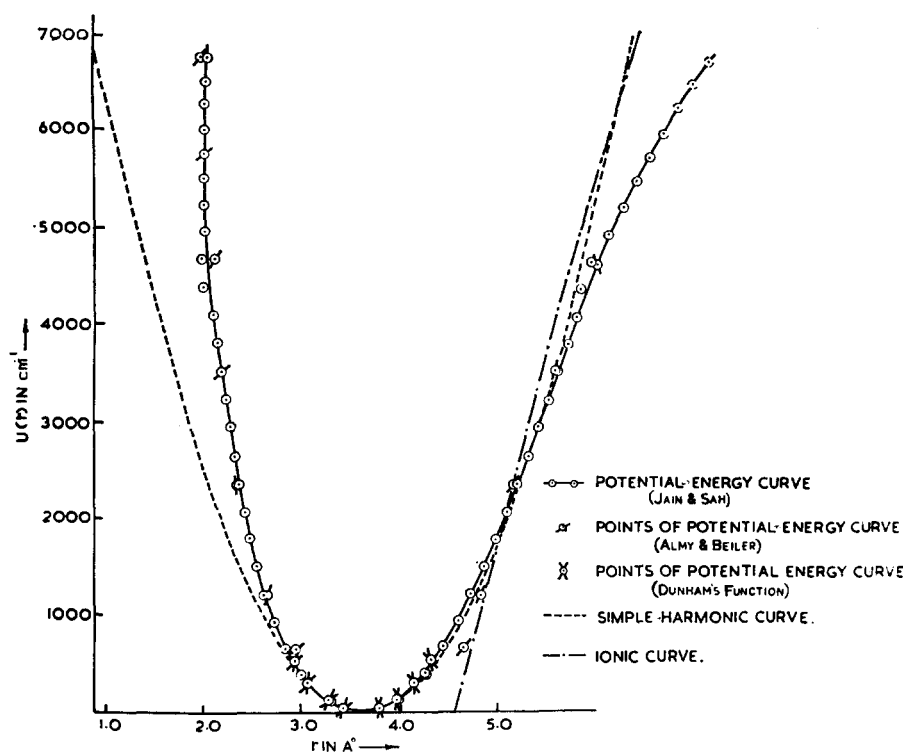


FIG. 3. The potential-energy curve of the  $A\ 1\Sigma^+$  state of the KH molecule.

been used. The values of  $Bv'$  given by Olsson<sup>13</sup> have been adopted for higher vibrational levels. For KH, the experimental data of Hori<sup>14</sup> have been adopted for  $v \leq 8$  and those of Almy and Beiler<sup>3</sup> for  $v > 8$ . The vibrational and rotational constants obtained have been listed in Table I. The vibrational constants for LiH and RbH reported by Singh and Jain<sup>7</sup> have also been included in the table.

For obtaining the potential-energy curves of the excited states of NaH and KH, the vibrational terms have been calculated by using the observed  $\Delta G_{v+1/2}$  values. The constants  $\omega_i$  and  $(\omega x)_i$  for the intervals between successive vibrational levels have been calculated by least-squaring four vibrational terms at a time. The constants thus obtained have been used for the interval between the middle two levels only, and then another overlapping group of four vibrational terms considered.<sup>6</sup> Similarly, the values of  $B_i$  and  $\alpha_i$  for the intervals between successive vibrational levels have been calculated by using the observed  $B_v$  values. The excited states of both these molecules possess discontinuities in the law of force in the sense that the  $(\omega x)_i$  values for vibrational levels below the discontinuity are negative and for those above it are positive. The change of sign takes place at  $v=15$  for NaH and at  $v=16$  for KH. Accordingly, for calculating  $f$ , Eq. (7) or (5) has been used for vibrational levels having negative or positive values of  $(\omega x)_i$ . For NaH, Olsson

has given the values of  $B_v'$  up to  $v=13$  only. Therefore the values of  $r_{\min}$  for  $v > 13$  have been obtained by a graphical extrapolation of the left branch of the potential-energy curve and the values of  $r_{\max}$ , by using the relation

$$r_{\max} = r_{\min} + 2f.$$

In the case of KH, the value of  $g$  is somewhat sensitive to the values of  $\omega_i$  and  $(\omega x)_i$  in the region of the observed discontinuity in the law of force. In this situation,  $\omega_i$  and  $(\omega x)_i$  for the interval between the 14th and 15th vibrational levels have been obtained by using the vibrational terms for these levels only. The values of  $Z_{i-1}$  [Eq. (6)] for the interval between the 15th and 16th vibrational levels has been obtained by using the  $\omega_i$  and  $(\omega x)_i$  values for this interval. Even then a slight discontinuity is observed in the potential-energy curve at the 15th and 16th vibrational levels (see Fig. 3). The results for the potential-energy curves have been entered in Tables II and III.

The simple-harmonic curves have been obtained by using the molecular constants listed in Table I, and the ionic curves, by using the relation

$$U(r) = A - (\alpha/r),$$

where  $A$  and  $\alpha$  are constants. The numerical value of  $\alpha=14.4$  if  $U(r)$  is in electron volts and  $r$  in Å. Referred to  $M(^2S) + H(^2S)$  as zero energy, the constant  $A$  is equal to (ionization potential of  $M$ ) - (electron affinity of  $H$ ). The potential-energy curves have been

<sup>13</sup> E. Olsson, Z. Physik **93**, 206 (1935).

<sup>14</sup> T. Hori, Mem. Ryojun Coll. Eng. **6**, 1 (1933).

plotted in Figs. 1–4 along with the simple-harmonic and ionic curves. The results of Singh and Jain<sup>5</sup> have been used for plotting the potential-energy curves for LiH and RbH. The portions of the curves for NaH and RbH obtained by extrapolation are shown by dotted lines. The potential-energy curve of the excited state of KH obtained by Almy and Beiler<sup>4</sup> has also been plotted in Fig. 3. They obtained the  $r_{\min}$  and  $r_{\max}$  values for  $V \geq 2$  by the graphical method of Rydberg and Klein and the portion of the curve near the equilibrium internuclear separation by Dunham's power series.

### DISCUSSION

The potential-energy curves for LiH and KH were constructed by Rosenbaum<sup>2</sup> and by Almy and Beiler,<sup>3</sup> respectively, by the graphical method of Rydberg and Klein. These, in general, agree with the curves reported by Singh and Jain<sup>4</sup> and by us. In the case of LiH, Rosenbaum has concluded that the potential-energy curve partly supports Mulliken's explanation as to the anomalous character of its excited state. Almy and Beiler have drawn similar conclusion in the case of KH. From the figures it is seen that the potential-energy curves for LiH, NaH, and KH at first rise faster on both sides of equilibrium internuclear separation than the corresponding simple-harmonic curves. The curve for LiH lies wholly within the parabola while the right limbs of those for NaH and KH cross the right limbs of the respective simple harmonic curves. The right limb of the potential-energy curve for RbH lies slightly to the right of the corresponding limb of the simple-harmonic curve. Thus one finds a gradual change in the position of the potential-energy curves from LiH to RbH.

The ionic curves for LiH, NaH, and KH cross the potential-energy curves indicating that the excited states do involve some interaction between the ionic  $^1\Sigma^+$  state derived from  $M^+ + H^-$  and a similar state derived from unexcited neutral atoms. Further, these potential-energy curves indicate that the excited states most probably dissociate into  $M(^2P) + H(^2S)$  atoms which would mean another interaction between the ionic state and the  $^1\Sigma^+$  state derived from  $M(^2P) + H(^2S)$ . We have neglected the repulsion term  $\beta/r^n$ ,

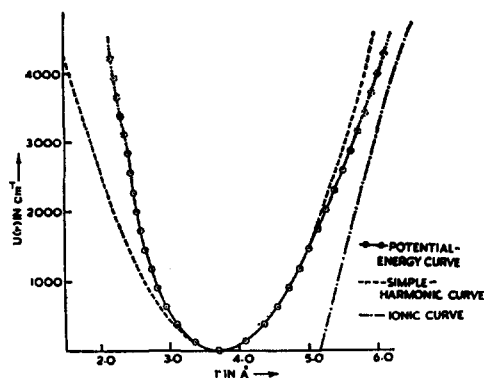


FIG. 4. The potential-energy curve of the  $A\ ^1\Sigma^+$  state of the RbH molecule.

which would raise the ionic curves through a few hundredths of an electron volt. However, this would not affect these conclusions. Considering that the excited states dissociate into  $M(^2P) + H(^2S)$  atoms, we find that the ranges of observed vibrational levels lie sufficiently below the dissociation limits, and thus the experimental data are not sufficient to give us adequate information regarding the potential-energy curves in that region. The potential-energy curve for RbH (Fig. 4) does not cross the ionic curve, and thus the above remarks may not hold for it. Mulliken<sup>15</sup> has remarked that the potential-energy curves, although attempting to follow the ionic curve, bend over to dissociate into  $^2P + ^2S$ ; this would account for their less steep slope than for the ionic curve. In other words, at larger  $r$  values the wavefunctions may be mostly ionic with not much  $^2S + ^2S$ , but then increasingly mixed with  $^2P + ^2S$  and going completely to this as  $r \rightarrow \infty$ .

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<sup>15</sup> R. S. Mulliken (private communication).