A Theoretical Investigation of HeH⁺

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Results are reported for the ground state ($X^1\Sigma^+$) of the HeH⁺ ion. They include an improved Born–Oppenheimer potential curve, adiabatic corrections, and rovibronic energies for the three lowest vibrational states. The dissociation energy in the adiabatic approximation is found to be 14 873.6 cm⁻¹, and adiabatic effects decrease the two lowest vibrational spacings $\Delta G(\frac{1}{2})$ and $\Delta G(\frac{3}{2})$ by 0.9 and 0.8 cm⁻¹, respectively. The adiabatic rovibronic energies reported are thought to be accurate to within 1 cm⁻¹.

INTRODUCTION

In this paper we report on an improved calculation of the Born–Oppenheimer potential energy curve for the electronic ground state ($X^1\Sigma^+$) of HeH⁺ and a first-time calculation of the adiabatic corrections to this curve. We use these results to determine the lowest-lying rovibronic energy levels of HeH⁺. The prime motivation for this work is to aid and complement the experimental studies (via infrared spectroscopy) presently being carried out on this ion by G. Herzberg and H. Liu at the National Research Council of Canada.

There have been many theoretical investigations of HeH⁺, one going back as far as 1933 (*1*), but the majority have been made within the framework of conventional molecular-orbital theory (with or without configuration interaction); references to work of this nature are cited in the paper by Green *et al.* (*2*). Notable exceptions to this rule are the studies by Wolniewicz (*3*), Kołos (*4*), and Kołos and Peek (*5*), in which the framework used was the same as that which had been successfully applied to the hydrogen molecule. Nonetheless, none of these calculations took account of corrections for the use of the Born–Oppenheimer approximation. Therefore it seemed to us necessary, if theory was to help experiment, to attempt an evaluation of these corrections as well as to improve upon the previous Born–Oppenheimer calculations. Our goal was to increase the accuracy of the theoretical rovibronic energies to less than one reciprocal centimeter. This we believe we have achieved. We have not, however, considered nonadiabatic effects since these are of much less importance than the adiabatic corrections.

The paper is divided into three parts: The first part deals with improving the Born–Oppenheimer potential energy curve for the electronic ground state, the second part with the calculation of the adiabatic corrections to this curve, and the last part with the calculation of the rovibronic energies.

All computations were done on an IBM 360/65 computer in double-precision arithmetic. In general, atomic units are used: 1 hartree $= 2R_\infty \simeq 219\ 474.64$ cm⁻¹ and 1 bohr $= a_0 \simeq 0.52917706$ Å. The isotopic species of HeH⁺ considered

throughout is $^4\text{He}^1\text{H}^+$, and the mass ratios used for the electron (e), proton (p), and helium nucleus ($^4\text{He}^{2+}$) are: $m_p/m_e = 1836.152$ and $m_{\text{He}}/m_e = 7294.300$. These values were derived from data in Ref. (6).

THE BORN–OPPENHEIMER POTENTIAL CURVE

To determine the Born–Oppenheimer potential energy curve $E(R)$ we have used the same basic approach which we have already applied to H_2 (7). $E(R)$ is defined as the eigenvalue of the Schrödinger equation

$$H\Psi = E(R)\Psi, \tag{1}$$

where the Hamiltonian H is given by:

$$H = -\tfrac{1}{2}(\nabla_1^2 + \nabla_2^2) - r_{1a}^{-1} - 2r_{1b}^{-1} - r_{2a}^{-1} - 2r_{2b}^{-1} + r_{12}^{-1} + 2R^{-1}. \tag{2}$$

In this equation ∇_i^2 is the Laplacian operator for electron i relative to the geometric center of the nuclei; r_{ia} and r_{ib} are the distances of electron i from nucleus a (H^+) and nucleus b ($^4\text{He}^{2+}$), respectively; r_{12} and R are the interelectronic and internuclear separations, respectively.

Equation (1) was solved by using for Ψ a variational wavefunction of the form

$$\Psi = \sum_{i=1}^{N} c_i[\Phi_i(1,2) + \Phi_i(2,1)], \tag{3}$$

where

$$\Phi_i(1,2) = \exp(-\alpha_1\xi_1 - \alpha_2\xi_2)\exp(\beta_1\eta_1 + \beta_2\eta_2)\xi_1^{m_i}\xi_2^{n_i}\eta_1^{k_i}\eta_2^{l_i}\rho^{q_i}, \tag{4}$$

and

$$\rho = 2r_{12}/R. \tag{5}$$

In Eq. (4), ξ_i and η_i ($i = 1, 2$) are the usual elliptical coordinates of the ith electron. Ψ therefore contains N linear variational parameters (c_i) and four nonlinear variational parameters ($\alpha_1, \alpha_2, \beta_1,$ and β_2), and each basis function Φ_i is prescribed by the values of the powers (integers) of the coordinates, i.e., m_i, n_i, k_i, l_i, and q_i.

Following the work on H_2 described in Ref. (7), we have used a 255-term wavefunction which includes all possible basis functions within the following constraints: (a) the maximum values of either ($m_i + k_i$) or ($n_i + l_i$) are 5, 3, 2, 1 for $q_i = 0, 1, 2, 3$, respectively; (b) the maximum value of ($m_i + n_i + k_i + l_i$) is 5; and (c) the maximum value of q_i is 3.

In the notation of Ref. (7) the wavefunction Ψ would be written as (5321/5). Our choice of basis functions in this fashion worked well for H_2, and we have no reason to believe that this should not also be the case for HeH⁺.

The optimum values of the nonlinear parameters ($\alpha_1,\alpha_2,\beta_1,\beta_2$) for $R = 0.9$, 1.46, 1.8, 3.0, 4.5, and 6.0 bohrs were kindly supplied to us by Professor W. Kołos and are listed in Table I together with the values for $R = 1.2$ and 2.4 bohrs, which were used in the adiabatic calculations and were obtained by fifth-order-polynomial interpolation. The values of the 255 coefficients, c_i, were found by solving the usual secular equations, which were simplified by first orthonormalizing the basis functions with Löwdin's canonical method (8). Unlike the situation

TABLE I

Values of the Nonlinear Parameters for Different Internuclear Separations (R)[a]

R (bohrs)	α_1	α_2	β_1	β_2
0.9	1.004	0.926	0.530	0.281
1.2	1.334	1.158	0.868	0.595
1.46	1.565	1.387	1.173	0.854
1.8	1.838	1.694	1.587	1.125
2.4	2.350	2.196	2.341	1.383
3.0	2.973	2.640	3.095	1.497
4.5	4.789	3.969	4.821	2.954
6.0	6.537	5.524	6.560	5.026

[a] See text.

in H_2 there is some near-linear dependence between the original basis functions for HeH$^+$. This was avoided by excluding those orthonormal functions which corresponded to the smallest eigenvalues given in the diagonalization of the original overlap matrix. It is this near-linear dependence which prevented us from increasing the size of the basis set beyond 255 functions; only with higher-precision arithmetic, and consequently a great increase in computational cost, would this be possible.

In Table II values of $E(R)$ are given for $R = 0.9$, 1.46, 1.8, 3.0, 4.5, and 6.0 bohrs. The value listed for $R = \infty$ (the He atom) was obtained by making the calculation at $R = 6.0$ bohrs and with a zero charge on the proton; it is only 0.322 cm^{-1} greater than Pekeris' exact value (9). This is just one indication of the superiority of our wavefunction over the 83-term wavefunction used in Refs. (4,5): for that wavefunction the difference was 2.42 cm^{-1}. Also in Table II we list the differences $\Delta E(R)$ between the Born–Oppenheimer energies we have calculated

TABLE II

Born–Oppenheimer Energies $E(R)$, and Improvements over the Values Given in Refs. (4,5), $\Delta E(R)$, for Different Internuclear Separations, R

R(bohrs)	E(R) (hartrees)	$\Delta E(R)$ (cm^{-1})
0.9	-2.845 643 82	4.122
1.46	-2.978 702 62	2.976
1.8	-2.967 560 43	3.406
3.0	-2.918 588 37	5.017
4.5	-2.905 922 11	5.379
6.0	-2.904 310 68	2.267
∞	-2.903 722 91	2.105

and those of Kołos and Peek (5) and Kołos (4). Our values were all lower than theirs by at least 2 cm⁻¹. A plot of these differences is given in Fig. 1. In making this plot the $\Delta E(R)$ values for the six finite values of R in Table II were fitted to the polynomial:

$$\Delta E(R) = \sum_{k=-3}^{k=2} a_k R^k. \tag{6}$$

It is clear from Fig. 1 that our 255-term wavefunction gives a marked, though not uniform, improvement over the 83-term wavefunction of Refs. (4, 5), and this is due to the greater flexibility stemming from the additional 172 linear parameters. We cannot, however, make *accurate* predictions about the convergence of our basis set since to do so would require increasing the basis-set size and monitoring the change in energy. As stated before, because of near-linear dependence, this is computationally impossible in double-precision arithmetic. Nonetheless, experience with variational calculations on H_2^+ and H_2 leads us to believe that the energies in Table II are accurate to within 0.5 cm⁻¹, and, at the very least, we can say that they are better than any previously published values.
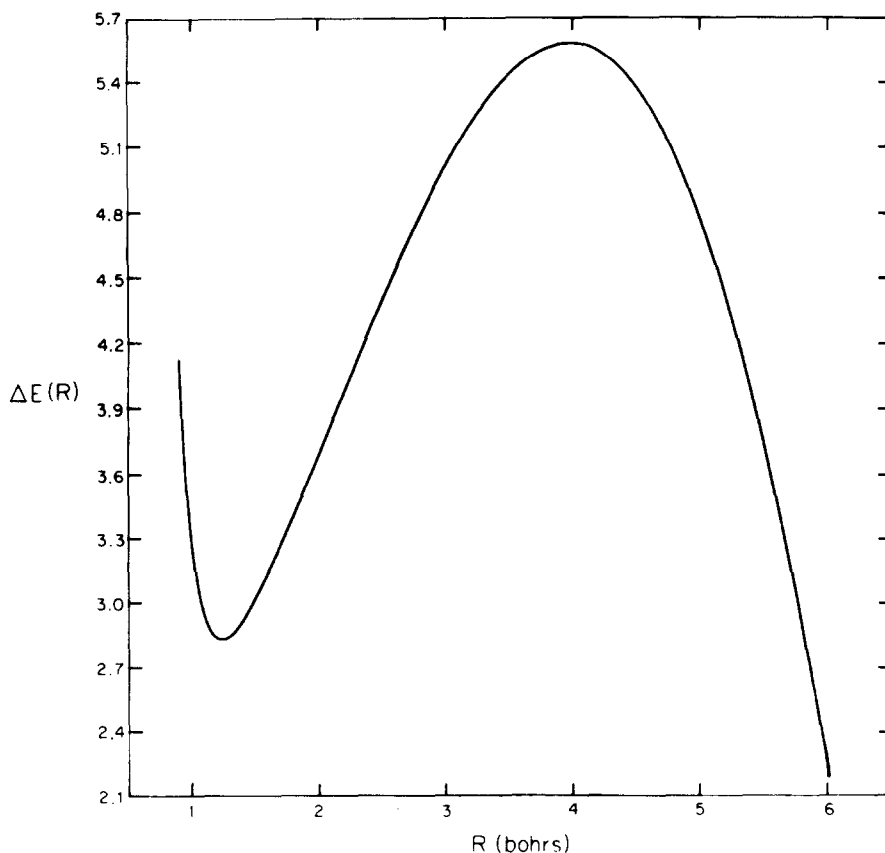

FIG. 1. Basis-set energy corrections $\Delta E(R)$ (in cm⁻¹) for different internuclear separations R (in bohrs).

THE ADIABATIC CORRECTIONS

To go beyond the Born–Oppenheimer approximation (i.e., to take account of the coupling between electronic and nuclear motion) and yet still retain the potential energy curve one can use the Born method (10). This changes the $E(R)$ curve to a new curve $U(R)$ in the following way (11, 12):

$$U(R) = E(R) - \langle(\nabla_1 + \nabla_2)^2\rangle/8\mu - \langle\nabla_R^2\rangle/2\mu - \langle\nabla_R\cdot(\nabla_1 + \nabla_2)\rangle/2\mu_a, \quad (7)$$

where ∇_R^2 is the Laplacian operator for one nucleus relative to the other, μ is the reduced nuclear mass ($=1466.898$ in atomic units), and μ_a is the mass ratio $m_p m_{He}/(m_{He} - m_p)$ ($=2453.844$ in atomic units). The correction terms are expectation values of the operators over the Born–Oppenheimer electronic wavefunctions, and we have used the same techniques as those described in Ref. (7) to evaluate them.

The electronic wavefunctions used in calculating the adiabatic corrections need not be as refined as those used for calculating $E(R)$; for example, in their pioneering work on H_2, Kołos and Wolniewicz used only a 54-term wavefunction for the

TABLE III

The Basis Functions (Defined by Coordinate Powers) Used in the 45-Term Wavefunction[a]

i	q_i	m_i	k_i	n_i	l_i	i	q_i	m_i	k_i	n_i	l_i
1	0	0	0	0	0	24	1	0	1	1	0
2	0	0	0	0	1	25	1	1	0	0	1
3	0	0	0	1	0	26	2	0	0	0	2
4	1	0	0	0	0	27	0	1	0	0	0
5	0	0	0	2	0	28	0	1	1	0	0
6	0	1	0	1	0	29	2	0	0	1	1
7	0	0	0	0	2	30	1	0	0	1	2
8	0	0	1	0	1	31	1	0	2	0	0
9	0	0	0	1	1	32	2	0	1	0	0
10	1	0	0	0	1	33	1	0	1	0	1
11	0	2	0	2	0	34	2	0	0	1	0
12	0	0	0	0	3	35	0	0	0	0	4
13	0	2	0	0	0	36	1	0	0	3	0
14	0	0	1	0	2	37	1	0	0	2	1
15	0	0	0	2	1	38	2	1	0	0	0
16	1	0	0	0	2	39	0	0	1	1	0
17	0	0	0	3	0	40	0	2	0	1	0
18	2	0	0	0	1	41	1	3	0	0	0
19	1	0	0	1	0	42	0	0	0	1	3
20	1	1	1	0	0	43	0	0	0	0	5
21	2	0	0	0	0	44	0	0	0	1	4
22	0	0	0	1	2	45	1	1	0	0	0
23	1	0	0	0	3						

[a] See text.

TABLE IV

Convergence of the Adiabatic Corrections (cm⁻¹) with Number of Terms (N)
in the Wavefunction for $R = 1.46$ bohrs

N	$-\langle(\nabla_1 + \nabla_2)^2\rangle/8\mu$	$-\langle\nabla_R^2\rangle/2\mu$	$-\langle\nabla_R\cdot(\nabla_1 + \nabla_2)\rangle/2\mu_a$	Total
26	117.717	102.503	-119.927	100.293
27	117.751	102.243	-119.798	100.195
28	117.748	102.284	-119.855	100.177
29	117.749	102.277	-119.858	100.168
30	117.750	102.283	-119.849	100.184
31	117.705	102.301	-119.840	100.166
32	117.738	102.238	-119.800	100.177
33	117.716	102.178	-119.763	100.131
34	117.717	102.148	-119.756	100.107
35	117.744	102.199	-119.671	100.272
36	117.737	102.203	-119.668	100.271
37	117.730	102.206	-119.669	100.268
38	117.728	102.191	-119.665	100.254
39	117.718	102.200	-119.659	100.259
40	117.718	102.199	-119.657	100.260
41	117.720	102.221	-119.665	100.276
42	117.720	102.222	-119.662	100.280
43	117.722	102.227	-119.649	100.301
44	117.722	102.224	-119.651	100.295
45	117.719	102.226	-119.655	100.291

TABLE V

The Adiabatic Corrections (in cm⁻¹) Using the 45-Term Wavefunction for Different
Internuclear Separations, R (in bohrs)

R	$-\langle(\nabla_1+\nabla_2)^2\rangle/8\mu$	$-\langle\nabla_R^2\rangle/2\mu$	$-\langle\nabla_R\cdot(\nabla_1+\nabla_2)\rangle/2\mu_a$	Total	$\Delta(R)$[a]
0.9	138.970	93.962	-113.225	119.706	-27.551
1.2	124.473	98.614	-116.506	106.582	-14.427
1.46	117.719	102.226	-119.655	100.291	-8.136
1.8	113.375	106.348	-123.775	95.947	-3.792
2.4	111.686	111.650	-130.026	93.311	-1.156
3.0	112.572	113.921	-133.913	92.580	-0.425
4.5	114.225	114.446	-136.617	92.054	0.101
6.0	114.484	114.510	-136.885	92.109	0.046
∞	114.562	114.562	-136.970	92.155	0

[a] $\Delta(R)$ is the total adiabatic correction at ∞ less the value at R.
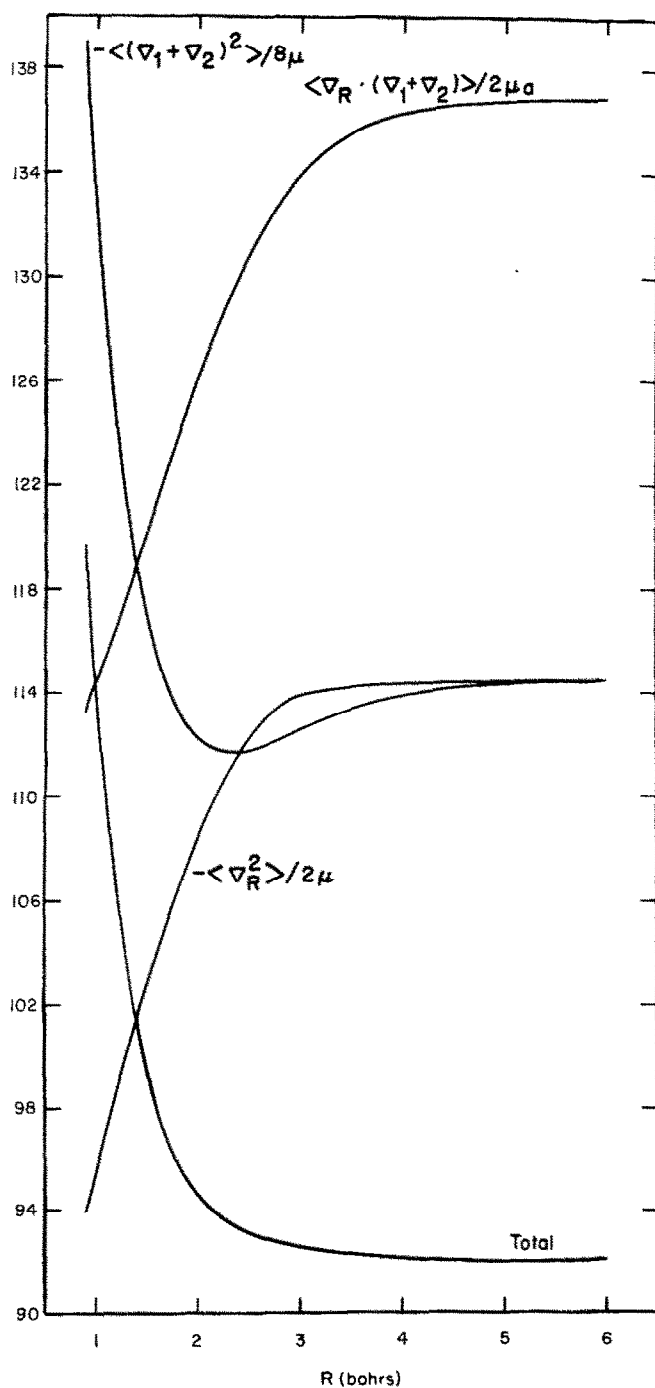
FIG. 2. Adiabatic corrections (in cm^{-1}) for different internuclear separations R (in bohrs): $-\langle(\nabla_1 + \nabla_2)^2\rangle/8\mu$, $-\langle\nabla_R^2\rangle/2\mu$, $\langle\nabla_R\cdot(\nabla_1 + \nabla_2)\rangle/2\mu_a$, and total. Note that in the total correction $\langle\nabla_R\cdot(\nabla_1 + \nabla_2)\rangle/2\mu_a$ is subtracted.

corrections (*12*) but a 100-term wavefunction for $E(R)$ (*13*). We have therefore used the same 45-term wavefunction for these corrections that Kołos (*4*) used to optimize the nonlinear parameters in his calculation of $E(R)$ for HeH⁺; it is listed in Table III. The fact that the corrections are accurate for this wavefunction is demonstrated in Table IV, in which values are given for $R = 1.46$ bohrs for increasing basis-set size. The nonlinear parameters of Table I were used.

The corrections for $R = 0.9$, 1.2, 1.46, 1.8, 2.4, 3.0, 4.5, and 6.0 bohrs are displayed in Table V and plotted in Fig. 2. The formula $\sum_{k=-5}^{k=2} b_k R^k$ was used to interpolate the total adiabatic correction. We estimate that the corrections in Table V have converged to within 0.1 cm⁻¹.

It can be easily shown, by changing the origin of the coordinates from the geometric midpoint to the helium nucleus as $R \rightarrow \infty$, that at $R = \infty$

$$\langle (\nabla_1 + \nabla_2)^2 \rangle = 4\langle \nabla_R^2 \rangle = -2\langle \nabla_R \cdot (\nabla_1 + \nabla_2) \rangle, \tag{8}$$

and from the data of Table I of Ref. (*9*), namely, ϵ^2 and $\epsilon^2(A/N)$, one can obtain

$$\tfrac{1}{2}\langle (\nabla_1 + \nabla_2)^2 \rangle = -3.06279386 \text{ hartrees.} \tag{9}$$

From this information we have found the values of the corrections at $R = \infty$ (last row of Table V); it is clear that the finite-R values are converging nicely to these values.

TABLE VI

Rovibronic Energies (hartrees) Obtained from the Born–Oppenheimer Potential Curve of Refs. (*4, 5*)

J	v = 0	v = 1	v = 2
0	-2.971 514 10	-2.958 244 36	-2.946 373 47
1	-2.971 208 46	-2.957 963 50	-2.946 117 59
2	-2.970 598 96	-2.957 403 52	-2.945 607 55
3	-2.969 689 10	-2.956 567 85	-2.944 846 73
4	-2.968 484 12	-2.955 461 61	-2.943 840 19
5	-2.966 990 90	-2.954 091 54	-2.942 594 59
6	-2.965 217 92	-2.952 465 94	-2.941 118 18
7	-2.963 175 13	-2.950 594 62	-2.939 420 67
8	-2.960 873 91	-2.948 488 76	-2.937 513 24
9	-2.958 326 94	-2.946 160 87	-2.935 408 42
10	-2.955 548 09	-2.943 624 69	-2.933 120 02
11	-2.952 552 32	-2.940 895 09	-2.930 663 15
12	-2.949 355 59	-2.937 988 02	-2.928 054 09
13	-2.945 974 73	-2.934 920 41	-2.925 310 36
14	-2.942 427 39	-2.931 710 15	-2.922 450 74
15	-2.938 731 97	-2.928 376 10	-2.919 495 35
16	-2.934 907 51	-2.924 938 06	-2.916 465 90
17	-2.930 973 78	-2.921 416 92	-2.913 386 03
18	-2.926 951 18	-2.917 834 79	-2.910 281 97
19	-2.922 860 89	-2.914 215 38	-2.907 183 73
20	-2.918 724 99	-2.910 584 52	-2.904 127 44
21	-2.914 566 69	-2.906 971 20	
22	-2.910 410 83	-2.903 409 51	
23	-2.906 284 57		
24	-2.902 218 87		

TABLE VII

The Rovibronic Energies of Table VI Less those Obtained from the Basis-Set-Corrected
Born–Oppenheimer Potential Curve (in 10^{-8} hartrees)

J	v = 0	v = 1	v = 2
0	1395	1474	1562
1	1396	1475	1563
2	1397	1476	1565
3	1400	1479	1568
4	1403	1482	1571
5	1406	1487	1577
6	1410	1493	1583
7	1416	1498	1591
8	1422	1506	1600
9	1429	1514	1610
10	1437	1524	1623
11	1447	1536	1636
12	1457	1548	1652
13	1469	1562	1671
14	1483	1579	1691
15	1496	1597	1714
16	1513	1617	1741
17	1530	1639	1771
18	1550	1665	1806
19	1572	1693	1848
20	1597	1727	1898
21	1625	1766	
22	1655	1811	
23	1690		
24	1731		

It may be noted that the total adiabatic correction has a small minimum near $R = 4.5$ bohrs. In the hydrogen molecule there is also a minimum, but it is deeper and at a smaller internuclear separation (*12*). Other than this there is little similarity between the adiabatic corrections for H_2 and HeH^+: for example, the difference between the total correction at $R = \infty$ and at a given R in the region of the equilibrium internuclear separation (1.46 bohrs)—see the last column of Table V—is larger than and of opposite sign to the corresponding value for H_2 (*12*). One reason for this lack of similarity is the existence of the correction $-\langle \nabla_R \cdot (\nabla_1 + \nabla_2) \rangle / 2\mu_a$ in the heteronuclear case.

ROVIBRONIC ENERGY LEVELS

In this section we give the values of the rovibronic energies $E(v,J)$, where v and J are the vibrational and rotational quantum numbers, respectively. They were found by solving the vibrational–rotational Schrödinger equation

$$[-(2\mu)^{-1}(d^2/dR^2) + E(R) + (2\mu R^2)^{-1}J(J + 1)]\chi(R) = E(v,J)\chi(R) \qquad (10)$$

with the Numerov–Cooley method (*14*). In this equation $E(R)$ is replaced by $U(R)$ if adiabatic results are required. $\chi(R)$ is the vibrational wavefunction.

In Table VI the $E(v,J)$ are displayed for a Born–Oppenheimer potential curve which has for data points the energies of Ref. (5) for $0.9 \leqslant R \leqslant 4.5$ bohrs (but excluding the values at $R = 1.4631$, 1.4632, and 1.4633 bohrs) and of Ref. (4) for $R = 5.0$, 5.5, and 6.0 bohrs. Next the $E(v,J)$ are obtained from a Born–Oppenheimer potential curve but this time the data points are those of the previous curve changed by the corrections shown in Fig. 1. This curve therefore incorporates the effects of using a 255-term as opposed to a 83-term wavefunction. These $E(v,J)$ are subtracted from those of Table VI and the differences are given in Table VII. Finally, the total adiabatic corrections (Fig. 2) are added to the basis-set-corrected curve and this leads to the rovibronic energies in Table VIII.

Since there are only a limited number of data points for each of the three curves, results are shown only for $v \leqslant 2$. Trials with an H_2^+ potential curve using a comparable number of points showed that for $v > 2$ less than seven-figure accuracy was obtained in comparison with the use of a curve determined by 129 data points (15). Consequently, energy levels above $v = 2$ would be less accurate than 0.2 cm^{-1}. Taking this into account and the fact that the corrected Born–Oppenheimer energies and adiabatic corrections have probably not completely converged, we estimate (conservatively) that the errors on the adiabatic rovibronic energies in Table VIII are less than 1 cm^{-1}. Due to error cancellation, the errors are likely to be less than this for energy differences (i.e., transition frequencies).

TABLE VIII

Rovibronic Energies (hartrees) Obtained from the Adiabatic Potential Curve

J	v = 0	v = 1	v = 2
0	-2.971 073 59	-2.957 808 75	-2.945 942 57
1	-2.970 768 07	-2.957 528 00	-2.945 686 80
2	-2.970 158 80	-2.956 968 23	-2.945 176 96
3	-2.969 249 29	-2.956 132 89	-2.944 416 44
4	-2.968 044 76	-2.955 027 07	-2.943 410 31
5	-2.966 552 11	-2.953 657 53	-2.942 165 22
6	-2.964 779 80	-2.952 032 57	-2.940 689 40
7	-2.962 737 78	-2.950 161 97	-2.938 992 59
8	-2.960 437 44	-2.948 056 92	-2.937 085 94
9	-2.957 891 43	-2.945 729 94	-2.934 981 99
10	-2.955 113 63	-2.943 194 75	-2.932 694 55
11	-2.952 118 99	-2.940 466 22	-2.930 238 71
12	-2.948 923 47	-2.937 560 29	-2.927 630 77
13	-2.945 543 89	-2.934 493 90	-2.924 888 24
14	-2.941 997 89	-2.931 284 93	-2.922 029 88
15	-2.938 303 86	-2.927 952 22	-2.919 075 85
16	-2.934 480 86	-2.924 515 59	-2.916 047 83
17	-2.930 548 62	-2.920 995 91	-2.912 969 47
18	-2.926 527 56	-2.917 415 31	-2.909 867 03
19	-2.922 438 84	-2.913 797 49	-2.906 770 53
20	-2.918 304 56	-2.910 168 29	-2.903 716 14
21	-2.914 147 92	-2.906 556 73	
22	-2.909 993 74	-2.902 996 91	
23	-2.905 869 23		
24	-2.901 805 34		

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TABLE IX

Vibrationally Averaged Powers of R (Internuclear Separation in bohrs) Using the Born–Oppenheimer Approximation (Enlarged Basis Set) and Corrections for Adiabatic Effects ($J = 0$)

Power	Average	Correction
	$v = 0$	
-3	0.3056	-0.0002
-2	0.4488	-0.0002
-1	0.6662	-0.0001
1	1.5174	0.0003
2	2.3274	0.0008
3	3.6084	0.0019
4	5.6540	0.0040
5	8.9532	0.0079
	$v = 1$	
-3	0.2784	-0.0001
-2	0.4124	0.0001
-1	0.6316	-0.0001
1	1.6336	0.0003
2	2.7463	0.0010
3	4.7353	0.0025
4	8.3455	0.0058
5	14.985	0.013
	$v = 2$	
-3	0.2506	-0.0001
-2	0.3757	-0.0001
-1	0.5961	-0.0001
1	1.7648	0.0003
2	3.2519	0.0012
3	6.2059	0.0033
4	12.175	0.009
5	24.402	0.022

Dabrowski and Herzberg (16) have also calculated the rovibronic energies using the data of Refs. (4, 5). A comparison of their results for $v = 0, 1, 2$ with ours (Table VI) shows differences of the order of 0.1 cm^{-1}. We speculate that this is caused by the use of different interpolation schemes in the Numerov–Cooley method. Several workers (17, 18) have discussed this situation, and it becomes particularly acute when the potential curve is defined by only a few points. This would also explain why Dabrowski and Herzberg's energies for some $v > 2$ agree only to within 0.5 cm^{-1} with the unpublished results of Kołos [see the comment made in Ref. (16)].

From the results in Tables VI–VIII it is apparent that the dissociation energy of HeH$^+$ (dissociating to He + H$^+$) is increased by 3.1 cm^{-1}, to give 14 881.2 cm^{-1}, by enlarging the size of the basis set and decreased by 7.6 cm^{-1}, to give 14 873.6 cm^{-1}, by the inclusion of adiabatic effects. Note that for H$_2$, adiabatic effects *increase* the dissociation energy (17). The vibrational spacings $\Delta G(\frac{1}{2})$ and $\Delta G(\frac{3}{2})$ are both decreased by 0.2 cm^{-1} when the larger basis set is used; $\Delta G(\frac{1}{2})$ is decreased by 0.9 cm^{-1} and $\Delta G(\frac{3}{2})$ is decreased by 0.8 cm^{-1} when adiabatic effects are included. For H$_2$ the vibrational spacings are also decreased (though by a larger amount) when adiabatic effects are taken into account (17).

Unfortunately, the number of accurate rovibronic energies we have obtained is too limited for a determination of the conventional spectroscopic constants. However, we have calculated the expectation values of various powers of R (Table IX) over the vibrational wavefunctions $\chi(R)$, and these could be of use for averaging over vibrations those quantities which can be expressed as polynomials

in R. It is seen from this table that adiabatic effects increase the expectation values of the positive powers of R. This has also been shown to be the case for H$_2^+$ (*19*).

ACKNOWLEDGMENTS

RECEIVED: October 2, 1978

Note added in proof. Since this work was completed, R. I. Price (*Chem. Phys.* **31**, 309–317 (1978)) has published a paper which includes an *approximate* calculation of the adiabatic corrections for HeH$^+$. The differences between his values for $\Delta(R)$ (see his Table 2) and our values (see our Table V) are of the order of 1 cm^{-1}.

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