

## SOME ACCURATE RESULTS FOR THREE-PARTICLE SYSTEMS\*

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Results of a variational calculation of the nonadiabatic ground state energy of  $H_2^+$  are presented. Diagonal corrections for nuclear motion have also been calculated for the electronic ground state of  $H_2^+$ . The adiabatic potential energy curve has been employed to calculate the rotational and vibrational levels for the  $H_2^+$  ion and for muonic molecules. Nonadiabatic energy corrections are discussed. For  $pm\mu$  the adiabatic wave function is compared with the corresponding nonadiabatic result.

### I. Introduction

Three-particle molecular systems, such as  $H_2^+$ , are sufficiently simple to make accurate calculations of their properties feasible. Results of these calculations may give an insight into some fundamental approximations which are unavoidable when dealing with more complex molecules. In particular, this applies to the adiabatic approximation which plays a fundamental role in the theory of molecular structure.

In the present article new results are presented obtained for the  $H_2^+$  ion, and for muonic molecules. They are used to discuss some problems of the adiabatic approximation and of its accuracy.

### II. The adiabatic approximation

Let us express [1] the exact Hamiltonian of a diatomic molecule in the centre of mass system as

$$H = H^0 + H', \quad (1)$$

where  $H^0$  is the "electronic" Hamiltonian which is independent of the nuclear masses  $M_a$  and  $M_b$ , and  $H'$  represents the kinetic energy of the relative motion of the nuclei and the coupling between electronic and nuclear motion. Explicitly,  $H'$  has the form

$$H' = H_1 + H_2 + H_3, \quad (2)$$

\* Dedicated to Prof. P. GOMBÁS on his 60th birthday.

where

$$\begin{aligned} H_1 &= -\frac{1}{2\mu} \Delta_R, \\ H_2 &= -\frac{1}{8\mu} \left( \sum_i \nabla_i \right)^2, \\ H_3 &= -\frac{1}{2\mu_a} \nabla_R \sum_i \nabla_i, \end{aligned} \quad (3)$$

and the symbols used in (3) have the following meaning:  $\mathbf{R} = \mathbf{R}_a - \mathbf{R}_b$ , where  $\mathbf{R}_a$  and  $\mathbf{R}_b$  denote the radius vector for the nuclei a and b, respectively; the index  $i$  labels the electrons;  $\mathbf{r}_i$  are measured from the geometrical centre of the molecule;  $\mu^{-1} = M_a^{-1} + M_b^{-1}$  and  $\mu_a^{-1} = -M_a^{-1} + M_b^{-1}$ .

Let us also assume [2] the complete wave function in the form

$$\Psi = \sum_n \Psi_n(\mathbf{r}, \mathbf{R}) \chi_n(\mathbf{R}), \quad (4)$$

where  $\mathbf{r}$  denotes the coordinates of all the electrons and  $\Psi_n$  is the solution of

$$H^0 \Psi_n(\mathbf{r}, \mathbf{R}) = U_n(\mathbf{R}) \Psi_n(\mathbf{r}, \mathbf{R}). \quad (5)$$

Using (1) and (4) in the complete Schrödinger equation

$$H\Psi = E\Psi \quad (6)$$

one gets the following set of coupled differential equations for the functions  $\chi_n$

$$\left[ -\frac{1}{2\mu} \Delta_R + U_n(\mathbf{R}) + H'_{nn}(\mathbf{R}) - E \right] \chi_n(\mathbf{R}) = - \sum_{m \neq n} (H'_{nm} + B_{nm} \nabla_R) \chi_m(\mathbf{R}), \quad (7)$$

where

$$H'_{nm} = \int \Psi_n H' \Psi_m d\tau_r, \quad (8)$$

$$B_{nm} = - \int \Psi_n \left( \frac{1}{\mu} \nabla_R + \frac{1}{2\mu_a} \sum_i \nabla_i \right) \Psi_m d\tau_r. \quad (9)$$

The adiabatic approximation [2] is obtained by neglecting the right-hand side of Eqs. (7). In contrast to the Born—Oppenheimer (clamped nuclei) appro-

ximation it includes the diagonal corrections for nuclear motion,  $H'_{nn}$ , in the adiabatic potential

$$U_n^{ad}(R) = U_n(R) + H'_{nn}(R) \tag{10}$$

which governs the nuclear motion.

### III. Nonadiabatic energy for $H_2^+$

Nonadiabatic calculations for a diatomic molecule can be carried out in two different ways: (a) One can solve the set of Eqs. (7); (b) One can employ the Ritz variational method using the complete Hamiltonian (1) and assuming the trial function in the form

$$\Psi = \sum_{n=1}^{N'} c_n \Phi_n(\mathbf{r}, \mathbf{R}), \tag{11}$$

where  $\Phi_n(\mathbf{r}, \mathbf{R})$  is some set of functions in the space of  $\mathbf{r}, \mathbf{R}$ . For  $H_2^+$  both approaches are feasible.

Calculations based essentially on the set of Eqs. (7) have been carried out by HUNTER and PRITCHARD [3], and with only a few terms in the expansion (4) accurate energies have been obtained. This approach, however, does not seem to be practical for more complex systems and, therefore, in the present work the second approach has been tested. This method has already been used by several authors [4, 5, 6], but the wave functions employed were not flexible enough to yield accurate results.

For a non-rotational state the wave function does not depend on the orientation of  $\mathbf{R}$ , and in the present calculation the following basis set was employed

$$\Phi_n = \exp(-\alpha\xi) \cosh(\beta\eta) \xi^{r_n} \eta^{s_n} \exp(-x^2/2) \mathcal{H}_{k_n}(x) R^{-3/2}. \tag{12}$$

The symbols used in (12) have the following meanings:  $\xi$  and  $\eta$  denote the elliptic coordinates;  $\mathcal{H}_k$  is the  $k$ -th Hermitian polynomial;  $x = \gamma(R - R_e)$ ; and  $\alpha, \beta, \gamma, R_e$  are treated as variational parameters, in addition to the linear parameters  $c_i$  in the expansion (11).

Convergence of the energy resulting from the wave function (11) with the basis set (12) is displayed in Table I for the ground state of  $H_2^+$ .  $N$  denotes the number of terms in the expansion (11),  $(r + s)_{\max}$  the maximum value of the sum of powers of  $\xi$  and  $\eta$  included in the expansion, and  $k_{\max}$  the maximum degree of the Hermitian polynomials. All energies given in Table I were obtained with one set of the nonlinear parameters which were optimized for the maximum number of terms. The proton mass used was  $M_p = 1836.12$ . For the second lowest vibrational state a still larger number of terms was needed to get the final value of the energy.

Table I

Convergence of the nonadiabatic energy,  $E$ , and of the binding energy,  $D$ , for the ground state of  $\text{H}_2^+$

$N$	$(r+s)_{\max}$	$k_{\max}$	$E$ (a. u.)	$D$ (cm $^{-1}$ )
24	3	3	-0.5971166	21 374.3
30	3	4	-0.5971356	21 378.5
40	4	4	-0.5971367	21 378.8
44	4	5	-0.5971380	21 379.0 <sub>6</sub>
51	5	5	-0.5971381	21 379.0 <sub>8</sub>
55	5	6	-0.5971385	21 379.1 <sub>7</sub>
57	5	7	-0.5971387	21 379.2 <sub>1</sub>

#### IV. Adiabatic energy for $\text{H}_2^+$

The adiabatic energy is obtained by solving Equ. (7) with the right-hand side equal to zero. Assuming  $\chi(R) = f_{vk}(R) Y_K^M(\theta, \varphi) R^{-1}$  the appropriate equation for the vibrational wave function reads

$$\left[ -\frac{1}{2\mu} \frac{d^2}{dR^2} + U_n(R) + H'_{nn}(R) + \frac{J(J+1)}{2\mu R^2} - E \right] f_{vk}(R) = 0, \quad (13)$$

where  $v$  and  $J$  denote the vibrational and rotational quantum numbers, respectively.

Very accurate clamped nuclei potential has recently been published [7, 8], and adiabatic energies have also been computed [7]. However, in the latter calculation relatively poor values [9] of  $H'_{nn}$  were used. To get reliable non-adiabatic effects, which are very small and which are represented by the differences between the non-adiabatic and adiabatic values, highly accurate results are indispensable. Therefore the diagonal nuclear motion corrections (3) have been computed using for the wave function an expansion in terms of 10 basis functions of the form

$$\Phi_n = \exp(-\alpha\xi) \cosh(\beta\eta) \xi^r \eta^s \quad (14)$$

and the results are listed in Table II.  $\Delta D$  given in the last column (in cm $^{-1}$ ) is defined as  $\langle H'(\infty) \rangle - \langle H'(R) \rangle$  and represents the correction to the binding energy due to the diagonal nuclear motion corrections.

Using the calculated values of  $H'_{nn}$ , and accurate clamped nuclei potential  $U_n$ , the vibrational equation (13) has been solved for several vibrational

Table II

Clamped nuclei energy,  $E$ , and diagonal corrections for nuclear motion (2) for  $H_2^+$  calculated for various internuclear distances  $R$ 

$R$	$E$	$H_1 \times 10^3$	$H_2 \times 10^3$	$\Delta D$
0			0.54463	-59.766
0.3	1.4666385	0.07470	0.45537	-56.571
0.4	0.6992462	0.08327	0.41811	-50.275
0.5	0.2650120	0.09104	0.38414	-44.526
0.6	-0.0048180	0.09556	0.35388	-38.875
0.7	-0.1826248	0.09794	0.32718	-33.537
0.8	-0.3044800	0.09899	0.30371	-28.617
0.9	-0.3902705	0.09925	0.28307	-24.144
1.0	-0.4517863	0.09905	0.26489	-20.109
1.1	-0.4964118	0.09859	0.24884	-16.486
1.2	-0.5289745	0.09803	0.23462	-13.241
1.3	-0.5527406	0.09743	0.22199	-10.338
1.4	-0.5699835	0.09686	0.21074	-7.744
1.5	-0.5823232	0.09635	0.20069	-5.426
1.6	-0.5909372	0.09592	0.19169	-3.358
1.7	-0.5966963	0.09559	0.18362	-1.513
1.8	-0.6002536	0.09536	0.17636	0.131
1.9	-0.6021058	0.09522	0.16983	1.593
2.0	-0.6026342	0.09519	0.16395	2.891
2.1	-0.6021349	0.09527	0.15864	4.039
2.2	-0.6008396	0.09544	0.15386	5.052
2.3	-0.5989309	0.09570	0.14954	5.941
2.4	-0.5965536	0.09606	0.14565	6.718
2.5	-0.5938235	0.09650	0.14214	7.391
2.6	-0.5908332	0.09702	0.13898	7.968
2.7	-0.5876573	0.09762	0.13615	8.459
2.8	-0.5843560	0.09830	0.13361	8.868
2.9	-0.5809780	0.09904	0.13134	9.204
3.0	-0.5775628	0.09984	0.12932	9.471
3.1	-0.5741424	0.10070	0.12753	9.676
3.2	-0.5707425	0.10161	0.12595	9.822
3.3	-0.5673841	0.10257	0.12457	9.915
3.4	-0.5640840	0.10357	0.12337	9.959
3.5	-0.5608555	0.10461	0.12233	9.958
3.6	-0.5577092	0.10567	0.12146	9.917
3.7	-0.5546535	0.10676	0.12073	9.838

Table II (continued)

$R$	$E$	$H_1 \times 10^3$	$H_2 \times 10^3$	$AD$
3.8	-0.5516947	0.10787	0.12013	9.725
3.9	-0.5488373	0.10899	0.11966	9.582
4.0	-0.5460848	0.11012	0.11930	9.412
4.1	-0.5434394	0.11126	0.11905	9.219
4.2	-0.5409022	0.11239	0.11890	9.005
4.3	-0.5384735	0.11351	0.11883	8.772
4.4	-0.5361531	0.11463	0.11884	8.525
4.5	-0.5339400	0.11572	0.11893	8.265
4.6	-0.5318328	0.11680	0.11908	7.996
4.7	-0.5298295	0.11785	0.11930	7.718
4.8	-0.5279281	0.11888	0.11956	7.435
4.9	-0.5261259	0.11987	0.11987	7.148
5.0	-0.5244202	0.12084	0.12022	6.859
5.1	-0.5228082	0.12176	0.12061	6.571
5.2	-0.5212866	0.12265	0.12103	6.284
5.3	-0.5198521	0.12350	0.12147	6.000
5.4	-0.5185016	0.12432	0.12193	5.720
5.5	-0.5172315	0.12509	0.12241	5.446
5.6	-0.5160385	0.12582	0.12290	5.177
5.7	-0.5149192	0.12652	0.12340	4.916
5.8	-0.5138701	0.12718	0.12390	4.661
5.9	-0.5128878	0.12779	0.12440	4.415
6.0	-0.5119690	0.12838	0.12490	4.178
6.1	-0.5111105	0.12892	0.12540	3.949
6.2	-0.5103089	0.12943	0.12589	3.729
6.3	-0.5095612	0.12991	0.12638	3.518
6.4	-0.5088644	0.13035	0.12685	3.317
6.5	-0.5082155	0.13077	0.12731	3.124
6.6	-0.5076116	0.13115	0.12776	2.940
6.7	-0.5070501	0.13151	0.12820	2.766
6.8	-0.5065282	0.13185	0.12862	2.600
6.9	-0.5060437	0.13216	0.12903	2.442
7.0	-0.5055940	0.13245	0.12942	2.292
7.1	-0.5051769	0.13271	0.12980	2.151
7.2	-0.5047902	0.13296	0.13016	2.017
7.3	-0.5044319	0.13319	0.13051	1.891
7.4	-0.5041001	0.13340	0.13084	1.772
7.5	-0.5037929	0.13360	0.13115	1.660

Table II (continued)

$R$	$E$	$H_1 \times 10^3$	$H_2 \times 10^3$	$\Delta D$
7.6	-0.5035087	0.13378	0.13145	1.554
7.7	-0.5032458	0.13395	0.13174	1.454
7.8	-0.5030027	0.13411	0.13201	1.361
7.9	-0.5027780	0.13425	0.13226	1.273
8.0	-0.5025704	0.13438	0.13251	1.190
8.2	-0.5022013	0.13462	0.13295	1.040
8.4	-0.5018866	0.13483	0.13335	0.908
8.6	-0.5016184	0.13500	0.13370	0.792
8.8	-0.5013900	0.13516	0.13401	0.691
9.0	-0.5011954	0.13529	0.13428	0.603
9.2	-0.5010298	0.13540	0.13452	0.526
9.4	-0.5008887	0.13549	0.13473	0.458
9.6	-0.5007685	0.13558	0.13492	0.400
9.8	-0.5006661	0.13565	0.13508	0.349
10.0	-0.5005787	0.13571	0.13522	0.305
10.5	-0.5004121	0.13583	0.13549	0.218
11.0	-0.5002992	0.13591	0.13568	0.158
11.5	-0.5002221	0.13597	0.13582	0.115
12.0	-0.5001683	0.13601	0.13591	0.085
13.0	-0.5001035	0.13607	0.13602	0.049
14.0	-0.5000689	0.13610	0.13608	0.030
15.0	-0.5000490	0.13611	0.13611	0.020
17.5	-0.5000247	0.13614	0.13613	0.009
20.0	-0.5000143	0.13615	0.13614	0.005
$\infty$	-0.5000000	0.13616	0.13616	0.000

All results in a. u. only  $\Delta D$  in  $\text{cm}^{-1}$ .

and rotational states. The resulting adiabatic energies for the ground electronic state of  $H_2^+$  are shown in Table III.

By comparing the adiabatic energies for  $K = 0$  and  $v = 0, 1, 2$  with the corresponding nonadiabatic results [3] one gets the nonadiabatic energy correction  $\Delta E = E_{\text{nonad}} - E_{\text{ad}} = 0.12, 0.21$  and  $0.35 \text{ cm}^{-1}$  for the three lowest vibrational states, respectively. The correction is very small and is seen to be roughly a linear function of the vibrational excitation. The differences between the adiabatic and clamped nuclei [10] dissociation energies (for  $J = 0$ ) are shown in Table IV. Their maximum for  $v = 8$  results from the shape of the  $H'_{nn}$  versus  $R$  curve which has a minimum at  $R = 3.4$  a.u., and the expectation value of the internuclear distance for  $v = 8$  is just  $\langle R \rangle = 3.362$  a.u.

Table III  
Adiabatic energies (in a.u.) for various vibrational ( $v$ ) and rotational ( $J$ ) levels in the ground electronic state of  $H_2^+$

$v$	$J$	0	1	2	3	4	5	6
0	0	-0.5971382	-0.5968729	-0.5963443	-0.5955567	-0.5945162	-0.5932307	-0.5917097
0	1	-0.5871538	-0.5869025	-0.5864018	-0.5856657	-0.5846702	-0.5834528	-0.5820126
0	2	-0.5777492	-0.5775113	-0.5770375	-0.5763316	-0.5753992	-0.5742476	-0.5728856
0	3	-0.5689050	-0.5686802	-0.5682324	-0.5675654	-0.5666846	-0.5655969	-0.5643107
0	4	-0.5606050	-0.5603929	-0.5599706	-0.5593415	-0.5585109	-0.5574855	-0.5562733
0	5	-0.5528359	-0.5526363	-0.5522388	-0.5516469	-0.5508655	-0.5499012	-0.5487615
0	6	-0.5455872	-0.5453999	-0.5450269	-0.5444716	-0.5437387	-0.5428344	-0.5417663
0	7	-0.5388515	-0.5386763	-0.5383276	-0.5378085	-0.5371235	-0.5362789	-0.5352817
0	8	-0.5326241	-0.5324611	-0.5321365	-0.5316534	-0.5310164	-0.5302311	-0.5293048
0	9	-0.5269037	-0.5267527	-0.5264523	-0.5260055	-0.5254165	-0.5246910	-0.5238358
0	10	-0.5216918	-0.5215531	-0.5212772	-0.5208670	-0.5203266	-0.5196617	-0.5188788
0	11	-0.5169938	-0.5168676	-0.5166167	-0.5162438	-0.5157531	-0.5151500	-0.5144411
0	12	-0.5128188	-0.5127055	-0.5124802	-0.5121459	-0.5117064	-0.5111673	-0.5105349
0	13	-0.5091802	-0.5090803	-0.5088818	-0.5085875	-0.5082015	-0.5077292	-0.5071770
0	14	-0.5060962	-0.5060104	-0.5058401	-0.5055881	-0.5052587	-0.5048572	-0.5043904
0	15	-0.5035904	-0.5035197	-0.5033796	-0.5031730	-0.5029044	-0.5025794	-0.5022052
0	16	-0.5016922	-0.5016379	-0.5015307	-0.5013740	-0.5011722	-0.5009319	-0.5006612
0	17	-0.5004349	-0.5003989	-0.5003287				



Table IV

Differences between the adiabatic and clamped nuclei dissociation energies (in  $\text{cm}^{-1}$ ) for various vibrational levels of  $\text{H}_2^+$

$v$	$D_{\text{ad.}} - D_{\text{cl.n.}}$	$v$	$D_{\text{ad.}} - D_{\text{cl.n.}}$
0	3.23	9	6.13
1	3.96	10	5.95
2	4.60	11	5.66
3	5.12	12	5.27
4	5.54	13	4.76
5	5.86	14	4.15
6	6.08	15	3.43
7	6.19	16	2.57
8	6.22	17	1.59

### V. Adiabatic results for muonic molecules

The clamped nuclei potential energy curve with diagonal corrections for nuclear motion, computed for the  $\text{H}_2^+$  ion, can be directly employed, by changing only the mass ratio, to calculate the adiabatic energies for muonic molecules. These consist of two singly-charged nuclei (proton,  $p$ , deuteron,  $d$ , triton,  $t$ ) bound by a muon  $\mu$ . The results are listed in Table V where, in addition to the energy, the expectation values of  $R$  and  $R^{-2}$  are also given. In the same Table we give the nonadiabatic energies calculated recently by CARTER [11] using the Ritz variational method. Convergence of the energy becomes slower with decreasing ratio of the muon mass,  $m$ , to the reduced mass of the two nuclei. Inspection of CARTER's results shows that they have converged to roughly 4 figures except for the excited state of  $d\mu d$  where the accuracy is significantly lower and therefore this energy is not given in Table V. The previous nonadiabatic results (see e.g. [12]) also seem to be of a lower accuracy and are not included in the Table. For comparison the results for the  $\text{H}_2^+$  ion are listed in the last column. The corresponding nonadiabatic results are those of HUNTER and PRITCHARD [3].

The  $\Delta E$  values given in Table V represent the nonadiabatic energy correction, i.e.,  $\Delta E = E_{\text{nonad}} - E_{\text{ad}}$ . They are seen to be of the expected order of magnitude, i.e., of the order of  $(m/\mu)^2$ . They are also seen to be larger for the excited vibrational states than for the ground states. For the states under consideration the nonadiabatic effects are due to interaction with higher states of the same  $A$ , where  $A$  is the quantum number for the component of the angular momentum along the internuclear axis. The energy differences between these upper states and the state under consideration are smaller when the

Table V  
Energies and other properties of the muonic molecules

Molecule $m(M_a + M_b)/M_a M_b$	$E_{\text{HP}}$ 4.4400	$E_{\text{HD}}$ 5.9185	$E_{\text{HT}}$ 6.65648	$d_{\text{HD}}$ 8.87324	$d_{\text{HT}}$ 10.64216	$f_{\text{HD}}$ 13.29192	$H_{\text{I}}$ 917.86
$E_{\text{ad}}$	-0.4885066	-0.5080172	-0.5148851	-0.5294507	-0.5372619	-0.5455846	-0.5971382
$E_{\text{nonad}}$	-0.49437	-0.51266		-0.53097	-0.53840		-0.5971387
$v = 0 \Delta E$	-0.00586	-0.00464		-0.00152	-0.00114		-0.0000005
$\langle R \rangle$	3.303708	3.081971	3.003851	2.838290	2.749622	2.655254	2.063922
$\langle R^{-2} \rangle$	0.1492881	0.1618795	0.1667037	0.1776637	0.1839713	0.1910392	0.2439225
$E_{\text{ad}}$				-0.4777144	-0.4860214	-0.4957138	-0.5871537
$E_{\text{nonad}}$					-0.48773		-0.5871548
$v = 1 \Delta E$					-0.00171		-0.0000011
$\langle R \rangle$				5.743900	5.067744	4.481494	2.199147
$\langle R^{-2} \rangle$				0.0720091	0.0870771	0.1036442	0.2310860

All results in "natural units", i.e. assuming  $m = 1$ , where for the muonic molecules and for the  $H_{\text{I}}^+$  ion  $m$  denotes the muon and electron mass, respectively.

latter is an excited vibrational state. Therefore, by a common argument of the perturbation theory one may conclude that the nonadiabatic effects should increase with increasing vibrational excitation. Table V proves that this is indeed the case, and the results given in the previous Section show that the conclusion is also valid for higher vibrational states of  $H_2^+$ .

### VI. Adiabatic and nonadiabatic vibrational wave functions

It may be also of some interest to compare the adiabatic and nonadiabatic vibrational wave functions. A comparison of this type has already been made [13] for the ground state of the hydrogen molecule. However, in that

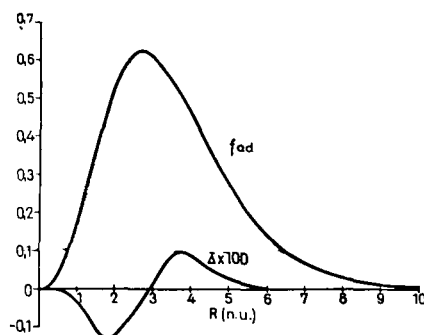


Fig. 1

case the nonadiabatic calculations [14] were not sufficiently accurate to make such a fine comparison of the wave functions meaningful. Similar and more accurate calculations have recently been carried out for the  $p\mu d$  system [15]. In this case one may expect that the nonadiabatic effect in the wave function is sufficiently large to be reliably detectable in a fairly accurate calculation. The 128-term nonadiabatic wavefunction calculated [15] for  $p\mu d$  has been used in the present work to calculate the vibrational pseudo-wave function defined as

$$f_{\text{nonad}}(R) = R \left[ \int |\Psi(\mathbf{r}, R)|^2 d\tau_\mu \right]^{1/2}, \quad (15)$$

where  $\Psi$  denotes the complete wave function for  $p\mu d$  and the integration is to be carried out only over the coordinates of the muon. The calculated pseudo-wave function can be compared with the adiabatic vibrational wave function  $f_{vK}(\equiv f_{\text{ad}})$  discussed in Section IV.

The calculated difference  $f_{\text{nonad}} - f_{\text{ad}}$  does not vanish with increasing internuclear distance (for  $R \leq 10$  n.u.) which is probably due to a relatively large error in the wave function for large  $R$ . Therefore, it seems that a weighted difference, i.e.,

$$A = (f_{\text{nonad}} - f_{\text{ad}}) f_{\text{ad}}^2 \quad (16)$$

has more physical meaning, and this difference is presented in Fig. 1 where the adiabatic vibrational wave function is also shown. Thus the nonadiabatic effects seem to increase the mean value of the internuclear distance in spite of the fact that they increase the binding of the two nuclei. This is supported by the results of TIPPING and HERMAN [16] who concluded that the nonadiabatic effects decrease the rotational constant of  $H_2$ . The binding is more directly related to the piling up of negative charge between the two nuclei. For  $H_2$  it has been found [13, 14] that the nonadiabatic value of  $\langle z^2 \rangle$  is smaller than the adiabatic one, where  $z$  denotes the sum of the electronic coordinates in the direction of the molecular axis. This is consistent with the increase of binding by the nonadiabatic effects.

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### REFERENCES

1. W. KOŁOS and L. WOLNIEWICZ, *Rev. Mod. Phys.*, **35**, 473, 1964.
2. M. BORN and R. OPPENHEIMER, *Ann. Phys.*, **84**, 457, 1927; M. BORN, *Nachr. Akad. Wiss. Göttingen*, **1**, 1951; M. BORN and K. HUANG, *Dynamical Theory of Crystal Lattices*, Oxford University Press, New York, 1956.
3. G. HUNTER and H. O. PRITCHARD, *J. Chem. Phys.*, **46**, 2153, 1967.
4. W. KOŁOS, C. C. J. ROOTHAAN and R. A. SACK, *Rev. Mod. Phys.*, **32**, 178 1960.
5. H. DIEHL and S. FLÜGGE, *Z. Physik*, **162**, 21, 1961.
6. A. FRÖMAN and J. L. KINSEY, *Phys. Rev.*, **123**, 2077, 1961.
7. H. WIND, Thesis, University of Utrecht, 1965; *J. Chem. Phys.*, **42**, 2371, 1965.
8. J. M. PEEK, Sandia Corporation Report No. SC-RR-65-77, 1965.
9. S. COHEN, D. L. JUDD and R. J. RIDDELL, Univ. of California, Lawrence Radiation Lab. Report No. UCRL-8802, 1959.
10. J. M. PEEK, private communication, 1968.
11. B. P. CARTER, *Phys. Rev.*, **165**, 139, 1968.
12. B. P. CARTER, *Phys. Rev.*, **141**, 863, 1966.
13. L. WOLNIEWICZ, *J. Chem. Phys.*, **45**, 515, 1966.
14. W. KOŁOS and L. WOLNIEWICZ, *J. Chem. Phys.*, **41**, 3674, 1964.
15. W. KOŁOS, *Phys. Rev.*, **165**, 165, 1968.
16. R. TIPPING and R. M. HERMAN, *J. Chem. Phys.*, **44**, 3112, 1966.

### НЕСКОЛЬКО ТОЧНЫХ РЕЗУЛЬТАТОВ ДЛЯ СИСТЕМ ТРЕХ ЧАСТИЦ

В. КОЛОС

#### Резюме

Сообщается о результатах вариационного вычисления неадиабатической энергии основного состояния  $H_2^+$ . Для электронного основного состояния  $H_2^+$  определялись и диагональные поправки для ядерного движения. Кривая адиабатической потенциальной энергии используется для вычисления ротационных и вибрационных уровней молекулярного иона  $H_2^+$  и для мюонных молекул. Дискутируются поправки к неадиабатической энергии. Адиабатическая волновая функция для  $pid$  сравнивается с соответствующим неадиабатическим результатом.