It is only possible with the information available to offer a partial indication as to which of the proton groups I_1, I_2, I_3 is associated with which of the nuclei Mg^{24}, Mg^{25}, Mg^{26}. It is reasonably certain, however, that the group I_1 is produced by Mg^{24}, since at a scattering angle of 90° it is nearly 1.7 times as large as the E group and could scarcely be produced by the other two rarer isotopes. This observation is supported by Henderson's[27] measurement of the gamma-ray energy of radio-sodium in the proposed reaction,

$$Na^{*24} \rightarrow Mg^{24} + \beta + \gamma,$$

in which he finds, by the absorption coefficient method, that the gamma-ray energy has an approximate value of 1.3 Mev which compares with our value of 1.37 Mev. However, from a number of published results, Livingston and Bethe[24] list gamma-rays for this reaction of energies 0.95 Mev, 1.93 Mev, and 3.08 Mev, none of which is closely comparable with the excitation energies or their differences as reported here.

From published studies of the proton groups from the reaction

$$Na^{23} + He^4 \rightarrow Mg^{26} + H^1,$$

Livingston and Bethe[24] have assigned excitation energies to Mg^{26} of 2.2 Mev, 4.0 Mev and 5.0 Mev. Of these, the first mentioned is not observed in our results, while the last value quoted is not in the range of our experiment. However, the group I_3 of measured excitation energy 4.07 Mev might perhaps correspond to the remaining proton group, thus associating this group with Mg^{26}.

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[27] M. C. Henderson, Phys. Rev. **48**, 855 (1935).

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Correction for Nuclear Motion in H_2^+

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The forced separation of variables usually employed in the quantum-mechanical treatment of molecular problems introduces certain small errors into the wave function. If the exact Hamiltonian is used, energy values can be computed very accurately because first-order errors in a wave function give rise to second-order errors in the energy. The energy of H_2^+ is ordinarily computed by using a separable, approximate Hamiltonian instead of an exact one. From a consideration of the terms which must be added to the approximate Hamiltonian to make it exact, Van Vleck has derived the correction terms needed to reduce the first-order error in the computed energy to a second-order error. The correction term is a function of R, the internuclear distance, and its calculation requires a knowledge of the wave function. In this paper the ground state wave function of H_2^+ is accurately determined over values of R from 1.20 to 2.75 atomic units and a table of the wave function coefficients is given, along with the corresponding energy values. Then, correction terms are calculated for a set of values of R. Including the proper correction term, the total negative energy of H_2^+ for the equilibrium internuclear distance is found to be $1.20472 \pm 0.00001 E_H = 132{,}132 \pm 10$ cm^{-1}. This result is compared with the consequences of certain experimental data.

1. THE PROBLEM

THE usual quantum-mechanical treatment of molecular problems is based upon a forced separation of variables.[1] This introduces certain small errors into the wave function, which, as such, is still as accurate as necessary. Since energy values are subject to much closer check by experimental data, it is desirable to determine energies as accurately as possible. They can be computed very accurately in some cases because first-order errors in a wave function give rise to second-order errors in the energy if the *exact* Hamiltonian is used in calculating the energy. The energy of H_2^+ is computed in the ordinary way by using, not the exact Hamil-

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[1] Cf. A. S. Coolidge and H. M. James, J. Chem. Phys. **6**, 730 (1938).

tonian, but the separable, approximate one. From a consideration of the terms which must be added to the approximate Hamiltonian to make it exact, Van Vleck[2] has derived the correction terms needed to reduce the first-order error in the computed energy due to total neglect of the motion of the nuclei to a second-order error due to carrying out the computation with approximate wave functions. The correction term, denoted by $P_{nn}+Q_{nn}+S_{nn}$, is a function of R, the internuclear distance. The potential energy at each value of R is obtained by adding this correction to the energy value of the corresponding fixed-nuclei solution. For infinite separation this correction becomes that required to convert the fixed- into the free-nuclei problem, hence it may be termed "the correction for nuclear motion." In this paper the ground state wave function of H_2^+ is accurately determined over values of R from 1.20 to 2.75 atomic units and the corresponding corrections for nuclear motion evaluated. A corrected value of the energy of H_2^+ for equilibrium internuclear distance is obtained and compared with certain experimental results.

2. Calculation of the Wave Function

The calculation of the wave functions of H_2^+ has been discussed in numerous papers in recent years;[3–11] but, due to the difficulties of calculation described below, the various authors have calculated only the energy values and not the wave function itself. Hence the first step in calculating the correction for nuclear motion is to make an accurate determination of the ground state wave function.

If elliptical coordinates, ξ, η, φ, are inserted in the Schrödinger equation, the latter becomes separable and the wave function for the ground state may be written:

$$\Psi(\xi,\eta,\varphi)=\frac{C}{(2\pi)^{\frac{1}{2}}}X(\xi)Y(\eta), \tag{1}$$

where C is the normalization constant. $Y(\eta)$ and $X(\xi)$ are defined by the differential equations:

$$\frac{d}{d\eta}(1-\eta^2)\frac{dY}{d\eta}+(\lambda^2\eta^2+\mu')Y=0, \tag{2}$$

$$\frac{d}{d\xi}(1-\xi^2)\frac{dX}{d\xi}+(\lambda^2\xi^2-2R\xi+\mu')X=0, \tag{3}$$

in which $\lambda^2=-E'R^2/2$, E' being the electronic part of the energy.

The solution of (2) is given by

$$Y(\eta)=1+a_2(\lambda)P_2(\eta)+a_4(\lambda)P_4(\eta)+a_6(\lambda)P_6(\eta)+\cdots \tag{4}$$

where, in order that the series may converge, the a_l must satisfy the relation:

$$a_{l-2}\lambda^2\frac{l(l-1)}{(2l-3)(2l-1)}+a_l\left[\mu'-l(l+1)+\lambda^2\left\{\frac{(l+1)^2}{(2l+1)(2l+3)}+\frac{l^2}{(2l+1)(2l-1)}\right\}\right]+a_{l+2}\lambda^2\frac{(l+1)(l+2)}{(2l+3)(2l+5)}=0.$$

So that the above equation may be satisfied by values of a_l other than zero, μ' and λ^2 must satisfy a functional relation, given in continued fraction form by Wilson[4] and solved in series form (accurate to the sixth decimal place) by Sandeman:[9]

$$-\mu'=\frac{\lambda^2}{3}+\frac{2\lambda^4}{3^3\cdot5}+\frac{4\lambda^6}{3^5\cdot5\cdot7}-\frac{26\lambda^8}{3^7\cdot5^3\cdot7}-\frac{92\lambda^{10}}{3^9\cdot5^2\cdot7\cdot11}-\frac{513988\lambda^{12}}{3^{10}\cdot5^5\cdot7^3\cdot11\cdot13}+\frac{2894282\lambda^{14}}{3^{12}\cdot5^6\cdot7^3\cdot11\cdot13}\cdots. \tag{5}$$

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[2] J. H. Van Vleck, J. Chem. Phys. **4**, 327 (1936).

[3] Ø. Burrau, Kgl. Danske, Vid. Selsk. **7**, No. 14 (1927).

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[8] G. Jaffe, Zeits. f. Physik **87**, 535 (1934).

[9] I. Sandeman, Proc. Roy. Soc. Edinburgh **55**, 72 (1935).

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[11] S. K. Chakravarty, Phil. Mag. **28**, 423 (1939).

TABLE I. *Wave function coefficients and energy values.*

λ	R	a_2	a_4	a_6	b_1	b_2	b_3	C	E'*	E*
1.0	1.214301	0.114518	0.001978	0.0000137	0.008496	0.0003706	0.0000411	3.612652	−2.712737	−1.065698
1.1	1.366077	.139388	.002919	.0000243	.010137	.0003908	.0000406	3.660361	−2.593552	−1.129506
1.2	1.523336	.166929	.004159	.0000410	.011831	.0004032	.0000392	3.723734	−2.482167	−1.169259
1.3	1.685909	.197207	.005770	.0000663	.013559	.0004086	.0000373	3.802924	−2.378365	−1.192061
1.4	1.853595	.230283	.007815	.0001035	.015301	.0004077	.0000348	3.898359	−2.281847	−1.202863
1.5	2.026162	.266212	.010364	.0001565	.017039	.0004014	.0000323	4.010611	−2.192272	−1.205184
1.6	2.203349	.305038	.013487	.0002306	.018757	.0003906	.0000294	4.140736	−2.109276	−1.201567
1.7	2.384868	.346787	.017253	.0003317	.020438	.0003762	.0000267	4.292105	−2.032493	−1.193872
1.8	2.570407	.391465	.021719	.0004674	.022068	.0003590	.0000239	4.459978	−1.961558	−1.183471
1.9	2.759633	.439049	.026927	.0006465	.023634	.0003399	.0000214	4.653078	−1.896115	−1.171381
1.483559	1.997466**	0.260107	0.009908	0.0001465	0.016754	0.0004028	0.0000328	3.991018	−2.206537	−1.205268

* E' and E are given in terms of $E_H = 109{,}679\ \text{cm}^{-1} = 13.530$ ev.
** Equilibrium internuclear distance.

The solution of (3) is written

$$X(\xi) = e^{-\lambda\xi}\left(\frac{2}{\xi+1}\right)^{\rho}\left\{1 + b_1(\lambda)\frac{\xi-1}{\xi+1} + b_2(\lambda)\left(\frac{\xi-1}{\xi+1}\right)^2 + b_3(\lambda)\left(\frac{\xi-1}{\xi+1}\right)^3 + \cdots\right\}, \tag{6}$$

where $\rho = 1 - (R/\lambda)$. In order that the series may converge, b_m must satisfy the relation

$$b_{m+1} = -u_m b_m + v_{m-1} b_{m-1}, \quad b_{-1} = 0, \tag{7}$$

where

$$-u_m = \frac{2m^2 + 2m(\rho+2\lambda) + (\rho + 2\rho\lambda + \lambda^2 + \mu')}{(m+1)^2}, \quad -v_{m-1} = (m-1+\rho)^2/(m+1)^2.$$

So that (7) may be satisfied by values of b_m other than zero, μ', λ, and ρ (or R) must be related in the manner indicated by the continued fraction:

$$-u_0 = \frac{v_0}{u_1+}\,\frac{v_1}{u_2+}\,\frac{v_2}{u_3+\cdots}. \tag{8}$$

In theory it is possible to eliminate μ' between (5) and (8) to obtain a relation between λ and R;[10, 11] in practice it is extremely difficult to determine an algebraic relation between λ and R sufficiently accurate to yield reliable values for the wave function coefficients. In the present work this calculation has been done numerically to insure maximum accuracy; for an arbitrary value of λ, μ' was found from (5), and then (8) was solved for the corresponding unique value of ρ (and hence R). From these values (all accurate to the sixth decimal place), corresponding values of a_l, b_m, C, and the energies E' and $E[=E'+(e^2/R)]$ were determined with like accuracy. Table I gives these results over a range of values of λ (or R); the last row gives results for the equilibrium value of R.

The value of the energy for the equilibrium value of R is exactly equal to that found by Hylleraas.[7] Sandeman[9] calculated a somewhat smaller absolute value. His result probably is slightly in error because the empirical formula relating λ and R, from which he obtained the energy minimum by the appropriate differentiation, was obtained from pairs of values of λ and R which fail to give agreement in Eq. (8) by about two percent.

The pairs of values of λ and R tabulated in Table I give rise to the empirical relation:

$$R = 0.0099234 + 0.9302959\lambda + 0.2461946\lambda^2 + 0.0449322\lambda^3 - 0.0176366\lambda^4 + 0.0006485\lambda^5 - 0.0000972\lambda^6 + 0.0000397\lambda^7 \cdots. \tag{9}$$

3. CALCULATION OF $P_{nn}+Q_{nn}+S_{nn}$ AND DISCUSSION OF RESULTS

Van Vleck's[2] expression for S_{nn}, which represents the energy difference due to the fact that the center of gravity of the molecule does not exactly coincide with the center of gravity of the nuclei, becomes for H_2^+:

$$\begin{aligned}\frac{S_{nn}}{E_H}&=-\frac{2}{M_PR^2}\int\frac{1}{\xi^2-\eta^2}\Psi\left\{\frac{\partial}{\partial\xi}(\xi^2-1)\frac{\partial\Psi}{\partial\xi}+\frac{\partial}{\partial\eta}(1-\eta^2)\frac{\partial\Psi}{\partial\eta}\right\}d\tau\\&=\frac{C^2R}{4M_P}\left[\int_{-1}^{1}Y^2d\eta\int_{1}^{\infty}(\xi^2-1)\left(\frac{\partial X}{\partial\xi}\right)^2d\xi+\int_{1}^{\infty}X^2d\xi\int_{-1}^{1}(1-\eta^2)\left(\frac{\partial Y}{\partial\eta}\right)^2d\eta\right],\end{aligned}\tag{10}$$

where M_P = mass of proton, E_H = ionization potential of hydrogen.

The corresponding expression for $P_{nn}+Q_{nn}$, which may be qualitatively described as representing coupling between vibrational and electronic motion, is

$$\begin{aligned}\frac{P_{nn}+Q_{nn}}{E_H}&=\frac{2}{M_P}\int\left(\frac{\partial\Psi}{\partial R}\right)^2d\tau-\frac{4}{M_PR}\int\frac{1}{\xi^2-\eta^2}\frac{\partial\Psi}{\partial R}\left\{\xi(\xi^2-1)\frac{\partial\Psi}{\partial\xi}+\eta(1-\eta^2)\frac{\partial\Psi}{\partial\eta}\right\}d\tau\\&\quad+\frac{2}{M_PR^2}\int\frac{\xi^2+\eta^2-1}{\xi^2-\eta^2}\left\{(\xi^2-1)\left(\frac{\partial\Psi}{\partial\xi}\right)^2+(1-\eta^2)\left(\frac{\partial\Psi}{\partial\eta}\right)^2\right\}d\tau\\&=\frac{C^2R^3}{4M_P}\int_{-1}^{1}\int_{1}^{\infty}\left[\frac{\partial}{\partial R}(XY)\right]^2(\xi^2-\eta^2)d\xi d\eta\\&\quad-\frac{C^2R^2}{2M_P}\int_{-1}^{1}\int_{1}^{\infty}\frac{\partial}{\partial R}\{XY\}\left\{Y\xi(\xi^2-1)\frac{\partial X}{\partial\xi}+X\eta(1-\eta^2)\frac{\partial Y}{\partial\eta}\right\}d\xi d\eta\\&\quad+\frac{C^2R}{4M_P}\int_{-1}^{1}\int_{1}^{\infty}(\xi^2+\eta^2)\left\{Y^2(\xi^2-1)\left(\frac{\partial X}{\partial\xi}\right)^2+X^2(1-\eta^2)\left(\frac{\partial Y}{\partial\eta}\right)^2\right\}d\xi d\eta-\frac{S_{nn}}{E_H}.\end{aligned}\tag{11}$$

The expression defined in Eq. (10) has been evaluated in a straightforward manner for a series of values of λ. The evaluation of expression (11) involves the calculation of the derivatives of the coefficients a_l and b_m and of λ and ρ with respect to R.[12] The appropriate derivatives have been calculated for different values of λ by use of the Gregory-Newton interpolation formula for derivatives of tabulated functions. Otherwise the evaluation of (11) involves only lengthy, but straightforward, integrations. Figure 1 shows the variation of S_{nn}, $P_{nn}+Q_{nn}$, and $P_{nn}+Q_{nn}+S_{nn}$ with internuclear distance. The total correction for nuclear motion at the equilibrium distance is 0.00055 ± 0.00001 E_H (60 $\text{cm}^{-1}=0.0075$ ev). Van Vleck[1] has estimated this quantity as 114 $\text{cm}^{-1}=0.014$ ev.

By combining the correction for nuclear motion with the value of the energy at equilibrium internuclear distance given in Table I, the total negative energy of H_2^+ becomes, for this value of R,

$$\begin{aligned}W(H_2^+)&=1.20472\pm0.00001E_H\\&=132{,}132\pm10\ \text{cm}^{-1}\\&=16.300\pm0.001\ \text{ev}.\end{aligned}\tag{12}$$

This value now can be compared with the results of experiment.

The total energy of H_2 equals twice the ionization energy of the H atom plus the dissociation energy of H_2. Beutler and Junger[13] have obtained a direct experimental value of the dissociation energy:

$$D(H_2)=36{,}116\pm6\ \text{cm}^{-1}.$$

With this value, the energy of H_2 becomes

$$\begin{aligned}W(H_2)&=2(109{,}679)+36{,}116\\&=255{,}474\pm6\ \text{cm}^{-1}.\end{aligned}\tag{13}$$

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[12] The normalization constant C is also a function of R, but calculation shows that terms involving $\partial C/\partial R$ are negligible compared to the others; hence such terms are omitted in Eq. (11).

[13] H. Beutler and H. O. Junger, Zeits. f. Physik **101**, 304 (1936).

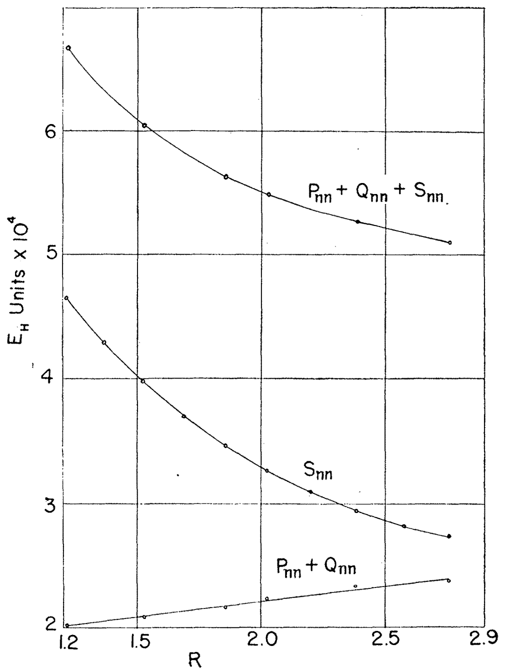

FIG. 1. Variation of $P_{nn}+Q_{nn}+S_{nn}$, S_{nn} and $P_{nn}+Q_{nn}$ with internuclear distance.

The ionization energy of H_2 can now be calculated, for the total energy of H_2 equals the ionization energy of H_2 plus the energy of H_2^+ minus the zero-point vibrational energy of H_2^+. By extrapolation from a singlet series of H_2, Richardson[14] has obtained for the zero-point energy the value 0.1399±0.0007 ev; Sandeman's theoretical work gives 0.1390 ev. The computations of this paper lead to the value

$$0.1389 \text{ ev} = 1126 \text{ cm}^{-1} \quad \text{(error not exceeding } 10 \text{ cm}^{-1}\text{)}. \qquad (14)$$

This value of the zero-point energy and the value of the energy of H_2^+ given in (12) give for the ionization energy of H_2:

$$\begin{aligned} I(H_2) &= 255{,}474 - 132{,}132 + 1126 \qquad (15) \\ &= 124{,}468 \pm 20 \text{ cm}^{-1}. \end{aligned}$$

Beutler and Junger, noting that the ionization energy of H_2 cannot be measured with the same accuracy as the dissociation energy, have obtained the experimental value

$$I(H_2) = 124{,}427 \pm 10 \text{ cm}^{-1}.$$

The small discrepancy may indicate that the probable error has been underestimated in one or both cases.

The dissociation energy of H_2^+ equals the energy of H_2^+ minus the zero-point vibrational energy of H_2^+ minus the ionization energy of the H atom. Using the theoretical values (12) and (14), one obtains:

$$\begin{aligned} D(H_2^+) &= 132{,}132 - 1126 - 109{,}679 \qquad (16) \\ &= 21{,}327 \pm 20 \text{ cm}^{-1}. \end{aligned}$$

This result cannot be directly compared with experiment because direct observations on the H_2^+ spectrum are completely lacking. The experimental value, 21,366±15 cm^{-1}, given by Beutler and Junger is a combination of the ionization and dissociation energies of H_2; hence the small discrepancy between calculated and experimental values of $I(H_2)$ appears again here.

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[14] O. W. Richardson, Proc. Roy. Soc. **A152**, 503 (1935); *Molecular Hydrogen and Its Spectrum* (Yale University Press, New York, 1934), p. 158.