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Vibrational States of the Hydrogen Molecular Ion*

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The eigenvalues and eigenfunctions of the vibrational states belonging to the ground electronic state of the hydrogen molecular ion have been calculated. The calculations have been done for the $J=0$, 2, 4, and 7 rotational states. Included is a discussion of the dependence of the eigenvalues as a function of the lowest-order dynamic corrections to the internuclear potential. Also, a calculation has been done to determine the number of bound states of the D_2^+ system.

I. INTRODUCTION

IN a study of the collision processes of the hydrogen molecular ion with electrons and other atomic systems, one is concerned in general with contributions from all the vibrational states belonging to the ground electronic state of the system. This follows from the fact that of the various mechanisms which lead to the formation of the molecular ion, whether in the laboratory or under astrophysical conditions, the ion is left in an excited vibrational state, and further transitions to the ground state must proceed via quadrupole emission. These quadrupole lifetimes are sufficiently long that the collision processes of the interest can occur before the ion has settled into the ground state. With respect to the interpretation of most experiments performed in the laboratory, these states are sufficiently long-lived to be considered stable.[1–3]

Calculations have been done to determine the eigenvalues and eigenfunctions of the vibrational states belonging to the ground electronic state of the H_2^+ system. These calculations have been carried out for several rotational states of the ion. We have included in these calculations a discussion of the dependence of the eigenvalues on the lowest-order dynamic corrections to the internuclear potential. In addition, a calculation has been done which gives the number of bound states for the D_2^+ ion. The eigenvalues for the H_2^+ ion are listed in the tables; the eigenfunctions have been tabulated elsewhere.[4]

II. QUANTITATIVE DISCUSSION

A general discussion of the three-body problem has been given in a previous paper[5]; here we reproduce only that portion which is essential for the continuity of this discussion.

The Hamiltonian for the hydrogen molecular ion is given by

$$\left\{-\frac{\hbar^2}{2M}[\nabla_1^2+\nabla_2^2]-\frac{\hbar^2}{2m}\nabla_e^2 + \frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}-\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_e|}-\frac{e^2}{|\mathbf{r}_2-\mathbf{r}_e|}\right\}\psi=E\psi, \quad (1)$$

where 1, 2 refer to the proton coordinates, and e to the electron coordinates. Upon introduction of the transformation

$$\begin{aligned}\mathbf{r}_c&=(2M+m)^{-1}(M\mathbf{r}_1+M\mathbf{r}_2+m\mathbf{r}_e),\\ \mathbf{R}_e&=\mathbf{r}_e-\tfrac{1}{2}(\mathbf{r}_1+\mathbf{r}_2),\\ \mathbf{r}_n&=\mathbf{r}_1-\mathbf{r}_2,\end{aligned} \quad (2)$$

the center-of-mass motion is separated from the internal motion, and the equation for the internal motion becomes

$$\left[-\frac{\hbar^2}{2}\left(\frac{1}{M_n}\nabla_n^2+\frac{1}{M_e}\nabla_e^2\right)+\frac{e^2}{r_n} -\frac{e^2}{|\mathbf{R}_e-\frac{1}{2}\mathbf{r}_n|}-\frac{e^2}{|\mathbf{R}_e+\frac{1}{2}\mathbf{r}_n|}\right]\psi(\mathbf{R}_e,\mathbf{r}_n)=W\psi(\mathbf{R}_e,\mathbf{r}_n), \quad (3)$$

where

$$M_n=\frac{M}{2},\quad M_e=\frac{m}{1+(m/2M)}.$$

To treat the equation for the internal motions, we introduce a solution of the form

$$\psi(\mathbf{R}_e,\mathbf{r}_n)=\textstyle\sum_i\psi_i(\mathbf{R}_e,\mathbf{r}_n)\chi_i(\mathbf{r}_n). \quad (4)$$

Upon insertion of Eq. (4) into Eq. (3), multiplication by ψ_j^*, and integration over all values of $\mathbf{R}_e$, Eq. (3) becomes

$$-\frac{\hbar^2}{2M_n}\nabla_n^2\chi_j+\left[\frac{e^2}{r_n}+W_j(r_n)-W\right]\chi_j +\mathcal{O}_{ij}-\sum_i\chi_i\int\psi_j^*\left[\frac{\hbar^2}{2M_e}\nabla_e^2+W_j(r_n) +\frac{e^2}{|\mathbf{R}_e-\frac{1}{2}\mathbf{r}_n|}+\frac{e^2}{|\mathbf{R}_e+\frac{1}{2}\mathbf{r}_n|}\right]\psi_i d^3\mathbf{R}_e=0; \quad (5)$$

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TABLE I. Comparison of eigenvalues with and without the lowest order dynamic corrections to the potential.

	$g_{00}=0$	$g_{00}\neq 0$
$v=0$	−1.1947414	−1.1944982
$v=2$	−1.1559646	−1.1557255
$v=4$	−1.1216770	−1.1214401
$v=6$	−1.0916400	−1.0914036
$v=8$	−1.0657038	−1.0654659
$v=10$	−1.0438166	−1.0435752
$v=12$	−1.0260434	−1.0257969
$v=14$	−1.0125960	−1.0123427
$v=16$	−1.0038738	−1.0003612
$v=18$	−1.0004024	−1.0001323
$W_0(\infty)$	−1.0002723	−1.0000000

here

$$\Theta_{ij}=-\frac{\hbar^2}{2M_n}\sum_i\left[\chi_i\int\psi_j{}^*\nabla_n{}^2\psi_i d^3\mathbf{R}_e+2\int\psi_j{}^*\nabla_n\chi_i\cdot\nabla_n\psi_i d^3\mathbf{R}_e\right].$$

The electronic eigenfunctions, ψ_i, are defined by setting the integrand of the last term in Eq. (5) to zero; the electronic eigenvalues, $W_j(r_n)$, are then determined as a function of the internuclear separation, r_n. The values of $W_j(r_n)$ used here have been determined by a variational calculation described elsewhere.[5,6]

The remaining terms in Eq. (5) serve to define the nuclear motion. The calculations discussed here have been done in two approximations; in the first approximation all the Θ_{ij} are set to zero, in the second only the lowest order term, Θ_{00}, is retained. When atomic units are introduced, the equation for the vibrational motion is written

$$\{\nabla_n{}^2+(M_n/M_e)[W_v-W_0(r_n)-2/r_n]\}\chi_{0v}(r_n)=-\Theta_{00}\chi_{0v}(r_n).\quad(6)$$

Here the first subscript on the χ designates the lowest electronic state of the system, and the second subscript is introduced to distinguish the various vibrational states belonging to this lowest electronic state.

The radial equation for a state of total orbital angular momentum J is obtained by introducing the substitution $\phi_{0v}=r_n\chi_{0v}$ and separating off the angular part of ϕ_{0v}. The first index on ϕ can be suppressed, and the radial equation becomes

$$\frac{d^2\phi_v}{dr_n{}^2}+\left\{\frac{M_n}{M_e}\left[W_v-W_0(r_n)-\frac{2}{r_n}\right]-\frac{J(J+1)}{r_n{}^2}-g_{00}\right\}\phi_v=0,\quad(7)$$

where $g_{00}=-\Theta_{00}$; g_{00} is tabulated by Cohen et al.[6]

The solutions for the ϕ_v and the W_v have been obtained by numerical solution of Eq. (7) using the IBM 701. The integrations extended over the range $0\leqslant r_n\leqslant 20$ (in units of the Bohr radius a_0), the integration proceeding in steps of $\Delta r_n=0.05$. For these calculations we have taken $M_n/M_e=918.334$. The calculations have been done for the $J=0$ and $J=2$ rotational states, and for a few of the upper states for $J=4$ and $J=7$.

In the first approximation the g_{00} is set equal to zero. In this approximation the potential function for large r_n tends to the limiting value

$$W_0(\infty)=-\frac{m}{1+(m/2M)}\frac{e^4}{2\hbar^2},$$

which differs from the correct limiting value, i.e., the atomic rydberg,

$$R=-\frac{m}{1+(m/M)}\frac{e^4}{2\hbar^2}.$$

In second approximation the lowest order coupling term, g_{00}, has been included. The inclusion of this term removes to lowest order in m/M the discrepancy in the asymptotic value of the potential present in the first approximation.[5] Table I is a comparison of some of the eigenvalues in first and second approximation, given in units of the atomic rydberg.

The eigenvalues calculated in second approximation are listed in Table II. For the $J=0$ (parahydrogen) state we find nineteen bound vibrational states. For the higher rotational quanta the potential function deforms in such a way as to reduce the number of bound states; at $J=4$ there are eighteen bound states, at $J=7$, seventeen bound states.

The error in the eigenvalues is determined primarily by the inaccuracies in the potential function. On the

TABLE II. Vibrational eigenvalues for the $J=0$, 2, 4, and 7 rotational states.

	$J=0$	$J=2$	$J=4$	$J=7$
$v=0$	−1.1944982	−1.1929112		
$v=1$	−1.1745327	−1.1730291		
$v=2$	−1.1557255	−1.1543024		
$v=3$	−1.1380388	−1.1366937		
$v=4$	−1.1214401	−1.1201708		
$v=5$	−1.1059022	−1.1047073		
$v=6$	−1.0914036	−1.0902817		
$v=7$	−1.0779281	−1.0768785		
$v=8$	−1.0654659	−1.0644884		
$v=9$	−1.0540136	−1.0531084		
$v=10$	−1.0435752	−1.0427433		
$v=11$	−1.0341627	−1.0334056		
$v=12$	−1.0257969	−1.0251171		−1.0197711
$v=13$	−1.0185092	−1.0179104		−1.0132400
$v=14$	−1.0123427	−1.0118297		−1.0078827
$v=15$	−1.0073536	−1.0069335	−1.0059878	−1.0037775
$v=16$	−1.0036121	−1.0032941	−1.0025902	−1.0010305
$v=17$	−1.0011962	−1.0009937	−1.0005668	
$v=18$	−1.0001323	−1.0000669		

Dissociation limit $=W_0(\infty)=-1.0000000$

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[6] S. Cohen, D. L. Judd, and R. J. Riddell, Jr., University of California Radiation Laboratory Report UCRL-8802, June, 1959 (unpublished).

basis of the comparison of the first-approximation potential function used here with the previous exact calculations,[7,8] we conclude that the correct eigenvalues are systematically lower by 4 to 5×10^{-3} electron volt than the values calculated here. Note that this absolute error is of the same order of magnitude as the g_{00} term. We believe the differences in the eigenvalues are more accurate than this error in the absolute values, however.

To test the convergence of the numerical integration for the rapidly varying higher state wave functions, the integration was done for an interval $\Delta r_n=0.025$, and by using a linear interpolation for the potential at the intermediate points; this test shifted the eigenvalues downward approximately three parts in 10^5, which is small compared with the effect of the uncertainties in the potential.

III. D_2^+ ION

As a final calculation we have determined the number of bound states of the D_2^+ ion. The number of bound states is one less than the number of nodes of the lowest free-state solution. For this calculation the g_{00} term appropriate to D_2^+ was neglected; the integration proceeded in steps of $\Delta r_n=0.025$, using a linear interpolation of the potential. In this approximation and for $J=0$ we find 27 bound states for the D_2^+ ion.

Note that for D_2^+ there are $\sqrt{2}$ times as many levels as for H_2^+. This result would follow rigorously for a parabolic potential or in the limit of applicability of the WKB solution.

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Hyperfine Structure of the Microwave Spectra of the NO Molecule and the Nuclear Quadrupole Moment of Nitrogen

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The frequencies of the magnetic resonance spectrum of the NO molecule has been recalculated by using the new value of spin-orbit coupling constants and by taking the effect of l uncoupling into consideration. The agreement between the theoretical and experimental results is improved over the previous calculation. By combining the magnetic hyperfine and nuclear quadrupole coupling constants the ratio of the quadrupole moment to the magnetic moment of the nitrogen nucleus is obtained. The nuclear quadrupole moment of nitrogen is found to be $(0.016\pm0.007)\times10^{-24}$ cm^2. The uncertainty of this value is chiefly due to that of the coupling constants rather than to the nature of the method itself.

THE theory of the hyperfine structure of the microwave spectra of NO and the interactions between the various spin angular momenta have been discussed in several papers in the literature.[1–9] Recently Favero, Mirri, and Gordy[10] have measured the rotational transitions of the NO molecule in the $^2\pi_{\frac{3}{2}}$ state and by combining the frequencies of this set of lines with those associated with the $^2\pi_{\frac{1}{2}}$ levels they made an accurate determination of the hyperfine coupling constants. They also obtained the spin-orbit coupling constant as 122.094 cm^{-1} instead of 124.2 cm^{-1}, the value determined by optical spectroscopy.[11] The theory of magnetic resonance spectrum of NO has been given by Lin and Mizushima.[8] These authors used the old value of spin-orbit interaction constant in their calculation and were able to fit the experimental data only within 5 Mc/sec. They suggested that this discrepancy might be due to the uncertainty in the spin-orbit term. With the new value of the various coupling constants given by Favero, Mirri, and Gordy[10] we have recalculated the frequencies of the resonance spectrum. The calculation has also been slightly modified to include the effect of l uncoupling[9] which was neglected in reference 8. The results are given in Table I. It may be noted that with the exception of H_7 the theoretical frequencies agree with experiment within 1 Mc/sec.

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