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Magnetic dipole transitions in the $H_2{}^+$ ion

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The magnetic dipole transitions in the homonuclear molecular ion $H_2{}^+$ are obtained for a range of v and L, vibrational and total orbital momentum quantum numbers, respectively. Calculations are performed in the nonrelativistic approximation. Spin consideration is also included.

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I. INTRODUCTION

The hydrogen molecular ion is the simplest stable molecule, which may be studied both theoretically and experimentally with high precision. In recent years laser spectroscopy of the heteronuclear hydrogen molecular ions HD^+ achieved spectacular progress [1–3], which allowed one to get valuable information on fundamental constants such as proton-to-electron mass ratio and set new limits on the possible manifestations of new interactions between hadrons, on the hypothetical "fifth force" [4,5].

$H_2{}^+$ is difficult to study experimentally since the electric dipole transitions are strongly suppressed. Nevertheless, the hydrogen molecular ion is of significant interest for metrology, especially as a direct way to measure the proton-to-electron mass ratio, and new experiments are coming to attack the problem using quantum logic spectroscopy [6].

In all the cases it is very important to know the strength of various transitions, which may be induced by the laser light. In our previous studies [7,8] quadrupole $E2$ and forbidden $E1$ transitions for the $H_2{}^+$ ions were investigated. In the present work we consider $M1$ transitions for the hydrogen molecular ion $H_2{}^+$ at low v and L.

The $M1$ transitions in H_2 molecule were studied in [9] within the adiabatic approximation; it was found that they are significantly weaker than the quadrupole transitions for low rotational states. The magnetic properties of the $H_2{}^+$ ion differ from the one of the H_2 molecule, since the total electron spin S is zero for the case of H_2. Still, we come to a similar conclusion for the $H_2{}^+$ molecular ion. Our calculation is based on *ab initio* three-body variational approximation of the bound-state nonrelativistic wave function and a direct evaluation of the orbital magnetic moment operator; see Eq. (3) below. No adiabatic approximation is used. Another point is that the spin-dependent structure of the transitions, which allow one to study the hyperfine spectrum of the $H_2{}^+$ ion, is carefully considered.

In what follows we assume atomic units: $\hbar = |e| = m_e = 1$.

II. THEORY

Throughout we keep to the following notation: v is the vibrational quantum number and L is the total orbital angular momentum of the nonrelativistic wave function. The spin part is described by the spin operators of two protons, $\mathbf{I}_1$, $\mathbf{I}_2$, and the spin of an electron, $\mathbf{s}_e$, $\mathbf{I} = \mathbf{I}_1 + \mathbf{I}_2$ is the total nuclear spin, $\mathbf{F} = \mathbf{I} + \mathbf{s}_e$ is the total spin of the $H_2{}^+$ ion, and $\mathbf{J} = \mathbf{F} + \mathbf{L}$ is the total angular momentum. Thus the ground "para" state is denoted $(v = 0, L = 0, I = 0, F = 1/2, J = 1/2)$. Since the $M1$ transition preserves spatial parity and we will consider the spatial wave function in the nonrelativistic approximation only, we have thus a selection rule for these states: $L \to L' = L$.

The nonrelativistic Hamiltonian in the center-of-mass frame may be written as

$$H_0 = \frac{\mathbf{p}_1^2}{2M} + \frac{\mathbf{p}_2^2}{2M} + \frac{\mathbf{p}_e^2}{2m_e} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{Z^2}{R}, \tag{1}$$

where $\mathbf{r}_i = \mathbf{r}_e - \mathbf{R}_i$ and $\mathbf{R} = \mathbf{R}_2 - \mathbf{R}_1$ are electron coordinates relative to nuclei and internuclear position vector in the molecular coordinate notations, $(\mathbf{R}_1, \mathbf{R}_2, \mathbf{r}_e \equiv \mathbf{R}_3)$ and $(\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_e \equiv \mathbf{p}_3)$ are the position vectors and momenta of particles in the center-of-mass frame, $M = m_p$ is the proton mass, and $Z = 1$ is the proton charge.

The transition magnetic moment $\boldsymbol{\mu}_{nn'}$ for a bound system of particles is expressed (see [10], Sec. 47):

$$\boldsymbol{\mu}_{nn'} = \langle\psi_n|\hat{\boldsymbol{\mu}}|\psi_{n'}\rangle = \mu_B\langle\psi_n|g_L(v,v')\mathbf{L} + g_e\mathbf{s}_e + \frac{g_p}{m_p}\mathbf{I}|\psi_{n'}\rangle, \tag{2}$$

where $\hat{\boldsymbol{\mu}}$ is the operator of the magnetic moment of the bound system, $g_e = -2.002\,319$ is the electron g factor, $g_p = 5.585\,694$ is the proton g factor [11], $\mu_B = |e|\hbar/(2m_e c)$ is the Bohr magneton, and $g_L(v,v')$ is the orbital g factor of the transition:

$$g_L(v,v') = \frac{1}{\mu_B\langle L\|\mathbf{L}\|L\rangle}\sum_{a=1}^{3}\langle\psi_n\|\frac{z_a}{m_a}[\mathbf{R}_a\times\mathbf{p}_a]\|\psi_{n'}\rangle. \tag{3}$$

TABLE I. Orbital g factor for transition, $g_L(v, v')$, for the orbital states $L = 1$ and $L = 2$. [$a(b) = a \times 10^b$.]

	$L=1$			$L=2$		
$v \to v'$	$v=0$	$v=1$	$v=2$	$v=0$	$v=1$	$v=2$
$v'=0$	5.0113(−4)			5.0095(−4)		
1	7.6094(−6)	4.9606(−4)		7.6324(−6)	4.9587(−4)	
2	6.5530(−7)	1.1257(−5)	4.9060(−4)	6.5775(−7)	1.1291(−5)	4.9039(−4)
3	1.2180(−7)	1.1844(−6)	1.4421(−5)	1.2221(−7)	1.1892(−6)	1.4465(−5)
4	3.4906(−8)	2.4674(−7)	1.7594(−6)	3.5029(−8)	2.4765(−7)	1.7670(−6)
5	1.2655(−8)	7.7464(−8)	3.9817(−7)	1.2705(−8)	7.7754(−8)	3.9977(−7)
6	5.3465(−9)	3.0371(−8)	1.3402(−7)	5.3693(−9)	3.0498(−8)	1.3456(−7)
7	2.5135(−9)	1.3718(−8)	5.6022(−8)	2.5417(−9)	1.3783(−8)	5.6268(−8)
8	1.3084(−9)	6.8817(−9)	2.6810(−8)	1.3164(−9)	6.9173(−9)	2.6953(−8)
9	7.3091(−10)	3.7398(−9)	1.4170(−8)	7.3522(−10)	3.7732(−9)	1.4225(−8)
10	4.3382(−10)	2.2204(−9)	7.9503(−9)	4.3783(−10)	2.2064(−9)	8.0930(−9)

Here the sum is over all the particles of the system, and z_a and m_a are corresponding charges and masses of the particles.

When $n \neq n'$ the initial- and final-state functions are orthogonal and the spin terms in (2) are exactly zero. Thus the transition amplitudes are determined solely by g_L, the orbital g factor of the transition. The spin-dependent transition amplitudes between hyperfine states are then expressed as

$$\langle vIFLJ\|\hat{\boldsymbol{\mu}}\|v'IF'LJ'\rangle = \delta_{FF'}(-1)^{J+F+L+1}\sqrt{(2J+1)(2J'+1)} \times \begin{Bmatrix} L & 1 & L \\ J' & F & J \end{Bmatrix} \langle vL\|\hat{\boldsymbol{\mu}}\|v'L\rangle \tag{4}$$

and we have an additional selection rule for the hyperfine transition lines: $F \to F' = F$.

The transition probability for spontaneous emission of a magnetic dipole photon from state n to state n' is expressed as follows:

$$A_{nn'} = \frac{1}{\tau}\frac{4\alpha^3}{3}\, w_{nn'}^3 \frac{|\langle\psi_n\|\hat{\boldsymbol{\mu}}\|\psi_{n'}\rangle|^2}{2J_n+1} = \frac{1}{\tau}\frac{\alpha^5}{3}\, w_{nn'}^3 \frac{g_L^2(v,v')}{2J_n+1}. \tag{5}$$

Here $w_{nn'} = E_n - E_{n'}$ is the transition frequency and τ is a unit of time in atomic units: $\tau = 2.41888 \times 10^{-17}$ s.

If $v = v'$, transitions occur between hyperfine states of the same vibrational level and all the terms in (2) contribute to the transition strength. For the "pure" HFS states [for definition see [7], Eq. (10)] the matrix of the magnetic moment is expressed by

$$\boldsymbol{\mu}_{nn'} = \mu_B\langle vIFLJ\|g_L\mathbf{L}+g_e\mathbf{s}_e+\frac{g_p}{m_p}\mathbf{I}\|vI'F'LJ'\rangle. \tag{6}$$

Then for the real hyperfine eigenstates the matrix is modified by orthogonal transformation, which connects pure and real HF eigenstates. The matrix elements for particular terms in (6) may be evaluated using 6-j symbols as is shown in the Appendix, Eq. (A2).

TABLE II. Dependence of g_L on the orbital momentum L for two vibrational transitions.

$v \to v'$	$L=1$	$L=2$	$L=3$	$L=4$
$0 \to 1$	7.6094(−6)	7.6324(−6)	7.6670(−6)	7.7132(−6)
$0 \to 9$	7.3091(−10)	7.3522(−10)	7.4243(−10)	7.5216(−10)

III. RESULTS AND DISCUSSION

Numerical calculations were based on the "exponential" variational expansion [12]. By averaging Eq. (3) over the spatial degrees of freedom, we obtained the orbital g factors and, eventually, the Einstein coefficients $A_{nn'}$ for the spontaneous emission of a photon from the state $n = (v, L, F, J)$ to the state $n' = (v', L', F', J')$; see Eq. (5).

In Table I the results of our numerical calculations for $L=1$ and $L=2$ transitions are presented. The transition probability calculated from the orbital g factors for the $(L = 1, v = 1) \to (1, 0)$ transition is $A^{M1}_{nn'} = 5.45 \times 10^{-12}$ s^{-1}, which must be compared with the quadruple transition probability for the same transition $A^{E2}_{nn'} = 2.65 \times 10^{-7}$ s^{-1} [7]. Thus the $M1$ transition is five orders of magnitude weaker than the quadrupole one.

Variation of the orbital g factor with a change of L is expectedly small due to the adiabatic nature of the system

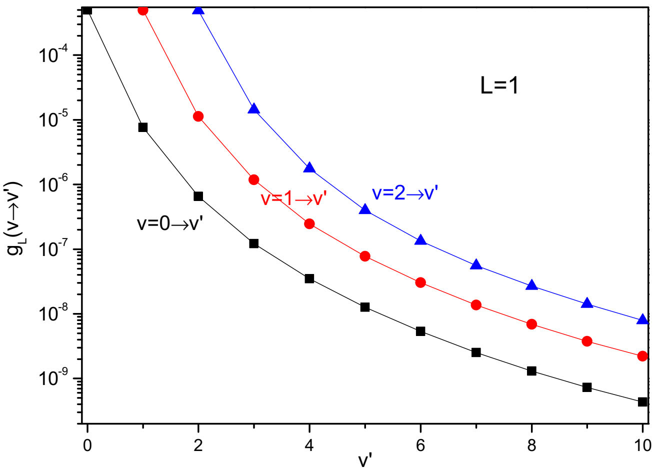

FIG. 1. Dependence of g_L for various $v \to v'$ transitions. $L = 1$.

and this is confirmed numerically in Table II. Since the L dependence is small we do not present calculations for higher L states. On the other hand, the orbital magnetic moment is proportional to $\sqrt{L(L+1)(2L+1)}$ and transition probability $A_{nn'}$ increases with L, similarly to the case of the molecule H_2 (see Fig. 1, Ref. [9]) and at some $L > 20$ the $M1$ transition becomes dominant.

On Fig. 1 three series of vibrational transitions for the $L = 1$ states are shown.

In conclusion, we obtained the $M1$ transition strengths for the hydrogen molecular ion $H_2{}^+$. Along with our previous calculations of the quadruple $E2$ transitions and forbidden dipole $E1$ transitions it completes the study of the transition rates, which are necessary for planning future experiments and allow one to estimate the laser intensity required for precision spectroscopy of the $H_2{}^+$ ion.

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APPENDIX: REDUCED MATRIX ELEMENTS FOR THE SPIN AND ORBITAL ANGULAR MOMENTUM OPERATORS

In this section we will apply the formula for the tensor product of irreducible tensor operators [13].

Let $\mathbf{V}_{k\mu} \equiv \{\mathbf{T}_{k_1} \otimes \mathbf{U}_{k_2}\}_{k\mu}$, where $\mathbf{T}_{k_1}$ acts on subsystem 1 with angular moment $\mathbf{J}_1$ and $\mathbf{U}_{k_2}$ acts on subsystem 2 with angular momentum $\mathbf{J}_2$. Then

$$\langle v_1 v_2 J_1 J_2 J \| \mathbf{V}_k \| v_1' v_2' J_1' J_2' J' \rangle = \Pi_{JJ'k} \begin{Bmatrix} J_1' & J_2' & J' \\ k_1 & k_2 & k \\ J_1 & J_2 & J \end{Bmatrix} \langle v_1 J_1 \| \mathbf{T}_{k_1} \| v_1' J_1' \rangle \langle v_2 J_2 \| \mathbf{U}_{k_2} \| v_2' J_2' \rangle. \tag{A1}$$

The reduced matrix elements for operators $\mathbf{I}$, $\mathbf{s}_e$, and $\mathbf{L}$ in the basis of the pure hyperfine states are

$$\begin{aligned} \langle IFLJ \| \mathbf{I} \| IF'LJ' \rangle &= \Pi_{FF'JJ'} (-1)^{I+s_e+L+J'+1} \begin{Bmatrix} I & 1 & I \\ F' & s_e & F \end{Bmatrix} \begin{Bmatrix} F & 1 & F' \\ J' & 1 & J \end{Bmatrix} \langle I \| \mathbf{I} \| I \rangle, \\ \langle IFLJ \| \mathbf{s}_e \| IF'LJ' \rangle &= \Pi_{FF'JJ'} (-1)^{I+s_e+L+J'+1} \begin{Bmatrix} s_e & 1 & s_e \\ F' & I & F \end{Bmatrix} \begin{Bmatrix} F & 1 & F' \\ J' & L & J \end{Bmatrix} \langle s_e \| \mathbf{s}_e \| s_e \rangle, \\ \langle IFLJ \| \mathbf{L} \| IF'LJ' \rangle &= \delta_{FF'} \Pi_{JJ'} (-1)^{F+L+J+1} \begin{Bmatrix} L & 1 & L \\ J' & F & J \end{Bmatrix} \langle L \| \mathbf{L} \| L \rangle, \end{aligned} \tag{A2}$$

where $\Pi_S = \sqrt{2S+1}$ and $\langle S \| \mathbf{S} \| S \rangle = \sqrt{S(S+1)(2S+1)}$ for any angular momentum operator $\mathbf{S}$.

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