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"Forbidden" Electric Dipole Transitions in the Hydrogen Molecular Ion – first estimates

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Abstract. The H_2^+ molecular ion is a simple three body homonuclear system. It has zero electrical dipole momentum and small spectral lines natural width, features making H_2^+ a suitable candidate for a high precision time standard. In order to select the optimal transition lines for such purposes, a complete understanding of the structure and the characteristics of all lines of interest is needed. In the present work we have contributed in solving this problem by extending the class of possible candidates with a detailed study of the so-called "forbidden" electric dipole transitions, i.e. transitions that are forbidden by selection rules in the non-relativistic limit. By adding spin interactions, due to mixing of states with opposite parity under nucleus exchange, these transitions receive a small, but different from zero intensity.

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1 H_2^+ structure and symmetries

1.1 Hyper-fine structure

Recently, the spectrum of the low ro-vibrational excitations of the hydrogen molecular ion H_2^+ has been evaluated with a very high precision [1, 2]. It has been shown that the narrow natural width and the suppressed sensitivity to external fields of selected levels makes this ion suitable for application as time standard. In [3, 4] the most appropriate E1 and two-photon transition lines for such purposes were selected. In [5] "forbidden" E1 transitions between the high ro-vibrational states of H_2^+ are studied with a view to their application in astronomy. In this work, we have computed "forbidden" dipole transitions between low excited rotational-vibrational levels which are of interest for the precision spectroscopy experiments.

The molecular hydrogen ion has hyper-fine structure, consisting of one, two, five, and six hypefine splitted levels when the total orbital momentum of the molecule is L = 0, 1, 2n, 2n+1 respectively. On Figure 1.1, the splitting of $(v, L) = (0, 0)$ and $(1, 1)$ states is shown. The "forbidden" electric dipole

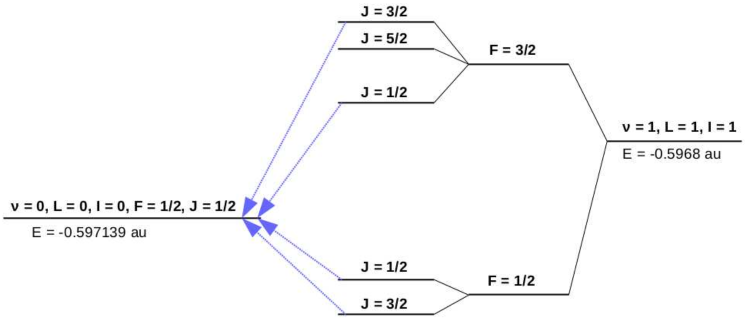

Figure 1. *H_2^+ molecular ion*

transitions between these states are given with dotted arrows. The selection rules prohibit the transition $|vLIF5/2\rangle \rightarrow |v'L'I'F'1/2\rangle$ even when the spin interaction corrections are taken in account. The angular momentum quantum numbers correspond to the following coupling scheme: $\mathbf{I} = \mathbf{S}_1 + \mathbf{S}_2$, $\mathbf{F} = \mathbf{I} + \mathbf{S}_e$, $\mathbf{J} = \mathbf{F} + \mathbf{L}$. Here ν is the vibrational quantum number, $\mathbf{S}_1, \mathbf{S}_2$, and $\mathbf{S}_e$ are the spin vectors of the two protons and the electron.

1.2 Symmetries of the hydrogen molecular ion

The hydrogen molecular ion is three particle system with two identical nuclei. Thus, in addition to the spatial parity it has a definite parity with respect to exchanging the two protons. In the non-relativistic limit the operators commuting with the Hamiltonian are: $\mathbf{L}^2$, $\mathbf{L}_z$ - the total orbital angular momentum squared and orbital momentum projection on the z axis, Π - spatial parity operator, and $\mathbf{X}$ - the operator of the exchange of the two nuclei. Then the stationary states could be labeled by the eigenvalues of these operators:

$$\begin{aligned} &\mathbf{L}^2|\nu x\lambda LL_z\rangle = L(L+1)|\nu x\lambda LL_z\rangle, \quad \mathbf{L}_z|\nu x\lambda LL_z\rangle = L_z|\nu x\lambda LL_z\rangle, \\ &\mathbf{\Pi}|\nu x\lambda LL_z\rangle = \lambda|\nu x\lambda LL_z\rangle, \quad \mathbf{X}|\nu x\lambda LL_z\rangle = x|\nu x\lambda LL_z\rangle. \end{aligned} \tag{1}$$

We consider transitions between states with normal parity $\mathbf{\Pi} = (-1)^L$ in which the electron is in its ground state. For these states the following relations holds:

$$\mathbf{X}|\nu x\lambda L L_z\rangle = (-1)^L|\nu x\lambda L L_z\rangle, \tag{2}$$

$$\text{i.}e.\ x = \lambda. \tag{3}$$

Let $\mathbf{D}$ be the dipole moment operator

$$\mathbf{D} = \sum_{i=1}^{3} Z_i \mathbf{R}_i, \tag{4}$$

where Z_i is the particle charge in atomic units and $\mathbf{R}_i$ ($\mathbf{R}_3 \equiv \mathbf{R}_e$) is its radius-vector. The commutators of $\mathbf{D}$ with $\mathbf{X}$ and $\mathbf{P}$ are

$$X\mathbf{D}X^{-1} = \mathbf{D}, \Pi\mathbf{D}\Pi^{-1} = -\mathbf{D}. \tag{5}$$

Then, from Eq. (1),(3), and (5) for dipole transitions between states of interest - $|\nu x\lambda L L_z\rangle$ and $|\nu x\lambda L' L'_z\rangle, L' = L \pm 1$

$$\langle\nu' x'\lambda' L' L'_z|\mathbf{D}|\nu x\lambda L L_z\rangle = \langle\nu' x'\lambda' L' L'_z|X^{-1}\left(X\mathbf{D}X^{-1}\right)X|\nu x\lambda L L_z\rangle = 0, \tag{6}$$

i.e. for transitions between states of H_2^+ with normal spatial parity $\lambda = (-1)^L$, the electric dipole transitions are forbidden in the nonrelativistic limit.

2 Computation of the electric dipole moments

2.1 Non-relativistic limit

The non-relativistic Hamiltonian of H_2^+ is:

$$H_0 = \frac{\mathbf{p}_1^2}{2m_p} + \frac{\mathbf{p}_2^2}{2m_p} + \frac{\mathbf{p}_e^2}{2m_e} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R}, \tag{7}$$

R and $r_{1,2}$ are the distances between the two nucleus and the distance between each of the protons and the electron, $\mathbf{p}_{1,2}$, $\mathbf{p}_e$ are the momentum vectors of the first and the second proton and the e^-, and m_p, m_e are the masses of the proton and electron respectively.
We use the following decomposition of the nonrelativistic wavefunction

$$\Psi_M^{L\lambda x}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{l_1,l_2}^{L} r_1^{l_1} r_2^{l_2} \mathbf{Y}_{LM}^{l_1 l_2}(\hat{r}_1, \hat{r}_2) F_{l_1 l_2}^{L\lambda x}(r_1, r_2, \Theta), \tag{8}$$

$$F_{l_1 l_2}^{L\lambda x}(r_1, r_2, \Theta) = \sum_{i=1}^{i_{max}} [C_i \cos(\nu_i R) + D_i \sin(\nu_i R)] e^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i R}.$$

Here $\mathbf{Y}^{l_1 l_2}_{LM}(\hat{r}_1, \hat{r}_2)$ are the bispherical harmonics, $\mathbf{r}_{1,2} = \mathbf{R}_e - \mathbf{R}_{1,2}$, $\hat{r}_{1,2}$ is the angular part of $\mathbf{r}_{1,2}$, and Θ is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$. l_1, l_2 are the angular momentums associated with each of the spherical harmonics constituting the bispherical harmonics. The numerical solution for the expansion parameters $\alpha_i, \beta_i, \gamma_i, C_i, D_i, \nu_i$, and for the corresponding state vectors is done with V. Korobov's code [2] using variational method.

2.2 Breit interaction Hamiltonian

In the relativistic picture of H_2^+ the state vectors are direct products of the nonrelativistic states $|\nu p \lambda L L_z\rangle$ (see Eq.(8)) with the spin state vectors of the electron and the two protons $|S_i \zeta_i\rangle$, with eigenvalue identities $\mathbf{S}_i^2 - S_i(S_i + 1))|S_i\zeta_i\rangle = (\mathbf{S}_{zi} - \zeta_i)|S_i\zeta_i\rangle = 0$:

$$|\nu x \lambda L L_z\rangle \otimes |S_1\zeta_1\rangle \otimes |S_2\zeta_2\rangle \otimes |s_e\zeta_e\rangle. \tag{9}$$

In the total angular momentum representation the basis has the form

$$|\nu x \lambda L I F J M\rangle = \tag{10}$$
$$\sum_{\zeta_1\zeta_1\zeta_2\zeta_s L_z} C^{II_z}_{S_1\zeta_1 S_2\zeta_2} C^{FF_z}_{II_z s_e \zeta} C^{JM}_{FF_z L L_z} |S_1\zeta_1\rangle |S_2\zeta_2\rangle |S_e\zeta\rangle |\nu x \lambda L L_z\rangle.$$

In this case, the concerved quantities are $\mathbf{J}$ and $\mathbf{M}$.
As shown in Eq. (6), in the nonrelativistic approximation the matrix elements of the electric dipole transitions in H_2^+ are zero. The Breit Hamiltonian includes operators which mix states with different nuclei exchange parity x. The relativistic corrections to the wave function are calculated in the first order of perturbation theory in the Breit Hamiltonian. The terms that have the most important contribution to the ortho-para mixing (or equivalently mixing with regard to $\mathbf{X}$ parity) of H_2^+ are:

$$H_{ss} = \alpha^2 \, \frac{\pi}{3} \frac{g_e g_p}{m_p} \, (\mathbf{s}_e \cdot \mathbf{I}_-)[\delta(\mathbf{r}_1) - \delta(\mathbf{r}_2)], \tag{11}$$
$$H_{so} = \alpha^2 \frac{g_p}{4m_p} \left(\frac{\mathbf{r}_1 \times \mathbf{p}_e}{r_1^3} - \frac{\mathbf{r}_2 \times \mathbf{p}_e}{r_2^3} \right) \mathbf{I}_-,$$

$\mathbf{I}_- = (\mathbf{S}_1 - \mathbf{S}_2)$ being the $\mathbf{X}$ symmetry breaking operator. In the expression above $\hbar = \mathrm{m_e} = \mathrm{e} = 1, \alpha = 1/\mathrm{c}$, where c is the speed of light and g_e, g_p are the gyromagnetic ratios for the electron and the proton. The next step is the calculation of the corrections to the nonrelativistic wavefunction by using the perturbation theory. The numerical computation of these corrections is the nontrivial part in obtaining the dipole transition matrix elements.

$$|\nu p\lambda LIFJM_{(1)}\rangle = |\nu p\lambda LIFJM_{(0)}\rangle + \tag{12}$$
$$\sum_{\nu' x' L' I' F'} \frac{\langle \nu' x' \lambda L' I' F' JM_{(0)}|H_{ss} + H_{so}|\nu x\lambda LIFJM_{(0)}\rangle}{E_{(0)}^{\lambda\nu xL} - E_{(0)}^{\lambda\nu' x' L'}} |\nu' x' \lambda L' I' F' JM_{(0)}\rangle$$

or in short notation

$$\begin{aligned} &\Psi_1 = \Psi_0 + \Delta\Psi, \\ &\Delta\Psi = Q(E_0 - H_0)QH_{op}, \;\; H_{op} = H_{ss} + H_{so}. \end{aligned} \tag{13}$$

The indices (0) and (1) label the vawefunctions in zeroeth and first order in perturbation theory.

In dipole approximation (longwave approximation), we compute the transition matrix element by using the molecule-photon dipole interaction operator (4)

$$\begin{aligned} &\langle \Psi_1^{'}|\mathbf{D}|\Psi_1\rangle = \langle \Psi_0^{'}|\mathbf{D}|\Psi_0\rangle + \\ &\langle \Psi_0^{'}|\mathbf{D}Q(E_0 - H_0)^{-1}QH_{op}|\Psi_0\rangle + \langle \Psi_0^{'}|H_{op}Q'(E_0' - H_0)^{-1}Q'\mathbf{D}|\Psi_0\rangle + \\ &\langle \Psi_0^{'}|H_{op}Q'(E_0' - H_0)^{-1}Q'\mathbf{D}Q(E_0 - H_0)^{-1}QH_{gu}|\Psi_0\rangle. \end{aligned} \tag{14}$$

Here Ψ and Ψ' stand for the initial and final state vectors $|vx\lambda JIFJM\rangle$ and $|v'x'\lambda' J'I'F'J'M'\rangle$, E_0 and E_0' are the corresponding non-perturbed energies, and Q and Q' project out of the subspaces spanned by the eigenvectors with eigenvalues E_0 and E_0', respectively. The first term in the righthand side is the electrical dipole transition matrix element in nonrelativistic approximation and is zero. The forth term has both left and right side corrections to the vawefunctions and is too small in comparison with the others. The second and the third term are the only ones that significantly contribute to the "forbidden" E1 transitions matrix elements $\mathbf{T}_{if}$:

$$\mathbf{T}_{if} = \langle \Psi_0^{'}|\mathbf{D}Q(E_0 - H_0)^{-1}QH_{op}|\Psi_0\rangle + \langle \Psi_0^{'}|H_{op}Q'(E_0' - H_0)^{-1}Q'\mathbf{D}|\Psi_0\rangle \tag{15}$$

Denote by T_{if} the reduced transition matrix element. We have

$$\begin{aligned}
&\langle\Psi_0^{'}\|\mathbf{D}Q(E_0-H_0)^{-1}QH_{op}\|\Psi_0\rangle = \\
&\alpha^2\frac{g_e g_p}{m_p}\frac{\pi}{3}\frac{\sqrt{3}}{2}(-1)^{L+J'+1/2}\sqrt{(2J+1)(2J'+1)} \\
&\begin{Bmatrix} L\,1/2\,J \\ J'\ 1\ L' \end{Bmatrix}\sum_{v''}\frac{\langle v'L'\|\mathbf{J}_{E1}\|v''L\rangle\langle v''L|\,\delta(\mathbf{r}_1)-\delta(\mathbf{r}_2)\,|vL\rangle}{E_0-E_{v''}} \qquad (16)\\
&\alpha^2\frac{g_p}{4m_p}\sqrt{3}\sum_{L''}(-1)^{F'+J'-J-1/2} \\
&\sqrt{(2J+1)(2J'+1)(2F'+1)(2F+1)}\begin{Bmatrix} L''\,F'\,J \\ J'\ 1\ L' \end{Bmatrix}\begin{Bmatrix} I'\ 1\ \ I \\ F\,1/2\,F' \end{Bmatrix}\begin{Bmatrix} F'\ F\ 1 \\ L\ L''\,J \end{Bmatrix} \\
&\sum_{v''}\frac{\langle v'L'\|\mathbf{J}_{E1}\|v''L''\rangle\langle v''L''\|\mathbf{h}_{so}^{(-)}\|vL\rangle}{E_0-E_{v''}}\,.
\end{aligned}$$

A similar expression are derived for the second term of T_{if}, $\langle\Psi_0^{'}\|H_{op}Q'(E_0'-H_0)^{-1}Q'\mathbf{D}\|\Psi_0\rangle$ as well.

The rate of the “forbidden” dipole transitions in H_2^+ stimulated by an oscillating electric field $\mathbf{E}\sin\omega t$ is then obtained by summing $|\mathbf{E}.\mathbf{T}_{if}|^2$ over the final state and averaging over the initial state polarizations and integrating over the laser line profile. In the present paper we focus our attention on the calculation of the transition matrix elements and discuss the values of T_{if} only.

3 Results

In Table 1 the results for the reduced matrix elements are given for a few transitions between hyperfine levels of the hydrogen molecular ion.

In their work [5], Bunker and Moss have calculated electric dipole "forbidden" transitions between high ro-vibrational levels $|\nu L\rangle$ of the H_2^+. They use the Born-Oppenheimer approximation. In Table 2 we make a comparison between their results and our variational method computations of the same reduced transition matrix elements $\mu = \langle\nu' L'||D||\nu L\rangle$. As seen, there is a reasonable agreement between the transition matrix element we get (third column) and the ones of Bunker and Moss (forth column). As the square of the transition matrix element enter into the transition rate expression its sign is not essential. The numerical calculations are done in quadruple precision but are to be improved by using higher (sextuple etc.) precision of the computations.

Table 1: Selected electric dipole “forbidden” transitions between low ro-vibrational hyperfine levels of H_2^+ molecular ion. The numbers in brackets are powers of ten.

$\lvert vLIFJ\rangle \to \lvert v'L'I'F'J'\rangle$	$\omega, [cm^{-1}]$	$T_{if}, [au]$
$\lvert 0,1,1,1/2,1/2\rangle \to \lvert 0,0,0,1/2,1/2\rangle$	58.23	$-1.62642[-8]$
$\lvert 0,1,1,1/2,3/2\rangle \to \lvert 0,0,0,1/2,1/2\rangle$	58.23	$2.26111[-8]$
$\lvert 0,1,1,3/2,1/2\rangle \to \lvert 0,0,0,1/2,1/2\rangle$	58.23	$1.14030[-8]$
$\lvert 0,1,1,3/2,3/2\rangle \to \lvert 0,0,0,1/2,1/2\rangle$	58.23	$-1.61263[-8]$
$\lvert 1,1,1,1/2,1/2\rangle \to \lvert 0,0,0,1/2,1/2\rangle$	2246.26	$-1.15774[-9]$
$\lvert 1,1,1,1/2,3/2\rangle \to \lvert 0,0,0,1/2,1/2\rangle$	2246.26	$4.66020[-9]$
$\lvert 1,1,1,3/2,1/2\rangle \to \lvert 0,0,0,1/2,1/2\rangle$	2246.26	$1.57437[-9]$
$\lvert 1,1,1,3/2,3/2\rangle \to \lvert 0,0,0,1/2,1/2\rangle$	2246.26	$-2.22650[-9]$
$\lvert 1,1,1,1/2,1/2\rangle \to \lvert 1,0,0,1/2,1/2\rangle$	55.17	$-1.54293[-8]$
$\lvert 1,1,1,1/2,3/2\rangle \to \lvert 1,0,0,1/2,1/2\rangle$	55.17	$1.28176[-8]$
$\lvert 1,1,1,3/2,1/2\rangle \to \lvert 1,0,0,1/2,1/2\rangle$	55.17	$1.08022[-8]$
$\lvert 1,1,1,3/2,3/2\rangle \to \lvert 1,0,0,1/2,1/2\rangle$	55.17	$-1.52766[-8]$
$\lvert 1,0,0,1/2,1/2\rangle \to \lvert 0,1,1,1/2,3/2\rangle$	2132.88	$-7.13890[-10]$

Table 2: Comparison between the non-relativistic high ro-vibrational transition dipole matrix elements calculated here μ and the ones given in [5]. ω is the transition frequency in units cm^{-1}

$\lvert vL\rangle \to \lvert v'L'\rangle$	$\omega, [cm^{-1}]$	$\mu, [au]$	$\mu_{B\&M}, [au]$
$\lvert 19,0\rangle \to \lvert 18,1\rangle$	19.88	$4.17[-2]$	$2.70[-2]$
$\lvert 19,0\rangle \to \lvert 17,1\rangle$	146.99	$7.76[-3]$	$5.05[-3]$
$\lvert 19,0\rangle \to \lvert 16,1\rangle$	419.23	$-1.25[-3]$	$8.20[-4]$
$\lvert 19,0\rangle \to \lvert 15,1\rangle$	832.48	$-2.15[-4]$	$1.40[-4]$
$\lvert 19,0\rangle \to \lvert 14,1\rangle$	1379.30	$-3.85[-5]$	$3.00[-5]$
$\lvert 19,1\rangle \to \lvert 19,0\rangle$	0.52	$-4.34[-1]$	$-1.66[-1]$
$\lvert 19,1\rangle \to \lvert 18,0\rangle$	23.83	$5.31[-2]$	$3.24[-2]$
$\lvert 19,1\rangle \to \lvert 17,0\rangle$	155.43	$9.02[-3]$	$5.53[-3]$
$\lvert 19,1\rangle \to \lvert 16,0\rangle$	431.69	$-1.44[-3]$	$8.90[-4]$
$\lvert 19,1\rangle \to \lvert 15,0\rangle$	848.54	$-2.47[-4]$	$1.50[-4]$
$\lvert 19,1\rangle \to \lvert 14,0\rangle$	1398.68	$4.41[-5]$	$2.00[-5]$
$\lvert 19,1\rangle \to \lvert 18,1\rangle$	14.03	$8.38[-2]$	$3.54[-2]$
$\lvert 19,1\rangle \to \lvert 17,1\rangle$	132.08	$-1.50[-2]$	$6.50[-3]$
$\lvert 19,1\rangle \to \lvert 16,1\rangle$	396.22	$-2.34[-3]$	$1.05[-3]$
$\lvert 19,1\rangle \to \lvert 15,1\rangle$	802.24	$-3.96[-4]$	$1.70[-4]$
$\lvert 19,1\rangle \to \lvert 14,1\rangle$	1342.44	$-7.03[-5]$	$3.00[-5]$

4 Conclusion

In this work we have studied the "forbidden" electrical dipole transitions of the H_2^+. The corrections to the wave function were calculated in first order of perturbation theory using the Breit three particle Hamiltonian. Laser induced electric dipole transition rates between H_2^+ hyperfine levels were computed and a comparison with the results in [5] for E1 transition matrix elements between highly excited ro-vibrational states of the hydrogen molecule is done. A more comprehensive study, including additional low ro-vibrational E1 "forbidden" transitions of the H_2^+, which are of experimental interest, and with improved precision will be published elsewhere. H_2^+ has characteristics which make it a suitable candidate for a high precision time standard. The study of the "forbidden" E1 transitions is a step to the understanding of the characteristics of H_2^+. The detailed picture requires a computation of the quadrupole and two-photon transitions between the states of this molecular ion. This, as well as the study of the D_2^+, a ion with simmilar properties to H_2^+, will be addressed in subsequent works.

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