Precision studies of the hydrogen molecular ion and its isotopologues

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Abstract We present systematic calculations of the leading order relativistic corrections including the hyperfine splitting (HFS) for a wide range of rotational and vibrational states of the HT^+ molecular ion. We also calculate the DC and AC Stark effects for the molecular hydrogen ions H_2^+ and HD^+ in the non-relativistic approximation. The influence of the DC Stark polarizability effect on the hyperfine substates of a ro-vibrational state is carefully analyzed. Our results enable the detailed evaluation of certain systematic shifts of the transition frequencies for the purpose of ultra-high-precision optical, microwave, or radio-frequency spectroscopy of the hydrogen molecular ions in a trap.

Keywords Molecular hydrogen ions · Fine and hyperfine splitting · Relativistic correction · Breit-Pauli Hamiltonian

1 Introduction

The ro-vibrational spectroscopy of the hydrogen molecular ions has been proposed to improve the determination of m_p/m_e, the proton-to-electron mass ratio [1, 2].

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We present results for a wide range of states of the total orbital angular momentum $L = 0 - 5$ and vibrational quantum number $v = 0 - 5$

We carry out extended calculations of the leading order relativistic corrections for HT^+ ro-vibrational states. It includes as well calculations of the hyperfine structure (HFS), which to our knowledge have never been published before for this isotopomer of the hydrogen molecular ion. The HFS may be of great importance for studies of the finite size properties of a triton, such as form factors, Zemach radius, etc.

For numerical three-body calculations we use the variational expansion [3]. Namely, the wave function for a state with a total orbital angular momentum L and of a total spatial parity $\pi = (-1)^L$ is expanded as

$$\psi_{LM}^\pi = \sum_{l_1+l_2=L} Y_{LM}^{l_1 l_2}(\hat{\mathbf{R}}, \hat{\mathbf{r}}_1) G_{LM}^{l_1 l_2}(R, r_1, r_2)$$

$$G_{l_1 l_2}^{L\pi}(R, r_1, r_2) = \sum_{n=1}^{N} C_n Re \left[e^{\alpha_n R - \beta_n r_1 - \gamma_n r_2} \right] + D_n Im \left[e^{\alpha_n R - \beta_n r_1 - \gamma_n r_2} \right] \quad (1)$$

2 Fine and hyperfine splitting of the levels in HT$^+$

The leading correction to the nonrelativistic energy is the relativistic correction of order $m\alpha^4$ determined by the Breit-Pauli Hamiltonian [4, 5].

The spin-dependent part of the Breit-Pauli Hamiltonian for a system of particles of spin 1/2 has the following form:

$$\begin{aligned}
H_{\text{HFS}} = &- \frac{e^2}{c^2} \sum_{j \neq i} \frac{Z_i Z_j c_S^{(j)} \left[\mathbf{r}_{ij} \times \mathbf{p}_j \right] \mathbf{s}_j}{2m_j^2 r_{ij}^3} \\
&- \frac{e^2}{c^2} \sum_{j > i} \frac{Z_i Z_j c_F^{(i)} \left[\mathbf{r}_{ij} \times \mathbf{p}_j \right] \mathbf{s}_i - c_F^{(j)} \left[\mathbf{r}_{ij} \times \mathbf{p}_j \right] \mathbf{s}_j}{m_i m_j r_{ij}^3} \\
&+ \sum_{i > j} \left[\frac{\boldsymbol{\mu}_i \boldsymbol{\mu}_j}{r_{ij}^3} - 3 \frac{(\boldsymbol{\mu}_i \mathbf{r}_{ij})(\boldsymbol{\mu}_j \mathbf{r}_{ij})}{r_{ij}^5} \right] - \frac{8\pi}{3} \boldsymbol{\mu}_i \boldsymbol{\mu}_j \delta(r_{ij}) \quad (2)
\end{aligned}$$

Here $\boldsymbol{\mu}_i = \left(c_F^{(i)} Z_i / 2m_i c \right) \boldsymbol{\sigma}_i$ is an operator of magnetic moment, coefficients c_F and c_S are defined

$$c_F^{(i)} = 1 + k_i, \qquad c_S^{(i)} = 1 + 2k_i \quad (3)$$

where k_i is an anomalous magnetic moment of a particle. We adopt the following coupling scheme:

$$\mathbf{F} = \mathbf{I}_p + \mathbf{I}_t \qquad \mathbf{S} = \mathbf{F} + \mathbf{s_e} \qquad \mathbf{J} = \mathbf{S} + \mathbf{L} \quad (4)$$

Averaging over spatial degrees of freedom we obtain the effective Hamiltonian, which depends on the spin and orbital angular momentum variables (see [5] for numerical results):

$$\begin{aligned}
H_{\text{eff}} = &\ E_1 \left(\mathbf{s}_e \cdot \mathbf{I}_p \right) + E_2 \left(\mathbf{s}_e \cdot \mathbf{I}_t \right) + E_3 (\mathbf{s}_e \cdot \mathbf{L}) + E_4 \left(\mathbf{I}_p \cdot \mathbf{L} \right) + E_5 \left(\mathbf{I}_t \cdot \mathbf{L} \right) \\
&+ E_6 \left\{ 2L(L+1) \left(\mathbf{s}_e \cdot \mathbf{I}_p \right) - 3 \left[(\mathbf{L} \cdot \mathbf{s}_e) \left(\mathbf{L} \cdot \mathbf{I}_p \right) + \left(\mathbf{L} \cdot \mathbf{I}_p \right) (\mathbf{L} \cdot \mathbf{s}_e) \right] \right\} \\
&+ E_7 \left\{ 2L(L+1) \left(\mathbf{s}_e \cdot \mathbf{I}_t \right) - 3 \left[(\mathbf{L} \cdot \mathbf{s}_e) \left(\mathbf{L} \cdot \mathbf{I}_t \right) + \left(\mathbf{L} \cdot \mathbf{I}_t \right) (\mathbf{L} \cdot \mathbf{s}_e) \right] \right\} \\
&+ E_8 \left\{ 2L(L+1) \left(\mathbf{I}_p \cdot \mathbf{I}_t \right) - 3 \left[(\mathbf{L} \cdot \mathbf{I}_p) \left(\mathbf{L} \cdot \mathbf{I}_t \right) + (\mathbf{L} \cdot \mathbf{I}_t) \left(\mathbf{L} \cdot \mathbf{I}_p \right) \right] \right\} \quad (5)
\end{aligned}$$

Table 1 Polarizabilities of the HD$^+$ molecular ion in atomic units

v	$L=0$	$L=1$		$L=2$		$L=3$		$L=4$		$L=5$	
	α_s	α_s	α_t	α_s	α_t	α_s	α_t	α_s	α_t	α_s	α_s
0	395.30633	3.99015	175.48275	4.00956	13.82797	4.03878	3.19075	4.07794	1.10141	4.12721	0.47319
1	462.65271	4.70314	205.20067	4.72694	16.14340	4.76278	3.71557	4.81084	1.27799	4.87136	0.54642
2	540.68636	5.56925	239.58035	5.59871	18.81611	5.64313	4.31921	5.70273	1.48001	5.77786	0.62955
3	631.40288	6.63284	279.47585	6.66965	21.91000	6.72541	5.01516	6.80017	1.71152	6.89451	0.72396
4	737.31802	7.95478	325.95893	8.00132	25.50477	8.07195	5.82011	8.16691	1.97742	8.28690	0.83127
5	861.64968	9.61839	380.39514	9.67856	29.70139	9.76943	6.75494	9.89175	2.28374	10.04654	0.95337
6	1008.5802	11.74323	444.54814	11.82178	34.62944	11.94052	7.84610	12.10056	2.63789	12.30342	1.09241
7	1183.6432	14.50032	520.73882	14.60466	40.45801	14.76254	9.12757	14.97563	3.04910	15.24624	1.25088
8	1394.3075	18.14238	612.07821	18.28368	47.41173	18.49776	10.64364	18.78717	3.52889	19.15548	1.43147
9	1650.8846	23.05215	722.82833	23.24788	55.79504	23.54473	12.45301	23.94684	4.09171	24.45984	1.63690
10	1967.9875	29.82774	858.97404	30.10584	66.03006	30.52844	14.63477	31.10210	4.75562	31.83608	1.86935

Table 2 Polarizabilities of the H_2^+ molecular ion in atomic units

v	$L=0$	$L=1$		$L=2$		$L=3$		$L=4$		$L=5$	
	α_s	α_s	α_t	α_s	α_t	α_s	α_t	α_s	α_t	α_s	α_s
0	3.1687258	3.1783035	−0.8033729	3.1975081	−0.1931423	3.2264392	−0.0914467	3.2652493	−0.0544769	3.3141473	−0.0367142
1	3.8975634	3.9101018	−1.1442051	3.9352574	−0.2751013	3.9731892	−0.1302653	4.0241411	−0.0776138	4.0884471	−0.0523179
2	4.8215004	4.8380889	−1.6000689	4.8713900	−0.3847653	4.9216560	−0.1822373	4.9892726	−0.1086157	5.0747693	−0.0732474
3	6.0093275	6.0315483	−2.2129563	6.0761862	−0.5322759	6.1436389	−0.2521973	6.2345166	−0.1503892	6.3496578	−0.1014845
4	7.5604532	7.5906530	−3.0434869	7.6513642	−0.7322875	7.7432180	−0.3471422	7.8671844	−0.2071498	8.0246002	−0.1399110
5	9.6217735	9.6635170	−4.1811566	9.7475033	−1.0064626	9.8747452	−0.4774336	10.046804	−0.2851555	10.265837	−0.1928182
6	12.416000	12.474853	−5.7615823	12.593371	−1.3876723	12.773211	−0.6588274	13.016932	−0.3939491	13.328069	−0.2667729
7	16.290999	16.375936	−7.9965515	16.547168	−1.9273337	16.807463	−0.9160304	17.161118	−0.5485440	17.614095	−0.3721509
8	21.809473	21.935532	−11.228720	22.189990	−2.7087984	22.577626	−1.2892120	23.105870	−0.7734466	23.785138	−0.5259729
9	29.920328	30.113886	−16.036300	30.505195	−3.8730473	31.102847	−1.8465559	31.920266	−1.1104555	32.976407	−0.7574477
10	42.306330	42.616316	−23.445884	43.244200	−5.6711124	44.206257	−2.7100058	45.528094	−1.6347702	47.246181	−1.1195247

Table 3 Polarizabilities of the D_2^+ molecular ion in atomic units

v	$L=0$	$L=1$		$L=2$		$L=3$		$L=4$		$L=5$	
	α_s	α_s	α_t	α_s	α_t	α_s	α_t	α_s	α_t	α_s	α_t
0	3.0719887	3.0765904	−0.7579521	3.0858052	−0.1813435	3.0996560	−0.0852443	3.1181777	−0.0503016	3.1414173	−0.0335048
1	3.5530258	3.5585822	−0.9782731	3.5697111	−0.2340592	3.5864444	−0.1100266	3.6088309	−0.0649271	3.6369364	−0.0432481
2	4.1195817	4.1263238	−1.2485988	4.1398301	−0.2987476	4.1601453	−0.1404432	4.1873367	−0.0828824	4.2214959	−0.0552137
3	4.7912827	4.7995087	−1.5808716	4.8159913	−0.3782716	4.8407920	−0.1778439	4.8740043	−0.1049671	4.9157545	−0.0699367
4	5.5933149	5.6034134	−1.9904009	5.6236531	−0.4763025	5.6541185	−0.2239603	5.6949390	−0.1322078	5.7462891	−0.0881048
5	6.5583187	6.5708021	−2.4970077	6.5958274	−0.5975951	6.6335113	−0.2810366	6.6840342	−0.1659357	6.7476365	−0.1106108
6	7.7290547	7.7446049	−3.1266348	7.7757864	−0.7483752	7.8227607	−0.3520126	7.8857801	−0.2078964	7.9651778	−0.1386263
7	9.1622096	9.1817469	−3.9136471	9.2209342	−0.9368936	9.2799934	−0.4407873	9.3592871	−0.2604068	9.4592730	−0.1737083
8	10.933925	10.958708	−4.9041723	11.008431	−1.1742306	11.083398	−0.5526002	11.184144	−0.3265836	11.311297	−0.2179539
9	13.147977	13.179752	−6.1610454	13.243527	−1.4754879	13.339760	−0.6946003	13.469145	−0.4106838	13.632624	−0.2742310
10	15.948121	15.989359	−7.7712809	16.072159	−1.8615919	16.197178	−0.8766990	16.365416	−0.5186172	16.578236	−0.3465280

3 Spin-independent relativistic corrections

The leading order relativistic corrections are described by the Breit-Pauli Ha-mil-to-nian. The complete spin-independent contribution at this order is

$$E_{\alpha^2} = E_{rc}^{(2)} + E_{kin}^{(2)} + E_{tr-ph}^{(2)} + E_{Darwin}^{(2)} + E_{nuc}^{(2)}, \tag{6}$$

where $E_{rc}^{(2)}$ — relativistic correction for the bound electron, $E_{kin}^{(2)}$ — relativistic kinetic energy correction for heavy particles, $E_{tr-phs}^{(2)}$ — recoil corrections, $E_{Darwin}^{(2)}$ — for the proton (triton), spin 1/2 point-like particle, $E_{nuc}^{(2)}$ — nuclear spin-dependent recoil corrections.

Detailed calculations of the relativistic corrections to the ro-vibrational energies of the HT^+ ion at this order are given in [5].

4 Polarizability

The static dipole polarizability tensor is reduced to scalar α_s and tensor α_t terms, which may be expressed in terms of three contributions corresponding to the possible values of the rotational angular momentum quantum number of the intermediate state: $L' = L \pm 1$ or $L' = L$

$$
\begin{aligned}
a_+ &= \frac{2}{2L+1} \sum_p \frac{\langle vL\|\mathbf{d}\|p(L+1)\rangle\langle p(L+1)\|\mathbf{d}\|vL\rangle}{E_0 - E_p}, \\
a_0 &= -\frac{2}{2L+1} \sum_p \frac{\langle vL\|\mathbf{d}\|pL\rangle\langle pL\|\mathbf{d}\|vL\rangle}{E_0 - E_p}, \\
a_- &= \frac{2}{2L+1} \sum_p \frac{\langle vL\|\mathbf{d}\|p(L-1)\rangle\langle p(L-1)\|\mathbf{d}\|vL\rangle}{E_0 - E_p},
\end{aligned}
\tag{7}
$$

and

$$
\begin{aligned}
\alpha_s &= \alpha_0 + \frac{L(L+1)}{3}\alpha_1 = \frac{1}{3}[a_+ + a_0 + a_-], \\
\alpha_t &= \alpha_1/2 = -\frac{a_+}{2(L+1)(2L+3)} + \frac{a_0}{2L(L+1)} - \frac{a_-}{2L(2L-1)}.
\end{aligned}
\tag{8}
$$

Our results are presented in Tables 1-3, details may be found in [5].

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