Leading-order relativistic corrections to the dipole polarizability of hydrogen molecular ions

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Abstract
The static dipole polarizability for the hydrogen molecular ions H_2^+, HD^+, and D_2^+ are calculated. These new data for polarizability take into account the leading-order relativistic corrections to the wave function of the three-body system resulting from the Breit–Pauli Hamiltonian of $m\alpha^4$ order. Our study covers a wide range of rotational ($J = 0 - 5$) and vibrational ($v = 0 - 10$) states, which are of practical interest for precision spectroscopy of the hydrogen molecular ions.

Keywords: hydrogen molecular ions, laser spectroscopy, static polarizability, relativistic corrections

1. Introduction

It has been shown recently [1] that simple molecular ions have potential uses as optical clocks with very good stability. An essential ingredient for the high fidelity of such clocks is a good knowledge of the molecule reaction on the external fields appeared in the experimental setup. For hydrogen molecular ions (HMIs), as the simplest three-body system, such data can be rigorously obtained from the *ab initio* calculations with very high precision. The nonrelativistic polarizability of ro-vibrational states with up to eight or sometimes even more significant digits is now available for a wide range of states [2–5]. It is easy to show that relativistic corrections to polarizability enters at a relative order of $\mathcal{O}(\alpha^2)$ or contribute to about 10^{-4} of relative precision [6].

Furthermore, there are many experiments being carried out at present with the aim of obtaining a better determination of the proton-to-electron-mass ratio by using ro-vibrational transition spectroscopy [7, 8] and to study the hyperfine structure of the HMI states [9, 10]. The present status of theory for the ro-vibrational transitions is the fractional uncertainty of $\sim 7 \times 10^{-12}$ for the fundamental transitions in HMI [11] and for the hyperfine structure, precision achieved is at 1 ppm level [12].

In this work we carry out calculations of the leading-order relativistic correction to the dipole polarizability of the hydrogen molecular ions H_2^+, HD^+, and D_2^+. We take into consideration a wide range of ro-vibrational states: $J = 0 - 5$, $v = 0 - 10$. This is the first systematic study of the relativistic effects to polarizability of the HMIs for a variety of states. The higher order ($\mathcal{O}(\alpha^3)$) radiative corrections in principle may be also taken into account, so far that has been done rigorously only for the helium ground state [13, 14]. In our present work we do not touch this issue, thus our current predictions are limited to 6–7 significant digits as a physically meaninful quantity.

We adopt atomic units ($m_e = \hbar = e = 1$) throughout this work.

2. Theory

2.1. Nonrelativistic dipole polarizability

We start from the nonrelativistic Schrödinger equation:

$$(H_0 - E_0)\Psi_0 = 0, \quad H_0 = \frac{\mathbf{P}_1^2}{2M_1} + \frac{\mathbf{P}_2^2}{2M_2}$$

$$- \frac{\mathbf{p}_e^2}{2m_e} + \frac{Z_1 Z_2}{R} - \frac{Z_1}{r_1} - \frac{Z_2}{r_2}, \quad (1)$$

Table 1. Test of convergence of the numerical results. The groung state of H_2^+ molecular ion is chosen for consideration. N is the number of basis functions for initial and intermediate states used in calculations. For convenience of comparison with other authors the values of nuclear masses have been taken: $M_p = 1836.152701\, m_e$ and $M_d = 3670.483014\, m_e$. Atomic units are used for all quantities.

N	E_{NR}	α_d	$(1/c)^2 \alpha_B \times 10^2$
2000	$-0.59713\ 90631\ 23404\ 0757$	$3.16872\ 58022\ 7017$	-1.52753848
3000	$-0.59713\ 90631\ 23405\ 0374$	$3.16872\ 58026\ 7529$	-1.52753844
4000	$-0.59713\ 90631\ 23405\ 0730$	$3.16872\ 58026\ 7610$	-1.52753841
5000	$-0.59713\ 90631\ 23405\ 0747$	$3.16872\ 58026\ 7613$	-1.52753839

where $\mathbf{P}_i$ and M_i are impulses and masses of nuclei (proton or deuteron), R is the internuclear distance, r_1 and r_2 are the distances from nuclei 1 and 2 to the electron, respectively. Z_1 and Z_2 are charges of the nuclei, in what follows we assume $Z_1 = Z_2 = Z$. The nonrelativistic state $\Psi_0 = |v\,J\rangle$ is the unperturbed state characterized by the vibrational and rotational quantum numbers v, J, and E_0 is the state energy.

The interaction with an external electric field $\mathcal{E}$ in the electric dipole representation takes the form

$$V_p = -\boldsymbol{\mathcal{E}}\cdot\boldsymbol{d}, \qquad \mathbf{d} = e[Z(\mathbf{R}_1 + \mathbf{R}_2) - \mathbf{r}], \qquad (2)$$

where $\mathbf{d}$ is the electric dipole moment of the HMI, and $\mathbf{R}_{1,2}$ and $\mathbf{r}$ are the position vectors of the nuclei and of the electron with respect to the center of mass of the ion.

The change of energy due to polarizability of molecular ions is expressed by

$$
\begin{aligned}
E_p^{(2)} &= \langle\Psi_0|V_p(E_0 - H_0)^{-1}V_p|\Psi_0\rangle \\
&= \mathcal{E}^i \mathcal{E}^j \langle\Psi_0|d^i(E_0 - H_0)^{-1}d^j|\Psi_0\rangle \\
&= -\frac{1}{2}\alpha_d^{ij}\mathcal{E}^i\mathcal{E}^j,
\end{aligned} \qquad (3)
$$

where α^{ij} is a tensor of polarizability of rank 2,

$$\alpha_d^{ij} = -2\langle\Psi_0|d^i(E_0 - H_0)^{-1}d^j|\Psi_0\rangle. \qquad (4)$$

The static dipole polarizability tensor is then reduced [15] to scalar, α_s, and tensor, α_t, terms, which may be expressed by the three contributions corresponding to the possible values of J' for the angular momentum of the intermediate state: $J' = J \pm 1$, or $J' = J$.

$$
\begin{aligned}
a_+ &= \frac{2}{2J+1}\sum_n \frac{\langle 0J\|\mathbf{d}\|n(J+1)\rangle\langle n(J+1)\|\mathbf{d}\|0J\rangle}{E_0 - E_n}, \\
a_0 &= -\frac{2}{2J+1}\sum_n \frac{\langle 0J\|\mathbf{d}\|nJ\rangle\langle nJ\|\mathbf{d}\|0J\rangle}{E_0 - E_n}, \\
a_- &= \frac{2}{2J+1}\sum_n \frac{\langle 0J\|\mathbf{d}\|n(J-1)\rangle\langle n(J-1)\|\mathbf{d}\|0J\rangle}{E_0 - E_n}.
\end{aligned} \qquad (5)
$$

where E_n is the energy of the intermediate state $|nJ'\rangle$. The polarizability tensor operator on a subspace of fixed total orbital angular momentum J may now be expressed:

$$\alpha_d^{ij} = \alpha_s + \alpha_t\left[J^iJ^j + J^jJ^i - \frac{2}{3}\mathbf{J}^2\right], \qquad (6)$$

where

$$
\begin{aligned}
\alpha_s &= \frac{1}{3}[a_+ + a_0 + a_-], \\
\alpha_t &= -\frac{a_+}{2(J+1)(2J+3)} \\
&\quad + \frac{a_0}{2J(J+1)} - \frac{a_-}{2J(2J-1)}.
\end{aligned} \qquad (7)
$$

The basic formalism in a shorthand vector notation may be rewritten as follows:

$$
\begin{aligned}
\Psi_1 &= (E_0 - H_0)^{-1}\mathbf{d}|\Psi_0\rangle \\
\alpha_d &= \langle\Psi_0|\mathbf{d}|\Psi_1\rangle = \langle\Psi_0|\mathbf{d}(E_0 - H_0)^{-1}\mathbf{d}|\Psi_0\rangle.
\end{aligned} \qquad (8)
$$

The tables for a complete set of the nonrelativistic results for H_2^+, HD^+ and D_2^+ ions within the range of the ro-vibrational states under consideration are presented in [5].

2.2. Relativistic corrections to the dipole polarizability

Relativistic correction α_B to the static dipole polarizability:

$$\alpha_d = \alpha_d^{(\mathrm{nonrel})} + (1/c)^2\,\alpha^B, \qquad (9)$$

is expressed:

$$
\begin{aligned}
\alpha_B &= 2\langle\Psi_B|\mathbf{d}|\Psi_1\rangle + \langle\Psi_1|H_B - \langle H_B\rangle|\Psi_1\rangle \\
&= 2\langle\Psi_0|H_B Q(E_0 - H_0)^{-1}Q\mathbf{d}|(E_0 - H_0)^{-1}\mathbf{d}\Psi_0\rangle \\
&\quad + \langle\Psi_0|\mathbf{d}(E_0 - H_0)^{-1}(H_B - \langle H_B\rangle)(E_0 - H_0)^{-1}\mathbf{d}|\Psi_0\rangle,
\end{aligned} \qquad (10)
$$

here H_B is the Hamiltonian of the Breit-Pauli interaction for the three-body system [16, 17]:

$$
\begin{aligned}
H_B = &-\frac{\mathbf{p}_e^4}{8m_e^3} + \frac{4\pi}{8m_e^2}[Z_1\delta(\mathbf{r}_1) + Z_2\delta(\mathbf{r}_2)] \\
&-\frac{\mathbf{P}_1^4}{8M_1^3} - \frac{\mathbf{P}_2^4}{8M_2^3} + \frac{Z_1}{2m_eM_1}\left(\frac{\mathbf{p}_e\mathbf{P}_1}{r_1} + \frac{\mathbf{r}_1(\mathbf{r}_1\mathbf{p}_e)\mathbf{P}_1}{r_1^3}\right) \\
&+\frac{Z_2}{2m_eM_2}\left(\frac{\mathbf{p}_e\mathbf{P}_2}{r_2} + \frac{\mathbf{r}_2(\mathbf{r}_2\mathbf{p}_e)\mathbf{P}_2}{r_2^3}\right) \\
&-\frac{Z_1Z_2}{2M_1M_2}\left(\frac{\mathbf{P}_1\mathbf{P}_2}{R} + \frac{\mathbf{R}(\mathbf{R}\mathbf{P}_1)\mathbf{P}_2}{R^3}\right),
\end{aligned} \qquad (11)
$$

and Ψ_B is the relativistic correction to the nonrelativistic wave function Ψ_0:

$$\Psi_B = Q(E_0 - H)^{-1}QH_B|\Psi_0\rangle. \qquad (12)$$

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Table 2. Polarizability of the H_2^+ molecular ion (in a.u.).

v	$J = 0$	$J = 1$		$J = 2$		$J = 3$		$J = 4$		$J = 5$	
	α_s	α_s	α_t	α_s	α_t	α_s	α_t	α_s	α_t	α_s	α_t
0	3.1685731	3.1781425	−0.8033502	3.1973545	−0.1931356	3.2262879	−0.0914433	3.2650990	−0.0544748	3.3139976	−0.0367128
1	3.8973934	3.9099178	−1.1441799	3.9350819	−0.2750942	3.9730164	−0.1302617	4.0239695	−0.0776116	4.0882763	−0.0523165
2	4.8213113	4.8378793	−1.6000406	4.8711902	−0.3847577	4.9214594	−0.1822335	4.9890778	−0.1086134	5.0745756	−0.0732459
3	6.0091177	6.0313112	−2.2129254	6.0759600	−0.5322677	6.1434165	−0.2521933	6.2342968	−0.1503867	6.3494400	−0.1014829
4	7.5602216	7.5903867	−3.0434518	7.6511105	−0.7322788	7.7429690	−0.3471380	7.8669387	−0.2071473	8.0243574	−0.1399094
5	9.6215210	9.6632217	−4.1811193	9.7472225	−1.0064538	9.8744707	−0.4774294	10.046534	−0.2851531	10.265571	−0.1928167
6	12.415730	12.474532	−5.7615463	12.593067	−1.3876642	12.772916	−0.6588237	13.016644	−0.3939470	13.327789	−0.2667717
7	16.290723	16.375602	−7.9965248	16.546853	−1.9273285	16.807161	−0.9160282	17.160827	−0.5485430	17.613818	−0.3721506
8	21.809221	21.935211	−11.228720	22.189694	−2.7088006	22.577348	−1.2892136	23.105612	−0.7734482	23.784904	−0.5259745
9	29.920158	30.113640	−16.036365	30.504982	−3.8730665	31.102663	−1.8465662	31.920118	−1.1104628	32.976304	−0.7574536
10	42.306376	42.616282	−23.446097	43.244214	−5.6711694	44.206322	−2.7100353	45.528226	−1.6347899	47.246401	−1.1195399

Table 3. Polarizability of the D_2^+ molecular ion (in a.u.).

v	$J=0$	$J=1$		$J=2$		$J=3$		$J=4$		$J=5$	
	α_s	α_s	α_t	α_s	α_t	α_s	α_t	α_s	α_t	α_s	α_t
0	3.0718385	3.0764328	−0.7579298	3.0856549	−0.1813369	3.0995081	−0.0852409	3.1180309	−0.0502995	3.1412711	−0.0335034
1	3.5528638	3.5584089	−0.9782491	3.5695458	−0.2340523	3.5862817	−0.1100231	3.6086695	−0.0649249	3.6367756	−0.0432467
2	4.1194070	4.1261334	−1.2485728	4.1396485	−0.2987404	4.1599666	−0.1404395	4.1871595	−0.0828801	4.2213195	−0.0552122
3	4.7910944	4.7993001	−1.5808434	4.8157922	−0.3782640	4.8405962	−0.1778400	4.8738102	−0.1049648	4.9155614	−0.0699351
4	5.5931121	5.6031855	−1.9903702	5.6234356	−0.4762945	5.6539046	−0.2239563	5.694727	−0.1322053	5.7460784	−0.0881031
5	6.5581008	6.5705539	−2.4969746	6.5955906	−0.5975866	6.6332784	−0.2810323	6.6838036	−0.1659331	6.7474075	−0.1106091
6	7.7288214	7.7443358	−3.1265993	7.7755297	−0.7483664	7.8225084	−0.3520083	7.8855305	−0.2078938	7.9649300	−0.1386246
7	9.1619614	9.1814571	−3.9136098	9.2206579	−0.9368846	9.2797220	−0.4407829	9.3590190	−0.2604042	9.4590076	−0.1737066
8	10.933664	10.958399	−4.9041347	11.008137	−1.1742218	11.083110	−0.5525959	11.183859	−0.3265811	11.311016	−0.2179523
9	13.147705	13.179427	−6.1610100	13.243217	−1.4754799	13.339457	−0.6945965	13.468847	−0.4106816	13.632332	−0.2742296
10	15.947847	15.989024	−7.7712522	16.071842	−1.8615859	16.196869	−0.8766962	16.365114	−0.5186156	16.577941	−0.3465270

Table 4. Polarizability of the HD$^+$ molecular ion (in a.u.).

| v | $J = 0$ | $J = 1$ | | $J = 2$ | | $J = 3$ | | $J = 4$ | | $J = 5$ | |
	α_s	α_s	α_t	α_s	α_t	α_s	α_t	α_s	α_t	α_s	α_t
0	395.27754	3.9899486	175.46989	4.0093758	13.826954	4.0386030	3.1905097	4.0777634	1.1013280	4.1270299	0.4731528
1	462.62017	4.7029195	205.18613	4.7267328	16.142249	4.7625805	3.7153046	4.8106388	1.2779012	4.8711642	0.5463772
2	540.64963	5.5690125	239.56394	5.5984707	18.814812	5.6429097	4.3189073	5.7025090	1.4799073	5.7776380	0.6295018
3	631.36149	6.6325616	279.45735	6.6693071	21.908555	6.7251653	5.0148197	6.7999232	1.7113981	6.8942638	0.7239099
4	737.27142	7.9543692	325.93821	8.0010358	25.503117	8.0716799	5.8197299	8.1666401	1.9772885	8.2866362	0.8312163
5	861.59725	9.6180552	380.37171	9.6782520	29.699534	9.7691277	6.7545125	9.8914502	2.2835914	10.046247	0.9533009
6	1008.5213	11.742867	444.52180	11.821446	34.627354	11.940196	7.8456173	12.100244	2.6377250	12.303109	1.0923369
7	1183.5771	14.499937	520.70922	14.604304	40.455664	14.762192	9.1270207	14.975296	3.0489087	15.245914	1.2507930
8	1394.2333	18.141977	612.04499	18.283320	47.409088	18.497399	10.643024	18.786825	3.5286700	19.155146	1.4313721
9	1650.8015	23.051744	722.79107	23.247524	55.792076	23.544383	12.452318	23.946515	4.0914633	24.459532	1.6367943
10	1967.8945	29.827372	858.93232	30.105532	66.026733	30.528154	14.633990	31.101840	4.7553467	31.835850	1.8692259

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Table 5. Nonrelativistic static dipole polarizability (in a.u.). Comparison with previous calculations. For convenience of comparison the values of nuclear masses have been taken: $M_p = 1836.152701 \, m_e$ and $M_d = 3670.483014 \, m_e$.

	H_2^+	D_2^+	HD^+
Hilico *et al* [2]	3.16872 5803	3.07198 8696	395.30632 88
Olivares Pilón, Baye [3]	3.16872 58026 5		
Li-Yan Tang *et al* [19]	3.16872 58026 76(1)	3.07198 86956 6(7)	395.30632 87972(1)[a]
this work	3.16872 58026 7613(1)	3.07198 86956 7511(2)	395.30632 8797231(3)

[a] Zong-Chao Yan *et al* [20].

Operator Q in the above equations is the projection operator on the subspace orthogonal to $|\Psi_0\rangle$. It is worthwhile noting that in atomic units $c = \alpha^{-1}$, where α is the fine structure constant. Expressions (8) and (12) represent linear equations for the wave functions Ψ_1 and Ψ_B, respectively. And thus the final value for α_B may be obtain without full diagonalization of the Hamiltonian (1) on the subspace of the variational basis set and futher summation over states and pseudostates, whichmakes numerical procedure more fast and stable.

It is easily seen that the relativistic correction to the polarizability energy shift is the third-order contribution of the pertubation theory. It is linear in the parameter α^2, the natural parameter of the relativistic expansion, and is quadratic in the electric field density $\mathcal{E}$.

3. Results

In our calculations we use a variational method based on exponential expansion with randomly chosen exponents, which has been described in details in a variety of our previous works [5, 17] and we omit here an explicit formulation of the method.

First we study convergence of our numerical results. For demonstration we take the ground ($J = 0$, $v = 0$) state of the H_2^+ molecular ion. As is seen from the table 1, the relativistic contribution α_B may be determined with at least eight significant digits while the nonrelativistic polarizability obtained is more precise than the best known in the literature [19].

A complete set of data of our numerical calculations is collected in tables 2–4, the polarizabilities for H_2^+, D_2^+ and HD^+ molecular ions, respectively, and is the main result of the present work. In this case the values for masses of nuclei have been taken from the latest published adjustment [18] of the CODATA group: $M_p = 1836.15267245 \, m_e$ and $M_d = 3670.4829652 \, m_e$. They are also in accordance with our previous nonrelativistic calculations [5]. To avoid numerical errors we have used the sextuple precision arithmetics (48 decimal digits).

In table 5 we compare our results with previous ones. Due to an absence of data for relativistic polarizability we include in our table only the nonrelativistic values for polarizability. In all cases our results demonstrate perfect agreement with previous calculations.

In conclusion, we want to state that new data for the polarizabilities of the hydrogen molecular ions have been obtained, which is significant up to 6–7 digits as physically observable quantities, while the achieved numerical precision is of eight or even more digits. These data may be used to increase the precision of physically meaningful values by including higher order QED corrections [13]. We want to note that this is the first systematic calculation that includes the leading-order relativistic corrections.

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