PHYSICAL REVIEW A **74**, 052506 (2006)

Leading-order relativistic and radiative corrections to the rovibrational spectrum of H_2^+ and HD^+ molecular ions

Vladimir I. Korobov
Bogolyubov Laboratory of Theoretical Physics, Joint Institute for Nuclear Research, Dubna 141980, Russia

(Received 28 August 2006; published 28 November 2006)

High-precision variational calculations for the rovibrational states in the range of the total orbital momentum $L=0-4$ and vibrational quantum number $v=0-4$ for the H_2^+ and HD^+ molecular ions are presented. Relativistic and radiative corrections of orders $R_\infty\alpha^2$, $R_\infty\alpha^2(m/M)$, $R_\infty\alpha^3$, $R_\infty\alpha^3(m/M)$, and, partially, $R_\infty\alpha^4$ are taken into consideration as well as the finite size structure of proton and deuteron. It is found that the relative theoretical uncertainty due to uncalculated contributions of orders $R_\infty\alpha^4$ and higher to the *reference* transition frequency interval $(L=0,v=0)\rightarrow(0,1)$ is about 1 ppb.

DOI: 10.1103/PhysRevA.74.052506 PACS number(s): 31.30.Jv, 31.15.Pf, 31.15.Ar

I. INTRODUCTION

In recent years laser spectroscopy experiments have been proposed [1,2] for high precision measurements of the vibrational spectrum of the hydrogen molecular ions H_2^+ and HD^+. These experiments present metrological interest and are aimed at a sup-ppb precision. In order to improve the present accuracy of the electron-to-proton mass ratio [3] the uncertainty of the spectroscopic data (as well as of the theoretical calculations of the spectra to compare to) should be below 1 part per billion (1 ppb). To meet these stringent requirements, the theoretical calculations should achieve at least a level of 10 kHz (or $\sim 10^{-11}$ in atomic units).

The variational calculations of the nonrelativistic energies during past years have reached a numerical precision of $10^{-15}-10^{-24}$ a.u. [4–9]. The ultimate accuracy of $\sim 10^{-24}$ a.u. has been obtained for the H_2^+ molecular ion ground state [8]. These calculations demonstrate that at least the nonrelativistic rovibrational transition frequencies can be determined with the accuracy well below the 1 kHz level.

The next important step is evaluation of the relativistic and radiative corrections to the binding energies of the rovibrational levels. This can be systematically performed using series expansion of the binding energy in terms of the coupling constant, in our case, the fine structure constant, α. The key quantity for the leading order $R_\infty\alpha^3$ radiative correction, the Bethe logarithm, have been obtained in our previous works for a range of states of the total orbital momentum $(L=0-4)$ and vibrational quantum number $(v=0-4)$ for HD^+ [10] and H_2^+ [11]. This work is aimed to continue our program and to calculate contributions of orders $R_\infty\alpha^2$, $R_\infty\alpha^2(m/M)$, $R_\infty\alpha^3$, $R_\infty\alpha^3(m/M)$, and partially, $R_\infty\alpha^4$.

The following notations are used throughout this paper. $\mathbf{P}_1$, $\mathbf{P}_2$, and $\mathbf{p}_e$ are the momenta and $\mathbf{R}_1$, $\mathbf{R}_2$, $\mathbf{r}_e$ are the coordinates of nuclei and electron with respect to the center of mass of a molecule, and

$$\mathbf{r}_1=\mathbf{r}_e-\mathbf{R}_1, \quad \mathbf{r}_2=\mathbf{r}_e-\mathbf{R}_2, \quad \mathbf{R}=\mathbf{R}_2-\mathbf{R}_1.$$

Here we assume that indices 1 and 2 stand for the protons in case of H_2^+, and $\mathbf{R}_1\equiv\mathbf{R}_d$—the coordinate of a deuteron in case of HD^+. The atomic units $(\hbar=e=m_e=1)$ are employed. We use the CODATA02 recommended values of the fundamental constants [12] for all our calculations.

II. VARIATIONAL WAVE FUNCTION

The variational bound state wave functions were calculated by solving the three-body Schrödinger equation with Coulomb interaction using the variational approach based on the exponential expansion with randomly chosen exponents. This approach has been discussed in a variety of works [13–15]. Details and particular strategy of choice of the variational nonlinear parameters and basis structure that have been adopted in the present work can be found in Ref. [5].

Briefly, 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 follows:

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

$$\begin{aligned}G_{l_1 l_2}^{L\pi}(R,r_1,r_2)=\sum_{n=1}^{N}\big[&C_n\,\mathrm{Re}(e^{-\alpha_n R-\beta_n r_1-\gamma_n r_2})\\&+D_n\,\mathrm{Im}(e^{-\alpha_n R-\beta_n r_1-\gamma_n r_2})\big],\end{aligned} \qquad (1)$$

where the complex exponents, α, β, γ, are generated in a pseudorandom way.

When exponents α_n, β_n, and γ_n are real, the method reveals slow convergence for molecular type Coulomb systems. Thus the use of complex exponents allows to reproduce the oscillatory behavior of the vibrational part of the wave function and to improve convergence [5,15,16].

In Table I the most difficult cases of the last vibrational S

TABLE I. Convergence for the last vibrational state in H_2^+ and HD^+ molecular ions $(L=0)$.

N	$E_{\mathrm{nr}}[H_2^+(v=19)]$	$E_{\mathrm{nr}}[HD^+(v=22)]$
6000	−0.4997312306491204	−0.49986577736371
7000	−0.4997312306491499	−0.49986577838595
8000	−0.4997312306491572	−0.49986577850697
9000	−0.4997312306491612	−0.49986577853072
10000	−0.4997312306491616	−0.49986577853699
extrap	−0.499731230649163(1)	−0.499865778539(2)

1050-2947/2006/74(5)/052506(5)

TABLE II. Nonrelativistic energies, H_2^+.

	$v=0$	$v=1$	$v=2$	$v=3$	$v=4$
$L=0$	−0.59713906307939	−0.58715567909619	−0.57775190441508	−0.56890849873086	−0.56060922084967
$L=1$	−0.59687373878471	−0.58690432091919	−0.57751403405745	−0.56868370826019	−0.56039717140029
$L=2$	−0.59634520548939	−0.58640363152869	−0.57704023716302	−0.56823599297158	−0.55997486482005
$L=3$	−0.59555763898031	−0.58565761187766	−0.57633435021963	−0.56756903483351	−0.55934583822827
$L=4$	−0.59451716923896	−0.58467213422891	−0.57540200329884	−0.56668823662971	−0.55851528162590

states in H_2^+ and HD^+ are considered. It is worthy to note that the latter state has 22 nodes in the wave function and especially difficult for a variational computation. These two examples demonstrate flexibility and efficiency of the variational expansion (1).

Numerical values of the nonrelativistic energies for the rovibrational states are presented in Tables II and III. In general, an accuracy of about $10^{-14}-10^{-15}$ a.u. is achieved when the basis set of $N=3000-4000$ functions is used.

III. LEADING-ORDER RELATIVISTIC CORRECTIONS

The leading order relativistic corrections ($R_\infty\alpha^2$) at present are well understood and are described by the Breit-Pauli Hamiltonian. Consideration of this part can be found in many textbooks, see, for example, Refs. [17,18], or reviews [19]. Here we present in explicit form expressions for different terms, which contribute to this order.

The major contribution comes from the relativistic correction for the bound electron,

$$E_{\rm rc}^{(2)}=\alpha^2\left\langle-\frac{\mathbf{p}_e^4}{8m_e^3}+\frac{4\pi}{8m_e^2}[Z_1\delta(\mathbf{r}_1)+Z_2\delta(\mathbf{r}_2)]\right\rangle. \tag{2}$$

The other corrections are due to a finite mass of nuclei and are called the recoil corrections of orders $R_\infty\alpha^2(m/M)$, $R_\infty\alpha^2(m/M)^2$, etc. The first is the transverse photon exchange,

$$\begin{aligned}E_{\rm tr\text{-}ph}^{(2)}=&\frac{\alpha^2Z_1}{2m_eM_1}\left\langle\frac{\mathbf{p}_e\mathbf{P}_1}{r_1}+\frac{\mathbf{r}_1(\mathbf{r}_1\mathbf{p}_e)\mathbf{P}_1}{r_1^3}\right\rangle\\&+\frac{\alpha^2Z_2}{2m_eM_2}\left\langle\frac{\mathbf{p}_e\mathbf{P}_2}{r_2}+\frac{\mathbf{r}_2(\mathbf{r}_2\mathbf{p}_e)\mathbf{P}_2}{r_2^3}\right\rangle\\&-\frac{\alpha^2Z_1Z_2}{2M_1M_2}\left\langle\frac{\mathbf{P}_1\mathbf{P}_2}{R}+\frac{\mathbf{R}(\mathbf{R}\mathbf{P}_1)\mathbf{P}_2}{R^3}\right\rangle.\end{aligned} \tag{3}$$

The contribution of the last term in (3) is not negligible and amounts to about 10% of $E_{\rm tr\text{-}ph}^{(2)}$.

The next is the relativistic kinetic energy ($E_{\rm kin}=\sqrt{m^2+p^2}\approx m+p^2/2m+\cdots$) correction for heavy particles,

$$E_{\rm kin}^{(2)}=-\alpha^2\left\langle\frac{\mathbf{P}_1^4}{8M_1^3}+\frac{\mathbf{P}_2^4}{8M_2^3}\right\rangle. \tag{4}$$

Further in the $R_\infty\alpha^2$ order, one must consider the nuclear spin dependent recoil corrections. For the proton, spin-$\frac{1}{2}$ particle, one has

$$E_{\rm Darwin}^{(2)}=\frac{\alpha^2 4\pi Z_p}{8M_p^2}\langle\delta(\mathbf{r}_p)\rangle. \tag{5}$$

In case of deuteron (spin one) this term vanishes. The leading-order electric charge finite size correction is defined (both for proton and deuteron) by

$$E_{\rm nuc}^{(2)}=\sum_{i=1,2}\frac{2\pi Z_i(R_i/a_0)^2}{3}\langle\delta(\mathbf{r}_i)\rangle, \tag{6}$$

where R is the root-mean-square (rms) radius of the nuclear electric charge distribution. The rms radius for the proton is $R_p=0.8750(68)$ fm, and for the deuteron, $R_d=2.1394(28)$ fm. These contributions are connected with internal structure of complex particles. For a detailed discussion of this rather nontrivial problem we refer the reader to Refs. [20,21].

The complete contribution to this order thus is

$$E_{\alpha^2}=E_{\rm rc}^{(2)}+E_{\rm kin}^{(2)}+E_{\rm tr\text{-}ph}^{(2)}+E_{\rm Darwin}^{(2)}+E_{\rm nuc}^{(2)}. \tag{7}$$

IV. LEADING-ORDER RADIATIVE CORRECTIONS

The radiative corrections of an order $R_\infty\alpha^3$ for a one electron molecular system can be expressed by the following set

TABLE III. Nonrelativistic energies, HD^+.

	$v=0$	$v=1$	$v=2$	$v=3$	$v=4$
$L=0$	−0.59789796860903	−0.58918182955696	−0.58090370021837	−0.57305054655187	−0.56561104207681
$L=1$	−0.59769812819221	−0.58899111199204	−0.58072182812093	−0.57287727709421	−0.56544616627757
$L=2$	−0.59729964335178	−0.58861082938979	−0.58035919519988	−0.57253181032597	−0.56511744976373
$L=3$	−0.59670488276189	−0.58804326416284	−0.57981800202787	−0.57201626923251	−0.56462694206205
$L=4$	−0.59591734221281	−0.58729178437422	−0.57910149556549	−0.57133378604600	−0.56397766686762

TABLE IV. Mean values of the various operators for the ro vibrational states in the H_2^+ molecular ion.

(L,v)	$\langle \mathbf{p}_e^4 \rangle$	$\langle \delta(\mathbf{r}_1) \rangle$	$\langle \mathbf{P}_1^4 \rangle$	R_{pe}	R_{pp}	Q_{pe}
0 0	6.28566006	0.206736476	79.7976	1.17012	4.60193	−0.13443
0 1	6.12451981	0.201310665	334.898	1.14081	12.8961	−0.13129
0 2	5.97622857	0.196294589	762.804	1.11408	19.8790	−0.12839
0 3	5.84001186	0.191662497	1304.21	1.08980	25.6616	−0.12573
0 4	5.71519854	0.187391848	1908.37	1.06787	30.3383	−0.12329
1 0	6.27803905	0.206491321	85.0505	1.16881	4.83433	−0.13426
1 1	6.11739733	0.201081174	347.549	1.13960	13.0953	−0.13113
1 2	5.96957939	0.196079943	780.922	1.11296	20.0477	−0.12825
1 3	5.83381405	0.191461983	1326.12	1.08876	25.8023	−0.12560
1 4	5.70943357	0.187204849	1932.62	1.06691	30.4531	−0.12317
2 0	6.26290998	0.206004543	96.9109	1.16624	5.29343	−0.13395
2 1	6.10325966	0.200625549	373.998	1.13720	13.4883	−0.13084
2 2	5.95638294	0.195653844	818.125	1.11073	20.3802	−0.12798
2 3	5.82151544	0.191063990	1370.76	1.08670	26.0792	−0.12534
2 4	5.69799573	0.186833736	1981.78	1.06501	30.6783	−0.12293
3 0	6.24049435	0.205283078	117.976	1.16241	5.96806	−0.13348
3 1	6.08231719	0.199950377	416.435	1.13364	14.0648	−0.13040
3 2	5.93683922	0.195022551	876.247	1.10743	20.8670	−0.12756
3 3	5.80330618	0.190474472	1439.63	1.08365	26.4834	−0.12496
3 4	5.68106608	0.186284177	2057.10	1.06219	31.0059	−0.12257
4 0	6.21111375	0.204336991	151.874	1.15740	6.84220	−0.13287
4 1	6.05487522	0.199065216	477.892	1.12898	14.8100	−0.12983
4 2	5.91123830	0.194195146	957.799	1.10310	21.4943	−0.12703
4 3	5.77946208	0.189702063	1534.80	1.07964	27.0022	−0.12446
4 4	5.65890704	0.185564385	2160.23	1.05850	31.4240	−0.12210

of equations (see Refs. [10,22,23]). Only the spin-independent part is considered.

The one-loop self-energy correction ($R_\infty \alpha^3$),

$$E_{se}^{(3)} = \frac{4\alpha^3}{3m_e^2}\left(\ln\frac{1}{\alpha^2} - \beta(L,v) + \frac{5}{6} - \frac{3}{8}\right)\langle Z_1\delta(\mathbf{r}_1) + Z_2\delta(\mathbf{r}_2)\rangle, \tag{8}$$

where

$$\beta(L,v) = \frac{\langle \mathbf{J}(H_0 - E_0)\ln[(H_0 - E_0)/R_\infty]\mathbf{J}\rangle}{\langle [\mathbf{J},[H_0,\mathbf{J}]]/2\rangle} \tag{9}$$

is the Bethe logarithm. The latter quantity presents the most difficult numerical problem in computation of QED corrections for the three-body bound states. In Ref. [10,11] the calculations for the considered range of rovibrational states in H_2^+ and HD^+ have been performed. An operator $\mathbf{J}$ in (9) is the electric current density operator of the system, $\mathbf{J} = \Sigma_a z_a \mathbf{p}_a / m_a$.

The anomalous magnetic moment ($R_\infty \alpha^3$),

$$E_{\text{anom}}^{(3)} = \frac{\pi\alpha^2}{m_e^2}\left[\frac{1}{2}\left(\frac{\alpha}{\pi}\right)\right]\langle Z_1\delta(\mathbf{r}_1) + Z_2\delta(\mathbf{r}_2)\rangle. \tag{10}$$

Sometimes this term is incorporated into Eq. (2) as a contribution from the form factors of an electron [24].

The one-loop vacuum polarization ($R_\infty \alpha^3$),

$$E_{\text{vp}}^{(3)} = \frac{4\alpha^3}{3m^2}\left(-\frac{1}{5}\right)\langle Z_1\delta(\mathbf{r}_1) + Z_2\delta(\mathbf{r}_2)\rangle. \tag{11}$$

The one transverse photon exchange $[R_\infty \alpha^3 (m/M)]$,

$$E_{\text{tr-ph}}^{(3)} = \alpha^3 \sum_{i=1,2}\left[\frac{2Z_i^2}{3m_e M_i}\left(-\ln\alpha - 4\beta(L,v) + \frac{31}{3}\right)\langle\delta(\mathbf{r}_i)\rangle - \frac{14Z_i^2}{3m_e M_i}Q(r_i)\right], \tag{12}$$

where $Q(r)$ is the Q term introduced by Araki and Sucher [25]:

$$Q(r) = \lim_{\rho\to 0}\left\langle \frac{\Theta(r-\rho)}{4\pi r^3} + (\ln\rho + \gamma_E)\delta(\mathbf{r})\right\rangle. \tag{13}$$

It is worthy to note here that the splitting onto nonrecoil and recoil parts [Eqs. (8) and (12)] is not exactly rigorous, since the Bethe logarithm contains contributions both from the self-energy and exchange photon diagrams.

Summarizing the contributions one gets

$$E_{\alpha^3} = E_{se}^{(3)} + E_{\text{anom}}^{(3)} + E_{\text{vp}}^{(3)} + E_{\text{tr-ph}}^{(3)}. \tag{14}$$

TABLE V. Mean values of the various operators for the rovibrational states in the HD^+ molecular ion.

(L,v)	$\langle \mathbf{p}_e^4 \rangle$	$\langle \delta(\mathbf{r}_d) \rangle$	$\langle \delta(\mathbf{r}_p) \rangle$	$\langle \mathbf{P}_d^4 \rangle$	$\langle \mathbf{P}_p^4 \rangle$	R_{de}	R_{pe}	R_{pd}	Q_{de}	Q_{pe}
0 0	6.30019995	0.207348142	0.207042599	104.444	104.372	1.17449	1.17077	5.35463	−0.13486	−0.13459
0 1	6.15902236	0.202601179	0.202288865	449.739	449.457	1.15048	1.14337	15.1448	−0.13211	−0.13184
0 2	6.02761433	0.198166795	0.197845838	1043.443	1042.82	1.12824	1.11812	23.5990	−0.12955	−0.12927
0 3	5.90545344	0.194027841	0.193696014	1814.06	1813.00	1.10768	1.09494	30.8177	−0.12717	−0.12688
0 4	5.79207742	0.190169092	0.189823704	2699.24	2697.67	1.08874	1.07372	36.8881	−0.12496	−0.12466
1 0	6.29445075	0.207163242	0.206857700	110.461	110.385	1.17358	1.16972	5.58956	−0.13474	−0.13447
1 1	6.15359977	0.202426557	0.202114213	464.653	464.362	1.14963	1.14238	15.3506	−0.13200	−0.13172
1 2	6.02250376	0.198001983	0.197680957	1065.26	1064.62	1.12743	1.11720	23.7778	−0.12944	−0.12916
1 3	5.90064189	0.193872418	0.193540480	1841.03	1839.95	1.10692	1.09407	30.9713	−0.12707	−0.12678
1 4	5.78755367	0.190022692	0.189677140	2729.80	2728.21	1.08803	1.07291	37.0184	−0.12486	−0.12457
2 0	6.28301636	0.206795445	0.206489902	123.876	123.790	1.17177	1.16763	6.05510	−0.13450	−0.13423
2 1	6.14281577	0.202079231	0.201766822	495.678	495.368	1.14792	1.14042	15.7580	−0.13177	−0.13150
2 2	6.01234104	0.197674189	0.197353027	1109.94	1109.27	1.12583	1.11536	24.1315	−0.12923	−0.12895
2 3	5.89107470	0.193563325	0.193231163	1895.86	1894.75	1.10542	1.09236	31.2752	−0.12687	−0.12658
2 4	5.77855952	0.189731566	0.189385688	2791.68	2790.06	1.08663	1.07131	37.2756	−0.12467	−0.12438
3 0	6.26602281	0.206248697	0.205943148	147.360	147.259	1.16908	1.16452	6.74278	−0.13415	−0.13388
3 1	6.12679095	0.201562974	0.201250465	545.124	544.785	1.14539	1.13751	16.3592	−0.13144	−0.13116
3 2	5.99724165	0.197187028	0.196865656	1179.45	1178.75	1.12346	1.11263	24.6528	−0.12891	−0.12863
3 3	5.87686248	0.193104023	0.192771520	1980.25	1979.08	1.10319	1.08981	31.7222	−0.12657	−0.12628
3 4	5.76520094	0.189299034	0.188952656	2886.33	2884.65	1.08454	1.06893	37.6533	−0.12439	−0.12410
4 0	6.24365467	0.205528778	0.205223214	184.718	184.592	1.16553	1.16043	7.64024	−0.13368	−0.13341
4 1	6.10570175	0.200883313	0.200570663	616.262	615.880	1.14206	1.13367	17.1427	−0.13100	−0.13072
4 2	5.97737434	0.196545786	0.196224126	1276.61	1275.85	1.12032	1.10904	25.3308	−0.12850	−0.12822
4 3	5.85816669	0.192499571	0.192166604	2096.56	2095.34	1.10026	1.08645	32.3023	−0.12617	−0.12589
4 4	5.74763241	0.188729937	0.188382879	3015.73	3013.98	1.08180	1.06580	38.1419	−0.12402	−0.12373

V. RESULTS

Results of numerical calculation of the mean values of various operators encountered in formulas of the preceding sections are presented in Tables IV and V. The notation is as follows:

$$R_{ne} = -\left\langle \frac{\mathbf{p}_e \mathbf{P}_n}{r_n} + \frac{\mathbf{r}_n(\mathbf{r}_n \mathbf{p}_e)\mathbf{P}_n}{r_n^3} \right\rangle,$$

$$R_{nn} = -\left\langle \frac{\mathbf{P}_1 \mathbf{P}_2}{R} + \frac{\mathbf{R}(\mathbf{R}\mathbf{P}_1)\mathbf{P}_2}{R^3} \right\rangle, \tag{15}$$

Q_{ne} is the Q-term expectation value as it is defined in Eq. (13), n stands for one of the nuclei, p or d. From these data one can easily get rovibrational transition intervals with account of the relativistic and radiative corrections of orders $R_\infty \alpha^2$, $R_\infty \alpha^2(m/M)$, $R_\infty \alpha^3$, and $R_\infty \alpha^3(m/M)$. That allows to determine the reference transition in H_2^+ with relative precision of about 3×10^{-8} or 30 ppb (parts per billion).

Some higher order corrections (radiative corrections) in the *external field* approximation are known in an analytic form [19,26] and can be included into consideration,

$$E_{se}^{(4)} = \alpha^4 \frac{4\pi}{m_e^2}\left(\frac{139}{128} - \frac{1}{2}\ln 2\right)\langle Z_1^2 \delta(\mathbf{r}_1) + Z_2^2 \delta(\mathbf{r}_2)\rangle,$$

$$E_{\text{anom}}^{(4)} = \alpha^2 \frac{\pi}{m_e^2}\left[\left(\frac{\alpha}{\pi}\right)^2\left(\frac{197}{144} + \frac{\pi^2}{12} - \frac{\pi^2}{2}\ln 2 + \frac{3}{4}\zeta(3)\right)\right] \times \langle Z_1 \delta(\mathbf{r}_1) + Z_2 \delta(\mathbf{r}_2)\rangle,$$

$$E_{\text{vp}}^{(4)} = \frac{4\alpha^3}{3m^2}\left(\frac{5\pi\alpha}{64}\right)\langle Z_1^2 \delta(\mathbf{r}_1) + Z_2^2 \delta(\mathbf{r}_2)\rangle,$$

$$E_{2\ \text{loop}}^{(4)} = \frac{\alpha^4}{m_e^2 \pi}\left(-\frac{6131}{1296} - \frac{49\pi^2}{108} + 2\pi^2 \ln 2 - 3\zeta(3)\right) \times \langle Z_1 \delta(\mathbf{r}_1) + Z_2 \delta(\mathbf{r}_2)\rangle. \tag{16}$$

The last equation includes both Dirac form factor and polarization operator contributions. Recoil corrections of order $R_\infty \alpha^4(m/M)$ are small and may be neglected. The only contribution in the $R_\infty \alpha^4$ order, which has not been yet included into Eq. (16) is the relativistic correction for the bound electron. It can be obtained from expansion of the Dirac two-center problem energy for the bound electron. However, a rough estimate can be obtained using the following speculations.

The electron ground state wave function to a good extent may be approximated by $\psi_e(\mathbf{r}_e) = C[\psi_{1s}(\mathbf{r}_1) + \psi_{1s}(\mathbf{r}_2)]$, where ψ_{1s} is the hydrogen ground state wave function and C is a normalization coefficient. The $R_\infty\alpha^4$ order contribution to the Dirac energy for the hydrogenlike atom ground state is $E_{\rm rc}^{(4)}=-(1/16)m_e Z^6\alpha^4$, thus one can approximate the relativistic correction for the electron bound by the two-center electrostatic field as

$$E_{\rm rc}^{(4)} \approx -\frac{\pi Z^3\alpha^4}{16m_e^2}\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle. \tag{17}$$

For the reference transition in H_2^+ this correction amounts to about 40 kHz. This is an order of magnitude estimate. The more rigorous calculation of this correction in the framework of the adiabatic approximation is in progress.

The most important $R_\infty\alpha^5$ order contributions can be evaluated in a similar way as was done for the relativistic correction,

$$E_{se}^{(5)} = \alpha^5\sum_{i=1,2}\left[\frac{Z_i^3}{m_e^2}\left(-\ln^2\frac{1}{(Z_i\alpha)^2}+A_{61}\ln\frac{1}{(Z_i\alpha)^2}+A_{60}\right)\times\langle\delta(\mathbf{r}_i)\rangle\right],$$

$$E_{2\ \rm loop}^{(5)} = \frac{\alpha^5}{\pi m_e^2}(B_{50})\langle Z_1^2\delta(\mathbf{r}_1)+Z_2^2\delta(\mathbf{r}_2)\rangle, \tag{18}$$

where the constants A_{61}, A_{60}, and B_{50} are taken equal to the constants of the 1*s* state of the hydrogen atom $A_{61}=5.419\ldots$ [27], $A_{60}=-30.924\ldots$ [28], and $B_{50}=-21.556\ldots$ [29] (see Ref. [19] and references therein).

Inclusion of the higher order contributions allows to reduce the relative accuracy of the reference transition frequency in H_2^+ to about 10^{-9} or 1 ppb. Various contributions to the frequency interval of the reference transition are summarized in Table VI. The uncertainty in the E_{α^4} contribution is determined by the yet uncalculated relativistic correction and uncertainty in E_{α^5} is set equal to the absolute value of the $R_\infty\alpha^5 \ln\alpha$ contribution.

TABLE VI. Summary of contributions to the $(L=0,v=0)\to(0,1)$ transition frequency (in MHz).

	H_2^+	HD^+
ΔE_{nr}	65 687 511.0686	57 349 439.9717
ΔE_{α^2}	1091.041(03)	958.152(03)
ΔE_{α^3}	−276.544(02)	−242.118(02)
ΔE_{α^4}	−1.942(40)	−1.700(35)
ΔE_{α^5}	0.121(80)	0.106(70)
$\Delta E_{\rm tot}$	65 688 323.745(80)	57 350 154.412(70)

In conclusion, we present the first systematic calculation of the leading-order relativistic and radiative corrections for the rovibrational states of the hydrogen molecular ions H_2^+ and HD^+. The wave functions used in calculations are accurate enough, which allows to claim that all the quoted digits for the mean values presented in the tables are significant and numerical errors do not affect them.

ACKNOWLEDGMENTS

The author wants to express his gratitude to L. Hilico and K. Pachucki for helpful remarks. The support of the Russian Foundation for Basic Research under Grant No. 05-02-16618 is gratefully acknowledged.

---

[1] B. Grémaud, D. Delande, and N. Billy, J. Phys. B **31**, 383 (1998).
[2] S. Schiller and C. Lämmerzahl, Phys. Rev. A **68**, 053406 (2003).
[3] D. L. Farnham, R. S. Van Dyck, and P. B. Schwinberg, Phys. Rev. Lett. **75**, 3598 (1995); T. Beier, H. Häffner, N. Hermanspahn, S. G. Karshenboim, H.-J. Kluge, W. Quint, S. Stahl, J. Verdú, and G. Werth, *ibid.* **88**, 011603 (2002).
[4] L. Hilico, N. Billy, B. Grémaud, and D. Delande, Eur. Phys. J. D **12**, 449 (2000); J.-Ph. Karr, S. Kilic, and L. Hilico, J. Phys. B **38**, 853 (2005).
[5] V. I. Korobov, Phys. Rev. A **61**, 064503 (2000).
[6] D. H. Bailey and A. M. Frolov, J. Phys. B **35**, 4287 (2002).
[7] Zong-Chao Yan, Jun-Yi Zhang, and Yue Li, Phys. Rev. A **67**, 062504 (2003).
[8] M. M. Cassar and G. W. F. Drake, J. Phys. B **37**, 2485 (2004).
[9] S. Schiller and V. Korobov, Phys. Rev. A **71**, 032505 (2005).
[10] V. I. Korobov, Phys. Rev. A **70**, 012505 (2004).
[11] V. I. Korobov, Phys. Rev. A **73**, 024502 (2006).
[12] P. J. Mohr and B. N. Taylor, Rev. Mod. Phys. **77**, 1 (2005).
[13] C. M. Rosenthal, Chem. Phys. Lett. **10**, 381 (1971); R. L. Somorjai and J. D. Power, *ibid.* **12**, 502 (1972); J. D. Power and R. L. Somorjai, Phys. Rev. A **5**, 2401 (1972).
[14] A. J. Thakkar and V. H. Smith, Jr., Phys. Rev. A **15**, 1 (1977).
[15] A. M. Frolov and V. H. Smith, Jr., J. Biol. Phys. **28**, L449 (1995).
[16] V. I. Korobov, D. Bakalov, and H. J. Monkhorst, Phys. Rev. A **59**, R919 (1999).
[17] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Plenum, New York, 1977).
[18] V. B. Berestetsky, E. M. Lifshitz, and L. P. Pitaevsky, *Relativistic Quantum Theory* (Pergamon, Oxford, 1982).
[19] M. I. Eides, H. Grotch, and V. A. Shelyuto, Phys. Rep. **342**, 63 (2001).
[20] K. Pachucki and S. G. Karshenboim, Phys. Rep. **28**, L221 (1994).
[21] I. B. Khriplovich, A. I. Milstein, and R. A. Sen'kov, Phys. Lett. A **221**, 370 (1996).
[22] K. Pachucki, J. Phys. B **31**, 3547 (1998).
[23] A. Yelkhovsky, Phys. Rev. A **64**, 062104 (2001).
[24] T. Kinoshita and M. Nio, Phys. Rev. D **53**, 4909 (1996).
[25] H. Araki, Prog. Theor. Phys. **17**, 619 (1957); J. Sucher, Phys. Rev. **109**, 1010 (1958).
[26] J. R. Sapirstein and D. R. Yennie, in *Quantum Electrodynamics*, edited by T. Kinosnita (World Scientific, Singapore, 1990).
[27] A. J. Lazer, Phys. Rev. Lett. **4**, 580 (1960).
[28] K. Pachucki, Ann. Phys. (N.Y.) **226**, 1 (1993).
[29] K. Pachucki, Phys. Rev. Lett. **72**, 3154 (1994); M. I. Eides and V. A. Shelyuto, Phys. Rev. A **52**, 954 (1995).