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

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High-precision variational calculations of the operators for the relativistic corrections in the leading $m\alpha^4$ order are presented. The rovibrational states in the range of the total orbital angular momentum $L = 0$–4 and vibrational quantum number $v = 0$–10 for the H_2^+ and HD^+ molecular ions are considered. We estimate that about 10 significant digits are obtained. This high precision is required for making theoretical predictions for transition frequencies at the level of 10^{-12} relative uncertainty.

In recent years, several laser experiments have been performed to measure vibrational transitions with high precision in the hydrogen molecular ions HD^+ [1–3]. One of the trends of these and future experiments [4] is a substantial increase of the vibrational number of the final state from $v = 1$ to 8 or 9. This will entail new theoretical calculations, including states with high v, in order to comply with the requirements of the experiments.

Recently, a very promising pure rotational transition experiment was carried out [5], which realized conditions of the Lamb-Dicke regime where the trap width is smaller than the wavelength of the laser light [6], and for the first time an experimental value was obtained of the transition frequency with a relative precision of 3×10^{-10}. Realistically, this precision could be improved in the near future by about two orders of magnitude. This poses another theoretical challenge [7], since calculation of theoretical frequencies for pure vibrational transitions leads to strong cancelations, thus very high accuracy is required in calculation of the matrix elements of various contributions, at least those connected with leading-order relativistic corrections.

The variational calculations of nonrelativistic energies during recent years have reached a numerical precision of 10^{-15}–10^{-30} a.u. [8–11]. The ultimate accuracy of $\sim 10^{-34}$ a.u. has been obtained for the H_2^+ molecular ion ground state [12]. These calculations demonstrate that at least the nonrelativistic rovibrational transition frequencies can be determined with an accuracy well below the 1 Hz level.

Systematic calculations of leading-order relativistic and radiative corrections were performed in [13–16]. In each case, the vibrational quantum number was restricted to $v = 4$. It is worth noting that in Ref. [16], the precision of the matrix elements for the Breit-Pauli Hamiltonian for the ground vibrational states, $v = 0$, was very high and definitely sufficient for the pure rotational transition case. However, with an increase of v the numerical precision of the calculations based on the Hylleraas variational expansion drops down very rapidly. So, these challenges require further numerical efforts to extend and to make more precise the data on the leading-order relativistic corrections.

The next important step is evaluation of the relativistic and radiative corrections to the binding energies of the rovibrational levels. This can be performed systematically using a series expansion of the binding energy in terms of the coupling constant, which in our case is the fine-structure constant, α. The key quantity for the leading-order $R_\infty \alpha^3$ radiative correction (the Bethe logarithm) for HD^+ and H_2^+ has been obtained in our previous work [17]. The present work is aimed at extending the calculations of the leading-order relativistic corrections to a larger range of vibrational states, and improving the precision of the mean values of the operators for the high v states.

The following notation is used throughout this paper: $\mathbf{P}_1$, $\mathbf{P}_2$, and $\mathbf{p}_e$ are the momenta and $\mathbf{R}_1$, $\mathbf{R}_2$, and $\mathbf{r}_e$ are the coordinates of nuclei and electrons 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 the case of H_2^+, and $\mathbf{R}_1 \equiv \mathbf{R}_d$ is the coordinate of a deuteron in the case of HD^+. Atomic units ($\hbar = e = m_e = 1$) are employed. We use the CODATA14 recommended values of the fundamental constants [18] for all our calculations.

I. VARIATIONAL WAVE FUNCTION

The variational bound-state wave functions were calculated by solving the three-body Schrödinger equation with Coulomb interaction:

$$\left[\frac{\mathbf{P}_1^2}{2M_1} + \frac{\mathbf{P}_2^2}{2M_2} + \frac{\mathbf{p}_e^2}{2m_e} - \frac{Z_1}{r_1} - \frac{Z_2}{r_2} + \frac{Z_1 Z_2}{R} \right] \Psi_0 = E_0 \Psi_0,$$
(1)

using the variational approach based on the exponential expansion with randomly chosen exponents. This approach has been discussed and developed in a variety of works [19–21].

Details and the particular strategy for choosing the variational nonlinear parameters and basis structure that have been adopted in the present work can be found in [22].

Briefly, the wave function for a state with total orbital angular momentum L and total spatial parity $\pi = (-1)^L$ is expanded as follows ($\mathbf{r}_2 = \mathbf{r}_1 - \mathbf{R}$):

$$\Psi_{LM}^{\pi}(\mathbf{R}, \mathbf{r}_1) = \sum_{l_1+l_2=L} \mathcal{Y}_{LM}^{l_1l_2}(\mathbf{R}, \mathbf{r}_1)G_{l_1l_2}^{L\pi}(R, r_1, r_2),$$

$$G_{l_1l_2}^{L\pi}(R, r_1, r_2) = \sum_{n=1}^{N}\{C_n \operatorname{Re}[e^{-\alpha_n R - \beta_n r_1 - \gamma_n r_2}]$$
$$+ D_n \operatorname{Im}[e^{-\alpha_n R - \beta_n r_1 - \gamma_n r_2}]\}, \quad (2)$$

where $\mathcal{Y}_{LM}^{l_1l_2}(\mathbf{R}, \mathbf{r}_1)$ are the solid bipolar harmonics defined as in Ref. [23],

$$\mathcal{Y}_{LM}^{l_1l_2}(\mathbf{R}, \mathbf{r}_1) = R^{l_1}r_1^{l_2}\{Y_{l_1} \otimes Y_{l_2}\}_{LM},$$

and the complex exponents α, β, γ are generated in a pseudo-random way.

When exponents α_n, β_n, and γ_n are real, the method reveals a slow convergence for molecular-type Coulomb systems.

Thus the use of complex exponents allows us to reproduce the oscillatory behavior of the vibrational part of the wave function and to improve convergence [21,22].

II. 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. [24,25], or a comprehensive review [26]. 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,

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

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,

$$E_{\text{tr-ph}}^{(2)} = \frac{\alpha^2 Z_1}{2m_e M_1}\left\langle \frac{\mathbf{p}_e\mathbf{P}_1}{r_1} + \frac{\mathbf{r}_1(\mathbf{r}_1\mathbf{p}_e)\mathbf{P}_1}{r_1^3}\right\rangle + \frac{\alpha^2 Z_2}{2m_e M_2}\left\langle \frac{\mathbf{p}_e\mathbf{P}_2}{r_2} + \frac{\mathbf{r}_2(\mathbf{r}_2\mathbf{p}_e)\mathbf{P}_2}{r_2^3}\right\rangle - \frac{\alpha^2 Z_1 Z_2}{2M_1 M_2}\left\langle \frac{\mathbf{P}_1\mathbf{P}_2}{R} + \frac{\mathbf{R}(\mathbf{R}\mathbf{P}_1)\mathbf{P}_2}{R^3}\right\rangle. \quad (4)$$

The contribution of the last term in (4) is not negligible and amounts to about 10% of $E_{\text{tr-ph}}^{(2)}$.

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

$$E_{\text{kin}}^{(2)} = -\alpha^2\left\langle \frac{\mathbf{P}_1^4}{8M_1^3} + \frac{\mathbf{P}_2^4}{8M_2^3}\right\rangle. \quad (5)$$

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

$$E_{\text{Darwin}}^{(2)} = \frac{\alpha^2 4\pi Z_p}{8M_p^2}\langle\delta(\mathbf{r}_p)\rangle, \quad (6)$$

where Z_p, M_p, and $\mathbf{r}_p$ are the charge, mass, and position vector of the electron with respect to a proton. In the case of a deuteron (spin 1), this term vanishes [27,28]. The leading-order electric charge finite-size correction is defined (both for a proton and a deuteron) by

$$E_{\text{nuc}}^{(2)} = \sum_{i=1,2}\frac{2\pi Z_i(R_i/a_0)^2}{3}\langle\delta(\mathbf{r}_i)\rangle, \quad (7)$$

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 it is $R_d = 2.1394(28)$ fm. These contributions are connected with the internal structure of complex particles. For a detailed discussion of this problem, we refer the reader to [27,28].

The complete contribution to this order is thus

$$E_{\alpha^2} = E_{\text{rc}}^{(2)} + E_{\text{kin}}^{(2)} + E_{\text{tr-ph}}^{(2)} + E_{\text{Darwin}}^{(2)} + E_{\text{nuc}}^{(2)}. \quad (8)$$

III. LEADING-ORDER RADIATIVE CORRECTIONS

The radiative corrections of order $R_\infty\alpha^3$ for a one-electron molecular system can be expressed by the following set of equations (see Refs. [29–31]). Only the spin-independent part is considered.

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

$$E_{\text{se}}^{(3)} = \frac{4\alpha^3}{3m_e^2}\left(\ln\frac{1}{\alpha^2} - \beta(L, v) + \frac{5}{6} - \frac{3}{8}\right)$$
$$\times \langle Z_1\delta(\mathbf{r}_1) + Z_2\delta(\mathbf{r}_2)\rangle, \quad (9)$$

TABLE I. Convergence of the mean value of $\langle\mathbf{p}_e^4\rangle$ for the vibrational states $v = 4$ and 10 in HD$^+$ for various L.

	N	$L = 0$	$L = 3$
$v = 4$	8 000	5.792 077 3804	5.765 200 6482
	10 000	5.792 077 3799	5.765 200 6473
	12 000	5.792 077 3798	5.765 200 6468
	14 000	5.792 077 3798	5.765 200 6466
	∞	5.792 077 3798(1)	5.765 200 6465(1)
	Ref. [15]	5.792 077 379 5339(5)	5.765 200 6889(6)
$v = 10$	18 000	5.276 903 8407	5.259 382 5408
	20 000	5.276 903 8401	5.259 382 5364
	22 000	5.276 903 8397	5.259 382 5339
	24 000	5.276 903 8395	5.259 382 5328
	∞	5.276 903 8394(2)	5.259 382 5322(9)

TABLE II. Mean values of various operators for the rovibrational states (L, v) in the $H_2{}^+$ molecular ion.

	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}
$L = 0$	0	6.2856600594	0.20673647629	79.797649364	1.170117625	4.601934314	−0.1344262279
	1	6.1245198079	0.20131066471	334.89830216	1.140805227	12.89614650	−0.1312863754
	2	5.9762285601	0.19629458830	762.80369623	1.114077226	19.87898102	−0.1283925753
	3	5.8400118491	0.19166249726	1304.2092864	1.089801609	25.66162135	−0.1257315001
	4	5.7151984964	0.18739184669	1908.3716822	1.067868274	30.33829429	−0.1232916813
	5	5.6012112574	0.18346299199	2531.6173039	1.048187719	33.98804802	−0.1210633708
	6	5.4975592498	0.17985893910	3136.1167480	1.030690164	36.67618495	−0.1190384366
	7	5.4038319567	0.17656514348	3688.8844922	1.015325087	38.45539351	−0.1172102897
	8	5.3196946603	0.17356935365	4160.9753024	1.002061184	39.36661303	−0.1155738424
	9	5.2448852254	0.17086149709	4526.8597586	0.9908868010	39.43965837	−0.1141255007
	10	5.1792121777	0.16843360820	4763.9728538	0.9818108626	38.69362778	−0.1128631936
$L = 1$	0	6.2780390374	0.20649132016	85.050455667	1.168818664	4.834336475	−0.1342668169
	1	6.1173973078	0.20108117308	347.54872567	1.139597149	13.09529203	−0.1311369254
	2	5.9695793176	0.19607994205	780.92161614	1.112955682	20.04770789	−0.1282526561
	3	5.8338140029	0.19146198172	1326.1219910	1.088762926	25.80234570	−0.1256007425
	4	5.7094333595	0.18720484414	1932.6198442	1.066909426	30.45305169	−0.1231697745
	5	5.5958631574	0.18328897611	2556.9179839	1.047306308	34.07852553	−0.1209500612
	6	5.4926153921	0.17969747034	3161.3322085	1.029884418	36.74374470	−0.1189335254
	7	5.3992823972	0.17641586729	3712.9958575	1.014593872	38.50108793	−0.1171136355
	8	5.3155323072	0.17343199956	4183.0603098	1.001404040	39.39119123	−0.1154853623
	9	5.2411059278	0.17073588027	4546.0740115	0.9903039968	39.44356252	−0.1140451747
	10	5.1758148732	0.16831963269	4779.5341125	0.9813034913	38.67697691	−0.1127910691
$L = 2$	0	6.2629099578	0.20600454283	96.910905201	1.166239007	5.293427390	−0.1339504598
	1	6.1032596294	0.20062554856	373.99761897	1.137198302	13.48828656	−0.1308403800
	2	5.9563828602	0.19565384281	818.12463975	1.110729011	20.38024874	−0.1279750672
	3	5.8215153662	0.19106398834	1370.7553673	1.086701150	26.07923567	−0.1253413771
	4	5.6979954729	0.18683373048	1981.7828915	1.065006550	30.67833547	−0.1229280161
	5	5.5852549395	0.18294369775	2608.0596187	1.045557594	34.25555325	−0.1207254060
	6	5.4828115576	0.17937715716	3212.1889678	1.028286377	36.87521850	−0.1187255828
	7	5.3902633187	0.17611981800	3761.5395264	1.013144294	38.58909168	−0.1169221266
	8	5.3072840707	0.17315968126	4227.4536463	1.000102065	39.43720246	−0.1153101265
	9	5.2336204946	0.17048693110	4584.6333862	0.9891502316	39.44844397	−0.1138861763
	10	5.1690904704	0.16809387031	4810.6981087	0.9803002006	38.64094245	−0.1126484120
$L = 3$	0	6.2404943312	0.20528307706	117.97635160	1.162414502	5.968061524	−0.1334819874
	1	6.0823171617	0.19995037649	416.43490453	1.133642648	14.06480756	−0.1304013519
	2	5.9368391490	0.19502254993	876.24662762	1.107429423	20.86703769	−0.1275642145
	3	5.8033061164	0.19047447029	1439.6301087	1.083646859	26.48342299	−0.1249576135
	4	5.6810658304	0.18628417107	2057.1039760	1.062188713	31.00592204	−0.1225704294
	5	5.5695590038	0.18243255228	2686.0371498	1.042969244	34.51150425	−0.1203932534
	6	5.4683120665	0.17890314079	3289.4575739	1.025922422	37.06353165	−0.1184182891
	7	5.3769315140	0.17568189914	3835.0805572	1.011001564	38.71284003	−0.1166392866
	8	5.2950997615	0.17275708064	4294.5293028	0.9981794217	39.49855014	−0.1150515119
	9	5.2225723483	0.17011912691	4642.7309921	0.9874487559	39.44863056	−0.1136517483
	10	5.1591765901	0.16776061086	4857.4830325	0.9788234896	38.58022733	−0.1124383412
$L = 4$	0	6.2111137341	0.20433699022	151.87439790	1.157397265	6.842198150	−0.1328684048
	1	6.0548751988	0.19906521543	477.89237049	1.128979542	14.81002209	−0.1298265267
	2	5.9112382325	0.19419514510	957.79934933	1.103103711	21.49435017	−0.1270264811
	3	5.7794620170	0.18970206193	1534.8012769	1.079644470	27.00220305	−0.1244555480
	4	5.6589068100	0.18556438053	2160.2340467	1.058498128	31.42404737	−0.1221028394
	5	5.5490251876	0.18176336040	2792.1407251	1.039581440	34.83548285	−0.1199591710
	6	5.4493550513	0.17828287309	3394.1025379	1.022830872	37.29858981	−0.1180169703
	7	5.3595142132	0.17510921788	3934.2857135	0.1008202311	38.86297608	−0.1162702141
	8	5.2791965306	0.17223098447	4384.6775195	0.9956712337	39.56655122	−0.1147144056
	9	5.2081694237	0.16963895903	4720.4954258	0.9852333961	39.43604596	−0.1133465831
	10	5.1462729334	0.16732607784	4919.7643085	0.9769061357	38.48728563	−0.1121653755

TABLE III. Mean values of operators for HD$^+$.

	v	$\langle \delta(\mathbf{r}_d) \rangle$	$\langle \delta(\mathbf{r}_p) \rangle$	$\langle \mathbf{p}_e^4 \rangle$	$\langle \mathbf{P}_p^4 \rangle$	$\langle \mathbf{P}_d^4 \rangle$
$L = 0$	0	0.20734814178	0.20704259948	6.3001999477	104.37171376	104.44384898
	1	0.20260117861	0.20228886474	6.1590223524	449.45675982	449.73914662
	2	0.19816679513	0.19784583748	6.0276143229	1042.8168322	1043.4433174
	3	0.19402784139	0.19369601393	5.9054534327	1812.9975669	1814.0632379
	4	0.19016909090	0.18982370286	5.7920773798	2697.6692759	2699.2354173
	5	0.18657710159	0.18621484444	5.6870790520	3642.2321785	3644.3304724
	6	0.18324011137	0.18285684358	5.5901023863	4598.6380478	4601.2741340
	7	0.18014797184	0.17973840936	5.5008389477	5524.3976372	5527.5541366
	8	0.17729212821	0.17684938788	5.4190251466	6381.7503195	6385.3894083
	9	0.17466566245	0.17418056963	5.3444400643	7136.9787737	7141.0443898
	10	0.17226343214	0.17172343636	5.2769038394	7759.8577177	7764.2774745
$L = 1$	0	0.20716324168	0.20685769957	6.2944507461	110.38493989	110.46133144
	1	0.20242655717	0.20211421221	6.1535997460	464.36193851	464.65338756
	2	0.19800198124	0.19768095602	6.0225036793	1064.6241336	1065.2634075
	3	0.19387241680	0.19354047839	5.9006418101	1839.9516894	1841.0329235
	4	0.19002268724	0.18967713562	5.7875534291	2728.2144184	2729.7980540
	5	0.18643939814	0.18607691220	5.6828329367	3674.9819497	3677.0989179
	6	0.18311083326	0.18272725426	5.5861257049	4632.3495498	4635.0048177
	7	0.18002688970	0.17961690940	5.4971246933	5557.9490993	5561.1246812
	8	0.17717905975	0.17673576024	5.4155677242	6414.1217749	6417.7792967
	9	0.17456047384	0.17407462955	5.3412352361	7167.2353693	7171.3182658
	10	0.17216604459	0.17162502783	5.2739488088	7787.1353273	7791.5707486
$L = 2$	0	0.20679544434	0.20648990098	6.2830163299	123.79001421	123.87565882
	1	0.20207923036	0.20176682151	6.1428157396	495.36790199	495.67811676
	2	0.19767418733	0.19735302514	6.0123409636	1109.2715320	1109.9369362
	3	0.19356332376	0.19323116142	5.8910746483	1894.7472178	1895.8600523
	4	0.18973156234	0.18938568123	5.7785592512	2790.0612338	2791.6802614
	5	0.18616560334	0.18580265714	5.6743921721	3741.1197981	3743.2744544
	6	0.18285382284	0.18246961801	5.5782216799	4700.3031879	4702.9971004
	7	0.17978620914	0.17937538868	5.4897435379	5625.4837721	5628.6977473
	8	0.17695434714	0.17650992330	5.4086983151	6479.2047371	6482.8993039
	9	0.17435146623	0.17386411066	5.3348692560	7228.0026311	7232.1202214
	10	0.17197258810	0.17142951724	5.2680807597	7841.8629641	7846.3298040
$L = 3$	0	0.20624869702	0.20594314769	6.2660227900	147.25876390	147.36009301
	1	0.20156297374	0.20125046479	6.1267909226	544.78450154	545.12442395
	2	0.19718702656	0.19686565434	5.9972415658	1178.7470290	1179.4529692
	3	0.19310402154	0.19277151828	5.8768624098	1979.0846625	1980.2460433
	4	0.18929902981	0.18895264869	5.7652006466	2884.6520623	2886.3251483
	5	0.18575889338	0.18539524983	5.6618581670	3841.8547847	3844.0667859
	6	0.18247212603	0.18208697377	5.5664875531	4803.4957133	4806.2482620
	7	0.17942885267	0.17901676065	5.4787887613	5727.8035584	5731.0756611
	8	0.17662079781	0.17617467198	5.3985065094	6577.6205427	6581.3710932
	9	0.17404133892	0.17355169431	5.3254282095	7319.7326808	7323.9026143
	10	0.17168566289	0.17113947797	5.2593825328	7924.3321151	7928.8462782
$L = 4$	0	0.20552877799	0.20522321313	6.2436546662	184.59247486	184.71796048
	1	0.20088331252	0.20057066224	6.1057017312	615.88018454	616.26250830
	2	0.19654578490	0.19622412424	5.9773742631	1275.8456943	1276.6080718
	3	0.19249956988	0.19216660270	5.8581666316	2095.3366407	2096.5647803
	4	0.18872993534	0.18838287675	5.7476323025	3013.9805344	3015.7274073
	5	0.18522391134	0.18485932503	5.6453791232	3978.8384624	3981.1283423
	6	0.18197019460	0.18158376287	5.5510654021	4943.2676976	4946.0995834
	7	0.17895909192	0.17854528318	5.4643966701	5865.9639410	5869.3144615
	8	0.17618251410	0.17573408983	5.3851231705	6710.1607564	6713.9866433
	9	0.17363403687	0.17314129869	5.3130378763	7442.9699688	7447.2101770
	10	0.17130906936	0.17075867070	5.2479751736	8034.8527748	8039.4303232

TABLE III. (*Continued.*)

	v	R_{dp}	R_{de}	R_{pe}	$Q(r_1)$	$Q(r_{12})$
$L=0$	0	5.354630521	1.174487826	1.170770145	−0.1348622766	−0.1345911956
	1	15.14482590	1.150481264	1.143366405	−0.1321133551	−0.1318389778
	2	23.59899698	1.128236201	1.118123569	−0.1295519876	−0.1292729300
	3	30.81765302	1.107677206	1.094937543	−0.1271692905	−0.1268839283
	4	36.88807889	1.088739930	1.073718404	−0.1249574956	−0.1246638869
	5	41.88558857	1.071370643	1.054389416	−0.1229098904	−0.1226056689
	6	45.87457090	1.055526002	1.036886189	−0.1210207797	−0.1207030052
	7	48.90935198	1.041173055	1.021155946	−0.1192854727	−0.1189504164
	8	51.03489389	1.028289564	1.007156830	−0.1177003010	−0.1173431284
	9	52.28734536	1.016864765	0.9948571418	−0.1162626814	−0.1158769724
	10	52.69445717	1.006900770	0.9842343052	−0.1149712469	−0.1145482435
$L=1$	0	5.589562257	1.173578500	1.169719380	−0.1347420011	−0.1344709788
	1	15.35057529	1.149625859	1.142380740	−0.1319996114	−0.1317252681
	2	23.77776210	1.127432510	1.117200151	−0.1294445280	−0.1291654762
	3	30.97134961	1.106923322	1.094073892	−0.1270678978	−0.1267825086
	4	37.01836535	1.088034231	1.072912395	−0.1248619829	−0.1245683079
	5	41.99388641	1.070711790	1.053639261	−0.1228201001	−0.1225157644
	6	45.96208086	1.054912938	1.036190429	−0.1209365827	−0.1206186343
	7	48.97706610	1.040605011	1.020513443	−0.1192067694	−0.1188714628
	8	51.08360344	1.027766080	1.006566764	−0.1176270254	−0.1172695033
	9	52.31764454	1.016385716	0.9943190061	−0.1161947956	−0.1158086001
	10	52.70674195	1.006466421	0.9837479032	−0.1149087585	−0.1144850792
$L=2$	0	6.055104820	1.171769108	1.167629281	−0.1345028469	−0.1342319402
	1	15.75802764	1.147923889	1.140420315	−0.1317734666	−0.1314991895
	2	24.13150124	1.125833576	1.115363727	−0.1292308991	−0.1289518570
	3	31.27518973	1.105423632	1.092356539	−0.1268663534	−0.1265809080
	4	37.27560762	1.086630566	1.071309889	−0.1246721507	−0.1243783409
	5	42.20735955	1.069401494	1.052148054	−0.1226416657	−0.1223370994
	6	46.13417317	1.053693917	1.034807627	−0.1207692907	−0.1204509921
	7	49.10974929	1.039475752	1.019236796	−0.1190504235	−0.1187146132
	8	51.17844827	1.026725684	1.005394655	−0.1174814900	−0.1171232613
	9	52.37582778	1.015433961	0.9932504485	−0.1160600096	−0.1156728359
	10	52.72904363	1.005603867	0.9827825290	−0.1147847326	−0.1143596945
$L=3$	0	6.742776308	1.169077915	1.164522384	−0.1341475654	−0.1338768278
	1	16.35924481	1.145392790	1.137506628	−0.1314375645	−0.1311633820
	2	24.65278168	1.123456057	1.112634818	−0.1289136422	−0.1286346099
	3	31.72221154	1.103194065	1.089805086	−0.1265671000	−0.1262815654
	4	37.65328342	1.084544180	1.068929626	−0.1243903481	−0.1240963309
	5	42.51989667	1.067454360	1.049933725	−0.1223768484	−0.1220719301
	6	46.38512106	1.051882951	1.032754956	−0.1205210805	−0.1202022490
	7	49.30203456	1.037798741	1.017342469	−0.1188185314	−0.1184819561
	8	51.31439742	1.025181338	1.003656310	−0.1172657215	−0.1169064227
	9	52.45717674	1.014022013	0.9916666688	−0.1158602717	−0.1154716137
	10	52.75693246	1.004325230	0.9813528252	−0.1146010528	−0.1141739516
$L=4$	0	7.640242671	1.165531695	1.160431691	−0.1336801802	−0.1334096597
	1	17.14269529	1.142058117	1.133671151	−0.1309957699	−0.1307217054
	2	25.33081704	1.120324362	1.109043459	−0.1284964706	−0.1282174429
	3	32.30232202	1.100257958	1.086448221	−0.1261737066	−0.1258880439
	4	38.14194612	1.081797407	1.065799028	−0.1240200062	−0.1237257023
	5	42.92265458	1.064891788	1.047022508	−0.1220289475	−0.1217235484
	6	46.70664501	1.049500571	1.030057540	−0.1201951261	−0.1198755705
	7	49.54616878	1.035593705	1.014854552	−0.1185141481	−0.1181765359
	8	51.48418831	1.023152039	1.001374860	−0.1169826603	−0.1166219119
	9	52.55488390	1.012168214	0.9895899118	−0.1155984217	−0.1152077538
	10	52.78401937	1.002648292	0.9794802286	−0.1143604633	−0.1139305668

where

$$\beta(L, v) = \frac{\langle \mathbf{J}(H_0 - E_0) \ln[(H_0 - E_0)/R_\infty]\mathbf{J}\rangle}{\langle [\mathbf{J}, [H_0, \mathbf{J}]]/2\rangle}, \quad (10)$$

is the Bethe logarithm. The latter quantity presents the most difficult numerical problem in computation of QED corrections for three-body bound states. In [17], calculations for the rovibrational states in H_2^+ and HD^+ were performed with sufficient precision. An operator $\mathbf{J}$ in (10) is the nonrelativistic electric current density operator of the system: $\mathbf{J} = -\mathbf{p}_e/m_e + Z_1\mathbf{P}_1/M_1 + Z_2\mathbf{P}_2/M_2$.

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

$$E_{\text{anom}}^{(3)} = \frac{\pi\alpha^2}{m_e^2}\left[\frac{1}{2}\left(\frac{\alpha}{\pi}\right)\right]\langle Z_1\delta(\mathbf{r}_1) + Z_2\delta(\mathbf{r}_2)\rangle. \quad (11)$$

Sometimes this term is incorporated into Eq. (3) as a contribution from the form factors of an electron [32].

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

$$E_{\text{vp}}^{(3)} = \frac{4\alpha^3}{3m^2}\left[-\frac{1}{5}\right]\langle Z_1\delta(\mathbf{r}_1) + Z_2\delta(\mathbf{r}_2)\rangle. \quad (12)$$

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

$$E_{\text{tr-ph}}^{(3)} = \alpha^3 \sum_{i=1,2}\left[\frac{2Z_i^2}{3m_eM_i}\left(-\ln\alpha - 4\beta(L, v) + \frac{31}{3}\right)\langle\delta(\mathbf{r}_i)\rangle \right.$$
$$\left. - \frac{14Z_i^2}{3m_eM_i}Q(r_i)\right], \quad (13)$$

where $Q(r)$ is the Q-term introduced by Araki and Sucher [33]:

$$Q(r) = \lim_{\rho\to 0}\left\langle\frac{\Theta(r - \rho)}{4\pi r^3} + (\ln\rho + \gamma_E)\delta(\mathbf{r})\right\rangle. \quad (14)$$

It is worth noting here that the splitting into nonrecoil and recoil parts [Eqs. (9) and (13)] is not exact, since the Bethe logarithm contains contributions from both the self-energy and exchange photon diagrams.

Summarizing the contributions, one gets

$$E_{\alpha^3} = E_{\text{se}}^{(3)} + E_{\text{anom}}^{(3)} + E_{\text{vp}}^{(3)} + E_{\text{tr-ph}}^{(3)}. \quad (15)$$

IV. RESULTS

It appears that the mean value of the $\mathbf{p}_e^4$ operator is the most difficult quantity for numerical calculation. That is why we choose it to study the convergence of our results. Table I demonstrates convergence of this key quantity for the two vibrational states $v = 4$ and 10. The first case is needed to compare our numbers with previously obtained results in [15,16], while in the latter case $v = 4$ was the largest vibrational state considered. In general, there is very good agreement between our data and the data from [15]. For the case of the vibrational state $v = 10$, we were not able to

TABLE IV. Various transitions in HD^+ (in kHz) calculated using the improved values for the matrix elements from Table III.

$(L, v) \to (L', v')$	HD^+	$u_r(v)$
$(0, 0) \to (1, 0)$	1 314 925 752.627(18)	1.35×10^{-11}
$(0, 0) \to (0, 1)$	57 350 154 373.6(5)	7.9×10^{-12}
$(0, 0) \to (1, 1)$	58 605 052 157.4(5)	8.1×10^{-12}
$(2, 0) \to (3, 4)$	214 978 560 967.2(1.5)	7.8×10^{-12}
$(2, 0) \to (3, 8)$	383 407 177 207.0(2.9)	7.6×10^{-12}
$(3, 0) \to (3, 9)$	415 264 925 467.0(3.1)	7.5×10^{-12}

achieve convergence of the last digit (the tenth digit after the point). Still, we may claim that for states of $v = 9$ and 10 at least nine digits after the point are significant, and this precision is enough for theoretical predictions of vibrational transition energies at the level of 10^{-12} of relative uncertainty. As for other data shown in Tables II and III, all the digits presented should be fixed.

Our main results of numerical calculations are presented in Tables II and III. The notation is as follows:

$$R_{\text{ne}} = -\left\langle\frac{\mathbf{p}_e\mathbf{P}_n}{r_n} + \frac{\mathbf{r}_n(\mathbf{r}_n\mathbf{p}_e)\mathbf{P}_n}{r_n^3}\right\rangle,$$
$$R_{\text{nn}} = -\left\langle\frac{\mathbf{P}_1\mathbf{P}_2}{R} + \frac{\mathbf{R}(\mathbf{R}\mathbf{P}_1)\mathbf{P}_2}{R^3}\right\rangle, \quad (16)$$

Q_{ne} is the Q-term expectation value as it is defined in Eq. (14), where 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 $R_\infty\alpha^3(m/M)$.

Table IV demonstrates theoretical predictions for the rovibrational spin-averaged transitions in an HD^+ molecular ion obtained with the new data. These transitions correspond to those studied recently or considered at present in experiments [1–5]. The higher-order contributions are calculated in the same way as in [7]. The uncertainty indicated in the calculated frequencies is due to yet uncalculated theoretical contributions; the uncertainty due to mass inaccuracy in the CODATA14 values is not shown here.

In summary, we have presented the extended systematic calculation of the leading-order relativistic corrections for the rovibrational states of the hydrogen molecular ions H_2^+ and HD^+. We were able to comply with the present-day requirements of hydrogen molecular ion precision spectroscopy, providing relative uncertainty due to numerical imperfection to the rovibrational transition frequencies below 10^{-12}.

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