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Relativistic corrections of $m\alpha^6$ order to the rovibrational spectrum of H_2^+ and HD^+ molecular ions

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The major goal of high-precision studies of rovibrational states in the hydrogen molecular ions is to provide an alternative way for improving the electron-to-proton mass ratio, or the atomic mass of electron. By now the complete set of relativistic and radiative corrections have been obtained for a wide range of rovibrational states of H_2^+ and HD^+ up to order $R_\infty\alpha^4$. In this work we complete calculations of various contributions to the $R_\infty\alpha^4$ order by computing the relativistic corrections to the binding energy of electron.

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In recent years several 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 have 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).

While the variational calculations of the nonrelativistic energies have reached a numerical precision of 10^{-15}–10^{-30} a.u. [4–10], the radiative and relativistic corrections have not been presented in the literature with required accuracy. Only recently high-precision variational calculations for the ro-vibrational 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 along with 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, $R_\infty\alpha^4$ have been obtained [11]. Here m is a mass of an electron and M is a mass scale characteristic for molecular nuclei.

The total $R_\infty\alpha^4$ order contribution to the energy in a nonrecoil limit consist of the radiative one- and two-loop corrections and the relativistic correction for the Dirac electron. The spin-orbit contribution to the hyperfine structure, which arises from the anomalous magnetic moment, has been considered separately for H_2^+ in Ref. [12] and for HD^+ in Ref. [13]. The radiative corrections are known in an analytic form (see, for example, Refs. [14,15]).

The major aim of the present work is to calculate relativistic contribution due to a bound electron to the energies of rovibrational states of H_2^+ and HD^+ in the same range of total orbital angular momentum L and vibrational quantum number v as in Ref. [11]. The atomic units ($\hbar=e=m_e=1$) are used throughout.

I. RADIATIVE CORRECTIONS OF ORDER $R_\infty\alpha^4$

For a given relative accuracy of $\sim 10^{-10}$–10^{-11} recoil corrections of orders $R_\infty\alpha^4(m/M)$ and higher are small and may be neglected. That allows us to reduce calculation of higher order corrections for the Coulomb three-body system to the problem of a bound electron in an external field.

The radiative corrections of order $R_\infty\alpha^4$ in the external field approximation can be expressed as follows [14,15]:

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

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

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

$$E_{\rm 2loop}^{(4)} = \frac{\alpha^4}{m_e^2\pi}\left[-\frac{6131}{1296}-\frac{49\pi^2}{108}+2\pi^2\ln 2-3\zeta(3)\right]$$
$$\times\langle Z_1\delta(\mathbf{r}_1)+Z_2\delta(\mathbf{r}_2)\rangle. \tag{1}$$

The last equation includes both Dirac form factor and polarization operator contributions.

II. RELATIVISTIC CORRECTIONS OF ORDER $R_\infty\alpha^4$

The most problematic contribution of $R_\infty\alpha^4$ order is the relativistic correction for a Dirac electron. It can be obtain within the adiabatic two-center approximation as follows (for details, see Ref. [16]).

We start from the nonrelativistic Schrödinger equation with the Hamiltonian

$$H_0=\frac{p^2}{2m_e}+V,\qquad V=-\frac{Z_1}{r_1}-\frac{Z_2}{r_2}. \tag{2}$$

The total contribution to the energy of a bound electron at the $R_\infty\alpha^4\sim m_ec^2\alpha^6$ order is defined by

$$\Delta E^{(6)}=\langle H_BQ(E_0-H_0)^{-1}QH_B\rangle+\langle H^{(6)}\rangle. \tag{3}$$

Here $H^{(6)}$ is the effective Hamiltonian for the interaction of an electron with the external field of two centers in this order, which can be expressed in the form

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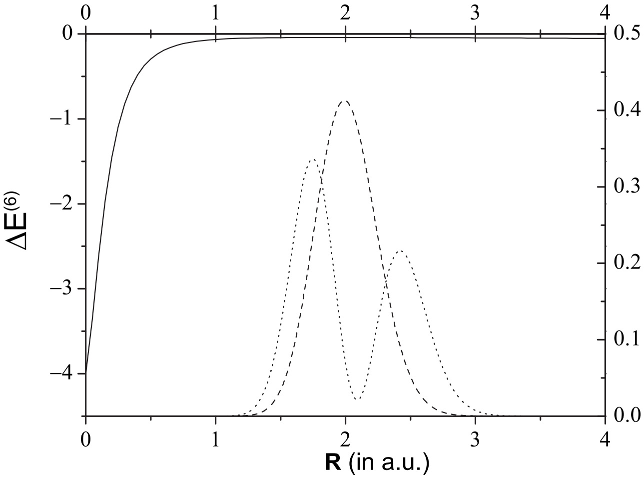

FIG. 1. Adiabatic "effective" potentials for the relativistic $m\alpha^6$ order correction for H_2^+ molecular ion ($Z_1{=}Z_2{=}1$). Energies are in (atomic units)$\times\alpha^4$.

$$H^{(6)} = \frac{p^6}{16m_e^5} + \frac{(\mathcal{E}_1+\mathcal{E}_2)^2}{8m_e^3} - \frac{3\pi}{16m_e^4}\{p^2[\rho_1+\rho_2]+[\rho_1+\rho_2]p^2\} + \frac{5}{128m_e^4}(p^4V+Vp^4) - \frac{5}{64m_e^4}(p^2Vp^2),$$

$$\mathcal{E}_i = -Z_i\mathbf{r}_i/r_i^3, \quad \rho_i = Z_i\delta(\mathbf{r}_i). \tag{4}$$

H_B is the Breit-Pauli interaction

$$H_B = -\frac{p^4}{8m_e^3} + \frac{\pi}{2m_e^2}[Z_1\delta(\mathbf{r}_1)+Z_2\delta(\mathbf{r}_2)] + \left(Z_1\frac{[\mathbf{r}_1\times\mathbf{p}]}{2m_e^2r_1^3} + Z_2\frac{[\mathbf{r}_2\times\mathbf{p}]}{2m_e^2r_2^3}\right)\mathbf{s}. \tag{5}$$

Both terms in Eq. (3) are divergent. In order to remove the infinities a transformation to the second order term can be applied which separates a divergent part

$$H_B' = H_B + (H_0-E_0)U + U(H_0-E_0),$$

$$\begin{aligned}\langle H_BQ(E_0-H_0)^{-1}QH_B\rangle &= \langle H_B'Q(E_0-H_0)^{-1}QH_B'\rangle + \langle UH_B+H_BU\rangle \\ &\quad - 2\langle U\rangle\langle H_B\rangle + \langle U(H_0-E_0)U\rangle \end{aligned} \tag{6}$$

with $U{=}\frac{1}{4m_e}[Z_1/r_1{+}Z_2/r_2]{=}{-}\frac{1}{4m_e}V$.

The last three terms of the second expression in Eq. (6) can be recast in a form of a new effective interaction

$$\begin{aligned} H'^{(6)} &= (UH_B+H_BU) - 2U\langle H_B\rangle - U(E_0-H_0)U \\ &= \frac{p^4V+Vp^4}{32m_e^4} - \frac{\pi V[\rho_1+\rho_2]}{4m_e^3} + \frac{(\mathcal{E}_1+\mathcal{E}_2)^2}{32m_e^3} + \frac{V}{2m_e}\langle H_B\rangle. \end{aligned} \tag{7}$$

Taking into account that Ψ_0 is a solution of the Schrödinger equation $H_0\Psi_0{=}E_0\Psi_0$, one may obtain from the above the following finite expression [16]

TABLE I. Relativistic corrections of $R_\infty\alpha^4$ order [in units $\alpha^4\times$(1 a.u.)], H_2^+.

	$v=0$	$v=1$	$v=2$	$v=3$	$v=4$
$L=0$	−0.042097	−0.042908	−0.043786	−0.044732	−0.045729
$L=1$	−0.042100	−0.042912	−0.043792	−0.044740	−0.045738
$L=2$	−0.042107	−0.042922	−0.043805	−0.044757	−0.045756
$L=3$	−0.042117	−0.042938	−0.043825	−0.044782	−0.045783
$L=4$	−0.042133	−0.042959	−0.043854	−0.044818	−0.045820

$$\begin{aligned}\Delta E^{(6)} &= \langle H_B'Q(E_0-H_0)^{-1}QH_B'\rangle + \langle H^{(6)}\rangle + \langle H'^{(6)}\rangle \\ &= \langle H_B'Q(E_0-H_0)^{-1}QH_B'\rangle + \frac{3E_0\langle V^2\rangle}{4m_e^2} - \frac{5E_0^2\langle V\rangle}{4m_e^2} \\ &\quad - \frac{3\pi E_0\langle(\rho_1+\rho_2)\rangle}{4m_e^3} + \frac{\langle\mathbf{p}V^2\mathbf{p}\rangle}{8m_e^3} + \frac{\langle V\rangle\langle H_B\rangle}{2m_e} + \frac{E_0^3}{2m_e^2}. \end{aligned} \tag{8}$$

This new expression can be now calculated numerically, since all the terms are finite.

The "effective" potentials of $\Delta E^{(6)}(R)$ have been obtained for different bond lengths in Ref. [16]. Results are shown in Fig. 1.

Averaging them over the radial wave function of particular state one may get corresponding contribution to the energy of that state of order $R_\infty\alpha^4$. Results of numerical calculation of the relativistic corrections at this order are presented in Tables I and II. For the transition frequency this adiabatic approach provides about three significant digits.

III. HIGHER ORDER RADIATIVE CORRECTIONS

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. So, the most important $R_\infty\alpha^5$ order contributions can be evaluated using this approximate wave function and the expressions

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

TABLE II. Relativistic corrections of $R_\infty\alpha^4$ order [in units $\alpha^4\times$(1 a.u.)], HD^+.

	$v=0$	$v=1$	$v=2$	$v=3$	$v=4$
$L=0$	−0.042043	−0.042738	−0.043483	−0.044278	−0.045126
$L=1$	−0.042045	−0.042741	−0.043487	−0.044284	−0.045132
$L=2$	−0.042050	−0.042748	−0.043496	−0.044295	−0.045146
$L=3$	−0.042058	−0.042759	−0.043510	−0.044312	−0.045167
$L=4$	−0.042069	−0.042773	−0.043529	−0.044336	−0.045195

TABLE III. Summary of contributions to the $(v=0,L=0) \to (v'=1,L'=0)$ transition frequency (in MHz). The nonrelativistic energies are obtained with the CODATA02 [20] recommended values.

	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)	−242.125(02)
ΔE_{α^4}	−1.997	−1.748
ΔE_{α^5}	0.120(23)	0.105(19)
ΔE_{tot}	65 688 323.688(25)	57 350 154.355(21)

$$E^{(5)}_{2\text{loop}} = \frac{\alpha^5}{\pi m_e^2}[B_{50}]\langle Z_1^2\delta(\mathbf{r}_1) + Z_2^2\delta(\mathbf{r}_2)\rangle, \qquad (9)$$

where the constants A_{61}, A_{60}, and B_{50} are taken equal to the constants of the $1s$ state of the hydrogen atom $A_{61}=5.419\cdots$ [17], $A_{60}=-30.924\cdots$ [18], and $B_{50}=-21.556\cdots$ [19]. We note that the leading contribution $(R_\infty\alpha^5 \ln^2 \alpha)$ is exact.

IV. RESULTS AND CONCLUSION

Various contributions to the frequency interval of the fundamental transition are summarized in Table III. Uncertainty in orders $R_\infty\alpha^2$ and $R_\infty\alpha^3$ are primarily due to numerical uncertainty in calculation of leading order terms such as $\langle \mathbf{p}^4 \rangle$ in the Breit-Pauli Hamiltonian or the Bethe logarithm $\beta(L,v)$ (see Refs. [21,22] for the details), and can be improved by more extensive calculations. We estimate uncertainty due to finite size of nuclei as $\sim 3\times10^{-4}$ MHz for these transitions. So, the latter is so far negligible for the rovibrational spectroscopy. For the contribution of order $R_\infty\alpha^5$ the error bars are determined by the total contribution of the terms with coefficients A and B in Eq. (9).

Recently, the $(v,L):(0,2)\to(4,3)$ rovibrational transition for the HD^+ ion has been precisely measured in the experiment at the Düsseldorf university [23]. Comparison with theoretical calculation demonstrates a very good agreement:

$$E_{\text{expt}} = 214\ 978\ 560.6(5)\ \text{MHz},$$

$$E_{\text{theor}} = 214\ 978\ 560.88(7)\ \text{MHz}.$$

In conclusion, the relativistic corrections of order $R_\infty\alpha^4$ allow us to reduce the relative accuracy of the fundamental transition frequency in H_2^+ to about 3×10^{-9} or 0.3 ppb. Further improvement we expect to achieve by numerical estimate of coefficients A_{61}, A_{60}, and B_{50} from Eq. (9) using the two-center adiabatic (or external field) approximation. That may reduce the final uncertainty by a factor of $5-10$ and the relative uncertainty to less than 10^{-10}. Eventually, it will make real the main goal of our studies: improving of the m_p/m_e mass ratio from the rovibrational spectroscopy of H_2^+ and HD^+.

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