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Bethe logarithm for the hydrogen molecular ion HD$^+$

Vladimir I. Korobov*
Joint Institute for Nuclear Research, 141980, Dubna, Russia

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The mean excitation energy (the Bethe logarithm) is calculated for the lowest rotational (up to $L=4$) and vibrational (up to $v=4$) states of the hydrogen molecular ion HD$^+$. The calculations are based on a method of the direct integration over photon momenta. The estimated accuracy of obtained values is about six significant digits.

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In the last few years an interest to precisely study the positive molecular ions of hydrogen isotopes is revived. Primarily it is due to the recent progress in variational calculations of this system, which improves the accuracy of nonrelativistic energies of the rovibrational states up to 18 significant digits [1–4]. These modern calculations are sensitive to proton/electron mass ratio, what as expected can lead to metrological application [1,5]. However for this purpose higher order relativistic and quantum electrodynamics (QED) corrections are required. In this work we will consider the contribution to the leading α^3 order radiative correction which is the most complicated quantity for numerical computation to this order. We will calculate the Bethe logarithm [6] for the HD$^+$ molecular ion.

The Bethe logarithm is a contribution, which comes mainly from the nonrelativistic energy region for the exchange photons and is defined in terms of the nonrelativistic quantum mechanics [6]. The complete spin independent contributions of order α^3 and $\alpha^3(m/M)$ in the case of a one electron molecular system can be derived from the nonrelativistic QED [7] in a way similar to what has been done for the helium case in Refs. [8] and [9] and can be expressed as follows:

$$\delta^{(3)}E = \alpha^3 \sum_i \left\{ \frac{4Z_i}{3}\left[-\ln\,\alpha^2 - \beta(L,v) + \frac{5}{6} - \frac{1}{5}\right]\langle\delta(\mathbf{r}_i)\rangle + \frac{2Z_i^2}{3M_i}\left[-\ln\,\alpha - 4\,\beta(L,v) + \frac{31}{3}\right]\langle\delta(\mathbf{r}_i)\rangle - \frac{14Z_i^2}{3M_i}Q(r_i)\right\}, \tag{1}$$

where

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

is the Bethe logarithm, H_0 is the three-body nonrelativistic Hamiltonian, $\mathbf{J}=\sum_a z_a\mathbf{p}_a/m_a$ is the electric current density operator of the system, and $Q(r)$ is the Q term introduced by Araki and Sucher [10]:

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

We use small z_i and m_i to denote charges and masses of a general few-body Coulomb system, and capital Z_i and M_i to denote charges and masses of nuclei in the hydrogenic molecular ion. Atomic units are adopted throughout this paper.

The numerical computation of the Bethe logarithm is one of the challenging problems in atomic and molecular physics [11,12]. There is spectacular progress in the last few years [13–16]. However, no *ab initio* calculations have been carried out for the positive hydrogen molecular ions so far. In Ref. [12] the "mean excitation energy" of an electron has been calculated for a range of bond lengths up to $6a_0$. The present work is an attempt to go beyond the "adiabatic" Born-Oppenheimer approximation and to include recoil effects into the calculation of $\beta(L,v)$ for this system.

I. THE LOW ENERGY PHOTON CONTRIBUTION AND THE BETHE LOGARITHM

The one transverse photon contribution to the energy of a bound system in the nonrelativistic QED is described by the diagrams shown on Fig. 1. The leading order effect enters into the Breit-Pauli Hamiltonian and the remaining part can be expressed as follows (in atomic units):

$$E_T = \frac{\alpha^3}{(2\pi)^3}\int \frac{d\mathbf{k}}{2k}\left(\delta^{ij} - \frac{k^i k^j}{k^2}\right)\left\langle \phi_0 \left| \sum_a j_a^i e^{i\mathrm{k}\cdot\mathrm{r}_a}\left(\frac{1}{E_0 - H_0 - k} + \frac{1}{k}\right)\sum_b e^{-i\mathrm{k}\cdot\mathrm{r}_b} j_b^j \right| \phi_0 \right\rangle, \tag{3}$$

where $\mathbf{j}_a = z_a\mathbf{p}_a/m_a$. The term $1/k$ in parentheses of Eq. (3) correspond to the subtracted leading α^2 order contribution to

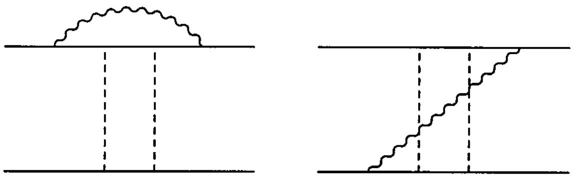

FIG. 1. Transverse self-energy and exchange photon diagrams in the nonrelativistic QED.

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*Electronic address: korobov@thsun1.jinr.ru

TABLE I. The Bethe logarithm for the lowest rotational, L, and vibrational, v, states of the hydrogen molecular ion HD^+.

	$v=0$	$v=1$	$v=2$	$v=3$	$v=4$
$L=0$	3.012349(1)	3.012645(1)	3.012803(1)	3.012818(2)	3.012692(2)
$L=1$	3.012328(1)	3.012621(1)	3.012776(1)	3.012789(2)	3.012663(2)
$L=2$	3.012285(1)	3.012572(1)	3.012721(1)	3.012729(2)	3.012597(2)
$L=3$	3.012222(1)	3.012500(1)	3.012640(2)	3.012640(2)	3.012500(3)
$L=4$	3.012139(1)	3.012406(1)	3.012534(2)	3.012524(2)	3.012377(4)

the Breit-Pauli interaction in case of the transverse photon exchange diagram [8] and to the "mass renormalization" counterterm in case of the self-energy diagram [6,7].

At low photon energies one can neglect the retardation, i.e., the exponential factors in Eq. (3) can be replaced by unity. In this "dipole" approximation expression (3) converts to a form

$$E_{TL} = \frac{\alpha^3}{(2\pi)^3}\int \frac{d\mathbf{k}}{2k}\left(\delta^{ij}-\frac{k^ik^j}{k^2}\right)\left\langle \phi_0 \left| J^i\left(\frac{1}{E_0-H_0-k} + \frac{1}{k}\right)J^j \right| \phi_0 \right\rangle. \qquad (4)$$

Averaging over angular variables one gets

$$E_{TL} = \frac{2\alpha^3}{3\pi}\int_0^\infty k\,dk\left\langle \phi_0 \left| \mathbf{J}\left(\frac{1}{E_0-H_0-k}+\frac{1}{k}\right)\mathbf{J} \right| \phi_0 \right\rangle; \qquad (5)$$

this integral is ultraviolet divergent. Using identity

$$\begin{aligned}(E_0-H_0-k)^{-1} &+ 1/k \\ &= -\frac{1}{k^2}(E_0-H_0) + \frac{1}{k^2}(E_0-H_0)(E_0-H_0-k)^{-1}(E_0-H_0)\end{aligned}$$

one can separate the logarithmically divergent term and then get

$$\begin{aligned}E_{TL} &= \frac{2\alpha^3}{3\pi}\int_0^{K_0} k\,dk\left\langle \phi_0 \left| \mathbf{J}\left(\frac{1}{E_0-H_0-k}+\frac{1}{k}\right)\mathbf{J} \right| \phi_0 \right\rangle \\ &\quad - \frac{2\alpha^3}{3\pi}\left(\int_{K_0}^{\Lambda}\frac{dk}{k}\right)\langle \phi_0|\mathbf{J}(E_0-H_0)\mathbf{J}|\phi_0\rangle \\ &\quad + \frac{2\alpha^3}{3\pi}\int_{K_0}^{\infty}\frac{dk}{k}\left\langle \phi_0 \left| \mathbf{J}\frac{(E_0-H_0)^2}{E_0-H_0-k}\mathbf{J} \right| \phi_0 \right\rangle \\ &= \frac{\alpha^3}{3\pi}\big[\ln(\Lambda/R_\infty) - \beta(L,v)\big]\langle \phi_0|[\mathbf{J},[H_0,\mathbf{J}]]|\phi_0\rangle, \qquad (6)\end{aligned}$$

where $\beta(L,v)$ is the Bethe logarithm as defined in Eq. (2). It now can be rewritten in terms of integrals over k (see also Ref. [11]):

$$\begin{aligned}\beta(L,v) &= \langle[\mathbf{J},[H_0,\mathbf{J}]]/2\rangle^{-1}\left[-\int_0^{K_0} k\,dk\langle \mathbf{J}(E_0-H_0-k)^{-1}\mathbf{J}\rangle \right. \\ &\quad \left. - K_0\langle \mathbf{J}^2\rangle\right] + \ln(K_0/R_\infty) - \int_{K_0}^{\infty}\frac{dk}{k} \\ &\quad \times \frac{\langle \mathbf{J}(E_0-H_0)(E_0-H_0-k)^{-1}(E_0-H_0)\mathbf{J}\rangle}{\langle[\mathbf{J},[H_0,\mathbf{J}]]/2\rangle}. \qquad (7)\end{aligned}$$

The final expressions in Eqs. (6) and (7) do not depend on a choice of $K_0(m\alpha^2 \ll K_0 \ll m\alpha)$, which is taken to split the ultrasoft and soft photon contributions.

The cutoff parameter Λ in Eq. (6) is introduced to define an upper limit of the integration over the photon momentum k and may be choosen as the rest mass of an electron, the typical mass scale of the problem. The cutoff parameter is eliminated when contribution from higher energy photons is taken into account [8].

Denominator in Eq. (7) can be expanded

$$\langle[\mathbf{J}[H_0,\mathbf{J}]]\rangle = -4\pi\sum_{i>j} z_i z_j\left(\frac{z_i}{m_i}-\frac{z_j}{m_j}\right)^2\langle\delta(\mathbf{r}_{ij})\rangle,$$

and in a limit of large m_e/M_i for molecular type systems is approximately expressed

$$\begin{aligned}\langle[\mathbf{J}[H_0,\mathbf{J}]]\rangle \approx 4\pi\Bigg\{&(Z_1\langle\delta(\mathbf{r}_1)\rangle + Z_2\langle\delta(\mathbf{r}_2)\rangle) \\ &+ 2\left[\frac{Z_1}{M_1}\langle\delta(\mathbf{r}_1)\rangle + \frac{Z_2}{M_2}\langle\delta(\mathbf{r}_2)\rangle\right]\Bigg\}.\end{aligned}$$

Substituting this expression into Eq. (6) we reproduce exactly a part of Eq. (1), which contains $\beta(L,v)$.

II. NUMERICAL EVALUATION OF THE INTEGRALS

In order to evaluate the value of $\beta(L,v)$ we shall use Eq. (7). To this end, let us introduce following Schwartz [11] the two functions, which enters as integrands into the ultrasoft and soft photons contributions of Eq. (7), respectively,

$$\begin{aligned}\tilde{J}(k) &= -\langle\psi_0|\mathbf{J}(E_0-H_0-k)^{-1}\mathbf{J}|\psi_0\rangle, \\ \tilde{w}(k) &= \langle\psi_0|[H_0,\mathbf{J}](E_0-H_0-k)^{-1}[H_0,\mathbf{J}]|\psi_0\rangle. \qquad (8)\end{aligned}$$

These functions are connected by the relation

$$\tilde{J}(k) = \frac{1}{k}\langle\mathbf{J}^2\rangle - \frac{1}{k^2}\langle[\mathbf{J},[H_0,\mathbf{J}]]/2\rangle + \frac{1}{k^2}\tilde{w}(k). \qquad (9)$$

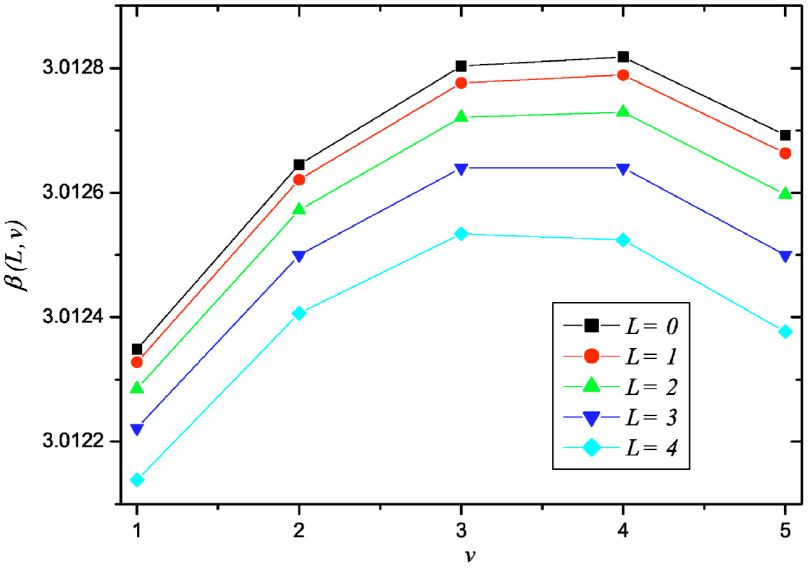

FIG. 2. (Color online) The logarithm of the mean excitation energy versus vibrational quantum number.

$\tilde{J}(k)$ can be obtained by solving an equation

$$(E_0 - H_0 - k)\psi^{(1)} = \mathbf{J}\psi_0, \tag{10}$$

for a set of k from zero to infinity. We solve this equation using the variational procedure. The solution $\psi^{(1)}$ is used to get $\tilde{J}(k) = -\langle\psi_0|\mathbf{J}|\psi^{(1)}\rangle$, which should obey the variational property, namely, the computed value of $\tilde{J}(k)$ provides a lower bound for this quantity. That allows one to find optimal variational parameters for the numerical solution of $\psi^{(1)}$. The function $\tilde{w}(k)$ can be obtained in a similar way. However, the operator $[H_0, \mathbf{J}]$, which appears in the equation, is singular that requires to introduce negative powers of r_i in the variational expansion for the first order perturbation wave function. In what follows we make use of the relation (9) in order to evaluate $\tilde{w}(k)$.

To provide with accurate numerical results, the variational wave function $\psi^{(1)}$ from Eq. (10) for large k should contain terms which behave as $e^{-\mu r_i}$, where $\mu = \sqrt{2k}$.

On the other hand, for the low energy part, when the Bethe logarithm for the excited vibrational states of the hydrogen molecular ion is evaluated, the integral contains poles which should be integrated in a sense of the Cauchy principal value. So, it is convenient for small values of k to use the following form:

$$\tilde{J}(k) = -\sum_n \frac{|\langle\psi_0|\mathbf{J}|\psi_n\rangle|^2}{E_0 - H_0 - k}, \tag{11}$$

where the summation proceeds along pseudostates ψ_n obtained by the diagonalization of the Hamiltonian for the finite variational basis set. That allows one to integrate this part analytically.

Finally, the function $\tilde{w}(k)$ at $k \to \infty$ can be approximated

$$\tilde{w}(k) \sim \frac{4\pi}{k}\sum_{i>j} z_i^2 z_j^2 \left(\frac{z_i}{m_i} - \frac{z_j}{m_j}\right)^2 [(2k)^{1/2} + z_i z_j \ln k]\langle\delta(\mathbf{r}_{ij})\rangle + \frac{1}{k}\sum_{m=0}^{M} C_m k^{-m/2}. \tag{12}$$

To estimate the contribution to the Bethe logarithm from the asymptotic region $[k_{\max}, \infty]$ ($k_{\max}$ is a maximal value for which the numerical calculation of the integrand is performed) we choose parameters C_m for $m = 0, \ldots, M$ to get a best fit for tabulated values of $\tilde{w}(k)$ in a range from $k_{\min} \approx 30$ to $k_{\max} \approx 1000$.

For numerical calculations presented in the next section we hold to the following rules:

(a) For $k = [0, 10]$, an analytical integration for $\tilde{J}(k)$ from Eq. (11) is used

$$\int_0^{K_0} k\, dk\tilde{J} = \sum_n |\langle\psi_0|\mathbf{J}|\psi_n\rangle|^2 \left[K_0 - (E_0 - E_n)\ln\left|\frac{E_0 - E_n}{E_0 - E_n - K_0}\right|\right].$$

(b) For $k = [10, 1000]$, we perform a numerical integration of the $\tilde{w}(k)$ function.

(c) For $k = [1000, \infty]$, the best fit for an asymptotic expansion (12) is integrated analytically.

III. VARIATIONAL APPROXIMATION AND NUMERICAL RESULTS

For the variational calculations presented here, the wave functions both for initial states and for intermediate ones are taken in the form (see Ref. [2] for details):

$$\Psi_L(l_1,l_2) = \sum_{i=1}^{\infty} \{U_i \,\mathrm{Re}[e^{-\alpha_i r_1-\beta_i r_2-\gamma_i r}] + W_i \,\mathrm{Im}[e^{-\alpha_i r_1-\beta_i r_2-\gamma_i r}]\}\mathcal{Y}^{l_1 l_2}_{LM}(\mathbf{r}_1,\mathbf{r}_2), \qquad (13)$$

where $\mathcal{Y}^{l_1 l_2}_{LM}(\mathbf{r}_1,\mathbf{r}_2)$ are the solid bipolar harmonics as defined in Refs. [17,18], L is a total orbital angular momentum of a state. Complex parameters α_i, β_i, and γ_i are generated in a quasirandom manner

$$\alpha_i = \left[\left\lfloor \tfrac{1}{2}i(i+1)\sqrt{p_\alpha}\right\rfloor (A_2 - A_1) + A_1\right] + i\left[\left\lfloor \tfrac{1}{2}i(i+1)\sqrt{q_\alpha}\right\rfloor (A_2' - A_1') + A_1'\right],$$

$\lfloor x \rfloor$ designates the fractional part of x, p_α, and q_α are some prime numbers, $[A_1,A_2]$ and $[A_1',A_2']$ are real variational intervals which need to be optimized. Parameters β_i and γ_i are obtained in a similar way.

Intermediate states, for the case of nonzero angular momentum L of the initial state, span over $L'=L,L\pm 1$ with the spatial parity $\pi=-(-1)^L$. For each L' we take a number of basis functions up to 5000 to achieve required accuracy. Especially it is important for large vibrational states.

Results of numerical calculations are shown in Table I. We estimate that the numerical precision for the Bethe logarithm for these states is about 10^{-6} and the number in parentheses indicates an uncertainty in the last digit. This accuracy is sufficient to provide the final precision for vibrational transition energies to be about 10^{-11}–10^{-12} on the assumption of higher order corrections to be included.

In Fig. 2, the logarithm of the mean excitation energy as a function of the vibrational quantum number is shown. For high values of v the Bethe logarithm should tend to the hydrogenic limit $\ln[k_0(1S)/R_\infty] \approx 2.984$, since the essential contribution to the wave function comes from configurations, when nuclei are located at large distances, and the electronic wave function can be approximated to a good extent by a superposition of the 1*s* state hydrogen functions. As is seen from this figure, the calculated vibrational states are not sufficient to make a reliable extrapolation to higher vibrational states. On the other hand, the numerical uncertainty in $\beta(L,v)$ grows very rapidly with increase of v, that makes difficult the numerical study of the high v states.

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