

Relativistic corrections to the dipole polarizability of the ground state of the molecular ion H_2^+

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The recently reported precise experimental determination of the dipole polarizability of the H_2^+ molecular ion ground state [P.L. Jacobson, R.A. Komara, W.G. Sturru, and S.R. Lundeen, Phys. Rev. A **62**, 012509 (2000)] reveals a discrepancy between theory and experiment of about $0.0007a_0^3$, which has been attributed to relativistic and QED effects. In the present work we analyze an influence of the relativistic effects on the scalar dipole polarizability of an isolated H_2^+ molecular ion. Our conclusion is that it accounts for only 1/5 of the measured discrepancy.

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I. INTRODUCTION

Recent measurements [1,2] of the scalar electric dipole polarizability of H_2^+ molecular ions through the study of H_2 molecule states with one Rydberg electron stimulated the introduction of methods [3–6] which are able to accurately describe wave functions of molecular ions with two heavy nuclei beyond the adiabatic approximation. The accuracy for the dipole polarizability constant ($\sim 10^{-7}a_0^3$) reached in the last work [6] in its turn becomes a challenge to experiment. The experimental work [2] substantially increases the accuracy of measurements and reveals a discrepancy of about $0.0007a_0^3$ between theory and experiment, which cannot be accounted for within purely nonrelativistic approximation. In the present work we consider relativistic corrections of order α^2 to the dipole polarizability of the ground state of an isolated H_2^+ molecular ion.

II. THEORY

The nonrelativistic Hamiltonian of the hydrogen molecular ion H_2^+ is

$$H_0 = -\frac{1}{2M}\nabla_1^2 - \frac{1}{2M}\nabla_2^2 - \frac{1}{2m}\nabla^2 + \frac{1}{R_{12}} - \frac{1}{r_1} - \frac{1}{r_2}. \quad (1)$$

We adopt atomic units ($e = \hbar = m = 1$) throughout this paper. The interaction with an external electric field (details of the nonrelativistic treatment of the problem can be found in previous papers [3–6]) is expressed by

$$V_p = \mathcal{E}\mathbf{n} \cdot \mathbf{d}, \quad (2)$$

where

$$\mathbf{d} = \mu\mathbf{r}_c = \left(\frac{2M}{2M+m} + 2\frac{m}{2M+m} \right) \left[\mathbf{r} - \frac{\mathbf{r}_1 + \mathbf{r}_2}{2} \right]$$

is the electric dipole moment of the three particles with respect to the center of mass of the system. Without loss of generality we assume that $\mathbf{n} \cdot \mathbf{d} = \mu z_c$.

The Breit α^2 correction to the nonrelativistic Hamiltonian is described by an operator

$$V_B = \alpha^2 \left\{ -\frac{p^4}{8m^3} + \frac{4\pi}{8m^2} [\delta(\mathbf{r}_1) + \delta(\mathbf{r}_2)] + \frac{1}{2m^2} \left[\frac{[\mathbf{r}_1 \times \mathbf{p}]}{r_1^3} + \frac{[\mathbf{r}_2 \times \mathbf{p}]}{r_2^3} \right] \frac{\boldsymbol{\sigma}}{2} \right\}. \quad (3)$$

Then the total Hamiltonian reads

$$H = H_0 + V_B + V_p. \quad (4)$$

Let us define the ground state nonrelativistic wave function as follows:

$$(H_0 - E_0)\Psi_0 = 0. \quad (5)$$

In the nonrelativistic case the change of energy due to polarizability of molecular ions is expressed by

$$\begin{aligned} E_p^{(2)} &= \langle \Psi_0 | V_p (E_0 - H_0)^{-1} V_p | \Psi_0 \rangle \\ &= \mathcal{E}^2 \mu^2 \langle \Psi_0 | z_c (E_0 - H_0)^{-1} z_c | \Psi_0 \rangle \\ &= -\frac{1}{2} \alpha_s^0 \mathcal{E}^2, \end{aligned} \quad (6)$$

and

$$\alpha_s^0 = -2\mu^2 \langle \Psi_0 | z_c (E_0 - H_0)^{-1} z_c | \Psi_0 \rangle. \quad (7)$$

Let us introduce $H_1 = H_0 + V_B$, then the scalar dipole polarizability α_s with account of relativistic corrections can be rewritten in the form (we assume that $V_B \approx \alpha^2 H_0$ and $\Psi_0^B = \Psi_0 + \Psi^B$)

$$\begin{aligned} \alpha_s^1 &= -2\mu^2 \langle \Psi_0^B | z_c (E_1 - H_1)^{-1} z_c | \Psi_0^B \rangle \\ &= -2\mu^2 \langle \Psi_0^B | z_c [(E_0 - H_0)^{-1} + (E_0 - H_0)^{-1} (V_B - \langle V_B \rangle) \\ &\quad \times (E_0 - H_0)^{-1} + \dots] z_c | \Psi_0^B \rangle \\ &= -2\mu^2 \langle \Psi_0 | z_c (E_0 - H_0)^{-1} z_c | \Psi_0 \rangle \\ &\quad - 2\mu^2 \langle \Psi_0 | z_c (E_0 - H_0)^{-1} (V_B - \langle V_B \rangle) (E_0 \\ &\quad - H_0)^{-1} z_c | \Psi_0 \rangle - 2\mu^2 (\langle \Psi^B | z_c (E_0 - H_0)^{-1} z_c | \Psi_0 \rangle \\ &\quad + \langle \Psi_0 | z_c (E_0 - H_0)^{-1} z_c | \Psi^B \rangle), \end{aligned} \quad (8)$$

TABLE I. Dipole polarizability of $H_2^+(0,0)$. Convergence of the numerical results with the size of the basis set.

	α_s^0	$\Delta\alpha_s$
$N=400$	3.168 596 2	-1.520 65[-4]
$N=600$	3.168 725 2	-1.521 40[-4]
$N=800$	3.168 725 76	-1.521 37[-4]

and $\Psi^B = (E_0 - H_0)^{-1} V_B |\Psi_0\rangle$. Thus the relativistic correction to the scalar dipole polarizability α_s is reduced to evaluation of the following matrix elements:

$$\begin{aligned} \Delta\alpha_s = & -2\mu^2 \langle \Psi_0 | z_c (E_0 - H_0)^{-1} (V_B - \langle V_B \rangle) \\ & \times (E_0 - H_0)^{-1} z_c |\Psi_0\rangle - 2\mu^2 \langle \Psi_0 | V_B E_0 - H_0)^{-1} z_c \\ & \times (E_0 - H_0)^{-1} z_c |\Psi_0\rangle - 2\mu^2 \langle \Psi_0 | z_c (E_0 - H_0)^{-1} z_c \\ & \times (E_0 - H_0)^{-1} V_B |\Psi_0\rangle. \end{aligned} \quad (9)$$

At this point we can note that the spin-orbit term does not contribute to α_s since the magnetic dipole operator has selection rules $m' = m \pm 1$.

III. VARIATIONAL NONRELATIVISTIC WAVE FUNCTION

A variational wave function describing the ground state of the hydrogen molecular ion is taken in a form

$$\begin{aligned} \Psi_0 = & \sum_{i=1}^{\infty} [C_i \cos(\nu_i R_{12}) + D_i \sin(\nu_i R_{12})] \\ & \times e^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i R_{12} + (\mathbf{r}_1 \leftrightarrow \mathbf{r}_2)}. \end{aligned} \quad (10)$$

Here α_i , β_i , γ_i , and ν_i are parameters generated in a quasirandom manner,

$$\alpha_i = \left[\left[\frac{1}{2} i (i+1) \sqrt{p_\alpha} \right] (A_2 - A_1) + A_1 \right],$$

where $[x]$ designates the fractional part of x , p_α and q_α are some prime numbers, and the end points of an interval $[A_1, A_2]$ are real variational parameters. Parameters β_i , γ_i , and ν_i are obtained in a similar way. Details of the method and discussion of various aspects of its application can be found in our previous papers [7,8].

The perturbed function $\Psi_1 = \mu(E_0 - H_0)^{-1} \mathbf{r}_c \Psi_0$ is expanded in a similar way

$$\begin{aligned} \Psi_1 = & \sum_{i=1}^{\infty} \mathbf{r}_1 [\hat{C}_i \cos(\nu_i R_{12}) + \hat{D}_i \sin(\nu_i R_{12})] \\ & \times e^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i R_{12} + (\mathbf{r}_1 \leftrightarrow \mathbf{r}_2)}. \end{aligned} \quad (11)$$

TABLE III. Dipole polarizability of $D_2^+(0,0)$.

	E_0	α_s^0	$\Delta\alpha_s$	α_s
$N=800$	-0.598 788 784 298 97	3.071 988 68	-1.499 14[-4]	3.071 838 77

TABLE II. Dipole polarizability of $H_2^+(0,0)$. Comparison with other calculations and experiment.

	α_s
Experiment [2]	3.167 96(15)
Shertzer and Greene [3]	3.1682(4)
Bhatia and Drachman [4]	3.1680
Moss [5]	3.168 50
Taylor, Dalgarno, and Babb [6]	3.168 725 6(1)
Present work	
Nonrelativistic	3.168 725 76
With α^2 corrections	3.168 573 62

Technically evaluation of the matrix elements in Eq. (9) can proceed in the following way. For the matrix element in the first line we need to solve one linear equation, $(E_0 - H_0)\Psi_1 = z_c \Psi_0$, and then average operator $(V_B - \langle V_B \rangle)$ over Ψ_1 . To get rid of singularities in the solutions of implicit equations of lines 2 and 3 of Eq. (9) one can solve a sequence of equations from the right to the left in the second line and in the reverse order for the third line. In the latter two cases the solution as well as the right-hand side of the last equation should be projected onto subspace orthogonal to Ψ_0 .

IV. RESULTS AND CONCLUSIONS

In Table I results of numerical calculations are presented. For the zeroth-order approximation a wave function with a basis set of $N=800$ has been used that yields the nonrelativistic energy

$$E_0 = -0.597 139 063 123 40(1), \quad (12)$$

which is in a good agreement with our previous accurate result [8]. Here $m_p = 1836.152 701 m_e$ is adopted. As seen from Table I convergence for the relativistic correction is slower due to singular operators encountered in the matrix elements. Nevertheless we can conclude from this table that the resulting value is

$$\Delta\alpha_s = -0.000 152 14(1). \quad (13)$$

Combining this result with the nonrelativistic value from Table I one obtains that the static electric dipole polarizability of H_2^+ molecular ion ground state with relativistic α^2 corrections is to be

$$\alpha_s = 3.168 573 7(1). \quad (14)$$

We see that the obtained value for the dipole polarizability does not fully account for present disagreement between

TABLE IV. Dipole polarizability of $D_2^+(0,0)$. Comparison with experiment.

	α_s
Experiment [2]	3.071 87(54)
Taylor, Dalgarno, and Babb [6]	3.071 988 7(2)
Present work	
Nonrelativistic	3.071 988 68
With α^2 corrections	3.071 838 77

theory and experiment (comparison of our results with results of previous calculations and experiment are presented in Table II). Our consideration does not include leading order QED corrections but usually they are one order of magnitude smaller than relativistic corrections and have a different sign. Thus they could not cover the remaining 4/5 of the discrepancy.

On the other hand the experimental value for the dipole polarizability has been deduced from the effective model Hamiltonian [9] which is a fully nonrelativistic Hamiltonian and it does not include the retardation Casimir-Polder effect [10] for the Rydberg electron. The importance of this phenomena has been pointed out in a paper of Babb and Spruch [11]. So, our conclusion is that the Casimir-Polder potential has to be included into the effective Hamiltonian to meet the requirements of the present level of experimental accuracy. That will enable one to deduce scalar electric dipole polarizability in a more reliable way. Results of similar calculations but for the D_2^+ molecular ion are presented in Tables III and IV.

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