Forbidden ortho-para electric dipole transitions in the H_2^+ ion

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We present a systematic calculation of the electric dipole forbidden transitions in the homonuclear molecular ion H_2^+. We get that the transition rate from the ground ortho ($v=0, N=1, J=1/2$) state to the ground para ($v=0, N=0, J=1/2$) state is 4.9×10^{-14} s^{-1}, which corresponds to the lifetime of 6.4×10^5 yr. The Einstein coefficient $A_{nn'}$ for the $(v=1, N=1, J=1/2)\to(v=0, N=0, J=1/2)$ transition is equal to 0.12×10^{-9} s^{-1}, which is of comparable order with the values for quadrupole transitions in H_2^+. It gives hope that the ortho-para transitions in H_2^+ can be explored by laser spectroscopy.

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I. INTRODUCTION

Forbidden E1 transitions between ortho (triplet in the proton spins, $I=1$) and para (singlet, $I=0$) states in the hydrogen molecular ion H_2^+ are of significant interest. So far, only transitions between near-threshold high vibrational $v\sim 18-19$ states were studied numerically [1] and experimentally [2], where it was discovered that due to strong g/u state mixing (*gerade*/*ungerade* electronic symmetry states) near threshold the transition rate is high enough for spectroscopic measurements. For example, the rate of the $(v=19, N=1)\to(v=18, N=0)$ transition is 9.6×10^{-6} s^{-1}.

In the case of a hydrogen molecule H_2, Wigner gave a qualitative estimate for the E1 radiative decay rate from ortho to para hydrogen as $R_{\rm est}=10^{-14}$ s^{-1} (see Ref. [3]). First calculations by Raich and Good [4] showed that the decay rate of the $X^1\Sigma_g^+(N=1)$ lowest vibrational ortho state is about $\sim2\times10^{-13}$ yr^{-1}, many orders of magnitude smaller than the nominal rate due to strong cancellations. Dodelson [3] reanalyzed the calculations of Raich and Good using a fully quantum electrodynamical approach, introduced by Feinberg and Sucher [5] for calculations in the helium atom, and derived additional terms, which change the previous result by about 20%. Later, Pachucki and Komasa [6] extended the calculations by taking into account both E1 and M2 transitions, resulting in an E1 decay rate of the $(v=0, N=1, J=1)$ ortho state equal to 1.68×10^{-13} yr^{-1} (or 5.3×10^{-21} s^{-1}). The radiative lifetimes of the $1s\sigma_g$ $(v=0, N=1, J=1/2)$ ortho state of the H_2^+ molecular ion have been only roughly estimated in Ref. [1]. Our calculation shows that this estimate was incorrect.

In the present work we intend to perform calculations of the E1 forbidden transitions for the hydrogen molecular ion H_2^+ at low v and N, which take into account all relativistic corrections of order $(m_e/m_p)(Z\alpha)^2$ to the transition amplitude. We intend to show that in the case of the E1 decay, transition rates are much higher than for the neutral molecule and are in agreement with Wigner's estimate for this quantity.

In what follows we assume atomic units: $\hbar=|e|=m_e=1$.

II. THE HAMILTONIAN

In this work we adopt the following notations: v is the vibrational quantum number, and N is the total orbital angular momentum of the nonrelativistic wave function. The spin part is described by the spin operators of two protons, $\mathbf{I}_1$, $\mathbf{I}_2$, and the spin of an electron, $\mathbf{s}_e$; $\mathbf{I}=\mathbf{I}_1+\mathbf{I}_2$ is the total nuclear spin; $\mathbf{F}=\mathbf{I}+\mathbf{s}_e$ is the total spin of the H_2^+ ion; and $\mathbf{J}=\mathbf{F}+\mathbf{N}$ is the total angular momentum. Thus, the ground para state is denoted $(v=0, N=0, I=0, F=1/2, J=1/2)$. The excited rotational ortho state of the ground vibrational level $(v=0, N=1)$ has two spin states: $F=1/2$ and $F=3/2$. We will call the first state the ground ortho state. The triplet states with the total spin $F=3/2$ are not coupled to the subspace of the singlet nuclear spin states, at least within the first-order corrections to the wave function considered in this work. For this reason we will ignore the $F=3/2$ states in our studies and will use the shorter notation for description of a state: (v, N, J).

The Hamiltonian for an ion interacting with the radiation electromagnetic field, which also includes the leading order Breit-Pauli corrections, is expressed as follows:

$$H=H_0+H_{\rm BP}+H_I, \tag{1}$$

where H_0 is the zero-order nonrelativistic Hamiltonian of the particles, $H_{\rm BP}$ is the Breit-Pauli Hamiltonian, and H_I is the part which describes the interaction of the ion with the electromagnetic field.

The nonrelativistic Hamiltonian in the center of mass frame may be written as

$$H_0 = \frac{\mathbf{p}_1^2}{2M} + \frac{\mathbf{p}_2^2}{2M} + \frac{\mathbf{p}_e^2}{2m_e} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{Z^2}{R}, \tag{2}$$

where $\mathbf{r}_i = \mathbf{r}_e - \mathbf{R}_i$ and $\mathbf{R} = \mathbf{R}_2 - \mathbf{R}_1$ are electron coordinates relative to nuclei and internuclear position vectors in the molecular coordinate notations, $(\mathbf{r}_e, \mathbf{R}_1, \mathbf{R}_2)$ and $(\mathbf{p}_e, \mathbf{p}_1, \mathbf{p}_2)$ are the position vectors and momenta of particles in the center of mass frame, $M = m_p$ is the proton mass, and $Z = 1$ is the proton charge. According to the tradition accepted in the theory of the light atoms, we will keep using Z for the proton charge in order to distinguish between two scales: α, fine structure constant, and $v/c \approx Z\alpha$, mean particle velocity in a bound system.

The Breit-Pauli Hamiltonian $H_{\rm BP}$ is the leading-order relativistic correction (see, for example, Ref. [7]). Here we need only the spin-spin and spin-orbit interactions responsible for the g/u mixing; we will follow the notations of Ref. [8]. The spin-spin and spin-orbit interactions are expressed, respectively, as

$$H_{ss} = \alpha^2 \frac{(1+\kappa_e)(1+\kappa_p)}{m_e m_p} \frac{8\pi}{3} [(\mathbf{s}_e \cdot \mathbf{I}_1)\delta(\mathbf{r}_1) + (\mathbf{s}_e \cdot \mathbf{I}_2)\delta(\mathbf{r}_2)]. \tag{3}$$

$$\begin{aligned} H_{\rm so} = \alpha^2 \Bigg\{ & \frac{1+2\kappa_e}{2m_e^2} \left[\frac{[\mathbf{r}_1 \times \mathbf{p}_e]}{r_1^3} + \frac{[\mathbf{r}_2 \times \mathbf{p}_e]}{r_2^3} \right] \mathbf{s}_e - \frac{1+\kappa_e}{m_e m_p} \left[\frac{[\mathbf{r}_1 \times \mathbf{p}_1]}{r_1^3} + \frac{[\mathbf{r}_2 \times \mathbf{p}_2]}{r_2^3} \right] \mathbf{s}_e \\ & - \frac{1+2\kappa_p}{2m_p^2} \left[\frac{[\mathbf{r}_1 \times \mathbf{p}_1]}{r_1^3} \mathbf{I}_1 + \frac{[\mathbf{r}_2 \times \mathbf{p}_2]}{r_2^3} \mathbf{I}_2 \right] + \frac{1+\kappa_p}{m_e m_p} \left[\frac{[\mathbf{r}_1 \times \mathbf{p}_e]}{r_1^3} \mathbf{I}_1 + \frac{[\mathbf{r}_2 \times \mathbf{p}_e]}{r_2^3} \mathbf{I}_2 \right] \Bigg\}. \end{aligned} \tag{4}$$

The operators which connect ortho and para states are

$$\begin{aligned} H_{ss}^{-} &= \alpha^2 \frac{(1+\kappa_e)(1+\kappa_p)}{m_e m_p} \frac{4\pi}{3} \{(\mathbf{s}_e \cdot \mathbf{I}_-)[\delta(\mathbf{r}_1) - \delta(\mathbf{r}_2)]\}, \\ H_{\rm so}^{-} &= \alpha^2 \left\{ \frac{1+\kappa_p}{2m_e m_p} \left(\frac{[\mathbf{r}_1 \times \mathbf{p}_e]}{r_1^3} - \frac{[\mathbf{r}_2 \times \mathbf{p}_e]}{r_2^3} \right) \mathbf{I}_- - \frac{1+2\kappa_p}{4m_p^2} \left(\frac{[\mathbf{r}_1 \times \mathbf{p}_1]}{r_1^3} - \frac{[\mathbf{r}_2 \times \mathbf{p}_2]}{r_2^3} \right) \mathbf{I}_- \right\}, \end{aligned} \tag{5}$$

where $\mathbf{I}_- = (\mathbf{I}_1 - \mathbf{I}_2)$, κ_e and κ_p are the magnetic moment anomaly of an electron and proton, respectively, while $\mu_p = 1 + \kappa_p$ is the magnetic moment of the proton in nuclear magnetons.

In our consideration we use the nonrelativistic quantum electrodynamics (NRQED) formalism [9–11]. For our needs only the leading-order terms of the Lagrangian [10], Eq. (19), are needed for both an electron and proton. We use the Coulomb gauge, and the one-photon interaction Hamiltonian (in the center of mass frame) may be expressed as

$$\begin{aligned} H_I = & \sum_a Z_a \alpha \frac{\mathbf{p}_a}{m_a} \mathbf{A}_r + \sum_a \frac{Z_a \alpha (1+\kappa_a)}{2m_a} \boldsymbol{\sigma}_a \mathbf{B}_r - \sum_a \frac{Z_a \alpha (1+2\kappa_a)}{8m_a^2} \boldsymbol{\sigma}_a (\mathbf{p}_a \times \mathbf{E}_\perp - \mathbf{E}_\perp \times \mathbf{p}_a) \\ & + \sum_a \frac{Z_a^2 \alpha^2}{2m_a} \mathbf{A} \cdot \mathbf{A}_r - \sum_a \frac{Z_a^2 \alpha^2 (1+2\kappa_a)}{4m_a^2} \boldsymbol{\sigma}_a (\mathbf{A}_r \times \mathbf{E}_\parallel) + \sum_a \frac{Z_a^2 \alpha^2 (1+2\kappa_a)}{4m_a^2} \boldsymbol{\sigma}_a (\mathbf{E}_\perp \times \mathbf{A}) + \cdots, \end{aligned} \tag{6}$$

where we use $\mathbf{A}_r$, $\mathbf{B}_r$, and $\mathbf{E}_\perp$ to denote operators of the external electromagnetic radiation field. The transverse fields $\mathbf{E}_\perp$ and $\mathbf{B}_\mathbf{r}$ depend on $\mathbf{A}_r$ as $\mathbf{E}_\perp = -\frac{1}{c}\frac{\partial}{\partial t}\mathbf{A}_r(\mathbf{r}, t)$ and $\mathbf{B}_r = \boldsymbol{\nabla} \times \mathbf{A}_r(\mathbf{r}, t)$.

Operators $\mathbf{E}_\parallel$ and $\mathbf{A}$ are the electric-field strength and the magnetic-field potential, which are induced by the particles constituting the molecular ion. For our derivations we need only the expression for the magnetic-field potential produced by the magnetic moment of the nuclei [corresponding to the $\mathbf{A} \cdot \mathbf{A}_r$ term of the electron line in (6)],

$$\mathbf{A} = -\frac{Z\alpha(1+\kappa_p)}{m_p} \left(\frac{[\mathbf{r}_1 \times \mathbf{I}_1]}{r_1^3} + \frac{[\mathbf{r}_2 \times \mathbf{I}_2]}{r_2^3} \right),$$

which results in correction to the nonrelativistic current $\mathbf{J}^{(0)} = \sum_a Z_a \alpha \mathbf{p}_a / m_a$:

$$\boldsymbol{\delta}\mathbf{J} = -\frac{Z\alpha^3(1+\kappa_p)}{2m_e m_p} \left\{ \frac{[\mathbf{r}_1 \times \mathbf{I}_1]}{r_1^3} + \frac{[\mathbf{r}_2 \times \mathbf{I}_2]}{r_2^3} \right\}. \tag{7}$$

The other terms in Eq. (6) produce corrections to the electric current which either do not contain the proton spin operator, or are of a higher order in m_e/m_p or $Z\alpha$ expansion and thus will be neglected.

III. TRANSITION AMPLITUDES

The transition amplitude for the forbidden E1 transitions is expressed as

$$\begin{aligned} \mathcal{T}_{E1}^i &= \langle \psi_n | J^i | \psi_{n'} \rangle + \langle \psi_n | J^{(0)i} | \psi_{n'}^{(1)} \rangle + \langle \psi_n^{(1)} | J^{(0)i} | \psi_{n'} \rangle \\ &= \langle \psi_n | \delta J^i | \psi_{n'} \rangle + \langle \psi_n | J^{(0)i} Q (E_{n'} - H_0)^{-1} Q H_{\rm gu} | \psi_{n'} \rangle \\ &\quad + \langle \psi_n | H_{\rm gu} Q (E_n - H_0)^{-1} Q J^{(0)i} | \psi_{n'} \rangle, \end{aligned} \tag{8}$$

where $\mathbf{J}$ is the electric current operator of the system of bound particles (ion), ψ_n and $\psi_{n'}$ are the nonrelativistic solutions of the Schrödinger equation, $\psi_n^{(1)}$ and $\psi_{n'}^{(1)}$ are the first-order relativistic corrections to the wave functions, Q is the projection operator on a subspace orthogonal to ψ_n (or $\psi_{n'}$), and the

TABLE I. Comparison with calculations by Bunker and Moss [1]. Averaged transition rates $\bar{A}_{nn'}$ (in 10^{-6} s^{-1}).

Transition	This work	Ref. [1]
$(19,0) \to (18,1)$	11.5	11.5
$(19,0) \to (17,1)$	161.4	163.7

operator

$$H_{\rm gu} = H_{\rm so}^{(-)} + H_{ss}^{(-)}$$

is the g/u symmetry breaking part of the Breit-Pauli Hamiltonian.

Transition amplitude in the length form may be obtained using relation $[H_0, \mathbf{r}_a] = -i\,\mathbf{p}_a/m_a$, or $\mathbf{J}^{(0)} = i\alpha[H_0, \mathbf{d}]$. Then one gets

$$\mathcal{T}^i_{E1} = \langle\psi_n|\mathcal{D}^i|\psi_{n'}\rangle + i\,\alpha\, w_{nn'}\langle\psi_n|d^i Q(E_{n'} - H_0)^{-1} Q H_{\rm gu}|\psi_{n'}\rangle + i\,\alpha\, w_{nn'}\langle\psi_n|H_{\rm gu} Q(E_n - H_0)^{-1} Q d^i|\psi_{n'}\rangle, \quad (9)$$

where $d^i = \sum_a Z_a r_a^i$ is the dipole operator in the length form, $w_{nn'} = E_n - E_{n'}$ is the transition frequency, and

$$\mathcal{D}^i = i\,\alpha\, w_{nn'} d^i - i\alpha[d^i, H_{\rm gu}] + \delta J^i.$$

Here the commutator is

$$i[\mathbf{d}, H_{\rm gu}] = -\frac{\alpha^2}{2}\left(1 + \frac{1}{m_p}\right)\frac{(1+\kappa_p)}{m_e m_p}\left(\frac{[\mathbf{r}_1 \times \mathbf{I}_1]}{r_1^3} + \frac{[\mathbf{r}_2 \times \mathbf{I}_2]}{r_2^3}\right), \quad (10)$$

and it cancels out the electric current correction term, Eq. (7), in the leading order in m_e/m_p.

The total transition probability for spontaneous emission from state n to state n' is expressed from the transition amplitude as follows:

$$A_{nn'} = \frac{1}{\tau}\,\frac{4\alpha}{3}\, w_{nn'}\,\frac{|\langle\psi_n\|\mathcal{T}^i_{E1}\|\psi_{n'}\rangle|^2}{2J_n + 1}, \quad (11)$$

where τ is a unit of time (in atomic units: $\tau = 2.41888 \times 10^{-17}$ s).

IV. RESULTS AND DISCUSSION

Numerical calculations were based on the exponential variational expansion [12]. Particularly, the nonrelativistic solutions ψ_n and the first-order corrections to the wave functions $\psi_n^{(1)}$ were calculated using this expansion method. By averaging Eq. (9), we obtained the transition amplitudes $T_{nn'}$ and, eventually, the Einstein coefficients $A_{nn'}$ for the spontaneous emission of a photon from the state $n = (v, N, J)$ to the state $n' = (v', N', J')$.

In Table I our results are compared with the results of Bunker and Moss [1]. In order to make this comparison, the transition rates are averaged over J',

$$\bar{A}_{nn'} = \bar{A}_{N=0,N'=1} = \tfrac{2}{3}A_{J=\frac{1}{2},J'=\frac{3}{2}} + \tfrac{1}{3}A_{J=\frac{1}{2},J'=\frac{1}{2}}. \quad (12)$$

In Ref. [1] only the spin-spin interaction has been taken into account as a source of the g/u breaking. That is justified for the weakly bound states where the spin-spin coupling becomes dominant due to proximity of the $2p\sigma_u$ states.

TABLE II. The Einstein coefficient $A_{nn'}$ (in 10^{-12} s^{-1}) for transitions between ortho and para states, $N = 0 \to N = 1$.

$v \to v'$	$J = \frac{1}{2} \to J' = \frac{1}{2}$	$J = \frac{1}{2} \to J' = \frac{3}{2}$
$0 \to 0$	0.0558	0.0494
$0 \to 1$	123.7	128.3
$0 \to 2$	0.1170	0.0708
$0 \to 3$	0.0429	0.0554
$0 \to 4$	0.0155	0.0183
$1 \to 0$	238.7	122.7
$1 \to 1$	0.0646	0.0585
$1 \to 2$	274.3	283.1
$1 \to 3$	0.8526	0.6433
$1 \to 4$	0.1131	0.1510

Tables II and III present the results of our numerical calculations for $N = 0 \to 1$ and $N = 1 \to 2$ transitions, respectively. As is seen, transition rates for $\Delta v = 1$ transitions are of comparable order of magnitude with the rate of quadrupole transitions in H_2^+ [13,14]. For example, the E2 transition $(v = 0, N = 0) \to (0, 2)$ has $A_{nn'} = 9.7 \times 10^{-12}$ s^{-1}, and the E2 transition $(v = 0, N = 0) \to (2, 2)$ has $A_{nn'} = 32. \times 10^{-9}$ s^{-1} [14]. This fact allows to hope that the ortho-para transitions may be studied in laser spectroscopic experiments.

It is interesting to note that the contribution of spin-orbit interactions to the decay rate of low v states is about 5%–10%. It turns out that a simple approach with only spin-spin coupling should give fairly good results. In this case, only the reduced matrix element of the transition $N \to N'$ can be calculated, and the spin part of the amplitude can be expressed using Wigner's 6-j symbols, as for allowed transitions:

$$\langle vFNJ\|\mathbf{d}\|v'FN'J'\rangle = (-1)^{J+F+N'+1}\sqrt{(2J+1)(2J'+1)} \times \begin{Bmatrix} N & 1 & N' \\ N' & F & J \end{Bmatrix}\langle vN\|\mathbf{d}\|v'N'\rangle.$$

TABLE III. The Einstein coefficient $A_{nn'}$ (in 10^{-12} s^{-1}) for transitions between ortho and para states, $N = 1 \to N = 2$.

$v \to v'$	$J = \frac{3}{2} \to J' = \frac{5}{2}$	$J = \frac{3}{2} \to J' = \frac{3}{2}$	$J = \frac{1}{2} \to J' = \frac{3}{2}$
$0 \to 0$	0.5229	0.0788	0.4186
$0 \to 1$	151.8	26.15	128.3
$0 \to 2$	0.0817	0.0070	0.0527
$0 \to 3$	0.0561	0.0121	0.0523
$0 \to 4$	0.0195	0.0039	0.0176
$1 \to 0$	211.3	23.96	236.6
$1 \to 1$	0.6076	0.0932	0.4899
$1 \to 2$	337.1	57.82	284.3
$1 \to 3$	0.7216	0.0865	0.5265
$1 \to 4$	0.1511	0.0335	0.1426

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