Eqs. (16) and (17) may be obtained also using the recursion relations for Coulomb matrix elements [see W. Gordon, Ann. Physik 2, 1031 (1929)].

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[9] See Ref. 7, p. 215, Eq.(11).

[10] See Ref. 8, p. 238, Eq.(3).

[11] P. Appell and Kampe de Feriet, Fonctions Hypergeométriques et Hypersphériques. (Polynômes d' Hermite, Paris, 1926) (unpublished).

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Multiphoton Processes in Heteropolar Diatomic Molecules

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Within the framework of the Born–Oppenheimer approximation and the theory of multiphoton molecular transitions, a method is proposed for calculating matrix elements of multiphoton processes in a heteropolar diatomic molecule. The method is based on the application of the explicit expressions of the Green's functions of the internuclear potentials. Analytical expressions are derived for the two-photon transitions. Results for higher-order processes are presented in a form which is convenient for numerical computation.

I. INTRODUCTION

In a previous paper[1] general expressions have been derived for the cross sections of multiphoton processes induced by radiation acting on a diatomic molecule.

Within the framework of time-dependent perturbation theory and the Born–Oppenheimer approximation, a method has been proposed for evaluating the sums over intermediate states. The method is based on the application of the explicit expressions for the Green's functions of the internuclear potentials. The Morse-type model of potential-energy curves has been used which gives a good representation of true curves of the ground and excited electronic states of some homopolar diatomic molecules.

It is evident that the description of the interaction of intense electromagnetic radiation with a heteropolar molecule would also be of interest from the different points of view. In the most clearly defined cases of what is called heteropolar binding all the valency electrons pass over from their own atoms to other atoms, so that the heteropolar molecule unlike the homopolar one has appreciable dipole moment in the ground state.

This gives rise to rich rotation-vibration spectra in ordinary spectroscopy of such diatomics. In the treatment of multiphoton processes it becomes necessary to take into account the intermediate transitions which occur without change in electronic state. Theoretically, two-photon vibrational transitions in a heteronuclear diatomic molecule have been considered using the Morse potential[2] and the Kratzer potential[3] as internuclear potential energy.

The application of the Green's functions of these potentials obtained in closed forms permits analytic solution of the problem. However, the potentials used do not give a particularly good representation of true curves in the case of heteropolar binding. At the same time the experimental investigation of the interaction of heteropolar diatomics with the electromagnetic field has been the subject of a large number of works. Terenin first initiated the study of spectra of heteropolar diatomics.[4] Actually, such research plays an important part both for the theory of molecular structure in general and for nonlinear optical phenomena in particular.

It is clear that the possibilities of the theoretical treatment of the processes induced by radiation acting on a molecule depend on the presence of the potential-energy-curve model for the ground and excited molecular states. Such a model must well describe the true curves and at the same time be simple enough to enable us to write analytic expressions for wave functions and a Green's function of all electron terms involved in the transition.

In the present paper we shall use the following internuclear potentials proposed in the paper[5]:

$$V_j(r) = \frac{A_j}{(r-\rho_j)^2} - \frac{B_j}{r-\rho_j} + Q_j \qquad (1)$$

for $r > \rho_j$ and $V_j(r) = \infty$ for $r \leqslant \rho_j$. Equation (1) gives a good representation of the true attractive ($B_j > 0$) and repulsive ($B_j < 0$) curves of heteropolar diatomics. The Schrödinger equation with potential (1) allows analytic solution.

The main difficulty in calculating the cross section of multiphoton molecular transitions lies in the correct evaluation of the radial parts of the matrix elements. (We shall use the general expressions derived in Ref. 1 for cross sections of multiphoton transitions in a diatomic molecule.) A method of calculating radial matrix elements being available, the problem of multiphoton transitions in diatomic heteropolar molecules may be considered as resolved in principle. The method used is based on the application of the internuclear-potential Green's functions obtained in closed form. In Sec. II the results are presented in a form which is convenient for numerical computation. In Sec. III analytic formulas are given for some two-photon transitions in heteropolar diatomics.

II. METHOD OF EVALUATING RADIAL MATRIX ELEMENTS

Within the framework of time-dependent perturbation theory and the Born–Oppenheimer approximation the treating of the multiphoton molecular transitions reduces essentially (after selection rules for rotational and electronic quantum numbers have been established) to evaluating radial matrix elements of the form

$$
\begin{aligned}
M(i_0, i_1, i_2, \ldots, i_{N-1}, i_f | E_p) &= \int_0^\infty \chi_f(r_N) D_N(r_N)\, dr_N \int_0^\infty D_{N-1}(r_{N-1}) \\
&\quad \times g_{N-1}(r_{N-1}, r_N | E_0 + (N-1)E_p)\, dr_{N-1} \cdots \\
&\quad \times \int_0^\infty D_1(r_1) g_1(r_1, r_2 | E_0 + E_p) \chi_0(r_1)\, dr_1
\end{aligned}
\tag{2}
$$

[see Eqs. (2), (8), and (14) of Ref. 1]. Here E_0 denotes the energy of the initial state of a molecule, E_p is the photon energy, and $\chi_0(r)$ and $\chi_f(r)$ are the radial functions of the initial $|i_0\rangle$ and final $|i_f\rangle$ states, respectively. $g_1, g_2, \ldots, g_{N-1}$ are the Green's functions of potentials $V_1(r)$, $V_2(r)$, $\ldots$, $V_{N-1}(r)$ of the intermediate electronic states $|i_1\rangle$, $|i_2\rangle$, $\ldots$, $|i_{N-1}\rangle$, respectively. $|i\rangle = |n, \Lambda, K\rangle$ denotes a state with definite values of the absolute value K and z component M of the total angular momentum of the molecule and a definite value Λ of the component of the electron angular momentum along the axis of the molecule; n denotes the assembly of the remaining quantum numbers which determine the molecular state.

The functions $D_1(r)$, $D_2(r)$, $\ldots$, $D_{N-1}(r)$ in Eq. (2) denote the dipole moments of the first, second, $\ldots$, $(N-1)$th intermediate electronic transitions calculated in the system of coordinates which rotates with the molecule; $D_j(r)$ corresponds to the transition from $|i_{j-1}\rangle$ into $|i_j\rangle$.

The Green's function of the radial Schrödinger equation

$$
\left[\frac{d^2}{dr^2} + \frac{2m}{\hbar^2}\left(E - \frac{\hbar^2}{2m} \times \frac{K_j(K_j+1)}{r_0^2}\left(\frac{r_0-\rho_j}{r-\rho_j}\right)^2 - V_j(r)\right)\right] rR(r) = 0 \,,
\tag{3}
$$

with the internuclear potential $V_j(r)$ of Eq. (1) and the centrifugal repulsion term treated approximately, is given by[5]

$$
g_j(r_1', r_2' | E) = -\frac{m}{\hbar^2 \zeta_j} \frac{\Gamma(1+s_j-n_j)}{\Gamma(2s_j+2)} \times M_{n_j, s_j+1/2}(2\zeta_j r_<') W_{n_j, s_j+1/2}(2\zeta_j r_>') \,.
\tag{4}
$$

Here the functions M and W are the Whittaker functions; $r_<'$ ($r_>'$) is the smaller (larger) of the quantities r_1' and r_2', $r' = r - \rho_j$; $\zeta_j = [-2m(E-Q_j)]^{1/2}\hbar^{-1}$, $n_j = mB_j/\hbar^2\zeta_j$; s_j is the positive root of the equation

$$
s_j(s_j+1) = \frac{2mA_j}{\hbar^2} + \frac{K_j(K_j+1)(r_0-\rho_j)^2}{r_0^2} \,,
\tag{5}
$$

where r_0 is the equilibrium internuclear distance in the ground state $|0\rangle$. When $B_j > 0$ the poles of the Γ function $\Gamma(1+s_j-n_j)$ at $1+s_j-n_j = -v$ ($v = 0, 1, 2, \ldots$) determine the infinite eigenenergy spectrum of bound states,

$$
E_v - Q_j = -\frac{B_j^2 m/\hbar^2}{2(s_j+1+v)^2} \,,
\tag{6}
$$

where $v = 0, 1, 2, ..$ is the vibrational quantum number. The normalized wave functions of the discrete spectrum ($\chi = rR$) are determined as the residues in the poles of the Green's function (4) and are given by

$$
\chi_v(r') = \frac{[mB_j \Gamma(2s_j+2+v)]^{1/2}}{\hbar(s_j+1+v)(v!)^{1/2}\Gamma(2s_j+2)} \times M_{s_j+1+v, s_j+1/2}\left(\frac{2r'}{a_j(s_j+1+v)}\right) ,
\tag{7}
$$

where $a_j = \hbar^2/B_j m$ ($B_j > 0$).

Continuum wave functions ($E - Q_j > 0$) in the attractive ($B_j > 0$) or in the repulsive ($B_j < 0$) field have the form

$$\chi_q(r') = \frac{e^{i\pi n_j/2}}{(2\pi)^{1/2}(i)^{s_j+1}} \frac{|\Gamma(s_j+1+n_j)|}{\Gamma(2s_j+2)} \times M_{n_j, s_j+1/2}(2iqr'), \tag{8}$$

where

$$n_j = mB_j/\hbar^2\zeta_j = -imB_j/\hbar^2 q,$$

$$\zeta_j = [-2m(E-Q_j)]^{1/2}/\hbar = iq;$$

q is the wave number of the relative motion of the particle. The normalization coefficient in (8) corresponds to the asymptotic form

$$\chi_q(r) \approx (2/\pi)^{1/2} \times \sin[qr + in_j \ln 2q(r-\rho_j) - \tfrac{1}{2}\pi s_j - q\rho_j + \delta_j],$$

where $\delta_j = \arg\Gamma(s_j+1+n_j)$.

Radial functions of the initial $|0\rangle$ and final $|f\rangle$ states are determined as the functions of their arguments $r' = r-\rho_0$ and $r' = r-\rho_f$, respectively, by Eqs. (7) and (8) [parameters $\rho_0, \rho_1, \ldots, \rho_{N-1}, \rho_f$ determine the positions of the singular points of potential-energy curves (1) of the gound $|0\rangle$, intermediate $|i_1\rangle$, $|i_2\rangle, \ldots, |i_{N-1}\rangle$, and final $|f\rangle$ electronic states]. The Green's function $g_1, g_2, \ldots, g_{N-1}$ of the internuclear potentials of the intermediate electronic states have explicit expressions (4) as the functions of the variables $(r-\rho_1)$, $(r-\rho_2), \ldots, (r-\rho_{N-1})$, respectively.

Let us introduce in Eq. (2) the new variables of integration

$$r_1' = r_1 - \rho_0,$$

$$r_2' = r_2 - \rho_0, \ldots, r_N' = r_N - \rho_0.$$

Taking into account that the wave functions and the Green's functions vanish to the left of the singular points of corresponding potentials (continuity of wave functions), we obtain

$$\begin{aligned} M(i_0, i_1, \ldots, i_{N-1}, i_f|E_p) = {} & \int_{(\Delta_{N-1},\Delta_f\rangle)}^{\infty} \bar{\chi}_f(r_N-\Delta_f) D_N(r_N+\rho_0)\, dr_N \int_{(\Delta_{N-2},\Delta_{N-1}^{>})}^{\infty} D_{N-1}(r_{N-1}+\rho_0) \\ & \times \bar{g}_{N-1}(r_N-\Delta_{N-1}, r_{N-1}-\Delta_{N-1}|E_0+(N-1)E_p)\, dr_{N-1} \cdots \\ & \times \int_{(\Delta_1,\Delta_2^{>})}^{\infty} D_2(r_2+\rho_0)\bar{g}_2(r_3-\Delta_2, r_2-\Delta_2|E_0+2E_p)\, dr_2 \\ & \times \int_{(\Delta_0,\Delta_1^{>})}^{\infty} D_1(r_1+\rho_0)\bar{g}_1(r_2-\Delta_1, r_1-\Delta_1|E_0+E_p)\bar{\chi}_0(r_1)\, dr_1. \end{aligned} \tag{9}$$

In Eq. (9) the primes on the variables of integration have been omitted, $\Delta_j = \rho_j - \rho_0$ $(j = 0, 1, 2, \ldots, N)$. The expressions $(\Delta_0, \Delta_1\rangle)$, $(\Delta_1, \Delta_2\rangle), \ldots$ denote the larger of two quantities in the bracket as the lower limit of integrations. The explicit expressions for the functions $\bar{g}$ and $\bar{\chi}$ in Eq. (9) are now these of Eqs. (4), (7), and (8). Substituting these equations into (9) we obtain

$$\begin{aligned} M(i_0, i_1, \ldots, i_{N-1}, i_f|E_p) = {} & \frac{(-1)^{N-1}[B_0\Gamma(2s_0+2+v_0)]^{1/2}N_f}{(s_0+1+v_0)(v_0!)^{1/2}\Gamma(2s_0+2)} \left(\frac{m}{\hbar^2}\right)^{N-1/2} \prod_{j=1}^{N-1} \frac{\Gamma(1+s_j-n_j)}{\zeta_j\Gamma(2s_j+2)} \\ & \times \int_{(\Delta_{N-1},\Delta_f^{>})}^{\infty} \bar{D}_N(r_N)\, dr_N M_{n_f, s_f+1/2}[2\zeta_f(r_N-\Delta_f)] \\ & \times \int_{(\Delta_{N-2},\Delta_{N-1}\rangle)}^{\infty} \bar{D}_{N-1}(r_{N-1})\, dr_{N-1}\, M_{n_{N-1}, s_{N-1}+1/2}[2\zeta_{N-1}(r_N-\Delta_{N-1}, r_{N-1}-\Delta_{N-1}\rangle)] \\ & \times W_{n_{N-1}, s_{N-1}+1/2}[2\zeta_{N-1}(r_N-\Delta_{N-1}, r_{N-1}-\Delta_{N-1}\rangle)] \ldots \\ & \times \int_{(0,\Delta_1\rangle)}^{\infty} M_{n_1, s_1+1/2}[2\zeta_1(r_2-\Delta_1, r_1-\Delta_1\rangle)]\, W_{n_1, s_1+1/2}[2\zeta_1(r_2-\Delta_1, r_1-\Delta_1,\rangle)] \\ & \times \bar{D}_1(r_1) M_{n_0, s_0+1/2}\left(\frac{2r_1}{an_0}\right) dr_1. \end{aligned} \tag{10}$$

Here parameters A_j, B_j, Q_j, and ρ_j are those of the potentials (1) of the electronic states involving a given multiphoton transition; E_0 is the energy and v_0 is the vibrational quantum number of the initial bound state, $n_0 = s_0 + 1 + v_0$;

$$n_j = mB_j/\hbar^2\zeta_j\,,$$
$$\zeta_j = [-2m(E_0 + jE_p - Q_j)]^{1/2}\hbar^{-1};$$

N_f is the normalization coefficient of the final state:

$$N_f = \frac{[B_f m\Gamma(2s_f + 2 + v_f)]^{1/2}}{\hbar(s_f + 1 + v_f)\,(v_f!)^{1/2}\,\Gamma(2s_f + 2)} \tag{11}$$

for the bound-bound transitions; v_f is the vibrational quantum number of the final state;

$$N_f = \frac{e^{i\pi n_f/2}}{(2\pi)^{1/2}(i)^{s_f+1}}\;\frac{|\Gamma(s_f + n_f + 1)|}{\Gamma(2s_f + 2)} \tag{12}$$

for the N-photon dissociation, where $n_f = -imB_f/\hbar^2 q$ and q is the wave number of dissociating particles.

The functions $\overline{D}_j$ in Eq. (10) describe the transition dipole moments and are defined according to relations $\overline{D}_j(r_j) = D_j(r_j + \rho_0)$. The functions $M_{n_j, s_j+1/2}(2\zeta_j(r_{j+1} - \Delta_j, r_j - \Delta_j^{<}))$ and $W_{n_j, s_j+1/2}(2\zeta_j(r_{j+1} - \Delta_j, r_j - \Delta_j^{>}))$ are the functions of the smaller and larger, respectively, of the two quantities $2\zeta_j(r_{j+1} - \Delta_j)$ and $2\zeta_j(r_j - \Delta_j)$.

Note, that the multiple integral in Eq. (10) may be represented as the sum of integrals of the Whittaker functions of the form

$$\begin{aligned}&\int_{(\Delta_{N-1}, \Delta_f^{>})}^{\infty} M_{n_f, s_f+1/2}[2\zeta_f(r_N - \Delta_f)]\overline{D}_N(r_N)\,dr_N M_{n_{N-1}, s_{N-1}+1/2}[2\zeta_{N-1}(r_N - \Delta_{N-1})]\\ &\times\int_{(r_N-\Delta_{N-1})}^{\infty} W_{n_{N-1}, s_{N-1}+1/2}[2\zeta_{N-1}(r_{N-1} - \Delta_{N-1})]\overline{D}_{N-1}(r_{N-1})\,dr_{N-1} M_{n_{N-2}, s_{N-2}+1/2}[2\zeta_{N-2}(r_{N-1} - \Delta_{N-2})]\\ &\times\ldots\int_{(r_2-\Delta_1)}^{\infty} W_{n_1, s_1+1/2}[2\zeta_1(r_1 - \Delta_1)]\overline{D}_1(r_1)\,dr_1 M_{n_0, s_0+1/2}(2\zeta_0 r_1)\,.\end{aligned} \tag{13}$$

Since each inner integral in (13) has a single-variable limit, an integration with a constant interval makes (13) actually equivalent to a simple integral. The Whittaker functions in Eq. (13) may be calculated using the expansions into power-series and integral representations given in Ref. 6.

The application of numerical methods to the problem of integration of Eq. (13) seems to be straightforward and will be considered in following papers. Without going into this problem, it may be noted that the cross sections of some two-photon transitions can be expressed in analytic form. Analytic expressions for one-photon matrix elements have been obtained in Ref. 5.

III. TWO-PHOTON TRANSITIONS

Let us consider two-photon transitions in the case when the potentials of states involving transition may be described by Eq. (1) with one and the same value of the parameter $\rho(\rho_f = \rho_1 = \rho_0)$. We shall use the integral representation of the Green's function (4) in symmetric coordinates,[7]

$$g(r_1, r_2|E_1) = \frac{2m(r_1 r_2)^{1/2}}{\hbar^2(1 - e^{-2\pi i(n_1 - s_1)})}\int_1^{(0+)} \frac{t^{-n_1-1/2}}{1-t}\exp\left(-\zeta_1(r_1 + r_2)\,\frac{1+t}{1-t}\right) I_{2s_1+1}\left(\frac{4\zeta_1(r_1 r_2 t)^{1/2}}{1-t}\right)dt\,, \tag{14}$$

where $\zeta_1 = [-2m(E_0 + E_p - Q_1)]^{1/2}\hbar^{-1}$, $n_1 = mB_1/\hbar^2\zeta_1$, and s_1 is defined in Eq. (5).

Then using the known relation[8] between the Whittaker functions M and the confluent hypergeometric functions, let us write the wave function of the final (bound or continuum) state in the following form:

$$\begin{aligned}\chi_f(r) = \frac{N_f}{r2\zeta_f(2s_f + 2)\,(2s_f + 3)}&[(1 - n_f + s_f)\,(2 - n_f + s_f)M_{n_f-1, s_f+3/2}(2\zeta_f r)\\ &+ 2(1 - n_f + s_f)(1 + n_f + s_f)M_{n_f, s_f+3/2}(2\zeta_f r) + (1 + n_f + s_f)\,(2 + n_f + s_f)M_{n_f+1, s+3/2}(2\zeta_f r)]\,.\end{aligned} \tag{15}$$

Here $\zeta_f = [-2m(E_0 + 2E_p - Q_f)]^{1/2}\hbar^{-1}$, $n_f = mB_f/\hbar^2\zeta_f$, and N_f is the corresponding normalization coefficient (11) or (12). Substituting Eqs. (7), (14), and (15) in (9) and integrating,[9] we obtain, for example

$$\int_0^\infty \chi_f(r_2) r_2 dr_2 \int_0^\infty g_1(r_1, r_2 | E_0 + E_p) \chi_0(r_1) r_1^i dr_1$$

$$= \frac{N_0 N_f m (-1)^{i+1} 2^{4s+4} \zeta_f^{s+1} \zeta_1^{2s+1} \Gamma(2s+2)}{\hbar^2 n_0^{s+1} a^{s-i} (\zeta_1^2 - \zeta_f^2)^{s+2}} \frac{\partial^{i+1}}{\partial \kappa^{i+1}} \Phi\left(-v_0, 2s+2, -\frac{2}{n_0}\frac{\partial}{\partial \kappa}\right)$$

$$\times \left[\left(\frac{\kappa}{a} + \zeta_1\right)^{-2s-2} \sum_{l=0,\pm 1} \delta^{-n_f-l} a_l \left(\frac{1}{\alpha} F(\alpha;\, \beta,\, \beta';\, \alpha+1;\, X, Y) - \frac{2b}{\alpha+1} F(\alpha+1;\, \beta,\, \beta';\, \alpha+2;\, X, Y) \right.\right.$$

$$\left.\left. + \frac{b^2}{\alpha+2} F(\alpha+2;\, \beta,\, \beta';\, \alpha+3;\, X, Y) \right)\right] \Bigg|_{\kappa = (s+1+v_0)^{-1}} . \qquad (16)$$

Here

$$a_{-1} = (1 - n_f + s)(2 - n_f + s),$$

$$a_0 = 2(1 - n_f + s)(1 + n_f + s),$$

$$a_1 = (1 + n_f + s)(2 + n_f + s);$$

$$b = (\kappa - a\zeta_1)/(\kappa + a\zeta_1);$$

$$X = -\delta(\kappa - a\zeta_1)(\kappa + a\zeta_1)^{-1}, \quad Y = -\beta/\delta;$$

$$\alpha = -n_1 + s + 1, \quad \beta = -n_f - l + s + 2,$$

$$\beta' = n_f + l + s + 2, \quad \delta = (\zeta_1 + \zeta_f)/(\zeta_1 - \zeta_f);$$

and the functions F are the Appell functions of the first kind.[8] To obtain Eq. (16) we have supported that $s = s_1 = s_f$.[10] The Appell functions in Eq. (16) reduce in the case of bound-bound transitions (that is, for $n_f = s + 1 + v_f$, $v_f = 0, 1, 2, \ldots$ is the vibrational quantum number of the bound final state) to ordinary hypergeometric functions. In some specific cases the functions F can be calculated using the asymptotic methods. Generally, the function F in Eq. (16) may be evaluated with the help of the following relation which can be obtained using the known relations for the Appell functions given in Ref. 11:

$$F(\alpha,\, \beta,\, \beta',\, \gamma;\, x,\, y) = (1+t)^\alpha \sum_{N=0}^\infty \frac{(\alpha)_N}{N!} (-t)^N F_1\left(-N,\, \beta,\, \beta',\, \gamma;\, \frac{1+t}{t} x,\, \frac{1+t}{t} y\right) = (1+t)^\alpha \sum_{N=0}^\infty s_N , \qquad (17)$$

where $s_{-N} = 0$, $s_0 = 1$, and

$$(N+1)(\gamma+N)(\gamma+N-1) s_{N+1} + (\alpha+N)(\gamma+N-1) t \left(3N + \gamma - (N+\beta)\frac{1+t}{t} x - (N+\beta')\frac{1+t}{t} y\right) s_N - (\alpha+N)(\alpha+N-1) t^2$$

$$\times \left[3 - 2\gamma - 3N + (\gamma+\beta-2+2N)\frac{1+t}{t} x + (\gamma+\beta'-2+2N)\frac{1+t}{t} y + (1-\beta-\beta'-N)\left(\frac{1+t}{t}\right)^2 xy\right] s_{N-1}$$

$$+ (\alpha+N)(\alpha+N-1)(\alpha+N-2) t^3 \left(1 - \frac{1+t}{t} x\right)\left(1 - \frac{1+t}{t} y\right) s_{N-2} = 0 . \qquad (18)$$

It should be noted that the presence of two alternative approaches to the calculation of two-photon processes gives us the possibility of comparing the results obtained within the general method of calculation (10) for $N = 2$ with those of Eq. (16). The application of the formulas derived in the present paper to real multiphoton transitions in heteronuclear diatomic molecules will be given in following papers.

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[9] A. Erdelyi, W. Magnus, F. Oberhettinger, and F. Tricomi, *Tables of Integral Transform* (McGraw-Hill, New York, 1954), Vol. 1. We use in Eq. (9) the following approximation for the transition dipole moments: $\bar{D}_j(r)=\sum_{i=0}^{n} d_{ji}\, r^i$. The radial matrix element (9) represents the sum of $(n+1)^2$ integrals considered analogously to that of Eq. (16).

[10] For the integration over r_1 in Eq. (16), we made use of Eq. (18) given in Ref. 9, p. 197. Then to integrate over r_2 we used Eq. (10) given in Ref. 9, p. 215. Finally we used the integral representation of the Appell function [see Ref. 8, p. 231, Eq. (5)]. It may be noted that the same order of integration in the two-photon radial matrix elements has been used in Ref. 3, where one can be referred for the details.

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Higher-Order Relativistic Contributions to the Combined Zeeman and Motional Stark Effects in Positronium*

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A calculation of higher-order relativistic contributions to the combined Zeeman and motional Stark effects in positronium is presented. These contributions are necessary for the determination of the fine-structure interval in the ground state from the Zeeman effect and may be important in future experiments on the first excited states of positronium. The contributions to the g_J factors have been calculated to order α^2 for all the S states and for the $2P$ states. The energy levels and the higher-order corrections to the motional Stark effect in the first excited state are also presented. Relativistic contributions are obtained from the matrix elements of a Hamiltonian containing the Breit interaction, a Pauli Hamiltonian, and the virtual annihilation interaction. For all nS states the relativistic contributions to the Zeeman effect may be accounted for by the replacement of g_e by $g_e(1-5\alpha^2/24n^2-T/2mc^2)$, where T is the kinetic energy of the atom and g_e is the gyromagnetic ratio of the free electron.

I. INTRODUCTION

Higher-order contributions to the combined Zeeman and motional Stark effects in positronium are needed for the determination of the fine-structure interval $\Delta\nu$ in the ground state from the Zeeman effect and may be important in future experiments on the first excited state. The measurement of $\Delta\nu$ is an important test of quantum electrodynamics and of the Bethe-Salpeter equation for the bound-state lepton-antilepton system.[1,2] In this paper the contributions to the Zeeman effect are calculated to order $\alpha^2\mu_B H$ for all the S states and for the $2P$ states of positronium. Also the energy levels and the higher-order corrections to the motional Stark effect in the first excited state are computed.[3–6]

The fine-structure interval in the ground state of positronium has been calculated to terms of order $\alpha^4\ln\alpha^{-1}\mathcal{R}$. The $\alpha^2\mathcal{R}$ contributions to $\Delta\nu$ were first determined by Pirenne,[7] Berestetski,[8,9] and Ferrell.[10] Karplus and Klein[11] have computed terms of order $\alpha^3\mathcal{R}$ that contribute to $\Delta\nu$. The $\alpha^4\ln\alpha^{-1}\mathcal{R}$ contributions to $\Delta\nu$ were calculated recently by Fulton, Owen, and Repko.[12] In the first excited state of positronium the fine-structure intervals have been calculated to order $\alpha^3\mathcal{R}$. Fulton and Martin[13] have computed all the contributions of order $\alpha^3\mathcal{R}$ to the energy levels of a bound two-fermion system. These values are to be added to the $\alpha^2\mathcal{R}$ contributions calculated by Ferrell.[10]

The relativistic contributions to the Zeeman and motional Stark effects are obtained from matrix elements of the positronium Hamiltonian $\mathcal{H}$. The three terms in $\mathcal{H}$ are the Breit interaction,[14] a Pauli Hamiltonian[15] introducing the anomalous magnetic moments of the electron and positron, and the virtual annihilation interaction.[11] A transformation of two-body equations[16] is used to decouple the positive and negative energy states. A unitary transformation[17] is used to reduce the dependence of the positronium Hamiltonian on the center-of-mass coordinate.

Margenau,[18] Lamb,[19] and Breit[20] have calculated