

## Second-order contributions to the fine structure of helium from all intermediate states\*

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For the theoretical assessment of the  $2^3P$  helium fine structure to become comparable to the precision measurements that have been made, it is necessary that the theory be calculated through order  $\alpha^6 mc^2$ . In particular, the second-order contribution from the Breit and mass-polarization operators must be evaluated to an accuracy of 1% or so. In this work, for each of five possible intermediate state symmetries the Dalgarno-Lewis method is used to obtain the first-order perturbed wave function, from which the second-order energy follows by integration. Both the perturbed and unperturbed wave functions are expanded in Hylleraas-type series with a progressively larger number of terms, the second-order energies being computed at each stage; up to 455 terms are used for  $^3P$  intermediate states and up to 286 for  $^1P$ ,  $^3D$ ,  $^1D$ , and  $^3F$ . The sequence of second-order energy results for each symmetry is extrapolated to the limit of an infinite number of basis functions to arrive at a final result. The  $^3P$ ,  $^1P$ , and  $^3D$  states will contribute to both the larger and the smaller fine-structure intervals  $\nu_{01}$  and  $\nu_{12}$ , respectively, while  $^3F$  and  $^1D$  states affect only  $\nu_{12}$ . The total theoretical result, up to order  $\alpha^6 mc^2$ , for  $\nu_{01}$  is much more accurate than that for  $\nu_{12}$ , allowing the fine-structure constant  $\alpha$  to be determined very precisely by comparison of theory to experiment, with the result  $\alpha^{-1} = 137.036\ 08(13)$ , good to 0.94 ppm.

### I. INTRODUCTION

Owing to the theoretical framework embodied in the Breit and Bethe-Salpeter equations and to the precise experiments carried out at Yale,<sup>1,2</sup> the accurate theoretical determination of the fine structure of helium-4 in the  $2^3P_J$  states has been a subject of great interest for many years. For one thing, it provides one more check on the consistency of quantum electrodynamics. From another point of view, assuming that quantum electrodynamics is indeed valid, the theoretical and experimental determinations of the fine-structure splitting can be combined to yield a precise value of the fine-structure constant. Specifically, given the precision of the experiment (1.2 ppm for the larger interval  $\nu_{01}$ ), the fine-structure constant can be determined to better than 1 ppm if the theoretical splitting is accurate to 1 ppm or better, which entails computations of order  $\alpha^6 mc^2$ .

Such a theoretical undertaking is comprised of four separate tasks. The first is the calculation of the fine-structure splitting to first order with the Breit operators and the mass-polarization operator, achieved by Schwartz<sup>3</sup> to an accuracy of about 0.2 ppm. Second, the splitting is calculated to second order with these operators to an accuracy of better than 1%; it is this aspect which is in fact the major concern of our research,<sup>4-6</sup> since the pioneering work by Hambro<sup>7</sup> only determined  $\alpha$  to 3 ppm. Third, a higher-order operator must be derived from quantum electrodynamics, a task that has been accomplished by Douglas and Kroll.<sup>8</sup> Fourth, the expectation value of this operator must be computed to 1% precision; this Daley *et al.*<sup>9</sup> have

succeeded in doing. Small corrections also must be made to account for nuclear recoil.<sup>9</sup> The anomalous moment of the electron contributes a term of leading order  $\alpha^5 mc^2$  in addition.<sup>3,9,10</sup> We have then for the  $2^3P_J$  helium energy level  $E_J$ , apart from the leading anomalous moment term, the formal expression

$$E_J = E_0 + \alpha^4 \langle H_4 \rangle_J + \alpha^6 \left\langle H_4 \frac{1}{E_0 - H_0} H_4 \right\rangle + \alpha^6 \langle H_6 \rangle_J + \dots,$$

where  $E_0$  is the nonrelativistic energy level,  $H_4$  is the Breit interaction, and  $H_6$  is the operator of Douglas and Kroll.

In this paper we will first calculate the major part of the second-order contribution to the fine structure, namely, that due to intermediate states of  $^3P$  character. The method used for obtaining the second-order energies circumvents the need to sum over all intermediate states, and is described in Sec. III. Second-order contributions from the other possible symmetries, namely,  $^1P$ ,  $^3D$ ,  $^1D$ , and  $^3F$ , are not negligible and these are treated in the remainder of the paper. To apply the second-order method, we need the nonrelativistic  $2^3P$  eigenvalue and eigenfunctions to some order of approximation, as well as matrix elements of the Breit operators between the  $^3P$  basis functions and the intermediate states. The calculation of these quantities for each intermediate state symmetry is described in the subsequent sections, beginning with the  $^3P$  case.

### II. FINE-STRUCTURE OPERATORS

The reduction of the Breit equation<sup>11</sup> to small components results in the six operators that con-

TABLE I. Nonrelativistic  $2^3P$  energy eigenvalues.

$\omega$	$N$	$E_0$ (a.u.)
1	4	-2.129 471 787 9
2	10	-2.132 678 402 0
3	20	-2.133 085 039 2
4	35	-2.133 140 222 3
5	56	-2.133 157 595 1
6	84	-2.133 162 287 6
7	120	-2.133 163 594 2
8	165	-2.133 163 981 5
9	220	-2.133 164 106 9
10	286	-2.133 164 153 1
11	364	-2.133 164 172 5
12	455	-2.133 164 181 4

tribute to the second-order energy. In addition, the mass-polarization operator mixes with the other operators and contributes to the fine structure. The Schrödinger Hamiltonian for helium ( $Z=2$ ) is

$$H_0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}. \quad (1)$$

The nonrelativistic wave function  $\Psi_0$  is needed to calculate the matrix elements of the Breit operators. The variational method is used to derive this wave function.  $\Psi_0$  is the solution of

$$H_0\Psi_0 = E_0\Psi_0 \quad (2)$$

where  $E_0$  is the zeroth-order energy, while the approximation used for  $\Psi_0$  is the Hylleraas-like basis<sup>12,13</sup>

$$\psi_0 = \sum_{l, m, n=0}^{l+m+n \leq \omega} C_{lmn} U_{lmn}, \quad (3)$$

where

$$U_{lmn} = \frac{1-P_{12}}{4\pi\sqrt{2}} \tilde{\mathbf{F}}_1 r_1^m r_2^n r_{12}^l e^{-\kappa\sigma r_1/2} e^{-\kappa r_2/2}. \quad (4)$$

$$\begin{aligned}
H_0 u_{lmn}(1, 2) T_1^{(l)}(\tilde{\mathbf{F}}_1) &= u_{lmn}(1, 2) T_1^{(l)}(\tilde{\mathbf{F}}_1) \left( -\frac{1}{8}(\kappa^2\sigma^2 + \kappa^2) + \frac{1}{r_1} \left[ \frac{1}{4}\kappa\sigma(4+2m+l) - Z \right] + \frac{1}{r_2} \left[ \frac{1}{4}\kappa(2+2n+l) - Z \right] \right. \\
&\quad - \frac{1}{r_1^2} \frac{m}{2} (m+3+l) - \frac{1}{r_2^2} \frac{n}{2} (n+1+l) \\
&\quad + \frac{1}{r_{12}} - \frac{1}{r_{12}^2} \frac{l}{2} (2l+4+m+n) + \frac{r_1}{r_{12}^2} \frac{\kappa\sigma l}{4} \\
&\quad \left. + \frac{r_2}{r_{12}^2} \frac{\kappa l}{4} - \frac{r_2^2}{r_1 r_{12}^2} \frac{\kappa\sigma l}{4} - \frac{r_1^2}{r_2 r_{12}^2} \frac{\kappa l}{4} + \frac{r_2^2}{r_1^2 r_{12}^2} \frac{ml}{2} + \frac{r_1^2}{r_2^2 r_{12}^2} \frac{nl}{2} \right) \\
&\quad + u_{lmn}(1, 2) T_1^{(l)}(\tilde{\mathbf{F}}_2) \frac{l}{r_{12}}. \quad (9)
\end{aligned}$$

The matrix elements are given in terms of a number of integrals described in Appendix A. Thus we have

The  $C_{lmn}$  are coefficients that are obtained by the variational method and  $P_{12}$  interchanges coordinates  $r_1$  and  $r_2$ , while  $\tilde{\mathbf{F}}_1$  indicates the  $P$  character of  $\Psi_0$ . This type of wave function was used by Schwartz<sup>3</sup> in the calculation of the major contribution to the helium fine structure. With 286 terms in  $\psi_0$  the first-order fine structure was calculated to 100 ppm. Schwartz changed the basis by replacing  $C_{lmn}$  by  $C_{lmn} + D_{lmn}(r_1 + r_2)^{1/2}$ . This new basis better describes the behavior of the helium wave function near the nucleus. With 439 terms Schwartz achieved better than 1-ppm accuracy in the first-order fine structure.

The variational principle is equivalent to finding  $\psi_0$  such that

$$\delta \langle \Psi_0 | H_0 - E_0 | \Psi_0 \rangle = 0. \quad (5)$$

In matrix form we obtain

$$\delta \left( \sum_{m=1}^N \sum_{n=1}^N C_m C_n (\langle U_m | H_0 | U_n \rangle - E_0 \langle U_m | U_n \rangle) \right) = 0$$

where  $N = \frac{1}{6}(\omega+1)(\omega+2)(\omega+3)$  is the number of terms in the expansion of  $\Psi_0$ . The eigenvalue problem is solved by an iterative method and the results are shown in Table I. The wave function  $\Psi_0$  is written in terms of spherical tensors<sup>14</sup>  $T_p^q(\tilde{\mathbf{F}})$  where, for example,

$$T_1^{(1)}(\tilde{\mathbf{F}}_1) = -(x_1 + iy_1)/\sqrt{2}, \quad (6)$$

$$U_{lmn} = \frac{1-P_{12}}{4\pi\sqrt{2}} T_1^{(l)}(\tilde{\mathbf{F}}_1) u_{lmn}(1, 2), \quad (7)$$

and

$$u_{lmn}(1, 2) = r_1^m r_2^n r_{12}^l e^{-\kappa\sigma r_1/2} e^{-\kappa r_2/2}. \quad (8)$$

The screening constants determined by Schwartz were used:

$$\kappa = 4.619\,999\,945\,163\,72,$$

$$\sigma = 0.289\,999\,999\,105\,93.$$

Thus

in general

$$\begin{aligned}
\langle H_0 \rangle_{pq} &= \langle U_{l',m',n'} | H_0 | U_{lmn} \rangle \\
&= \frac{1}{3} \left\{ -\frac{1}{8} (\kappa^2 \sigma^2 + \kappa^2) [A_d(L+2, M+4, N+2) - B_e(L+2, M'+3, N'+3)] \right. \\
&\quad + [\frac{1}{4} \kappa \sigma (4+2m+l) - Z] [A_d(L+2, M+3, N+2) - B_e(L+2, M'+2, N'+3)] \\
&\quad + [\frac{1}{4} \kappa (2+2n+l) - Z] [A_d(L+2, M+4, N+1) - B_e(L+2, M'+3, N'+2)] \\
&\quad - \frac{1}{2} m(m+3+l) [A_d(L+2, M+2, N+2) - B_e(L+2, M'+1, N'+3)] \\
&\quad - \frac{1}{2} n(n+1+l) [A_d(L+2, M+4, N) - B_e(L+2, M'+3, N'+1)] \\
&\quad + A_d(L+1, M+4, N+2) - B_e(L+1, M'+3, N'+3) \\
&\quad - \frac{1}{2} l(2l+4+m+n) [A_d(L, M+4, N+2) - B_e(L, M'+3, N'+3)] \\
&\quad + \frac{1}{4} \kappa \sigma l [A_d(L, M+5, N+2) - B_e(L, M'+4, N'+3)] \\
&\quad + \frac{1}{4} \kappa l [A_d(L, M+4, N+3) - B_e(L, M'+3, N'+4)] \\
&\quad - \frac{1}{4} \kappa \sigma l [A_d(L, M+3, N+4) - B_e(L, M'+2, N'+5)] \\
&\quad - \frac{1}{4} \kappa l [A_d(L, M+6, N+1) - B_e(L, M'+5, N'+2)] \\
&\quad + \frac{1}{2} ml [A_d(L, M+2, N+4) - B_e(L, M'+1, N'+5)] \\
&\quad + \frac{1}{2} nl [A_d(L, M+6, N) - B_e(L, M'+5, N'+1)] \\
&\quad \left. + l [B_d(L, M+3, N+3) - A_e(L, M'+2, N'+4)] \right\}, \quad (10)
\end{aligned}$$

where  $L = l + l'$ ,  $M = m + m'$ ,  $N = n + n'$ ,  $M' = m + n'$  and  $N' = n + m'$ .

With the wave function calculated from the variational principle above, one can find the matrix elements of the six Breit operators (which elements are needed in both the first- and second-order perturbation calculations):

$$\begin{aligned}
H_1^{(1)} &= \frac{1}{4} \alpha^2 Z \left( \frac{\vec{\sigma}_1 + \vec{\sigma}_2}{2} \right) \cdot \left( \frac{\vec{r}_1 \times \vec{p}_1}{r_1^3} + \frac{\vec{r}_2 \times \vec{p}_2}{r_2^3} \right), \\
H_1^{(2)} &= -\frac{3}{4} \alpha^2 \left( \frac{\vec{\sigma}_1 + \vec{\sigma}_2}{2} \right) \cdot \frac{(\vec{r}_1 - \vec{r}_2) \times (\vec{p}_1 - \vec{p}_2)}{r_{12}^3}, \\
H_1^{(3)} &= \frac{1}{4} \alpha^2 \frac{1}{r_{12}^3} \left( \vec{\sigma}_1 \cdot \vec{\sigma}_2 - \frac{3(\vec{\sigma}_1 \cdot \vec{r}_{12})(\vec{\sigma}_2 \cdot \vec{r}_{12})}{r_{12}^2} \right), \quad (11) \\
H_1^{(4)} &= -\frac{1}{2} \alpha^2 \frac{1}{r_{12}} \left( \vec{p}_1 \cdot \vec{p}_2 + \frac{\vec{r}_{12} \cdot (\vec{r}_{12} \cdot \vec{p}_1) \vec{p}_2}{r_{12}^2} \right), \\
H_1^{(5)} &= -\frac{1}{8} \alpha^2 (p_1^4 + p_2^4), \quad H_1^{(6)} = \frac{1}{2} Z \pi \alpha^2 [\delta^{(3)}(\vec{r}_1) + \delta^{(3)}(\vec{r}_2)];
\end{aligned}$$

$$H_1^{(1)} \alpha(1) \alpha(2) u_{lmn}(1, 2) T_1^{(1)}(\vec{r}_1)$$

$$\begin{aligned}
&= \frac{1}{4} \alpha^2 Z \left\{ \alpha(1) \alpha(2) u_{lmn}(1, 2) T_1^{(1)}(\vec{r}_1) \left[ \frac{1}{r_1^3} + \frac{l}{r_{12}^2} \frac{(\vec{r}_1 \times \vec{r}_2)_0}{i} \left( \frac{1}{r_2^3} - \frac{1}{r_1^3} \right) \right] \right. \\
&\quad \left. - \frac{1}{\sqrt{2}} [\alpha(1) \beta(2) + \beta(1) \alpha(2)] u_{lmn}(1, 2) T_1^{(1)}(\vec{r}_1) \left( \frac{1}{r_2^3} - \frac{1}{r_1^3} \right) \frac{l(\vec{r}_1 \times \vec{r}_2)_{+1}}{i r_{12}^2} \right\}. \quad (13)
\end{aligned}$$

The matrix element following from  $H_1^{(1)} \alpha(1) \alpha(2) u_{lmn}(1, 2) T_1^{(1)}(\vec{r}_1)$  is

and the mass-polarization operator

$$H_1^{(7)} = (m/M) \vec{p}_1 \cdot \vec{p}_2 \quad (12)$$

where  $m$  is the electron mass and  $M$  is the helium nuclear mass.  $H_1^{(1)}$  contains spin-orbit terms;  $H_1^{(2)}$  presents spin-other-orbit contributions. Spin-spin terms are present in  $H_1^{(3)}$  while  $H_1^{(4)}$  includes the effect of the retardation of the electromagnetic field. The relativistic increase of mass is given in  $H_1^{(5)}$  and the contact interaction is present in  $H_1^{(6)}$ .

With the use of the spinors

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

and defining, for a vector  $\vec{v}$ ,  $v_{\pm 1} = T_{\pm 1}^{(1)}(\vec{v})$  and  $v_0 = T_0^{(1)}(\vec{v}) = v_z$ , we obtain

$$\begin{aligned}
\langle H_1^{(1)} \rangle &= \left\langle \frac{1-P_{12}}{4\pi\sqrt{2}} \alpha(1) \alpha(2) u_{l'm'n'}(1, 2) T_1^{(1)}(\tilde{\mathbf{r}}_1) \middle| H_1^{(1)} \middle| \frac{1-P_{12}}{4\pi\sqrt{2}} \alpha(1) \alpha(2) u_{lmn}(1, 2) T_1^{(1)}(\tilde{\mathbf{r}}_1) \right\rangle \\
&= \frac{1}{(4\pi)^2} \langle (1-P_{12}) \alpha(1) \alpha(2) u_{l'm'n'}(1, 2) T_1^{(1)}(\tilde{\mathbf{r}}_1) | H_1^{(1)} | \alpha(1) \alpha(2) u_{lmn}(1, 2) T_1^{(1)}(\tilde{\mathbf{r}}_1) \rangle \\
&= \frac{1}{6} \alpha^2 [A_d(L+2, M+1, N+2) - (l/L) B_e(L+2, M'+3, N') - (l'/L) B_e(L+2, M', N'+3)]. \quad (14)
\end{aligned}$$

The general matrix elements of the other six operators are computed in like fashion as outlined elsewhere by Hambro.<sup>7</sup> The resulting expressions range in complexity from a single term for  $H_1^{(6)}$ , which vanishes unless  $n=n'=0$ , to 225 terms for  $H_1^{(5)}$ . Moreover the kinds of integrals appearing in these matrix elements demand various further computations depending on the operator being examined. Although the general integrals encountered can be computed recursively up to a point, many special cases arise when one or more of the variables  $r_1$ ,  $r_2$ , and  $r_{12}$  are raised to their lowest allowed powers in the integrands.

As an illustration, integrals involving  $r_{12}^{-2}$  occur in the matrix elements of four of the seven operators and this class of integrals must be computed separately as a special case. Integrals containing more negative powers of  $r_{12}$  generally diverge individually, but these always occur in combinations which cancel the divergences to yield a finite result. This is how the matrix elements of  $H_1^{(3)}$ , for example, are rendered finite in spite of the presence of an  $r_{12}^{-5}$  factor in the operator. Furthermore, in  $H_1^{(3)}$  matrix elements there are integrations over all space, for both the coordinate spaces of  $\tilde{\mathbf{r}}_1$  and  $\tilde{\mathbf{r}}_2$ , of terms that behave as  $r_{12}^{-2} r_2^{-2}$ , as  $r_2$  approaches zero. These again require special consideration, as described in Appendix A under the subject of  $F_L$  integrals one of whose arguments is zero.

### III. SECOND-ORDER METHOD

In order to calculate the second-order corrections to the  $2^3P$  helium energy levels, it is hardly feasible to compute the well-known sum over intermediate states, since the latter are not at hand. Instead, one returns to the inhomogeneous Schrödinger equation for the first-order perturbed wave function  $\Psi_1$ :

$$(H_0 - E_0) \Psi_1 = -(H_1 - E_1) \Psi_0, \quad (15)$$

where  $\Psi_0$  is the nonrelativistic helium  $2^3P$  eigenfunction and  $E_0$  its eigenvalue. Further,  $H_1$  is the perturbation Hamiltonian and  $E_1$  its expectation value in the (normalized) state  $\Psi_0$ .

Once this equation is solved for  $\Psi_1$ , the second-order energy is given by an integral involving  $\Psi_1$  and other knowns. If  $H_1$  is decomposed into a sum

of operators  $H_1^{(i)}$ , then in fact there are second-order energies  $E_2^{(i,j)}$  given by any of four (two, if  $i=j$ ) different expressions:

$$\begin{aligned}
E_2^{(i,j)} \langle \Psi_0 | \Psi_0 \rangle &= -\langle \Psi_1^{(i)} | H_0 - E_0 | \Psi_1^{(j)} \rangle \\
&= -\langle \Psi_1^{(j)} | H_0 - E_0 | \Psi_1^{(i)} \rangle \\
&= \langle \Psi_0 | H_1^{(i)} - E_1^{(i)} | \Psi_1^{(j)} \rangle \\
&= \langle \Psi_1^{(i)} | H_1^{(j)} - E_1^{(j)} | \Psi_0 \rangle. \quad (16)
\end{aligned}$$

Restricting ourselves for the time being to  $^3P$  intermediate states, we expand  $\Psi_1^{(i)}$  with the same basis functions as for  $\Psi_0$ :

$$\Psi_1^{(i)} = \sum_{l,m,n=0}^{l+m+n=\omega} X_{lmn}^{(i)} U_{lmn}(1, 2), \quad (17)$$

with  $U_{lmn}$  as in Sec. II. If we take  $\Psi_0$  and  $E_0$  as determined for a given  $\omega$  (see Sec. II) together with the expansion for  $\Psi_1^{(i)}$  above using the same  $\omega$  (this is not necessary, but is convenient for our purposes), Eq. (15) becomes

$$\begin{aligned}
\sum_{k=1}^{N(\omega)} X_k^{(i)} [\langle U_{k'} | H_0 | U_k \rangle - E_0(\omega) \langle U_{k'} | U_k \rangle] \\
= - \sum_{k=1}^{N(\omega)} C_k(\omega) \langle U_{k'} | H_1^{(i)} - E_1^{(i)} | U_k \rangle \quad (18)
\end{aligned}$$

for  $k'=1, 2, 3, \dots, N(\omega)$  and  $N(\omega) = \frac{1}{6}(\omega+1)(\omega+2)(\omega+3)$ . In the above, the indices  $(l, m, n)$  have been mapped bijectively into the set of indices  $k$ .

This last set of equations can be construed as a matrix equation for the column vector  $X$  with a special feature. This is that the matrix  $(H_0 - E_0)$  has 0 as an eigenvalue in the chosen basis, and so is de facto singular. If we set  $X_1^{(i)} = 0$  and solve the matrix equation remaining after the first row and first column of  $(H_0 - E_0)$  are deleted, then we will have a consistent set of  $N(\omega) - 1$  equations to be solved for the  $N(\omega) - 1$   $X_k$ ,  $k=2, 3, \dots, N(\omega)$ . Since  $\det(H_0 - E_0) \neq 0$  now, there is a unique solution for these  $X_k$ ; they may in fact be inserted into the  $k'=1$  equation to check for consistency and for roundoff errors.

Doing this for each  $i$ , we may then obtain mixed ( $i \neq j$ ) and unmixed second-order energies for given  $\omega$ . If both  $H_1^{(i)}$  and  $H_1^{(j)}$  are spin independent, then  $E_2^{(i,j)}$  shifts each fine-structure level by the same amount and so does not affect the splittings. Otherwise  $E_2^{(i,j)}$  is extrapolated by sev-

eral methods<sup>15</sup> to infinite  $\omega$ , and the total second-order spin-dependent shift of the  $2^3P_J$  level is then given by

$$(E_2)_J = \sum_i \left( E_2^{(i,i)} + 2 \sum_{j>i} E_2^{(i,j)} \right). \quad (19)$$

For the  $^3P$  intermediate states, we shall do the above calculations for  $J=2$  to obtain  $(E_2)_2$ . The level shifts for  $J=0$  and  $J=1$  are derived from the  $J=2$  result by the Wigner-Eckart theorem, and the change in the fine-structure intervals follows easily by subtraction.

#### IV. TEST OF METHOD

Hambro has shown that a simple test of this method of calculating second-order energies can be made. The nonrelativistic Hamiltonian is  $H_0 = T + V$ , where  $T$  is the kinetic and  $V$  is the potential energy. If  $T$  and  $V$  are considered perturbations,

$$\mathcal{H}_1^{(1)} = V \text{ and } \mathcal{H}_1^{(2)} = T,$$

then the virial theorem can be used to show the first-order energies:

$$E_1^{(1)} = 2E_0, \quad E_1^{(2)} = -E_0,$$

and one can further show that the second-order energies are

$$E_2^{(1,1)} = E_0, \quad E_2^{(2,2)} = E_0,$$

$$E_2^{(1,2)} = -E_0, \quad E_2^{(2,1)} = -E_0.$$

The results of this test calculation are shown in Tables II and III.

#### V. FINAL SECOND-ORDER EXTRAPOLATIONS FOR $^3P$ INTERMEDIATE STATES

For the  $^3P$  intermediate states, the first-order energies are presented in Table IV and the spin-dependent second-order energies are given in Table

V, for  $\omega=1$  to  $\omega=12$ . In addition, Table VI shows those second-order energies which do not affect the fine-structure splittings.

We have extrapolated the second-order results in Table V to infinite  $\omega$ . Following Schwartz, successive differences between second-order energies as a function of  $\omega$  are fitted to both exponential and inverse power types of behavior. This yields a best value for the (constant) ratio and inverse power, respectively, with an uncertainty in each case; these can then be used to obtain the individual extrapolated results. The final extrapolated result is a weighted average of the two already obtained, being closer to that one which has smaller uncertainty and best fits the data.

In some cases, we did not extrapolate the individual  $E_2^{(i,j)}$ , but instead took certain propitious combinations of several of them as they occur in the expressions for the changes in the larger and smaller fine-structure intervals. These expressions are

$$\begin{aligned} \Delta\nu_{01} = & 3 \sum_{i,j=1}^2 E_2^{(i,j)} - 50(E_2^{(1,3)} + E_2^{(2,3)}) \\ & + 75E_2^{(3,3)} - 2 \sum_{i=1}^2 \sum_{j=4}^7 E_2^{(i,j)} + 30 \sum_{j=4}^7 E_2^{(3,j)} \end{aligned} \quad (20)$$

and

$$\begin{aligned} \Delta\nu_{12} = & 8(E_2^{(1,3)} + E_2^{(2,3)}) + 24E_2^{(3,3)} \\ & - 4 \sum_{i=1}^2 \sum_{j=4}^7 E_2^{(i,j)} - 12 \sum_{j=4}^7 E_2^{(3,j)}. \end{aligned} \quad (21)$$

The behavior of most of the  $E_2^{(i,j)}$  as a function of  $\omega$  is either smooth or so rapidly convergent as to yield extrapolations accurate to 0.5% or better. The exceptions are  $E_2^{(1,1)}$ ,  $E_2^{(1,5)}$ , and  $E_2^{(3,3)}$ .  $E_2^{(1,1)}$  and  $E_2^{(3,3)}$  demonstrate a smooth but slow convergence with  $\omega$ , reflecting the pole-type singularities

TABLE II. First-order test calculation.

$\omega$	$\frac{1}{2}E_1^{(1)}$ (a.u.)	$E_1^{(2)}$ (a.u.)
1	-2.155 799 276 4	2.182 126 765 0
2	-2.134 972 042 3	2.137 265 682 6
3	-2.133 033 796 6	2.132 982 554 0
4	-2.133 102 833 5	2.133 065 444 7
5	-2.133 138 930 5	2.133 120 265 9
6	-2.133 155 707 2	2.133 149 126 7
7	-2.133 161 252 4	2.133 158 910 7
8	-2.133 163 114 4	2.133 162 247 2
9	-2.133 163 755 0	2.133 163 403 1
10	-2.133 163 993 8	2.133 163 834 6
11	-2.133 164 093 6	2.133 164 014 8
12	-2.133 164 140 0	2.133 164 098 5

TABLE III. Second-order test calculation.

$\omega$	$E_2^{(1,1)} = -E_2^{(1,2)} = -E_2^{(2,1)} = E_2^{(2,2)}$ (a.u.)
1	-1.801 314 478
2	-2.088 199 826
3	-2.128 536 110
4	-2.132 450 237
5	-2.132 976 961
6	-2.133 092 204
7	-2.133 137 444
8	-2.133 153 794
9	-2.133 159 927
10	-2.133 162 283
11	-2.133 163 254
12	-2.133 163 696

TABLE IV. First-order matrix elements of the Breit operators.

$\omega$	$E_1^{(1)}$ $\frac{1}{2}\alpha^2$ Ry	$E_1^{(2)}$ $\frac{1}{2}\alpha^2$ Ry	$E_1^{(3)}$ $\frac{1}{2}\alpha^2$ Ry	$E_1^{(4)}$ $2\alpha^2$ Ry	$E_1^{(5)}$ $2\alpha^2$ Ry	$E_1^{(6)}$ $2\alpha^2$ Ry	$E_1^{(7)}$ $2(m/M)$ Ry
1	0.136 215 710 56	-0.218 277 449 69	0.019 652 745 59	0.034 490 724 82	-9.650 521 361 45	7.802 284 919 27	-0.058 229 558 25
2	0.131 125 093 81	-0.201 776 410 02	0.018 015 107 57	0.032 904 898 33	-9.974 349 837 99	7.945 181 016 20	-0.059 299 556 96
3	0.134 790 079 01	-0.203 087 634 20	0.017 932 223 85	0.034 113 074 49	-9.901 429 363 52	7.905 371 791 37	-0.061 960 762 82
4	0.136 881 098 90	-0.204 591 378 82	0.017 982 384 06	0.034 672 686 86	-9.916 224 472 28	7.912 170 145 22	-0.063 377 555 23
5	0.137 897 972 83	-0.205 354 114 55	0.018 001 120 09	0.034 940 446 91	-9.910 320 049 11	7.908 943 677 56	-0.064 191 432 56
6	0.138 340 719 78	-0.205 676 309 11	0.018 009 443 47	0.035 035 684 54	-9.912 076 477 62	7.909 715 498 09	-0.064 463 462 23
7	0.138 519 492 64	-0.205 803 665 88	0.018 012 736 56	0.035 065 736 34	-9.911 766 902 75	7.909 518 589 99	-0.064 535 669 45
8	0.138 582 873 11	-0.205 860 183 20	0.018 014 279 24	0.035 075 957 702	-9.912 132 441 01	7.909 684 399 17	-0.064 563 045 96
9	0.138 621 686 32	-0.205 884 995 14	0.018 015 030 24	0.035 079 216 496	-9.912 055 028 99	7.909 638 947 50	-0.064 570 483 28
10	0.138 631 937 66	-0.205 896 528 36	0.018 015 436 59	0.035 080 235 99	-9.912 130 125 90	7.909 674 014 07	-0.064 572 273 11
11	0.138 635 457 22	-0.205 902 461 34	0.018 015 671 37	0.035 080 593 66	-9.912 097 717 43	7.909 656 906 80	-0.064 572 629 72
12	0.138 636 426 19	-0.205 905 734 29	0.018 015 814 35	0.035 080 727 33	-9.912 096 721 03	7.909 656 118 37	-0.064 572 454 06

of  $H_1^{(1)}$  and  $H_1^{(3)}$ , while  $E_2^{(1,5)}$  shows neither rapid nor smooth convergence, pointing to the influence of the  $\delta$ -function type of singularity appearing in  $H_1^{(5)}\psi_0$ .

The extrapolated results are shown in Table VII, where we obtain the total second-order contribution from  ${}^3P$  intermediate states as 5.062(38) and -0.413(79) MHz for  $\nu_{01}$  and  $\nu_{12}$ , respectively. Some of the individual error estimates for the  $E_2^{(i,j)}$  may be somewhat optimistic and others more or less conservative, but in any case only four or five of the  $E_2^{(i,j)}$  significantly affect the total uncertainty. Furthermore, our results for those energies for which Hambro obtained improved values are not inconsistent with his results, and we have used  $\omega = 10$  preliminary extrapolations to anticipate the  $\omega = 11$  and  $\omega = 12$  values for our  $E_2^{(i,j)}$  quite successfully, as a check on internal consistency of the method.

These results, together with those for the other intermediate states should allow  $\alpha$  to be determined to 1 ppm or better. The other contributions are discussed in the sections following.

## VI. ${}^1P$ INTERMEDIATE-STATE CONTRIBUTIONS

We now complete the second-order calculation by computing the effects of  ${}^1P$ ,  ${}^3D$ ,  ${}^1D$ , and  ${}^3F$  intermediate states. Of these symmetries, only the first two contribute to both the fine-structure intervals  $\nu_{01}$  and  $\nu_{12}$ ; the last two only affect  $\nu_{12}$ .

The second-order method has been described for  ${}^3P$  states already and its application to symmetries other than  ${}^3P$  is not much different. The major difference arises in the solution of the inhomogeneous Schrödinger equation for the  $i$ th perturbation wave function,

$$\sum_{k=1}^{N(\omega)} X_k^{(i)} [\langle \tilde{U}_i | H_0 | \tilde{U}_k \rangle - E_0(\omega) \langle \tilde{U}_i | \tilde{U}_k \rangle] = - \sum_{k=1}^{N(\omega)} c_k \langle \tilde{U}_i | H_1^{(i)} | U_k \rangle. \quad (22)$$

Here we have expanded  $\Psi_1^{(i)}(L, S, J, m_J = J)$  as

$$\Psi_1^{(i)} = \sum_{k=1}^{N(\omega)} X_k^{(i)} \tilde{U}_k(L, S, J, m_J = J), \quad (23)$$

where  $k \rightarrow (l, m, n)$  with  $l, m, n \geq 0$  and  $l + m + n \leq \omega$ , and  $N(\omega) = \frac{1}{6}(\omega + 1)(\omega + 2)(\omega + 3)$ . Furthermore,

$$\begin{aligned} \tilde{U}_{lmn}(L, S, J, m_J = J) &= \frac{1 + (-1)^S P_{12}}{4\pi\sqrt{2}} e^{-\kappa\sigma r_1/2} e^{-\kappa r_2/2} \\ &\times r_{12}^l r_1^m r_2^n Y(L, S, J, m_J = J) \end{aligned} \quad (24)$$

with  $\kappa$  and  $\sigma$  as before and  $Y$  a spherical tensor representing an  $L$ - $S$  coupling state of total angular momentum  $J$ , projection  $m_J$ , and odd parity. Now

TABLE V. Second-order energies.

$\omega$	$E_2^{(1,1)}$ $(\frac{1}{2}\alpha^2 \text{ Ry})\frac{1}{4}\alpha^2$	$E_2^{(2,2)}$ $(\frac{1}{2}\alpha^2 \text{ Ry})\frac{1}{4}\alpha^2$	$E_2^{(3,3)}$ $(\frac{1}{2}\alpha^2 \text{ Ry})\frac{1}{4}\alpha^2$	$E_2^{(2,2)}$ $(\frac{1}{2}\alpha^2 \text{ Ry})\frac{1}{4}\alpha^2$	$E_2^{(3,3)}$ $(\frac{1}{2}\alpha^2 \text{ Ry})\frac{1}{4}\alpha^2$	$E_2^{(4,2)}$ $(\frac{1}{2}\alpha^2 \text{ Ry})\frac{1}{4}\alpha^2$	$E_2^{(4,3)}$ $(\frac{1}{2}\alpha^2 \text{ Ry})\frac{1}{4}\alpha^2$	$E_2^{(4,4)}$ $(\frac{1}{2}\alpha^2 \text{ Ry})\alpha^2$
1	-0.246 939 977 80	-0.606 520 192 22	-0.003 914 987 988 60	0.375 263 457 93	-0.029 729 889 762	-0.039 027 567 208	-0.064 385 508 466	
2	-0.365 389 076 52	-0.796 511 077 86	-0.004 868 968 719 53	0.511 063 002 23	-0.039 027 567 208	-0.043 180 481 133	-0.096 387 812 985	
3	-0.442 532 341 41	-0.892 241 821 98	-0.005 258 842 720 89	0.579 233 469 60	-0.043 180 481 133	-0.045 005 653 530	-0.113 398 138 02	
4	-0.489 473 765 25	-0.950 705 903 29	-0.005 438 701 817 14	0.614 765 999 12	-0.045 005 653 530	-0.045 980 429 182	-0.122 737 003 56	
5	-0.522 678 106 11	-0.990 380 746 54	-0.005 554 941 074 46	0.636 515 482 79	-0.045 980 429 182	-0.046 520 836 115	-0.128 466 369 58	
6	-0.545 896 121 41	-1.017 181 339 0	-0.005 636 380 515 73	0.649 203 827 33	-0.046 520 836 115	-0.046 840 481 206	-0.131 587 859 13	
7	-0.562 411 923 01	-1.036 333 877 7	-0.005 697 942 319 22	0.656 672 855 32	-0.046 840 481 206	-0.047 042 908 573	-0.133 188 727 79	
8	-0.574 854 090 01	-1.050 929 231 4	-0.005 746 149 013 80	0.661 603 458 78	-0.047 042 908 573	-0.047 178 038 543	-0.134 120 841 93	
9	-0.584 638 721 61	-1.062 174 161 1	-0.005 784 833 878 29	0.664 955 847 80	-0.047 178 038 543	-0.047 271 371 260	-0.134 675 366 61	
10	-0.592 456 095 61	-1.071 011 789 7	-0.005 816 516 352 17	0.667 159 533 66	-0.047 271 371 260	-0.047 338 639 704	-0.134 969 486 68	
11	-0.598 880 112 47	-1.078 209 313 8	-0.005 842 900 396 76	0.668 724 917 70	-0.047 338 639 704	-0.047 388 457 435	-0.135 145 992 75	
12	-0.604 297 742 83	-1.084 176 114 5	-0.005 865 166 057 97	0.669 882 530 69	-0.047 388 457 435	$E_2^{(3,5)}$	-0.135 259 541 33	
	$E_2^{(4,5)}$	$E_2^{(4,6)}$	$E_2^{(4,7)}$	$E_2^{(3,5)}$	$E_2^{(3,6)}$	$E_2^{(3,7)}$	$E_2^{(3,7)}$	
$\omega$	$(\frac{1}{2}\alpha^2 \text{ Ry})\alpha^2$	$(\frac{1}{2}\alpha^2 \text{ Ry})\alpha^2$	$(\frac{1}{2}\alpha^2 \text{ Ry})m/M$	$(\frac{1}{2}\alpha^2 \text{ Ry})\frac{1}{4}\alpha^2$	$(\frac{1}{2}\alpha^2 \text{ Ry})\frac{1}{4}\alpha^2$	$(\frac{1}{2}\alpha^2 \text{ Ry})\alpha^2$	$(\frac{1}{2}\alpha^2 \text{ Ry})\alpha^2$	
1	-1.352 757 266 30	0.832 024 229 82	0.088 292 460 193	0.048 646 059 034	0.108 392 432 11	0.108 392 432 11	2.102 016 185 0	
2	0.034 234 318 757	0.122 374 672 03	0.160 089 879 020	0.061 924 185 653	0.145 649 986 24	0.145 649 986 24	-0.293 855 127 24	
3	-0.194 195 278 20	0.263 052 759 11	0.187 985 961 983	0.067 859 016 361	0.164 060 352 77	0.164 060 352 77	0.296 125 453 01	
4	-0.113 889 215 13	0.236 553 351 56	0.205 644 018 918	0.071 008 826 004	0.174 209 645 73	0.174 209 645 73	0.046 292 285 177	
5	-0.139 597 545 33	0.259 490 670 00	0.219 018 381 676	0.073 049 238 631	0.179 989 970 32	0.179 989 970 32	0.147 078 215 36	
6	-0.130 333 435 71	0.261 350 858 01	0.225 661 882 817	0.074 454 087 419	0.182 862 808 72	0.182 862 808 72	0.091 284 755 01	
7	-0.123 428 321 87	0.262 352 543 64	0.228 291 950 796	0.075 492 546 921	0.184 251 729 89	0.184 251 729 89	0.126 973 876 47	
8	-0.102 949 421 72	0.255 368 344 64	0.230 351 387 838	0.076 293 345 049	0.185 022 082 25	0.185 022 082 25	0.109 787 034 06	
9	-0.095 690 232 18	0.254 233 952 44	0.231 723 871 536	0.076 925 676 055	0.185 429 874 36	0.185 429 874 36	0.118 201 037 49	
10	-0.093 811 122 77	0.255 267 718 03	0.232 100 864 198	0.077 438 305 728	0.185 625 195 25	0.185 625 195 25	0.106 306 627 42	
11	-0.096 105 373 13	0.258 024 188 16	0.232 381 516 317	0.077 862 148 441	0.185 729 806 65	0.185 729 806 65	0.107 826 460 2	
12	-0.093 421 226	0.258 023 481	0.232 629 834 64	0.078 217 446 863	0.185 786 636 33	0.185 786 636 33	0.106 980 555	
	$E_2^{(3,6)}$	$E_2^{(3,7)}$	$E_2^{(3,4)}$	$E_2^{(3,5)}$	$E_2^{(3,6)}$	$E_2^{(3,7)}$	$E_2^{(3,7)}$	
$\omega$	$(\frac{1}{2}\alpha^2 \text{ Ry})\alpha^2$	$(\frac{1}{2}\alpha^2 \text{ Ry})m/M$	$(\frac{1}{2}\alpha^2 \text{ Ry})\alpha^2$	$(\frac{1}{2}\alpha^2 \text{ Ry})\alpha^2$	$(\frac{1}{2}\alpha^2 \text{ Ry})\alpha^2$	$(\frac{1}{2}\alpha^2 \text{ Ry})m/M$	$(\frac{1}{2}\alpha^2 \text{ Ry})m/M$	
1	-1.248 300 545 9	-0.169 152 046 28	-0.008 741 807 951 8	-0.135 463 626 50	0.079 731 206 176	0.079 731 206 176	0.013 890 400 158	
2	-0.009 042 191 679 9	-0.235 875 173 58	-0.011 210 409 140	0.025 656 689 317	-0.003 859 000 323	-0.003 859 000 323	0.018 025 837 945	
3	-0.321 767 155 43	-0.271 576 207 14	-0.012 264 960 517	0.000 874 551 492 39	0.009 283 318 773 7	0.009 283 318 773 7	0.020 086 284 655	
4	-0.206 227 869 68	-0.292 059 289 48	-0.012 751 258 084	0.007 095 695 115 8	0.006 632 136 734 7	0.006 632 136 734 7	0.020 936 916 568	
5	-0.262 354 201 27	-0.306 044 862 46	-0.012 982 926 713	0.006 688 362 400 5	0.007 082 592 722 2	0.007 082 592 722 2	0.021 347 172 299	
6	-0.237 308 703 05	-0.312 579 841 58	-0.013 091 136 660	0.007 088 273 926 3	0.007 001 481 814 6	0.007 001 481 814 6	0.021 498 040 345	
7	-0.256 639 740 30	-0.315 648 994 21	-0.013 144 105 726	0.006 515 381 810 7	0.007 346 763 955 8	0.007 346 763 955 8	0.021 572 087 018	
8	-0.248 892 796 00	-0.317 751 228 28	-0.013 171 239 018	0.006 269 440 363 1	0.007 499 789 959 1	0.007 499 789 959 1	0.021 604 339 147	
9	-0.253 600 714 02	-0.318 873 261 67	-0.013 184 916 583	0.006 391 486 302 9	0.007 454 210 052 8	0.007 454 210 052 8	0.021 611 864 122	
10	-0.247 932 108 20	-0.319 274 472 53	-0.013 192 271 426	0.006 742 887 330 0	0.007 285 904 956 8	0.007 285 904 956 8	0.021 617 230 998	
11	-0.248 853 577 3	-0.319 503 468 99	-0.013 196 263 747	0.006 899 529 484	0.007 210 588 665 8	0.007 210 588 665 8	0.021 620 011 407	
12	-0.248 523 394	-0.319 631 364 59	-0.013 198 291 862	0.006 779 555	0.007 271 201 4	0.007 271 201 4	0.021 619 651 675	

no equations are to be deleted in (22) because the matrix  $(H_0 - E_0)$  is nonsingular, and so the problem reduces to the one of inverting an  $N(\omega)$  by  $N(\omega)$  matrix.

In addition, we have new integrals appearing in the case of  $D$  and  $F$  symmetries involving spherical tensors more complicated than the  $T^{(1)}(\hat{r}_1)$  encountered previously. The calculation of these integrals is not too difficult but we nevertheless indicate as an example in Appendix B how the  ${}^3F$  integrals are reduced to the  $A$  and  $B$  integrals introduced earlier in this paper. We proceed now to examine the effect of  ${}^1P$  intermediate states.

The operators with nonvanishing matrix elements between  ${}^1P$  and  ${}^3P$  states are

$$\tilde{H}_1^{(1)} = \frac{1}{4} \alpha^2 Z \left( \frac{\vec{\sigma}_1 - \vec{\sigma}_2}{2} \right) \cdot \left( \frac{\hat{r}_1 \times \hat{p}_1}{r_1^3} - \frac{\hat{r}_2 \times \hat{p}_2}{r_2^3} \right) \tag{25}$$

and

$$\tilde{H}_1^{(2)} = \frac{1}{4} \alpha^2 \left( \frac{\vec{\sigma}_1 - \vec{\sigma}_2}{2} \right) \cdot \left( \frac{\hat{r}_1 - \hat{r}_2}{r_{12}^3} \times (\hat{p}_1 + \hat{p}_2) \right).$$

These are the spin-antisymmetric parts of  $H_1^{(1)}$  and  $H_1^{(2)}$ , the spin-orbit Breit operators; the spin-

symmetric parts are proportional to the total spin  $S$  and do not permit singlet-triplet transitions. Since  $J=1$  for  ${}^1P$  states and  $J$  is still a good quantum number we take as our nonrelativistic  $2{}^3P$  wave function

$$\Psi_0({}^3P_1, m_J = 1) = \sum_{l,m,n=0}^{l+m+n=\omega} C_{lmn} U_{lmn}({}^3P_1, m_J = 1) \tag{26}$$

where the  $C_{lmn}$  are as determined in Sec. II and

$$U_{lmn}({}^3P_1, m_J = 1) = \frac{1 - P_{12}}{4\pi\sqrt{2}} \frac{1}{\sqrt{2}} [S_0^{(1)} T_1^{(1)}(\hat{r}_1) - S_1^{(1)} T_0^{(1)}(\hat{r}_1)] u_{lmn}(1, 2). \tag{27}$$

The perturbed wave function is expanded as

$$\tilde{\Psi}_1^{(i)}({}^1P_1, m_J = 1) = \sum_{l,m,n=0}^{l+m+n=\omega} \tilde{C}_{lmn}^{(i)} \tilde{U}_{lmn}({}^1P_1, m_J = 1) \tag{28}$$

where

$$\tilde{U}_{lmn}({}^1P_1, m_J = 1) = \frac{1 + P_{12}}{4\pi\sqrt{2}} S_0^{(0)} T_1^{(1)}(\hat{r}_1) u_{lmn}(1, 2). \tag{29}$$

We compute the action of the operators on the unsymmetrized  ${}^1P$  basis functions:

TABLE VI. Second-order energies which do not contribute to the fine structure.

$\omega$	$E_2^{(4,4)}$ ( $2\alpha^4$ Ry)	$E_2^{(5,5)}$ ( $2\alpha^4$ Ry)	$E_2^{(6,6)}$ ( $2\alpha^4$ Ry)	$E_2^{(7,7)}$ ( $2(m/M)^2$ Ry)	$E_2^{(4,5)}$ ( $2\alpha^4$ Ry)
1	-0.019 941 220 294	-252.301 040 25	-89.151 341 771	-0.067 054 443 540	-0.509 634 666 84
2	-0.028 765 953 476	-349.313 294 68	-108.818 603 13	-0.121 394 680 800	0.038 090 731 754
3	-0.033 335 808 370	-442.934 748 19	-133.136 851 57	-0.142 266 384 01	-0.103 141 283 917
4	-0.035 906 828 850	-534.405 189 29	-155.751 708 50	-0.160 864 025 32	-0.040 353 494 222
5	-0.037 393 840 859	-621.794 445 183	-177.726 745 72	-0.180 662 910 46	-0.073 261 738 297
6	-0.038 073 570 418	-708.113 034 96	-199.266 653 29	-0.191 579 090 43	-0.055 513 108 990
7	-0.038 343 778 493	-793.054 988 05	-220.517 116 05	-0.196 151 002 74	-0.062 513 658 090
8	-0.038 477 869 851	-877.327 069 51	-241.565 720 19	-0.200 108 593 14	-0.055 928 749 109
9	-0.038 543 199 087	-960.906 702 83	-262.464 300 03	-0.202 827 567 19	-0.059 430 409 098
10	-0.038 567 915 521	-1 044.056 101	-283.246 293 60	-0.203 751 130 51	-0.057 381 527 590
11	-0.038 579 766 222	-1 126.807 270	-303.937 823 07	-0.204 267 306 21	-0.058 454 129 847
12	-0.038 586 551 825	-1 209.289 343	-324.558 334 79	-0.204 656 232 76	-0.057 551 914 63
$\omega$	$E_2^{(4,6)}$ ( $2\alpha^4$ Ry)	$E_2^{(4,7)}$ ( $2\alpha^2(m/M)$ Ry)	$E_2^{(5,6)}$ ( $2\alpha^4$ Ry)	$E_2^{(5,7)}$ ( $2\alpha^2(m/M)$ Ry)	$E_2^{(6,7)}$ ( $2\alpha^2(m/M)$ Ry)
1	0.297 444 545 402	0.033 581 361 651	149.929 739 78	1.180 015 618 3	-0.668 956 889 07
2	0.017 125 440 447	0.053 384 471 485	194.062 343 59	-0.128 252 515 86	-0.020 398 608 316
3	0.092 956 846 436	0.062 084 852 339	241.747 532 88	0.453 873 200 08	-0.320 344 711 78
4	0.064 126 858 647	0.067 951 065 502	287.233 174 83	0.068 616 519 845	-0.134 151 816 82
5	0.082 165 221 912	0.072 383 341 337	331.049 521 62	0.366 745 088 79	-0.287 356 668 50
6	0.074 066 349 412	0.074 449 032 058	374.168 123 84	0.167 663 976 64	-0.189 469 485 95
7	0.077 953 863 661	0.075 196 222 464	416.652 673 65	0.287 334 615 78	-0.249 909 273 77
8	0.074 878 198 038	0.075 703 313 069	458.768 590 78	0.198 833 876 04	-0.206 039 709 81
9	0.076 754 952 587	0.075 996 409 786	500.561 367 76	0.260 487 154 18	-0.237 101 855 03
10	0.075 798 997 017	0.076 080 170 556	542.130 222 82	0.221 424 235 45	-0.217 621 966 28
11	0.076 376 705 093	0.076 120 936 920	583.509 101 74	0.247 141 172 76	-0.230 525 267 83
12	0.075 951 579 96	0.076 149 073 589	624.749 778 88	0.229 279 678 4	-0.221 626 010 1

$$\begin{aligned} \tilde{H}_1^{(1)} \frac{1}{\sqrt{2}} [S_0^{(1)} T_1^{(1)}(\tilde{\mathbf{r}}_1) - S_1^{(1)} T_0^{(1)}(\tilde{\mathbf{r}}_1)] u_{imn}(1, 2) \\ = \frac{1}{4} \alpha^2 Z u_{imn}(1, 2) S_0^{(0)} \sqrt{2} \left[ \frac{1}{r_1^3} T_1^{(1)}(\tilde{\mathbf{r}}_1) - \frac{l}{2r_1^2} \left( \frac{1}{r_1^3} + \frac{1}{r_2^3} \right) [T_1^{(1)}(\tilde{\mathbf{r}}_1)(\tilde{\mathbf{r}}_1 \cdot \tilde{\mathbf{r}}_2) - T_1^{(1)}(\tilde{\mathbf{r}}_2)r_1^2] \right], \quad (30) \end{aligned}$$

and

$$\begin{aligned} \tilde{H}_1^{(2)} \frac{1}{\sqrt{2}} [S_0^{(1)} T_1^{(1)}(\tilde{\mathbf{r}}_1) - S_1^{(1)} T_0^{(1)}(\tilde{\mathbf{r}}_1)] u_{imn}(1, 2) \\ = \frac{1}{4} \alpha^2 \sqrt{2} S_0^{(0)} u_{imn}(1, 2) \frac{1}{r_{12}^3} \left[ T_1^{(1)}(\tilde{\mathbf{r}}_1) - T_1^{(1)}(\tilde{\mathbf{r}}_2) + \frac{1}{2} \left( \frac{m}{r_1^2} + \frac{n}{r_2^2} - \frac{\kappa\sigma}{2r_1} - \frac{\kappa}{2r_2} \right) [T_1^{(1)}(\tilde{\mathbf{r}}_1)(\tilde{\mathbf{r}}_1 \cdot \tilde{\mathbf{r}}_2) - T_1^{(1)}(\tilde{\mathbf{r}}_2)r_1^2] \right]. \quad (31) \end{aligned}$$

It should be pointed out here that the plus signs preceding "1/r<sub>2</sub><sup>3</sup>" in the  $\tilde{H}_1^{(1)}$  equation and "1/2" in the  $\tilde{H}_1^{(2)}$  equation, respectively, are reversed, incorrectly, in Hambro's paper. (His final results are, however, correct.) These computations suffice for obtaining the transition matrix elements

$$(\tilde{M}_1^{(i)})_{k', k},$$

where

$$(\tilde{M}_1^{(i)})_{k', k} = \langle \tilde{U}_{1', m', n'}(^1P_1, m_J = 1) | \tilde{H}_1^{(i)} | U_{imn}(^3P_1, m_J = 1) \rangle. \quad (32)$$

The  $(\tilde{M}_1^{(i)})_{k', k}$  so calculated differ from the  $(M_1^{(i)})_{k', k}$  of the <sup>3</sup>P case only in some sign changes and overall multiplicative factors. Also needed are the matrix elements of  $H_0$  and of unity between <sup>1</sup>P basis functions. These again are the same as the corresponding <sup>3</sup>P quantities save for a sign change preceding all the exchange integrals.

Having computed these matrix elements, we can solve for the  $\tilde{X}_k^{(i)}$  in the inhomogeneous Schrödinger equation (22) for a given  $\omega$  and thence obtain the  $\tilde{E}_2^{(i, j)}$  as described in Sec. III. The total shift of the <sup>2</sup><sup>3</sup>P<sub>1</sub> level is then given by  $(\tilde{E}_2)_{J=1} = \tilde{E}_2^{(1, 1)} + \tilde{E}_2^{(2, 2)}$

TABLE VII. <sup>3</sup>P contributions to the helium fine structure.

$(i, j)$	$E_2^{(i, j)}$ <sup>a</sup>	$\Delta \nu_{01}(\frac{1}{2} \alpha^4 \text{ Ry})$	$\Delta \nu_{12}(\frac{1}{2} \alpha^4 \text{ Ry})$
(1, 1)	-0.665 3(46)	-0.499(3)	0
(1, 2)	0.674 76(24)	1.012 1(4)	0
(1, 3)	-0.047 608(1)	0.595 10(1)	-0.095 216(2)
(1, 4)	-0.135 528(24)	0.271 06(5)	0.542 1(1)
(1, 5)+(1, 6)	0.174(4)	-0.348(8)	-0.696(16)
(2, 2)	-1.142 0(17)	-0.857(1)	0
(2, 3)	0.082 12(18)	-1.027(2)	0.164 2(4)
(2, 4)	0.185 863(14)	-0.371 73(3)	-0.743 45(6)
(2, 5)	0.107 252(46)	-0.214 50(9)	
(2, 6)	-0.248 618(17)		0.994 47(7)
(3, 3)	-0.006 11(4)	-0.114 6(8)	-0.036 7(2)
(3, 4)	-0.013 200 5(1)	-0.396 015(3)	0.158 406(1)
30[(3, 5)+(3, 6)]-2(2, 6)	0.919 502(37)	0.919 50(4)	
12[(3, 5)+(3, 6)]-4(2, 5)	-0.598 02(72)		-0.598 02(72)
		$\left( \frac{1}{2} \frac{m}{M} \alpha^2 \text{ Ry} \right)$	$\left( \frac{1}{2} \frac{m}{M} \alpha^2 \text{ Ry} \right)$
(1, 7)	0.233 3(4)	-0.466 6(8)	-0.933(2)
(2, 7)	-0.319 795(39)	0.639 59(8)	1.279 2(2)
(3, 7)	0.021 620 2(1)	0.648 606(3)	-0.259 442(1)
Totals		-0.515(4) $\alpha^4 \text{ Ry}$	-0.155(8) $\alpha^4 \text{ Ry}$
		+0.410 8(4) $\frac{m}{M} \alpha^2 \text{ Ry}$	+0.043(1) $\frac{m}{M} \alpha^2 \text{ Ry}$
		=5.062(38) MHz <sup>b</sup>	=-0.413(79) MHz <sup>b</sup>

<sup>a</sup> Units as in Table V.

<sup>b</sup> Values of  $\alpha$  (and  $c$ ) and the Ryberg constant  $R (=R_\infty)$  are taken from Refs. 18 and 19, respectively. We take  $m/M=1.370 934 \times 10^{-4}$  (see Ref. 22). Hence, e.g.,  $\alpha^4 R c=4.664 515 \text{ MHz}$ .

+2 $\bar{E}_2^{(1,2)}$ . Table VIII presents our results for the  $\bar{E}_2^{(i,j)}$  due to  ${}^1P$  intermediate states for  $\omega = 1$  to  $\omega = 10$ .

### VII. ${}^3D$ INTERMEDIATE-STATE CONTRIBUTIONS

The operators with nonvanishing matrix elements between  ${}^3D$  and  ${}^3P$  states are the spin-symmetric parts of the spin-dependent Breit operators, that is,  $H_1^{(1)}$ ,  $H_1^{(2)}$ , and  $H_1^{(3)}$  as presented in Sec. II. We shall evaluate the perturbation on the  $2{}^3P_2$  level by  ${}^3D_2$  states so that we take

$$U_{lmn}({}^3P_2, m_J = 2) = \frac{1 - P_{12}}{4\pi\sqrt{2}} S_1^{(1)} T_1^{(1)}(\vec{r}_1) u_{lmn}(1, 2),$$

as before. With

$$\begin{aligned} T_2^{(2)}(\vec{r}_1, \vec{r}_2) &= (\sqrt{2} S_0^{(1)} \{T^{(1)}(\vec{r}_1), \{T^{(1)}(\vec{r}_1), T^{(1)}(\vec{r}_2)\}^{(1)}\}_2^{(2)} \\ &\quad - S_1^{(1)} \{T^{(1)}(\vec{r}_1), \{T^{(1)}(\vec{r}_1), T^{(1)}(\vec{r}_2)\}^{(1)}\}_1^{(2)}) / \sqrt{3}, \end{aligned} \quad (33)$$

then the "D-part" of

$$\begin{aligned} H_1^{(1)} S_1^{(1)} T_1^{(1)}(\vec{r}_1) u_{lmn}(1, 2) &= \frac{1}{4} \alpha^2 Z \sqrt{3} \frac{l}{r_{12}^2} \left( \frac{1}{r_2^3} - \frac{1}{r_1^3} \right) T_2^{(2)}(\vec{r}_1, \vec{r}_2) u_{lmn}(1, 2). \end{aligned} \quad (34)$$

A note of explanation is in order here. It will be noted that  $T_2^{(2)}(\vec{r}_1, \vec{r}_2)$  is essentially a  ${}^3D$  Russell-Saunders term with  $J = 2$ ,  $m_J = 2$  constructed from the odd-parity configuration  $2p3d$ . The operation of the  $H_1^{(i)}$  on the  $2{}^3P$  basis functions produces terms containing products of  $P$ -type spherical tensors. These products can be decomposed by methods of vector-coupling algebra<sup>16</sup> into components which are pure  $S$ ,  $P$ , and  $D$  respectively, and it is the latter which we project out as the sole contributor to our matrix elements. Proceeding with  $H_1^{(2)}$ , we obtain that the  $D$  part of

$$\begin{aligned} H_1^{(2)} S_1^{(1)} T_1^{(1)}(\vec{r}_1) u_{lmn}(1, 2) &= -\frac{3}{4} \alpha^2 \sqrt{3} \frac{1}{r_{12}^3} \left( \frac{m}{r_1^2} - \frac{K\sigma}{2r_1} + \frac{K}{2r_2} - \frac{n}{r_2^2} \right) \\ &\quad \times T_2^{(2)}(\vec{r}_1, \vec{r}_2) u_{lmn}(1, 2), \end{aligned} \quad (35)$$

and

$$\begin{aligned} H_1^{(3)} S_1^{(1)} T_1^{(1)}(\vec{r}_1) u_{lmn}(1, 2) \quad (D \text{ part}) &= -\frac{1}{4} \alpha^2 \sqrt{3} \left( \frac{2}{r_{12}^5} \right) [T_2^{(2)}(\vec{r}_1, \vec{r}_2) \\ &\quad + T_2^{(2)}(\vec{r}_2, \vec{r}_1)] u_{lmn}(1, 2). \end{aligned} \quad (36)$$

We will expand the  ${}^3D$  intermediate states in two ways. One way is to multiply the usual Hylleraas expansion by the  ${}^3D_2$  form  $T_2^{(2)}(\vec{r}_1, \vec{r}_2)$ . The other way divides this tensor by  $r_1 r_2$ , so that we can match the  $P$  expansions (Secs. II and V) term by term and use integrals of the same order. The latter expansion has the feature that the lowest-order term is no longer a  $2p3d$  configuration, but with the factor  $(r_1 r_2)^{-1}$  it seems to better reflect the singularities in the  $H_1^{(i)}$  than the former expansion. Hence we develop the intermediate  $D$  states as

$$\Psi_P^{(i)}({}^3D_2, m_J = 2) = \sum_{l, m, n=0}^{l+m+n=\omega} Y_{lmn}^{(i)} V_{lmn}^P({}^3D_2, m_J = 2), \quad (37)$$

with

$$V_{lmn}^P({}^3D_2, m_J = 2) = \frac{1 - P_{12}}{4\pi\sqrt{2}} \frac{T_2^{(2)}(\vec{r}_1, \vec{r}_2)}{(r_1 r_2)^{2-P}} u_{lmn}(1, 2). \quad (38)$$

The integrals involved in deriving the required matrix elements can be expressed in terms of the  $A$  and  $B$  integrals in much the same way as is done in Appendix B for the  ${}^3F$  case. One then finds, for example,

TABLE VIII.  ${}^1P$  intermediate-state contributions.

$\omega$	$E_2^{(1,1)}$ ( $\alpha^4$ Ry)	$E_2^{(2,2)}$ ( $\frac{1}{2} \alpha^4$ Ry)	$E_2^{(1,2)}$ ( $\frac{1}{2} \alpha^4$ Ry)
1	-0.326 083 150 88	-0.184 644 064 08	-0.244 726 520 49
2	-0.331 131 174 24	-0.175 888 934 60	-0.239 969 803 09
3	-0.350 064 594 92	-0.173 445 981 92	-0.243 720 589 92
4	-0.365 313 359 75	-0.173 757 715 10	-0.247 748 058 84
5	-0.374 772 120 85	-0.173 362 964 16	-0.249 206 734 39
6	-0.381 096 250 54	-0.173 346 329 85	-0.250 114 866 10
7	-0.385 639 094 46	-0.173 480 325 43	-0.250 769 735 56
8	-0.388 981 850 16	-0.173 572 695 78	-0.251 163 261 55
9	-0.391 536 114 08	-0.173 644 366 53	-0.251 418 244 26
10	-0.393 581 108 70	-0.173 705 575 77	-0.251 606 646 81

$$\begin{aligned} \langle V_{l'm'n'}^1 | H_1^{(1)} | U_{lmn} \rangle = & -\frac{1}{40} \alpha^2 Z \sqrt{3} \frac{l}{L} \left( B_d(L+2, M+4, N-1) - B_d(L+2, M+1, N+2) \right. \\ & + A_e(L+2, M'+3, N') + \frac{3}{L+2} B_e(L+4, M'+2, N'-1) \\ & \left. - A_e(L+2, M', N'+3) - \frac{3}{L+2} B_e(L+4, M'-1, N'+2) \right), \end{aligned} \quad (39)$$

and similarly for  $H_1^{(2)}$  and  $H_1^{(3)}$ .

The action of  $H_0$  on the  ${}^3D$  basis functions is given by

$$\begin{aligned} H_0 \frac{u_{lmn}(1, 2)}{r_1 r_2} T_2^{(2)}(\vec{r}_1, \vec{r}_2) = & \frac{u_{lmn}(1, 2)}{r_1 r_2} T_2^{(2)}(\vec{r}_1, \vec{r}_2) \left( -\frac{1}{8} (\kappa^2 \sigma^2 + \kappa^2) + \frac{1}{r_1} \left[ \frac{1}{4} \kappa \sigma (2m+4+l) - 2 \right] + \frac{1}{r_2} \left[ \frac{1}{4} \kappa (2n+2+l) - 2 \right] \right. \\ & - \frac{1}{r_1^2} \frac{1}{2} (m-1)(m+l+4) - \frac{1}{r_2^2} \frac{1}{2} (n-1)(n+2+l) + \frac{1}{r_{12}} \\ & - \frac{1}{r_{12}^2} \frac{1}{2} l(2l+m+n+6) + \frac{r_1}{r_{12}^2} \frac{1}{4} \kappa \sigma l + \frac{r_2}{r_{12}^2} \frac{1}{4} \kappa l \\ & \left. - \frac{r_1^2}{r_1 r_{12}^2} \frac{1}{4} \kappa \sigma l - \frac{r_1^2}{r_2 r_{12}^2} \frac{1}{4} \kappa l + \frac{r_2^2}{r_1 r_{12}^2} \frac{1}{2} l(m-1) + \frac{r_1^2}{r_2 r_{12}^2} \frac{1}{2} l(n-1) \right) \\ & - \frac{u_{lmn}(1, 2)}{r_1 r_2} T_2^{(2)}(\vec{r}_2, \vec{r}_1) \frac{l}{r_{12}}. \end{aligned} \quad (40)$$

The matrix elements of unity and  $H_0$  can then be expressed as

$$\langle V_{l'm'n'}^1 | I | V_{lmn}^1 \rangle = -\frac{1}{10} \frac{1}{L+2} \left( B_d(L+4, M+3, N+1) + A_e(L+4, M'+2, N'+2) + \frac{3}{L+4} B_e(L+6, M'+1, N'+1) \right) \quad (41)$$

and a similar sum of 42 terms for

$$\langle V_{l'm'n'}^1 | H_0 | V_{lmn}^1 \rangle.$$

Having computed the matrix elements for  $P=1$ , those for  $P=2$  follow with little extra effort. For the transition matrix elements of the  $H_1^{(i)}$  for  $P=2$ , we simply raise by one the second and third indices in each  $A$  and  $B$  integral occurring in the corresponding expression for  $P=1$ . These indices are each increased by two in going from the  $P=1$  to the  $P=2$  matrix elements of unity. Finally, we get the new  $H_0$  matrix elements from the old by raising each of the last two indices in every  $A$  or  $B$  integral by two and by replacing the multiplicative factors  $m$  and  $n$  by  $m+1$  and  $n+1$ , respectively.

The perturbation equation to be solved now is quite similar in form to that for the  ${}^1P$  case. Tables IX and X give the second-order energies for  $P=2$  (undivided basis) and  $P=1$ , respectively. The convergence of the  $\tilde{E}_2^{(i,j)}$  as a function of  $\omega$  is clearly better for  $P=1$  than for  $P=2$ , although the total shift of the  $2^3P_2$  level, given by Eq. (19), does in fact have a reasonable convergence for  $P=2$ , not inconsistent with that for  $P=1$ . We use the  $P=1$  results for subsequent calculations. There is also a perturbation of the  $2^3P_1$  level due to  ${}^3D_1$  intermediate states, but this can be ex-

tracted simply from the  $J=2$  result by Racah algebra.<sup>16</sup> The shift of the  $J=1$  level is found to be

$$\begin{aligned} (\tilde{E}_2)_{J=1} = & \frac{5}{9} (\tilde{E}_2^{(1,1)} + \tilde{E}_2^{(2,2)} + 9\tilde{E}_2^{(3,3)} + 2\tilde{E}_2^{(1,2)} \\ & - 6\tilde{E}_2^{(1,3)} - 6\tilde{E}_2^{(2,3)}), \end{aligned} \quad (42)$$

from which the corrections to the values of the larger and smaller fine-structure intervals can be readily obtained.

#### VIII. ${}^1D$ INTERMEDIATE-STATE CONTRIBUTIONS

The operators with nonvanishing matrix elements between  ${}^1D$  and  ${}^3P$  states are precisely the operators  $\tilde{H}_1^{(1)}$  and  $\tilde{H}_1^{(2)}$  encountered in the  ${}^1P$  case. Since  $J$  must be 2 for  ${}^1D$  states, we again use for the unperturbed basis wave function  $U_{lmn}({}^3P_2, m_J=2)$  and as in the  ${}^3D$  case we use  ${}^1D$  expansions of both "divided" and "undivided" types:

$$\Psi_p^{(i)}({}^1D_2, m_J=2) = \sum_{l, m, n=0}^{l+m+n \leq \omega} Z_{lmn}^{(i)} W_{lmn}^p({}^1D_2, m_J=2), \quad (43)$$

where

$$\begin{aligned} W_{lmn}^p({}^1D_2, m_J=2) = & \frac{1+P_{12}}{4\pi\sqrt{2}} S_0^{(0)} \{ T^{(1)}(\vec{r}_1), \{ T^{(1)}(\vec{r}_1), T^{(1)}(\vec{r}_2) \}_{l_2}^{(1)} \}_{l_2}^{(2)} \\ & \times u_{lmn}(1, 2) (r_1 r_2)^{p-2}. \end{aligned} \quad (44)$$

TABLE IX.  ${}^3D$  intermediate-state contributions using the no division basis ( $P=2$ ).

$\omega$	$10^3 E_2^{(1,1)}$ ( $\frac{3}{2} \alpha^4$ Ry)	$10 E_2^{(2,2)}$ ( $\frac{3}{8} \alpha^4$ Ry)	$10^4 E_2^{(3,3)}$ ( $\frac{3}{8} \alpha^4$ Ry)
1	-1.366 652 850 12	-0.110 522 054 62	-0.196 787 902 47
2	-0.710 762 004 31	-0.134 681 778 27	-0.292 213 695 55
3	-0.593 612 876 99	-0.156 527 657 11	-0.389 078 840 77
4	-0.549 860 060 48	-0.174 044 176 04	-0.473 872 926 60
5	-0.533 246 090 44	-0.186 928 588 73	-0.543 953 979 09
6	-0.533 176 246 63	-0.196 770 450 60	-0.603 675 247 72
7	-0.543 482 651 29	-0.204 398 822 43	-0.654 697 179 54
8	-0.554 509 427 42	-0.210 423 708 73	-0.698 473 932 14
9	-0.565 547 781 04	-0.215 261 317 57	-0.736 216 766 51
10	-0.575 443 433 35	-0.219 201 295 09	-0.768 927 272 06
$\omega$	$10^2 E_2^{(1,2)}$ ( $\frac{3}{4} \alpha^4$ Ry)	$10^4 E_2^{(1,3)}$ ( $\frac{3}{4} \alpha^4$ Ry)	$10^2 E_2^{(2,3)}$ ( $\frac{3}{8} \alpha^4$ Ry)
1	0.269 421 855 46	0.954 201 753 99	-0.045 682 986 246
2	0.231 932 935 78	0.976 235 932 99	-0.060 560 051 902
3	0.221 376 481 83	0.935 950 772 89	-0.074 518 644 393
4	0.213 445 715 43	0.899 296 009 79	-0.085 877 848 210
5	0.206 611 671 24	0.865 411 361 94	-0.094 484 107 572
6	0.203 529 015 71	0.851 745 279 35	-0.101 234 385 10
7	0.202 560 072 80	0.848 837 570 39	-0.106 541 238 68
8	0.202 243 379 10	0.850 041 334 59	-0.110 743 057 70
9	0.202 215 966 45	0.852 603 275 54	-0.114 097 395 21
10	0.202 266 765 00	0.855 311 786 00	-0.116 797 502 33

TABLE X.  ${}^3D$  intermediate-state contributions using the division basis ( $P=1$ ).

$\omega$	$10^3 E_2^{(1,1)}$ ( $\frac{3}{2} \alpha^4$ Ry)	$10 E_2^{(2,2)}$ ( $\frac{3}{8} \alpha^4$ Ry)	$10^4 E_2^{(3,3)}$ ( $\frac{3}{8} \alpha^4$ Ry)
1	-2.932 459 627 1	-0.161 613 978 18	-0.340 106 185 53
2	-1.345 970 458 8	-0.193 730 641 96	-0.509 951 383 40
3	-0.986 885 949 59	-0.206 983 161 25	-0.617 724 847 50
4	-0.813 439 775 92	-0.216 153 189 19	-0.691 679 313 57
5	-0.727 979 098 18	-0.221 527 841 03	-0.742 831 054 85
6	-0.686 479 010 55	-0.225 483 193 54	-0.784 198 583 46
7	-0.671 969 372 27	-0.228 491 901 57	-0.818 640 721 67
8	-0.665 567 140 27	-0.230 877 940 84	-0.847 861 920 90
9	-0.663 931 617 18	-0.232 815 731 50	-0.872 896 591 04
10	-0.663 847 111 10	-0.234 416 689 75	-0.894 471 179 05
$\omega$	$10^2 E_2^{(1,2)}$ ( $\frac{3}{4} \alpha^4$ Ry)	$10^4 E_2^{(1,3)}$ ( $\frac{3}{4} \alpha^4$ Ry)	$10^2 E_2^{(2,3)}$ ( $\frac{3}{8} \alpha^4$ Ry)
1	0.328 098 345 95	1.255 716 596 9	-0.072 429 385 476
2	0.277 155 059 77	1.213 629 750 8	-0.095 083 262 108 2
3	0.244 649 667 46	1.067 712 341 3	-0.106 437 384 44
4	0.225 869 891 97	0.978 883 206 01	-0.113 632 335 96
5	0.212 961 405 81	0.916 156 610 90	-0.117 817 805 23
6	0.206 789 602 02	0.887 183 841 25	-0.120 779 024 40
7	0.204 177 659 42	0.874 988 242 93	-0.122 938 547 64
8	0.202 981 606 39	0.870 086 701 02	-0.124 566 401 58
9	0.202 482 686 92	0.868 347 560 64	-0.125 822 424 65
10	0.202 286 397 95	0.867 918 336 44	-0.126 809 404 34

TABLE XI.  ${}^1D$  intermediate-state contribution using the no division basis ( $p=2$ ).

$\omega$	$10^3 E_2^{(1,1)}$ ( $\alpha^4$ Ry)	$10^2 E_2^{(2,2)}$ ( $\frac{1}{4} \alpha^4$ Ry)	$10^3 E_2^{(1,2)}$ ( $\frac{1}{2} \alpha^4$ Ry)
1	-1.403 836 880 8	-0.152 544 006 96	-1.054 390 740 5
2	-0.773 893 759 10	-0.185 461 040 19	-0.959 573 356 37
3	-0.660 992 609 49	-0.215 273 127 77	-0.945 321 893 35
4	-0.616 474 229 94	-0.236 402 896 29	-0.931 279 989 99
5	-0.596 877 872 93	-0.250 532 046 75	-0.915 204 681 43
6	-0.595 291 903 61	-0.260 261 634 00	-0.911 221 516 74
7	-0.604 953 981 23	-0.267 086 203 57	-0.913 556 440 59
8	-0.615 759 058 98	-0.271 960 310 85	-0.917 023 005 68
9	-0.626 743 460 61	-0.275 500 274 25	-0.920 506 816 78
10	-0.636 639 608 90	-0.278 112 611 05	-0.923 460 456 18

Now the  $L=2$  components arising from the action of the  $\tilde{H}_1^{(i)}$  are found to be

$$\begin{aligned} & \tilde{H}_1^{(1)} S_1^{(1)} T_1^{(1)}(\vec{r}_1) u_{1mn}(1, 2) \text{ (D part)} \\ &= \frac{1}{4} \alpha^2 Z \sqrt{2} S_0^{(0)} \frac{l}{r_{12}^2} \left( \frac{1}{r_1^3} + \frac{1}{r_2^3} \right) \\ & \times \{ T^{(1)}(\vec{r}_1), \{ T^{(1)}(\vec{r}_1), T^{(1)}(\vec{r}_2) \}^{(1)} \}_{2}^{(1)(2)} u_{1mn}(1, 2), \end{aligned} \quad (45)$$

and

$$\begin{aligned} & \tilde{H}_1^{(2)} T_1^{(1)}(\vec{r}_1) S_1^{(1)} u_{1mn}(1, 2) \text{ (D part)} \\ &= -\frac{1}{4} \alpha^2 \sqrt{2} S_0^{(0)} \{ T^{(1)}(\vec{r}_1), \{ T^{(1)}(\vec{r}_1), T^{(1)}(\vec{r}_2) \}^{(1)} \}_{2}^{(1)(2)} \\ & \times \frac{1}{r_{12}^3} \left( \frac{m}{r_1^2} - \frac{\kappa \sigma}{2r_1} + \frac{n}{r_2^2} - \frac{\kappa}{2r_2} \right) u_{1mn}(1, 2). \end{aligned} \quad (46)$$

These results bear a close similarity to the corresponding  ${}^3D$  quantities and in fact the matrix elements  $\langle W_{i'm'n'}^p | \tilde{H}_1^{(i)} | U_{1mn} \rangle$  differ from the  $\langle V_{i'm'n'}^p | H_1^{(i)} | U_{1mn} \rangle$  only by a scale factor and a few sign changes between the  $A$  and  $B$  integrals. Like-

wise, the overlap integral for the  ${}^1D$  basis functions is found easily from the  ${}^3D$  inner product by reversing the signs of the exchange integrals therein.

Moreover, it should be evident that the action of  $H_0$  on the (unsymmetrized)  $W_{1mn}^1$  is the same as that computed for  $H_0$  on  $V_{1mn}^1$  (unsymmetrized) in the  ${}^3D$  case, with  $V_{1mn}^1$  simply replaced by  $W_{1mn}^1$ . Then the matrix element of  $H_0$  between  ${}^1D$  basis functions is readily obtained from that between  ${}^3D$  basis functions by merely changing the signs of the exchange integrals  $A_e, B_e$  appearing in the latter.

Using these matrix elements, we may proceed as before to determine the coefficients in the expansions for  $\psi_p^{(i)}$  and from this the second-order energies. The results are displayed in Tables XI and XII for  $p=2$  and  $p=1$ , respectively. The convergence as a function of  $\omega$  for both cases is qualitatively the same as that observed in the case of the  ${}^3D$  intermediate states previously encountered. As in the  ${}^1P$  calculation, only the  $J=L$  level is shifted with the same expression arising for  $(E_2)_{J=2}$  in the  ${}^1D$  case as for  $(\tilde{E}_2)_{J=1}$  in the  ${}^1P$  case.

TABLE XII.  ${}^1D$  intermediate-state contributions using the division basis ( $p=1$ ).

$\omega$	$10^3 E_2^{(1,1)}$ ( $\alpha^4$ Ry)	$10^2 E_2^{(2,2)}$ ( $\frac{1}{4} \alpha^4$ Ry)	$10^3 E_2^{(1,2)}$ ( $\frac{1}{2} \alpha^4$ Ry)
1	-2.985 471 476 1	-0.204 848 944 48	-1.265 533 625 1
2	-1.435 111 804 2	-0.244 466 231 44	-1.162 245 912 3
3	-1.073 798 711 5	-0.263 599 645 30	-1.079 803 585 8
4	-0.892 419 317 88	-0.274 064 211 14	-1.021 823 284 8
5	-0.798 649 580 10	-0.279 060 165 11	-0.974 308 838 76
6	-0.752 526 373 15	-0.281 913 777 77	-0.950 688 212 22
7	-0.735 613 931 83	-0.283 645 323 33	-0.940 455 886 35
8	-0.728 017 311 93	-0.284 765 357 40	-0.935 811 489 38
9	-0.725 784 609 47	-0.285 517 258 34	-0.933 929 325 18
10	-0.725 394 681 83	-0.286 038 366 24	-0.933 245 496 58

Thus, only the smaller interval is shifted in value by  ${}^1D$  intermediate states in second-order perturbation theory.

#### IX. ${}^3F$ INTERMEDIATE-STATE CONTRIBUTIONS

The only operator with nonvanishing matrix elements between  ${}^3F$  and  ${}^3P$  states is the spin-spin operator  $H_1^{(3)}$ . Since the only transitions conserving  $J$  are those for which  $J=2$ , we take

$H_1^{(3)}S_1^{(1)}T_1^{(1)}(\vec{r}_1)u_{1mn}(1,2)$  ( $F$  part)

$$= \frac{1}{4}\alpha^2 \left(-\frac{6}{r_{12}^5}\right) \left(\frac{7}{5}\right)^{1/2} \left[ \left(\frac{1}{21}\right)^{1/2} S_1^{(1)}X_1^{(3)} - \left(\frac{5}{21}\right)^{1/2} S_0^{(1)}X_2^{(3)} + \left(\frac{5}{7}\right)^{1/2} S_{-1}^{(1)}X_3^{(3)} \right] u_{1mn}(1,2), \quad (48)$$

where

$$X_M^{(3)} = \{ \{ T^{(1)}(\vec{r}_1), T^{(1)}(\vec{r}_1) \}^{(2)}, T^{(1)}(\vec{r}_1) \}_M^{(3)} \\ + \{ \{ T^{(1)}(\vec{r}_2), T^{(1)}(\vec{r}_2) \}^{(2)}, T^{(1)}(\vec{r}_1) \}_M^{(3)} \\ - 2 \{ \{ T^{(1)}(\vec{r}_1), T^{(1)}(\vec{r}_1) \}^{(2)}, T^{(1)}(\vec{r}_2) \}_M^{(3)}. \quad (49)$$

Hence we choose  $\tilde{W}$  to be

$$\tilde{W}_{1mn}({}^3F_2, m_J=2) \\ = \frac{(1-P_{12})}{4\pi\sqrt{2}} \left[ \left(\frac{1}{21}\right)^{1/2} S_1^{(1)}\tilde{X}_1^{(3)} - \left(\frac{5}{21}\right)^{1/2} S_0^{(1)}\tilde{X}_2^{(3)} \right. \\ \left. + \left(\frac{5}{7}\right)^{1/2} S_{-1}^{(1)}\tilde{X}_3^{(3)} \right] u_{1mn}(1,2), \quad (50)$$

where

$$\tilde{X}_M^{(3)} = \{ \{ T^{(1)}(\vec{r}_1), T^{(1)}(\vec{r}_1) \}^{(2)}, T^{(1)}(\vec{r}_1) \}_M^{(3)} \\ + \varphi \{ \{ T^{(1)}(\vec{r}_2), T^{(1)}(\vec{r}_2) \}^{(2)}, T^{(1)}(\vec{r}_1) \}_M^{(3)} \\ + \xi \{ \{ T^{(1)}(\vec{r}_1), T^{(1)}(\vec{r}_1) \}^{(2)}, T^{(1)}(\vec{r}_2) \}_M^{(3)} \quad (51)$$

and  $\varphi$  and  $\xi$  will be specified later. Looking at  $\tilde{X}_M^{(3)}$ , we discover that it represents a state of total orbital angular momentum 3 constructed via  $L$ - $S$  coupling from  $2p3d$  and  $1s4f$  two-electron configurations. As such it is an odd-parity object, as it must be to allow for nonvanishing transitions between states of different  $L$  and/or  $S$ , but with the same  $J$ . The bracketed part of the expression for  $\tilde{W}_{1mn}$  is then the coupling of  $L=3$  with  $S=1$  to obtain a state with total angular momentum  $J=2$  and  $m_J=2$ .

Now the coefficients  $\varphi$  and  $\xi$  are not *a priori*

$U_{1mn}({}^3P_2, m_J=2)$  as before, and we have one perturbation wave function to consider, which we write as

$$\psi^{(3)}({}^3F_2, m_J=2) = \sum_{l,m,n}^{l+m+n=\omega} \tilde{Z}_{lmn}^{(3)} \tilde{W}_{1mn}({}^3F_2, m_J=2). \quad (47)$$

The form of  $\tilde{W}$  is suggested by the operation of  $H_1^{(3)}$  on  $U$  and is discussed by Schwartz,<sup>17</sup>

determined, nor are they to be regarded as variational parameters to be optimized. Under the circumstances, it seems reasonable to take  $\phi=1$ ,  $\xi=-2$  as dictated by the operation of  $H_1^{(3)}$  on the  $2{}^3P$  basis functions, but we have also carried out the calculations with  $\phi=0$ ,  $\xi=-1$  for the sake of comparison. In point of fact, we should take  $\phi=0$  or  $\xi=0$  in  $\tilde{W}_{1mn}$  and treat  $\xi(\phi)$  as  $\xi_{1mn}(\phi_{1mn})$ , so that we have in effect twice as many coefficients to solve for in the perturbation equation as were required for the other intermediate states for a given  $\omega$ . However, this has been done and the results are very little different from those obtained with the choice  $\phi=1$ ,  $\xi=-2$ , so we proceed along these latter lines.

Using the general results derived in Appendix B, we find, e.g., that the matrix element of the spin-spin operator between  ${}^3P$  and  ${}^3F$  basis functions is

TABLE XIII.  ${}^3F$  intermediate-state contributions.

$\omega$	$10^3 E_{\xi}^{(3,3)}$ ( $\frac{14}{5}\alpha^4$ Ry)	
	$\xi=-2, \varphi=1$	$\xi=-1, \varphi=0$
1	-0.36189639177	-0.47531537046
2	-0.47697878743	-0.61647867358
3	-0.59965349682	-0.76322224644
4	-0.70972110772	-0.89165989091
5	-0.80644239861	-0.99815569634
6	-0.89680169469	-1.08671906458
7	-0.98067125919	-1.16054146726
8	-1.05404688402	-1.22242658793
9	-1.11962961974	-1.27465545881
10	-1.18002196767	-1.31908315805

$$\begin{aligned}
& \langle \tilde{W}_{l'm'n'} | H_1^{(3)} | U_{lmn} \rangle \\
&= -\frac{3}{2} \alpha^2 \left(\frac{7}{5}\right)^{1/2} \frac{2}{105} \left\{ 3A_d(L-3, M+8, N+2) - 6B_d(L-3, M+7, N+3) \right. \\
&\quad + 3(1+\varphi) \left( A_d(L-3, M+6, N+4) + \frac{3}{L-3} B_d(L-1, M+5, N+3) \right) \\
&\quad + (\xi - 2\varphi) \left[ 3B_d(L-3, M+5, N+5) + \frac{1}{L-3} \left( A_d(L-1, M+4, N+4) \right. \right. \\
&\quad \quad \quad \left. \left. + \frac{3}{L-1} B_d(L+1, M+3, N+3) \right) \right] \\
&\quad - 2\xi \left( 3A_d(L-3, M+6, N+4) + \frac{2}{L-3} B_d(L-1, M+5, N+3) - \frac{3}{2} B_d(L-3, M+7, N+3) \right) \\
&\quad + \varphi \left( 3A_d(L-3, M+4, N+6) + \frac{2}{L-3} B_d(L-1, M+3, N+5) \right) \\
&\quad - 3 \left[ B_e(L-3, M'+5, N'+5) + B_e(L-3, M'+3, N'+7) - 2A_e(L-3, M'+4, N'+6) \right. \\
&\quad \quad + \frac{1}{L-3} \left( 5A_e(L-1, M'+4, N'+4) + \frac{15}{L-1} B_e(L+1, M'+3, N'+3) \right. \\
&\quad \quad \quad \left. \left. - 6B_e(L-1, M'+3, N'+5) \right) \right] \\
&\quad - \xi \left( 3A_e(L-3, M'+6, N'+4) + 3A_e(L-3, M'+4, N'+6) \right. \\
&\quad \quad \left. + \frac{1}{L-3} [9B_e(L-1, M'+5, N'+3) + 2B_e(L-1, M'+3, N'+5)] \right) \\
&\quad + 2\varphi \left( 3A_e(L-3, M'+6, N'+4) - \frac{3}{2} B_e(L-3, M'+7, N'+3) \right. \\
&\quad \quad \left. + \frac{2}{L-3} B_e(L-1, M'+5, N'+3) \right) \\
&\quad - (\varphi - 2\xi) \left[ 3B_e(L-3, M'+5, N'+5) + \frac{1}{L-3} \left( A_e(L-1, M'+4, N'+4) \right. \right. \\
&\quad \quad \quad \left. \left. + \frac{3}{L-1} B_e(L+1, M'+3, N'+3) \right) \right] \left. \right\}. \tag{52}
\end{aligned}$$

Turning our attention next to the effect of  $H_0$  on the  ${}^3F$  basis functions, we may write

$$\begin{aligned}
H_0 \tilde{X}_M^{(3)} u_{lmn}(1, 2) &= u_{lmn}(1, 2) \left( \sum_{i=1}^{13} \gamma_1^i \gamma_2^i \gamma_{12}^i d_{1i} \{ \{ T^{(1)}(\tilde{\mathbf{r}}_1), T^{(1)}(\tilde{\mathbf{r}}_1) \}^{(2)}, T^{(1)}(\tilde{\mathbf{r}}_1) \}_M^{(3)} \right. \\
&\quad + \xi d_{2i} \{ \{ T^{(1)}(\tilde{\mathbf{r}}_1), T^{(1)}(\tilde{\mathbf{r}}_1) \}^{(2)}, T^{(1)}(\tilde{\mathbf{r}}_2) \}_M^{(3)} + \phi d_{3i} \{ \{ T^{(1)}(\tilde{\mathbf{r}}_2), T^{(1)}(\tilde{\mathbf{r}}_2) \}^{(2)}, T^{(1)}(\tilde{\mathbf{r}}_1) \}_M^{(3)} \} \\
&\quad \left. + \frac{\phi l}{\gamma_{12}^2} \{ \{ T^{(1)}(\tilde{\mathbf{r}}_2), T^{(1)}(\tilde{\mathbf{r}}_2) \}^{(2)}, T^{(1)}(\tilde{\mathbf{r}}_2) \}_M^{(3)} \right), \tag{53}
\end{aligned}$$

TABLE XIV. Final extrapolations for second-order contributions to  $2^3P$  helium fine structure from intermediate state symmetries other than  $^3P$ .

Intermediate state	Extrapolated quantities <sup>a,b</sup>	$(E_2)_1$ ( $\alpha^4$ Ry)	$(E_2)_2$ ( $\alpha^4$ Ry)	$\Delta\nu_{01}$ (MHz)	$\Delta\nu_{12}$ (MHz)
$^1P$	$(E_2)_1$	-0.704 08(198)		6.568(18)	-6.568(18)
$^3D$	$(E_2)_1, (E_2)_2$	-0.002 855(84)	-0.008 04(19)	0.027(1)	0.048(2)
$^1D$	$E_2^{(1,1)} = -0.000 725 26(5)$				
	$E_2^{(1,2)} = -0.000 932 79(5)$		-0.002 378(1)		0.022 18(1)
	$E_2^{(2,2)} = -0.002 878 0(22)$				
$^3F$	$E_2^{(3,3)} = -0.001 7(3)$		-0.004 8(8)		0.045(8)

<sup>a</sup> Expressions for  $(E_2)_j$  for given symmetries are given in the text.

<sup>b</sup> Units of the various  $E_2^{(i,j)}$  are as displayed in Tables XI–XIII.

where the variables indexed by the subscript “ $i$ ” are defined in the following tabulation:

$i$	$p_i$	$q_i$	$s_i$	$d_{ji}(j=1, 2, 3)$
1	-1	0	0	$\frac{1}{4}\kappa\sigma[2(m-j)+l+10]-2$
2	0	-1	0	$\frac{1}{4}\kappa[2(n+j)+l]-2$
3	-2	0	0	$-\frac{1}{2}m(m+l+9-2j)$
4	0	-2	0	$-\frac{1}{2}n(n+l+2j-1)$
5	0	0	-2	$-\frac{1}{2}l(2l+m+n+8)+ld'_j$
6	0	0	0	$-\frac{1}{8}\kappa^2(\sigma^2+1)$
7	0	0	-1	1
8	1	0	-2	$\frac{1}{4}\kappa\sigma l$
9	0	1	-2	$\frac{1}{4}\kappa l$
10	-2	2	-2	$\frac{1}{2}ml$
11	2	-2	-2	$\frac{1}{2}nl$
12	-1	2	-2	$-\frac{1}{4}\kappa\sigma l$
13	2	-1	-2	$-\frac{1}{4}\kappa l$

For  $i=5$ ,  $d'_j$  is given by

$$d'_1 = \xi, \quad d'_2 = (3+2\phi)/\xi, \quad d'_3 = 2\xi/\phi. \quad (54)$$

Each matrix element  $\langle \bar{W}_{\nu m' n'} | H_0 | \bar{W}_{l m n} \rangle$  can then be expressed as the sum of 478 terms. As a byproduct of this calculation, the inner product of the  $^3F$  basis functions is extracted as a linear combination of 27  $A$  and  $B$  integrals.

There is now one equation to be solved for the perturbation wave function and one energy  $E_2^{(3,3)}$  to be derived from this wave function. Table XIII indicates the results for  $E_2^{(3,3)}$  for two choices of the pair of parameters  $\xi$  and  $\phi$ . Although the results in column 2 of that table are uniformly lower than those in column 1 for a given  $\omega$ , the conver-

gence rates are comparable and, in fact, the extrapolated value from the latter column is lower than that from the former. There being no compelling argument in favor of the choice  $\xi=-1$ ,  $\phi=0$ , we will use the results for  $\xi=-2$ ,  $\phi=1$  to calculate the  $^3F$  second-order contributions in the next section.

## X. RESULTS

As in Sec. V, the second-order energies are extrapolated according to two types of convergence and a weighted average is obtained. For the  $^3D$  and  $^1P$  cases it is advantageous to extrapolate the expressions for the total level shifts rather than to extrapolate individual  $E_2^{(i,j)}$  and then sum them. This gives results that are consistent with those that would be obtained by the latter method, and in addition avoids minor irregularities inherent in those results. For the same reason we choose to extrapolate the  $E_2^{(i,j)}$  individually and then sum them in the case of  $^1D$  intermediate states. When this is done, the  $^1D$  contribution is found to be remarkably accurate for the case of the divided basis functions. The  $^3F$  energies exhibit a slow exponen-

TABLE XV. The second-order contributions to the fine structure of  $2^3P$  helium. ( $^1D$  and  $^3F$  intermediate states do not contribute to  $\nu_{01}$ .)

Intermediate state	Interval	
	$\nu_{01}$ (MHz)	$\nu_{12}$ (MHz)
$^3P$	$5.062 \pm 0.038$	$-0.413 \pm 0.079$
$^1P$	$6.568 \pm 0.018$	$-6.568 \pm 0.018$
$^3D$	$0.027 \pm 0.001$	$0.048 \pm 0.002$
$^1D$		$0.022 18 \pm 0.000 01$
$^3F$		$0.045 \pm 0.008$
Total	$11.657 \pm 0.042$	$-6.866 \pm 0.081$

TABLE XVI. Theoretical contributions to the fine-structure of  $2^3P$  helium in MHz. The values of  $\alpha^{-1}$ ,  $c$ ,  $R_\infty$  and  $m/M$  are 137.035987(29) (0.21 ppm),<sup>a</sup> 2.997 924 58(12)  $\times 10^{10}$  cm sec<sup>-1</sup> (0.004 ppm),<sup>a</sup> 109 737.314 3 cm<sup>-1</sup> (0.009 ppm)<sup>b</sup> and 1.370 934  $\times 10^{-4}$ , respectively. Thus  $\frac{1}{2}\alpha^2 c R_\infty = 87.594$  28 GHz (0.42 ppm).

Interval	$\alpha^4 m c^2$	$\alpha^5 m c^2$	$(m/M)\alpha^4 m c^2$	Second order	$\alpha^6 m c^2$	$\nu_{\text{theory}}$	$\nu_{\text{expt}}$	$\nu_{\text{theory}} - \nu_{\text{expt}}$
$\nu_{01}$	29 564.577 $\pm 0.006$ (0.21 ppm)	54.708	-10.707 $\pm 0.000$ 44 (0.015 ppm)	11.657 $\pm 0.042$ (1.42 ppm)	-3.331 $\pm 0.003$ 9 (0.13 ppm)	29 616.904 $\pm 0.043$ (1.44 ppm)	29 616.864 <sup>c</sup> $\pm 0.036$ (1.2 ppm)	0.040 = 1.35 ppm
	2 317.203 $\pm 0.001$ 8 (0.76 ppm)	-22.548	1.952 $\pm 0.000$ 88 (0.39 ppm)	-6.866 $\pm 0.081$ (35 ppm)	1.542 $\pm 0.006$ 8 (3.0 ppm)	2 291.283 $\pm 0.081$ (35 ppm)	2 291.196 <sup>d</sup> $\pm 0.005$ (2.2 ppm)	0.087 = 37 ppm

<sup>a</sup> See Ref. 18.

<sup>b</sup> See Ref. 19.

<sup>c</sup> See Ref. 1.

<sup>d</sup> See Ref. 2.

tial decrease with  $\omega$  that makes inferior any attempt to fit the behavior of the  $E_2^{(3,3)}$  to an inverse power law. Thus the extrapolated  $E_2^{(3,3)}$  is obtained directly by the first of these two methods.

We show in Table XIV the extrapolated second-order level shifts  $(E_2)_J$  ( $J=1, 2$ ) and the resulting contributions to  $\nu_{01}$  and  $\nu_{12}$  for  $^1P$ ,  $^3F$ , and  $^{1,3}D$  (divided basis) intermediate-state symmetries. [This involves a conversion from  $\alpha^4 R$  to MHz which uses  $\alpha^{-1} = 137.035987(29)^{18}$  and  $R = 109\,737.3143$  cm<sup>-1</sup> (0.009 ppm).<sup>19</sup>] It is to be noted that the  $^1P$  contribution is almost 40% larger than the shift calculated by Pekeris *et al.*<sup>20</sup> due to the effect of the  $2^1P_1$  state alone. That the  $^1P$  contribution is much larger than that from  $^3D$  is plausible in view of the fact that the intermediate states making the greatest contribution in each case are  $2^1P_1$  and  $3(2p3d)^3D$ . The energy of the former state is -2.123 a.u. while that of the latter is -0.559 a.u.,<sup>21</sup> so the energy denominator in the expression for the second-order energy perturbation is smaller and the contribution larger for  $2^1P$  than for  $3^3D$ . Furthermore,  $3(2p3d)^1D$  is less than 1% lower in energy than  $3^3D$ , and their respective contributions are not very different. The correction to  $\nu_{12}$  due to  $^3F$  states seems to us to be somewhat high, but again the greater closeness of the  $2^3P$  level in helium to  $4^3F$  as compared to  $3(2p3d)^{1,3}D$  is reflected in a larger value for the  $^3F$  correction than for either the  $^1D$  or the  $E_2^{(3,3)}$  component of the  $^3D$  correction.

Combining the calculations involving the five intermediate state symmetries to obtain the final respective contributions to the intervals  $\nu_{01}$  and  $\nu_{12}$ , we get the results shown in Table XV. These second-order results can then be incorporated with the other theoretical contributions referred to earlier in this paper to yield the total theoretical values for the splittings  $\nu_{01}$  and  $\nu_{12}$  through order  $\alpha^6 m c^2$ , as shown in Table XVI. It is seen that the agreement between theory and experiment is quite good in the case of the larger interval  $\nu_{01}$ , and certainly much better than in the  $\nu_{12}$  case. One reason for this last fact is that the  $\nu_{12}$  splitting depends more strongly and more predominantly than  $\nu_{01}$  on the most uncertain energies,  $E_2^{(1,5)}$  and  $E_2^{(1,6)}$ , from the  $^3P$  states. Even if the second-order calculation for  $\nu_{12}$  were to be greatly improved, it is highly unlikely that an output value of  $\alpha$  could be derived to an accuracy of better than 2 ppm by comparison of the theoretical to the experimental  $\nu_{12}$ .

However, if this is done for the larger interval  $\nu_{01}$ ,  $\alpha$  can be determined to an accuracy of 0.94 ppm. We obtain the results  $\alpha^{-1} = 137.036$  08(13), which is in good agreement with other determinations<sup>5, 18, 22-28</sup> of  $\alpha^{-1}$  (see Fig. 1). It should be re-

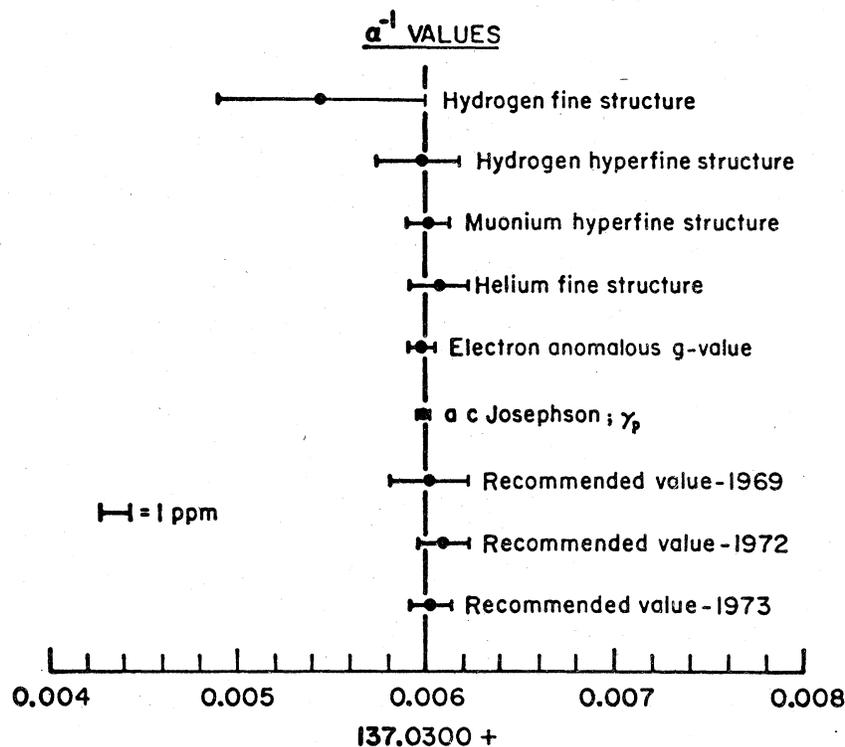


FIG. 1. Various determinations of the fine-structure constant  $\alpha$  (including this calculation).

marked that contributions of order  $\alpha^7 mc^2$  may affect the output  $\alpha$  at the fraction of a ppm level, so these contributions should be at least estimated in the near future. We are planning further improvements on the above findings by including terms with, e.g.,  $(r_1+r_2)^{1/2}$  or  $\log(r_1+r_2)$  in the expansions of the  $^3P$  and  $^1P$  wave functions. This should enable us to improve the precision of our  $\alpha$  determination toward the 0.5 ppm level or so.

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#### APPENDIX A

Many integrals<sup>7</sup> are needed to calculate the matrix elements of the  $H_1^{(i)}$  and  $H_0$ . The major integrals are

$$A(L, M, N) = \int \frac{d\tau_1}{4\pi} \int \frac{d\tau_2}{4\pi} e^{-ar_1} e^{-br_2} r_1^{M-2} r_2^{N-2} r_{12}^{L-2}, \quad (A1)$$

$$B(L, M, N) = \int \frac{d\tau_1}{4\pi} \int \frac{d\tau_2}{4\pi} e^{-ar_1} e^{-br_2} r_1^{M-2} \times r_2^{N-2} r_{12}^{L-2} \cos\theta_{12}. \quad (A2)$$

There are two types of  $A$  and  $B$  integrals.  $A_d(L, M, N)$  and  $B_d(L, M, N)$  are the direct integrals for  $a = \kappa\sigma$ ,  $b = \kappa$ .  $A_e(L, M, N)$  and  $B_e(L, M, N)$  are the exchange integrals for  $a = b = \frac{1}{2}\kappa(1 + \sigma)$ . The computer calculates these integrals by the use of recursion relations:

$$A(L, M, N) = A(L-2, M+2, N) + A(L-2, M, N+2) - 2B(L-2, M+1, N+1) \quad (A3)$$

and

$$B(L, M, N) = \frac{L-2}{L+2} [B(L-2, M+2, N) + B(L-2, M, N+2) - 2A(L-2, M+1, N+1)]. \quad (A4)$$

These relations may be obtained with

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_{12} \quad (A5)$$

and

$$\int \frac{d\Omega_1}{4\pi} \int \frac{d\Omega_2}{4\pi} \sin^2\theta_{12} r_{12}^L = -\frac{2}{L+2} \int \frac{d\Omega_1}{4\pi} \int \frac{d\Omega_2}{4\pi} \cos\theta_{12} \frac{r_{12}^{L+2}}{r_1 r_2}. \quad (A6)$$

If we define

$$F(M, N; \alpha, \beta) = \int_0^\infty dr e^{-\alpha r} r^{M-1} \int_r^\infty ds e^{-\beta s} s^{N-1}, \quad (\text{A7})$$

then we may show

$$A(2, M, N) = \frac{M!N!}{\alpha^{M+1}\beta^{N+1}}, \quad (\text{A8})$$

$$B(2, M, N) = 0, \quad (\text{A9})$$

$$A(1, M, N) = F(M+1, N; a, b) + F(N+1, M; b, a), \quad (\text{A10})$$

$$B(1, M, N) = \frac{1}{3} [F(M+2, N-1; a, b) + F(N+2, M-1; b, a)]. \quad (\text{A11})$$

The  $F$  integrals are calculated using

$$F(M, 1; \alpha, \beta) = \frac{1}{\beta} \frac{(M-1)!}{(\alpha+\beta)^M}, \quad (\text{A12})$$

$$F(M, N; \alpha, \beta) = \frac{(M+N-2)!}{\beta(\alpha+\beta)^{M+N-1}} + \frac{N-1}{\beta} F(M, N-1; \alpha, \beta). \quad (\text{A13})$$

The recursion relations above are valid for  $A$  integrals for  $L \geq 1, M \geq 1, N \geq 1$  and for  $B$  integrals with  $L \geq 1, M \geq 2, N \geq 2$ .

The lowest-order term in the expansion

$$r_{12}^{-2} = \frac{1}{2r_1 r_2} \ln \frac{r_1+r_2}{|r_1-r_2|} + \dots \quad (\text{A14})$$

appears in the  $A$  and  $B$  integrals when  $L=0$ . Thus

$$A_d(0, M, N) = \frac{1}{2} [F_{LA}(M, N) + F_{LB}(N, M)], \quad (\text{A15})$$

$$A_e(0, M, N) = \frac{1}{2} [F_{LC}(M, N) + F_{LC}(N, M)], \quad (\text{A16})$$

$$B_d(0, M, N) = \frac{1}{4} [F_{LA}(M+1, N-1) + F_{LA}(M-1, N+1) + F_{LB}(N+1, M-1) + F_{LB}(N-1, M+1)] - \frac{1}{2} [F(M, N; \kappa\sigma, \kappa) + F(N, M, \kappa, \kappa\sigma)], \quad (\text{A17})$$

$$B_e(0, M, N) = \frac{1}{4} [F_{LC}(M+1, N-1) + F_{LC}(M-1, N+1) + F_{LC}(N+1, M-1) + F_{LC}(N-1, M+1)] - \frac{1}{2} [F(M, N; \delta, \delta) + F(N, M; \delta, \delta)], \quad (\text{A18})$$

where  $\delta = \frac{1}{2}\kappa(1+\sigma)$ . The  $F_L$  integrals are

$$F_L(M, N; \alpha, \beta) = \int_0^\infty dr e^{-\alpha r} r^{M-1} \times \int_r^\infty ds e^{-\beta s} s^{N-1} \ln \frac{s+r}{s-r} \quad (\text{A19})$$

and

$$F_{LA}(M, N) = F_L(M, N; \kappa\sigma, \kappa), \\ F_{LB}(M, N) = F_L(M, N; \kappa, \kappa\sigma), \quad (\text{A20}) \\ F_{LC}(M, N) = F_L(M, N; \delta, \delta).$$

The  $F_L$  integrals may be written as sums of products of various functions.<sup>7</sup>

For the  $A$  and  $B$  integrals with  $M=0, N \geq 1$  and  $M \geq 1, N=0$  when  $L \geq 1$  we need  $F(M, N; \alpha, \beta)$  for  $N=0$  and  $N=-1$ .

$$F(M, -N; \alpha, \beta) = \frac{(M-N-1)!}{N(\alpha+\beta)^{M-N}} - \frac{\beta}{N} F(M, -N+1; \alpha, \beta). \quad (\text{A21})$$

Equation (A21) can be obtained by partial integration. The  $F(M, 0; \alpha, \beta)$  is evaluated by truncating an infinite series expansion:

$$F(M, 0; \alpha, \beta) = \frac{(M-1)!}{(\alpha+\beta)^M} \sum_{j=0}^{\infty} \frac{1}{M+j} \left(\frac{\alpha}{\alpha+\beta}\right)^j. \quad (\text{A22})$$

$F(M, -1; \alpha, \beta)$  is then obtained by application of (A21), for  $M \geq 2$ .

The  $B$  integrals with  $L=0, M=1, N \geq 1$  and  $L=0, M \geq 1, N=1$  require the calculation of  $F_L(M, 0; \alpha, \beta)$  and  $F_L(0, N; \alpha, \beta)$  where  $M, N \geq 2$ . The  $F_L(0, N; \alpha, \beta)$  can be written as an infinite series of products much like the usual  $F_L$  integrals, and can be truncated after 200–300 terms to yield values accurate to 30 decimal places or more, at least for those values of  $N$  of interest to us ( $N \leq 35$ ). The  $F_L(M, 0; \alpha, \beta)$  are written as integrals over the interval from 0 to  $\infty$  by a change of variables in the original integration between 0 and 1. By truncating the integrals at  $\chi=70$  and numerically integrating by Gaussian quadrature between  $\chi=0$  and  $\chi=70$  results are obtained that are good to 30 decimal places for  $M \leq 35$ .

## APPENDIX B

The integrals which arise in the evaluation of matrix elements in the case of  ${}^3F$  intermediate states are of the form

$$I_{i, j, k; i', j', k'}(\mu, \nu, \lambda) = \iint \frac{dv_1 dv_2}{(4\pi)^2} r_1^\mu r_2^\nu r_{12}^\lambda e^{-\alpha r_1 - \beta r_2} \times \{i, j, k\}_M^{(3)*} \{i', j', k'\}_M^{(3)} \quad (\text{B1})$$

where

$$\{i, j, k\}_M^{(3)} = \{ \{ T^{(1)}(\vec{r}_i), T^{(1)}(\vec{r}_j) \}^{(2)}, T^{(1)}(\vec{r}_k) \}_M^{(3)}$$

and  $i, j, k, i', j', k'$  can each assume the values 1 or 2. Now, if  $i=k$ , e.g., then

$$\{i, j, k\}_M^{(3)} = \{i, k, j\}_M^{(3)} \\ = \left(\frac{2}{3}\right)^{1/2} \{ T^{(2)}(\vec{r}_i), T^{(1)}(\vec{r}_j) \}_M^{(3)},$$

which derives from the relation

$$\{T^{(1)}, T^{(k)}\}^{(k+1)} = [(k+1)/(2k+1)]^{1/2} T^{(k+1)}.$$

If, in addition,  $i=j$ , then another application of

$$\{i, j, k\}_M^{(3)} = (2/3)^{1/2} \{ (4\pi/5)^{1/5} r_i^2 Y^{(2)}(\theta_i, \phi_i), (4\pi/3)^{1/2} r_j Y^{(1)}(\theta_j, \phi_j) \}_M^{(3)} \quad (\text{B2a})$$

$$= (4\pi/3)(2/5)^{1/2} r_i^2 r_j |l_i=2, l_j=1, L=3, m_L=M\rangle, \quad i=k \neq j, \quad (\text{B2b})$$

and

$$\{i, j, k\}_M^{(3)} = (2/5)^{1/2} (4\pi/7)^{1/2} (4\pi)^{1/2} r_i^3 Y_M^{(3)}(\theta_i, \phi_i) Y_0^{(0)}(\theta_{3-i}, \phi_{3-i}) \quad (\text{B3a})$$

$$= 4\pi(2/35)^{1/2} r_1^3 |l_1=3, l_2=0, L=3, m_L=M\rangle, \quad i=k=j=1, \text{ e.g.} \quad (\text{B3b})$$

As a result,  $I_{i,j,k;i',j',k'}(\mu, \nu, \lambda)$  is proportional to

$$\iint dr_1 dr_2 r_1^{\mu+2} r_2^{\nu+2} r_i r_j r_k r_{i'} r_{j'} r_{k'} e^{-ar_1 - br_2} \times \langle l_1, l_2, 3, M | r_{12}^\lambda | l'_1, l'_2, 3, M \rangle. \quad (\text{B4})$$

Now  $r_{12}^\lambda$  can be expanded as

$$r_{12}^\lambda = \sum_{i=0}^{\infty} R_{\lambda i}(r_1, r_2) P_i(\cos\theta_{12}), \quad (\text{B5})$$

where  $R_{\lambda i}(r_1, r_2)$  involves hypergeometric functions

$$\begin{aligned} \langle l_1, l_2, 3, M | r_{12}^\lambda | l'_1, l'_2, 3, M \rangle &= \sum_{i=0}^{\infty} R_{\lambda i} \langle l_1, l_2, 3, M | C^{(i)}_1 \cdot C^{(i)}_2 | l'_1, l'_2, 3, M \rangle \\ &= \sum_{i=0}^{\infty} R_{\lambda i} (-1)^{l_1+l_2+3} \left\{ \begin{matrix} l'_1 & l'_2 & 3 \\ l_2 & l_1 & l \end{matrix} \right\} \langle l_1 || C^{(i)} || l'_1 \rangle \langle l_2 || C^{(i)} || l'_2 \rangle \\ &= (-1)^{l_1+l_2+1} \sum_{i=0}^{\infty} R_{\lambda i} [(2l_1+1)(2l'_1+1)(2l_2+1)(2l'_2+1)]^{1/2} \left\{ \begin{matrix} l'_1 & l'_2 & 3 \\ l_2 & l_1 & l \end{matrix} \right\} \begin{pmatrix} l_1 & l & l'_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l & l'_2 \\ 0 & 0 & 0 \end{pmatrix}. \end{aligned} \quad (\text{B7})$$

In the above, the object enclosed by braces is a 6- $j$  symbol, while those within parentheses are 3- $j$  symbols. The reduced (double-bar) matrix elements of  $C^{(i)}$  indicate the use of the Wigner-Eckart theorem in this derivation.<sup>14</sup>

Since a 3- $j$  symbol like

$$\begin{pmatrix} l_1 & l & l'_1 \\ 0 & 0 & 0 \end{pmatrix}$$

vanishes unless  $(l_1+l+l'_1)$  is even and  $l_1, l$ , and  $l'_1$  satisfy a triangular condition, only a few terms will remain in the infinite sum above. We may then apply the relation

$$\iint d\Omega_1 d\Omega_2 r_{12}^\lambda P_i(\cos\theta_{12}) = (4\pi)^2 R_{\lambda i} / (2l+1) \quad (\text{B8})$$

to the final expression above to recast the angular matrix element in (B4) in the form

this relation yields

$$\{i, j, k\}_M^{(3)} = (2/5)^{1/2} T_M^{(3)}(\vec{r}_i).$$

Therefore, we have

and is described in the work of Sack.<sup>29</sup> Furthermore, we may write, following Judd,<sup>14</sup>

$$\begin{aligned} P_l(\cos\theta_{12}) &= \frac{4\pi}{2l+1} \sum_m Y_m^{(l)*}(\theta_1, \phi_1) Y_m^{(l)}(\theta_2, \phi_2) \\ &= C^{(l)}_1 \cdot C^{(l)}_2 \end{aligned} \quad (\text{B6})$$

using the spherical-harmonic addition theorem and the definition of the scalar product of tensor operators. The subscripts 1 and 2 refer to electrons 1 and 2, respectively. Thus for the angular integration we get successively

$$\iint \frac{d\Omega_1 d\Omega_2}{(4\pi)^2} r_{12}^\lambda f(\theta_{12}).$$

Finally, through use of such identities as

$$\iint \frac{d\Omega_1 d\Omega_2}{(4\pi)^2} r_{12}^\lambda \sin^2\theta_{12} = \frac{-2}{\lambda+2} \iint \frac{d\Omega_1 d\Omega_2}{(4\pi)^2} \frac{r_{12}^{\lambda+2}}{r_1 r_2} \cos\theta_{12} \quad (\text{B9a})$$

and

$$\begin{aligned} &\iint \frac{d\Omega_1 d\Omega_2}{(4\pi)^2} r_{12}^\lambda \sin^2\theta_{12} \cos\theta_{12} \\ &= \frac{-2}{\lambda+2} \iint \frac{d\Omega_1 d\Omega_2}{(4\pi)^2} \frac{r_{12}^{\lambda+2}}{r_1 r_2} \\ &\quad \times \left( 1 + \frac{3}{\lambda+4} \cos\theta_{12} \frac{r_{12}^2}{r_1 r_2} \right), \end{aligned} \quad (\text{B9b})$$

obtained by performing partial integrations, we may express  $I_{i,j,k;i',j',k'}(\mu, \nu, \lambda)$  solely in terms of the  $A$  and  $B$  integrals described in Appendix A.

The integrals  $I_{i,j,k;i',j',k'}$  are invariant under permutations of the  $i, j, k$  among themselves and/or the  $i', j', k'$  among themselves, leaving only six integrals to be actually computed. As an example, let us calculate  $I_{1,1,1;2,2,2}(\mu, \nu, \lambda)$ . The angular matrix element appearing in (B4) is then

$$\begin{aligned} \langle l_1=3, l_2=0, 3, M | r_{12}^\lambda | l_1'=0, l_2'=3, 3, M \rangle &= \sum_{l=0}^{\infty} R_{\lambda l}(\gamma) \begin{Bmatrix} 0 & 3 & 3 \\ 0 & 3 & l \end{Bmatrix} \begin{Bmatrix} 3 & l & 0 \\ 0 & 0 & 0 \end{Bmatrix} \\ &= 7R_{\lambda 3}(\frac{1}{7})(\sqrt{1/7})^2 = \frac{1}{7} R_{\lambda 3} \\ &= \iint \frac{d\Omega_1 d\Omega_2}{(4\pi)^2} r_{12}^\lambda P_3(\cos\theta_{12}). \end{aligned} \quad (\text{B10})$$

The constant of proportionality in (B4) is a product of the numerical factors appearing in (B2b) and/or (B3b) multiplying  $4\pi$ . In this example, it is the square of the factor in (B3b), namely  $\frac{2}{35}$ . So we have

$$\begin{aligned} I_{1,1,1;2,2,2}(\mu, \nu, \lambda) &= \frac{2}{35} \iint dr_1 dr_2 r_1^{\mu+2} r_2^{\nu+2} r_1^3 r_2^3 e^{-ar_1-br_2} \iint \frac{d\Omega_1 d\Omega_2}{(4\pi)^2} r_{12}^\lambda \cos\theta_{12} (1 - \frac{5}{2} \sin^2\theta_{12}) \\ &= \frac{2}{35} \iint \frac{dv_1 dv_2}{(4\pi)^2} r_1^{\mu+3} r_2^{\nu+3} e^{-ar_1-br_2} \left( \cos\theta_{12} r_{12}^\lambda + \frac{5}{\lambda+2} \frac{r_{12}^{\lambda+2}}{r_1 r_2} + \frac{15 \cos\theta_{12}}{(\lambda+2)(\lambda+4)} \frac{r_{12}^{\lambda+4}}{r_1^2 r_2^2} \right) \\ &= \frac{2}{35} \left( B(\lambda+2, \mu+5, \nu+5) + \frac{5}{\lambda+2} A(\lambda+4, \mu+4, \nu+4) + \frac{15}{(\lambda+2)(\lambda+4)} B(\lambda+6, \mu+3, \nu+3) \right). \end{aligned} \quad (\text{B11})$$

To conclude, we enumerate here the remaining five cases:

$$I_{1,1,1;1,1,1}(\mu, \nu, \lambda) = \frac{2}{35} A(\lambda+2, \mu+8, \nu+2), \quad (\text{B12})$$

$$I_{1,1,1;1,1,2}(\mu, \nu, \lambda) = \frac{2}{35} B(\lambda+2, \mu+7, \nu+3), \quad (\text{B13})$$

$$I_{1,1,1;1,2,2}(\mu, \nu, \lambda) = \frac{2}{35} \left( A(\lambda+2, \mu+6, \nu+4) + \frac{3}{\lambda+2} B(\lambda+4, \mu+5, \nu+3) \right), \quad (\text{B14})$$

$$I_{1,1,2;1,1,2}(\mu, \nu, \lambda) = \frac{2}{35} \left( A(\lambda+2, \mu+6, \nu+4) + \frac{2}{3(\lambda+2)} B(\lambda+4, \mu+5, \nu+3) \right), \quad (\text{B15})$$

$$I_{1,1,2;1,2,2}(\mu, \nu, \lambda) = \frac{2}{35} \left( B(\lambda+2, \mu+5, \nu+5) + \frac{1}{3(\lambda+2)} A(\lambda+4, \mu+4, \nu+4) + \frac{1}{(\lambda+2)(\lambda+4)} B(\lambda+6, \mu+3, \nu+3) \right). \quad (\text{B16})$$

*Note added in proof.* In the previous work by Lewis and Serafino all the second-order contributions to the  $2^3P$  helium fine structure have been calculated in order to complete the theoretical evaluation of the fine-structure splitting through order  $\alpha^6 mc^2$ . In such a way separate theoretical results have been obtained for the larger and smaller intervals  $\nu_{01}$  and  $\nu_{12}$ , respectively, with

$$\Delta\nu_{02} = 3 \sum_{i,j=1}^2 E_2^{(i,j)} - 42 [E_2^{(1,3)} + E_2^{(2,3)}] + 99 E_2^{(3,3)} - 6 \sum_{i=1}^2 \sum_{j=4}^7 E_2^{(i,j)} + 18 \sum_{j=4}^7 E_2^{(3,j)}$$

for the second-order contribution to  $\nu_{02}$  together with the values of the  $E_2^{(i,j)}$  from the previous work, we find that  $\Delta\nu_{02} = 4.649(115)$  MHz from intermediate  $^3P$  states alone, while the total second-order contribution is 4.791(115) MHz. The other theoretical contribution to  $\nu_{02}$  can be taken over quite readily from the corresponding results for

the determination of the former being accurate to 1.4 ppm. This in turn allows the fine structure constant  $\alpha$  to be determined to an accuracy of 0.94 ppm by comparing theory to experiment.

It is our aim here to complete these calculations by including the corresponding results for the interval  $\nu_{02}$  between the highest- and lowest-lying levels of the  $2^3P$  state. Using the equation

$\nu_{01}$  and  $\nu_{12}$  by addition. Combining all these contributions, we obtain the net result through order  $\alpha^6 mc^2$

$$\nu_{02} = 31908.187(116) \text{ MHz}$$

which determination is thus accurate to 3.6 ppm.

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- <sup>1</sup>A. Kponou, V. W. Hughes, C. E. Johnson, S. A. Lewis, and F. M. J. Pichanick, *Phys. Rev. Lett.* **26**, 1613 (1971).
- <sup>2</sup>S. A. Lewis, F. M. J. Pichanick, and V. W. Hughes, *Phys. Rev. A* **2**, 86 (1970).
- <sup>3</sup>Charles Schwartz, *Phys. Rev.* **134**, A1181 (1964).
- <sup>4</sup>M. L. Lewis and P. H. Serafino, *Bull. Am. Phys. Soc.* **18**, 1510 (1973).
- <sup>5</sup>Michael L. Lewis, *Atomic Physics 4*, edited by G. zu Putlitz, E. W. Weber, and A. Winnacker (Plenum, New York, 1975), p. 105.
- <sup>6</sup>M. L. Lewis, P. H. Serafino, and V. W. Hughes, *Phys. Lett.* **58A**, 125 (1976).
- <sup>7</sup>L. Hambro, *Phys. Rev. A* **5**, 2027 (1972); *Phys. Rev. A* **6**, 865 (1972); *Phys. Rev. A* **7**, 479 (1973).
- <sup>8</sup>M. Douglas and N. M. Kroll, *Ann. Phys. (N.Y.)* **82**, 89 (1974).
- <sup>9</sup>J. Daley, M. Douglas, L. Hambro, and N. M. Kroll, *Phys. Rev. Lett.* **29**, 12 (1972).
- <sup>10</sup>G. Araki, M. Ohta, and K. Mano, *Phys. Rev.* **116**, 651 (1959).
- <sup>11</sup>H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer, Berlin, 1957), p. 181.
- <sup>12</sup>E. A. Hylleraas, *Z. Phys.* **48**, 469 (1928); **54**, 347 (1929).
- <sup>13</sup>E. A. Hylleraas and J. Midtdal, *Phys. Rev.* **103**, 829 (1956).
- <sup>14</sup>B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill, New York, 1963).
- <sup>15</sup>Charles Schwartz, *Methods in Computational Physics* (Academic, New York, 1963), Vol. 2, p. 241.
- <sup>16</sup>M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).
- <sup>17</sup>C. Schwartz, *Phys. Rev.* **123**, 1700 (1961).
- <sup>18</sup>P. T. Olsen and E. R. Williams, *Atomic Masses and Fundamental Constants 5*, edited by J. H. Sanders and A. H. Wapstra (Plenum, New York, 1976), p. 538.
- <sup>19</sup>T. W. Hänsch, M. H. Nayfeh, S. A. Lee, S. M. Curry, and I. S. Shahin, *Phys. Rev. Lett.* **32**, 1336 (1974).
- <sup>20</sup>C. L. Pekeris, B. Schiff, and H. Lifson, *Phys. Rev.* **126**, 1057 (1962).
- <sup>21</sup>A. K. Bhatia, *Phys. Rev. A* **6**, 2498 (1972).
- <sup>22</sup>E. R. Cohen and B. N. Taylor, *J. Phys. Chem. Ref. Data* **2**, 663 (1973).
- <sup>23</sup>P. J. Mohr, *Atomic Physics 5*, edited by R. Marrus, M. Prior, and H. Shugart (Plenum, New York, 1977), p. 37.
- <sup>24</sup>D. E. Casperson *et al.*, *Phys. Rev. Lett.* **38**, 956 (1977); **38**, 1504 (1977).
- <sup>25</sup>P. Cvitanovic and T. Kinoshita, *Phys. Rev. D* **10**, 4007 (1974).
- <sup>26</sup>R. S. Van Dyck, Jr., P. B. Schwinberg, and H. G. Dehmelt, *Phys. Rev. Lett.* **38**, 310 (1977).
- <sup>27</sup>S. Calmet *et al.*, *Rev. Mod. Phys.* **49**, 21 (1977).
- <sup>28</sup>V. W. Hughes and T. Kinoshita, in *Muon Physics*, edited by V. W. Hughes and C. S. Wu (Academic, New York, 1977), Vol. I.
- <sup>29</sup>R. A. Sack, *J. Math. Phys.* **5**, 245 (1964); **5**, 252 (1964); **5**, 260 (1964).