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Second-Order Corrections to the Fine Structure of Helium. II. Contributions from ^1P and ^3D Intermediate States*

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The contributions from the three spin-dependent Breit operators in second-order perturbation theory are calculated when the symmetries of the intermediate states are odd ^1P or ^3D. Standard Hylleraas expansions with up to 165 terms are used for the perturbations of the wave functions. The large interval of the fine structure of the $2\,^3P$ level in helium is increased by $2.17(2)\times10^{-4}$ cm^{-1} by ^1P, and by $0.0089(6)\times10^{-4}$ cm^{-1} by ^3D. Two methods for handling angular integration over D tensors are described.

I. INTRODUCTION

In an earlier paper,[1] hereafter referred to as I, the contributions to the fine structure of the $2\,^3P$ level of helium from second-order perturbation theory with intermediate ^3P states were calculated. This fine structure consists of two intervals whose experimental values are $\nu_{12}=764.2606\,(17)$ cm^{-1} and $\nu_{01}=9879.121\,(12)$ cm^{-1}.[2] The relative accuracy of the large interval is thus better than for the small interval (1.2 ppm vs 2.2 ppm), and the results of I came much closer to the desired accuracy (which is to match the absolute experimental accuracy) for the large interval than for the small; so, in this paper the remaining second-order contributions to the large interval are calculated. These come from intermediate states with ^1P and ^3D symmetries. There are also contributions from ^1D and ^3F states to the small interval which have not yet been calculated. As in I, one solves an inhomogeneous Schrödinger equation for the odd ^1P and ^3D perturbations of the $2\,^3P$ wave function by the variational method; the second-order perturbation energies are then given by integrals. We emphasize that this is but one of many theoretical contributions to the fine structure. A summary of the complete calculation of the fine-structure intervals, including quantum-electrodynamic and nuclear-motion effects, with detailed comparison with experiment, will be reported.[3]

II. ^1P EXPANSION

The two spin-orbit operators which connect singlet and triplet states are ($Z=2$ for neutral helium)

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

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

which follow from the well-known operators with just one $\vec{\sigma}$.[4] The equation for the ^1P perturbation to the $2\,^3P$ wave function is

$$(H_0-E_0)\,\tilde{\Psi}_1^{(i)}(^1P_1)=-\tilde{H}_1^{(i)}\,\Psi_0(^3P_1),\quad i=1,2 \tag{1}$$

which differs from the basic equation [Eq. (6) of Paper I] because the expectation value of $\tilde{H}_1^{(i)}$ is zero in a state of definite multiplicity. H_0 is the nonrelativistic Hamiltonian in atomic units:

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

The unperturbed wave function with total angular momentum $J=1$ and $M_J=1$ is

$$\Psi_0(^3P_1,M_J=1)=\sum_{l,m,n=0}^{l+m+n=\omega'} C_{lmn}U_{lmn}(^3P_1,M_J=1), \tag{2}$$

where

$$U_{lmn}(^3P_1,M_J=1)=\frac{1-P_{12}}{4\pi\sqrt{2}}\,(S_0^{(1)}\{\vec{r}_1\}^{(1)}-S_1^{(1)}\{\vec{r}_1\}_0^{(1)})\,u_{lmn}(1,2),$$

P_{12} exchanges coordinates $\vec{r}_1$ and $\vec{r}_2$,

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

as in I ($\kappa=4.62$ and $\sigma=0.29$), and

$$\{\vec{r}_1\}_{\pm1}^{(1)} = (x_1 \pm iy_1)/(\mp\sqrt{2}) , \quad \{\vec{r}_1\}_0^{(1)} = z_1 .$$

In this paper, curly brackets are always used to denote spherical tensor components. $S_{-1,0,1}{}^{(1)}$ and $S_0{}^{(0)}$ are the usual spinors for two electrons having total spin 1 or 0. Ψ_0 is the eigenfunction of H_0 with odd ^3P symmetry which has the lowest-lying eigenvalue, and this eigenvalue is $E_0 = E_0(\omega)$. The calculation of C_{lmn} and E_0 (for $\omega = 1, 2, \ldots, 8$) was described in I.

The ^1P perturbation is now expanded in similar basis functions:

$$\tilde{\Psi}_1{}^{(i)}(^1P_1, M_J = 1) = \sum_{l,m,n=0}^{l+m+n \leq \omega} \tilde{X}_{lmn}{}^{(i)} \tilde{U}_{lmn}(^1P_1, M_J = 1) , \quad i = 1, 2 \qquad (3)$$

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

The variational approximations to $\tilde{\Psi}_1{}^{(i)}$ of (1) are obtained by solving

$$\sum_{k=1}^{N(\omega)} [\langle \tilde{U}_{k'} | H_0 | \tilde{U}_k \rangle - E_0(\omega') \langle \tilde{U}_{k'} | \tilde{U}_k \rangle] \tilde{X}_k{}^{(i)} = \tilde{b}_{k'}{}^{(i)} , \quad k' = 1, 2, \ldots, N(\omega) \qquad (4)$$

where $N(\omega)$ is the number of terms in these expansions, $(\omega+1)(\omega+2)(\omega+3)/6$, and

$$\tilde{b}_{k'}{}^{(i)} = -\langle \tilde{U}_{k'} | \tilde{H}_1{}^{(i)} | \Psi_0 \rangle = -\sum_{k=1}^{N(\omega')} C_k \langle \tilde{U}_{k'} | \tilde{H}_1{}^{(i)} | U_k \rangle .$$

Here the three indices (l, m, n) in the expansions (2) and (3) have been mapped into one, k or k'. The matrix elements of H_0 in the left-hand side of (4) are calculated as in I; the only difference is that the exchange-type integrals are added to the direct type instead of subtracted. The action of $\tilde{H}_1{}^{(1)}$ and $\tilde{H}_1{}^{(2)}$ on $\Psi_0(^3P_1, M_J = 1)$ is given by

$$\tilde{H}_1{}^{(i)} \frac{1}{\sqrt{2}} (S_0{}^{(1)} \{\vec{r}_1\}_1^{(1)} - S_1{}^{(1)} \{\vec{r}_1\}_0^{(1)}) u_{lmn}(1, 2) .$$

For $i = 1$ this is equal to

$$\tfrac{1}{4}\alpha^2 Z\sqrt{2} S_0{}^{(0)} \left[\frac{\{\vec{r}_1\}_1^{(1)}}{r_1^3} - \frac{l}{2r_{12}^2}\left(\frac{1}{r_1^3} - \frac{1}{r_2^3}\right) \times [\{\vec{r}_1\}_1^{(1)} (\vec{r}_1 \cdot \vec{r}_2) - \{\vec{r}_2\}_1^{(1)} r_1^2] \, u_{lmn}(1, 2) \right] \qquad (5)$$

and for $i = 2$ we obtain

$$\tfrac{1}{4}\alpha^2\sqrt{2} S_0{}^{(0)} \left[\{\vec{r}_1 - \vec{r}_2\}_1^{(1)} - \frac{1}{2}\left(\frac{m}{r_1^2} - \frac{\kappa\sigma}{2}\frac{1}{r_2} + \frac{n}{r_2^2} - \frac{\kappa}{2}\frac{1}{r_2}\right) \times [\{\vec{r}_1\}_1^{(1)} (\vec{r}_1 \cdot \vec{r}_2) - \{\vec{r}_2\}_1^{(1)} r_1^2] \right] \frac{1}{r_{12}^3} u_{lmn}(1, 2) , \qquad (6)$$

where the following tensor identities have been used:

$$\{\vec{r}_1 \times \vec{r}_2\}_M^{(1)} = -i\sqrt{2} \{\{\vec{r}_1\}^{(1)}, \{\vec{r}_2\}^{(1)}\}_M^{(1)} \equiv -i\sqrt{2} \{\vec{r}_1, \vec{r}_2\}_M^{(1)} ,$$

$$\{\{\vec{r}_1\}^{(1)}, \{\vec{r}_1, \vec{r}_2\}^{(1)}\}_1^{(1)} = \tfrac{1}{2}[r_1^2 \{\vec{r}_2\}_1^{(1)} - (\vec{r}_1 \cdot \vec{r}_2)\{\vec{r}_1\}_1^{(1)}] .$$

Spherical tensors are combined by Clebsch-Gordan coefficients using the well-known formula

$$\{\{A\}^{(j_1)}, \{B\}^{(j_2)}\}_M^J = \textstyle\sum_N C(N, M-N; j_1 j_2 J) \times \{A\}_N^{(j_1)} \{B\}_{M-N}^{(j_2)} .$$

Notice that expression (5) and (6) are pure ^1P; there is no ^1D part when $\tilde{H}_1{}^{(i)}$ acts on $\Psi_0(^3P_1)$. Only when $\tilde{H}_1{}^{(1)}$ acts on $\Psi_0(^3P_2)$ does one get a $^1D_2$ part; i.e., only the $J = 2$ level is shifted by perturbations from intermediate ^3D states.

The evaluation of the matrix elements $\langle \tilde{U}_{l'm'n'} | \times \tilde{H}_1{}^{(i)} | U_{lmn} \rangle$ in terms of the standard integrals of I now proceeds very much like the calculation of matrix elements of $H_1{}^{(1)}$ and $H_1{}^{(2)}$ between ^3P terms in Appendix B of I.

III. ^3D EXPANSION

The operators that give ^3D parts when they act on $\Psi_0(^3P)$ are the spin-dependent operators of I:

$$H_1{}^{(1)} = \tfrac{1}{4}\alpha^2 Z \left(\frac{\vec{\sigma}_1 + \vec{\sigma}_2}{2}\right) \cdot \left(\frac{\vec{r}_1 \times \vec{p}_1}{r_1^3} + \frac{\vec{r}_2 \times \vec{p}_2}{r_2^3}\right) ,$$

$$H_1{}^{(2)} = -\tfrac{3}{4}\alpha^2 \left(\frac{\vec{\sigma}_1 + \vec{\sigma}_2}{2}\right) \cdot \left(\frac{(\vec{r}_1 - \vec{r}_2) \times (\vec{p}_1 - \vec{p}_2)}{r_{12}^3}\right) ,$$

$$H_1{}^{(3)} = \tfrac{1}{4}\alpha^2 \frac{1}{r_{12}^3}\left(\vec{\sigma}_1 \cdot \vec{\sigma}_2 - \frac{3}{r_{12}^3}(\vec{\sigma}_1 \cdot \vec{r}_{12})(\vec{\sigma}_2 \cdot \vec{r}_{12})\right) .$$

It is now more practical to let these operators act on the "stretched" state with $J = M_J = 2$, $\Psi_0(^3P_2, M_J = 2)$. After some algebra, one obtains the D part of

$$H_1{}^{(i)} S_1{}^{(1)} \{\vec{r}_1\}_1^{(1)} u_{lmn}(1, 2) .$$

For $i = 1$ it is given by

$$\tfrac{1}{4}\alpha^2 Z\sqrt{3} \frac{l}{r_{12}^2}\left(\frac{1}{r_2^3} - \frac{1}{r_1^3}\right) T_2{}^{(2)}(1, 2) u_{lmn}(1, 2) ,$$

where

$$T_2{}^{(2)}(1, 2) = [\sqrt{2} S_0{}^{(1)} \{\{\vec{r}_1\}_1^{(1)}, \{\vec{r}_1, \vec{r}_2\}^{(1)}\}_2^{(2)} - S_1{}^{(1)} \{\{\vec{r}_1\}^{(1)}, \{\vec{r}_1, \vec{r}_2\}^{(1)}\}_1^{(2)}]/\sqrt{3} ,$$

so that the odd D tensors have just the form suggested by Schwartz,[5] and are similar to the D functions used by Doyle *et al.*:[6] For $i = 2$ we obtain

$$-\tfrac{3}{4}\alpha^2\sqrt{3}\left(\frac{m}{r_1^2} - \frac{\kappa\sigma}{2}\frac{1}{r_1} - \frac{n}{r_2^2} + \frac{\kappa}{2}\frac{1}{r_2}\right) \frac{1}{r_{12}^3} T_2^{(2)}(1, 2) u_{lmn}(1, 2)$$

and for $i = 3$ the result is

$$-\tfrac{1}{4}\alpha^2\sqrt{3}(2/r_{12}^5)[T_2^{(2)}(1, 2) + T_2^{(2)}(2, 1)] u_{lmn}(1, 2) .$$

Notice that with $\vec{r}_1 - \vec{r}_2 = \vec{r}_{12}$,

$$(1+P_{12})\{\{\vec{r}_1\}^{(1)}, \{\vec{r}_1, \vec{r}_2\}\}_M^{(2)}$$
$$= \{\{\vec{r}_{12}\}^{(1)}, \{\vec{r}_{12}, \vec{r}_2\}^{(1)}\}_M^{(2)}$$
$$= -\{\{\vec{r}_{12}\}^{(1)}, \{\vec{r}_1, \vec{r}_{12}\}^{(1)}\}_M^{(2)} .$$

The corresponding P parts were given in Appendix B of I. For completeness we also note that

$$F \text{ part of } H_1^{(3)} S_1^{(1)} \{\vec{r}_1\}_1^{(1)} u_{lmn}(1,2)$$
$$= \tfrac{1}{4}\alpha^2(-3/r_{12}^5)(\tfrac{7}{5})^{1/2}[(\tfrac{5}{7})^{1/2} S_{-1}^{(1)} X_3^{(3)}$$
$$- (\tfrac{5}{21})^{1/2} S_0^{(1)} X_2^{(3)} + (\tfrac{1}{21})^{1/2} S_1^{(1)} X_1^{(3)}] u_{lmn}(1,2) , \quad (7)$$

where the Clebsch-Gordan coefficients $C(M, 2-M; 1, 3, 3)$ in (7) appear as the result of lengthy manipulations and

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

The following expansion is chosen for the ^3D perturbations to Ψ_0:

$$\Psi^{(i)}(^3D_2, M_J = 2) = \sum_{l,m,n=0}^{l+m+n=\omega} y_{lmn}^{(i)} V_{lmn}(^3D_2, M_J = 2) , \quad (8)$$

where

$$V_{lmn}(^3D_2, M_J = 2) = \frac{1-P_{12}}{4\pi\sqrt{2}} \frac{T_2^{(2)}(1,2)}{r_1 r_2} u_{lmn}(1,2) . \quad (9)$$

The sum of powers of r_1, r_2, and r_{12} then has the same range as in the expansions (2) and (3). Notice that (8) is not a Hylleraas expansion for an odd (unperturbed) ^3D state because of the division by $r_1 r_2$ in (9). The equations to be solved are now

$$\sum_{k=1}^{N(\omega)} [\langle V_{k'}|H_0|V_k\rangle - E_0(\omega')\langle V_{k'}|V_k\rangle] y_k^{(i)}$$
$$= -\sum_{k=1}^{N(\omega')} C_k \langle V_{k'}|H_1^{(i)}|V_k\rangle . \quad (10)$$

To evaluate the matrix elements of H_0 and 1 in (10), we require the action of H_0 on (9) given by

$$H_0 \frac{\{\{\vec{r}_1\}^{(1)}, \{\vec{r}_1, \vec{r}_2\}^{(1)}\}_M^{(2)} u_{lmn}(1,2)}{r_1 r_2} = \Big[\{\{\vec{r}_1\}^{(1)}, \{\vec{r}_1, \vec{r}_2\}^{(1)}\}_M^{(2)}\Big(-\tfrac{1}{8}\kappa^2(\sigma^2+1)$$
$$+ [\tfrac{1}{4}\kappa\sigma(2m+4+l)-2]\frac{1}{r_1} + [\tfrac{1}{4}\kappa(2n+2+l)-2]\frac{1}{r_2} + \frac{1}{r_{12}} - \tfrac{1}{2}(m-1)(m+l+4)\frac{1}{r_1^2}$$
$$- \tfrac{1}{2}(n-1)(n+l+2)\frac{1}{r_2^2} - \tfrac{1}{2}l(m+2l+6+n)\frac{1}{r_{12}^2} + \tfrac{1}{4}\kappa\sigma l\frac{r_1}{r_{12}^2} + \tfrac{1}{4}\kappa l\frac{r_2}{r_{12}^2} - \tfrac{1}{4}\kappa\sigma l\frac{r_2^2}{r_1 r_{12}^2}$$
$$- \tfrac{1}{4}\kappa l\frac{r_1^2}{r_2 r_{12}^2} + \tfrac{1}{2}l(m-1)\frac{r_2^2}{r_1^2 r_{12}^2} + \tfrac{1}{2}l(n-1)\frac{r_1^2}{r_2^2 r_{12}^2}\Big) + \{\{\vec{r}_2\}^{(1)}, \{\vec{r}_1, \vec{r}_2\}^{(1)}\}_M^{(2)}\frac{l}{r_{12}^2}\Big]\frac{u_{lmn}(1,2)}{r_1 r_2} .$$

To express these matrix elements as linear combinations of the integrals of I, a reduction formula for

$$\int\frac{dv_1}{4\pi}\int\frac{dv_2}{4\pi} F(r_1, r_2, r_{12})[\{\{\vec{r}_{i'}\}^{(1)}, \{\vec{r}_{j'}, \vec{r}_{k'}\}^{(1)}\}_M^{(2)}]^*$$
$$\times\{\{\vec{r}_i\}^{(1)}, \{\vec{r}_j, \vec{r}_k\}^{(1)}\}^{(2)} \quad (11)$$

is required. One way of doing this is explained in the Appendix, where all angles, except the angle θ_{12} between $\vec{r}_1$ and $\vec{r}_2$, are integrated out. The reduction can also be done by using the formula

$$\sum_{M=-2}^{M=2}(-1)^M\{\{\vec{A}\}^{(1)}, \{\vec{B}\}^{(1)}\}_M^{(2)}\{\{\vec{C}\}^{(1)}, \{\vec{D}\}^{(1)}\}_{-M}^{(2)}$$
$$= \tfrac{1}{2}(\vec{A}\cdot\vec{C})(\vec{B}\cdot\vec{D}) + \tfrac{1}{2}(\vec{A}\cdot\vec{D})(\vec{B}\cdot\vec{C}) - \tfrac{1}{3}(\vec{A}\cdot\vec{B})(\vec{C}\cdot\vec{D}) , \quad (12)$$

which can be proved by writing out the left- and right-hand sides in Cartesian components. Using (12) we get

$$[\{\{\vec{r}_{i'}\}^{(1)}, \{\vec{r}_{j'}, \vec{r}_{k'}\}^{(1)}\}_M^{(2)}]^*\{\{\vec{r}_i\}^{(1)}, \{\vec{r}_j, \vec{r}_k\}^{(2)}\}_M^{(2)}$$
$$= \tfrac{1}{2}\{\{\vec{r}_{i'}\}^{(1)}, \{\vec{r}_{j'}\times\vec{r}_{k'}\}\}_{-M}^{(2)}\{\{\vec{r}_i\}^{(1)}, \{\vec{r}_j\times\vec{r}_k\}^{(1)}\}_M^{(2)}$$
$$= \tfrac{1}{20}(\vec{r}_{i'}\cdot\vec{r}_i)[(\vec{r}_{j'}\times\vec{r}_{k'})\cdot(\vec{r}_j\times\vec{r}_k)] ,$$

where the last two terms of (12) vanish, since i', j', k', i, j, and k are 1 or 2 and $j' \neq k'$, $j \neq k$. The integral (11) can now be written

$$\int\frac{dv_1}{4\pi}\int\frac{dv_2}{4\pi} F(r_1, r_2, r_{12}) f_{i'j'k', ijk}(r_1, r_2, \theta_{12}) ,$$

where the functions f required for this work are

$$f_{112,112} = \tfrac{1}{20} r_1^4 r_2^2 \sin^2\theta_{12} , \quad (13a)$$
$$f_{221,112} = -\tfrac{1}{20} r_1^3 r_2^3 \sin^2\theta_{12}\cos\theta_{12} , \quad (13b)$$
$$f_{112,212} = \tfrac{1}{20} r_1^3 r_2^3 \sin^2\theta_{12}\cos\theta_{12} , \quad (13c)$$
$$f_{221,212} = -\tfrac{1}{20} r_1^2 r_2^4 \sin^2\theta_{12} . \quad (13d)$$

The matrix elements of H_0 and unity can then be evaluated with the help of the formulas

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

$$\int \frac{d\Omega_1}{4\pi}\int \frac{d\Omega_2}{4\pi}\sin^2\theta_{12}\cos\theta_{12}\, r_{12}^{L}$$

$$= \frac{-2}{L+2}\int \frac{d\Omega_1}{4\pi}\int \frac{d\Omega_2}{4\pi}\,\frac{r_{12}^{L+2}}{r_1 r_2}\left(1+\frac{3}{L+4}\cos\theta_{12}\,\frac{r_{12}^2}{r_1 r_2}\right),$$

obtained by partial integration. The matrix elements of $H_1^{(i)}$ in (10) between ^3P and ^3D terms are calculated in the same manner.

IV. RESULTS AND DISCUSSION

Equations (4) are solved with $\omega' = \omega$ for $\omega = 1, 2, \ldots, 8$. The matrix of the equations is nonsingular since $E_0(\omega')$ is the 2^3P level. There is no nontrivial solution to the homogeneous equation corresponding to (4), and one does not have to delete one equation as was necessary in I. The resulting second-order energies are given by

$$\tilde{E}_2^{(i,j)} \times \langle \Psi_0 | \Psi_0 \rangle = \langle \tilde{\Psi}_1^{(i)} | \tilde{H}_1^{(j)} | \Psi_0 \rangle = \langle \Psi_0 | \tilde{H}_1^{(i)} | \tilde{\Psi}_1^{(j)} \rangle$$

$$= -\sum_{k=1}^{N(\omega)} \tilde{X}_k^{(j)} \tilde{b}_k^{(i)} = -\langle \tilde{\Psi}_1^{(i)} | H_0 - E_0 | \tilde{\Psi}_1^{(j)} \rangle$$

$$= -\langle \tilde{\Psi}_1^{(j)} | H_0 - E_0 | \tilde{\Psi}_1^{(i)} \rangle \qquad (14)$$

and the results reproduced in Table I. The numbers obtained by the different methods in (14) agreed to the digits quoted. There are four results to compare when $i \neq j$, and two when $i = j$. As in I, the difference between these numbers increases with ω owing to accumulating round-off errors. The extrapolation has been done by the methods of I; i.e., one tries to fit the difference between computed energies for successive values of ω to α^ω ("fast" convergence) or ω^{-p} ("slow" convergence), with α or p being determined empirically. $\tilde{E}_2^{(1,1)}$ has been extrapolated by the slow rate because more refined calculations of some of the results of I[7] came much closer to the extrapolated values obtained from the slow rate than to those obtained by the fast rate. For $\tilde{E}_2^{(1,2)}$ the fast and slow rates gave the same results. The values obtained for $\tilde{E}_2^{(2,2)}$ are rather puzzling. It was shown in Appendix C of I that, for the unmixed second-order energies, the calculated numbers are upper bounds to the exact value provided E_0, the lowest 2^3P eigenvalue, is lower than any approximation to a ^1P eigenvalue, i.e., eigenvalues of the matrices $\langle \tilde{U}_k' | H_0 | \tilde{U}_k \rangle$. The highest value of E_0 is -2.129471 a.u. (for $\omega = 1$), and this is lower than the best (lowest) 2^3P eigenvalue obtained by Schiff *et al.*,[8] which is -2.123843 (for $\omega = 13$). But the results for $\tilde{E}_2^{(2,2)}$ are fairly constant, so the extrapolated value has been taken close to the lowest calculated value with an uncertainty so that the extrapolation is consistent with all the computed numbers. The sum of these contributions ($\tilde{E}_2^{(1,2)} = \tilde{E}_2^{(2,1)}$ enters twice) has been extrapolated separately; the fast and slow rates were then in agreement. Notice that the extrapolated sum is not equal to the sum of the three extrapolated energies, but they agree to within their assigned uncertainties. With a conversion factor of $\alpha^4\mathcal{R} = 3.11134\times10^{-4}$ cm^{-1}, where $\mathcal{R}$ is the Rydberg constant for infinite mass, we obtain a shift of the $J = 1$ level by an amount

$$-2.17(2)\times10^{-4}\ \text{cm}^{-1}.$$

Pekeris *et al.*[9] have calculated the shift of the $J = 1$ level from the mixing with the nearby 2^1P state and found

$$\frac{|\langle \Psi_0(2^3P_1)|\tilde{H}_1^{(1)} + \tilde{H}_1^{(2)}|\Psi_0(2^1P_1)\rangle|^2}{E_0(2^3P_1) - E_0(2^1P_1)}$$

$$= -1.58\times10^{-4}\ \text{cm}^{-1}.$$

Since we have calculated the complete second-order sum (over all $^3P_1$ states) and not just the first (and presumably the biggest) term, our result is consistent with theirs. This shows that even if the first term of a second-order sum is dominating, it only gives an estimate of the order of magnitude of the complete sum.

The calculation of the contributions from odd ^3D

TABLE I. Second-order spin-dependent perturbation energies from intermediate ^1P states using the expansion (3) for $\tilde{\Psi}_1^{(i)}(^1P_1, M_J = 1)$.

ω	$N(\omega)$	$\tilde{E}_2^{(1,1)}(\alpha^4\mathcal{R})$	$\tilde{E}_2^{(2,2)}(\frac{1}{4}\alpha^4\mathcal{R})$	$\tilde{E}_2^{(1,2)}(\frac{1}{2}\alpha^4\mathcal{R})$	$(\tilde{E}_2^{(1,1)} + \frac{1}{4}\tilde{E}_2^{(2,2)} + \tilde{E}_2^{(1,2)})(\alpha^4\mathcal{R})$
1	4	−0.326 083 150 88	−0.184 644 064 08	−0.244 726 520 48	−0.616 97
2	10	−0.331 131 174 24	−0.175 888 934 60	−0.239 969 803 08	−0.615 07
3	20	−0.350 064 594 92	−0.173 445 981 91	−0.243 720 589 91	−0.637 14
4	35	−0.365 313 3625	−0.173 757 715 10	−0.247 748 059 07	−0.656 50
5	56	−0.374 772 0	−0.173 362 964 19	−0.249 206 7	−0.667 31
6	84	−0.381	−0.173 34	−0.250 0	−0.674
7	120	−0.3857	−0.173 480 3	−0.250 77	−0.679 8
8	165	−0.388 8	−0.173 572	−0.251 16	−0.683 3
Extrapolated		−0.41 (1)	−0.18 (1)	−0.252 (1)	−0.699 (7)

TABLE II. Second-order spin-dependent perturbation energies from intermediate ^3D states, using the expansion (8) for $\Psi_1^{(i)}(^3D_2, M_J = 2)$.

ω	$10^4 E_2^{(1,1)}(\frac{3}{2}\alpha^4\mathcal{R})$	$10^2 E_2^{(2,2)}(\frac{3}{8}\alpha^4\mathcal{R})$	$10^5 E_2^{(3,3)}(\frac{3}{8}\alpha^4\mathcal{R})$	$10^3 E_2^{(1,2)}(\frac{3}{4}\alpha^4\mathcal{R})$	$10^5 E_2^{(1,3)}(\frac{3}{4}\alpha^4\mathcal{R})$	$10^3 E_2^{(2,3)}(\frac{3}{8}\alpha^4\mathcal{R})$
1	−29.324 596 271	−1.616 139 772 9	−3.401 061 859 5	3.280 983 461 6	12.557 165 969	−0.724 293 851
2	−13.459 704 588	−1.937 306 250 3	−5.099 513 877 9	2.771 550 598 0	12.136 297 508	−0.950 832 530
3	− 9.868 859 497	−2.069 830 569	−6.177 248 34	2.446 496 533	10.677 123 37	−1.064 373 138
4	− 8.134 397 74	−2.161 528	−6.916 746	2.258 699 00	9.788 83	−1.136 318 9
5	− 7.279 791 5	−2.215 239	−7.426 12	2.129 620 1	9.161 73	−1.178 08
6	− 6.865 073	−2.258 9	−7.835 8	2.067 9	8.871	−1.206
7	− 6.719 363 6	−2.283	−8.16	2.041 7	8.750	−1.228
8	− 6.654 7	−2.303	−8.36	2.029	8.70	−1.238
∞	−6.51(7)	−2.5(1)	−9.7(7)	2.014(7)	8.63(3)	−1.28(2)

intermediate states proceeds in the same way. Equations (10) are solved with $\omega' = \omega$, and the second-order energies are given by formulas similar to (14). The extrapolations are all according to the slow convergence scheme, but in most cases the fast scheme gave results close to the ones quoted. Notice that the eight computed values for $E_2^{(1,1)}$ increase monotonically with ω. However, in these calculations we cannot expect the computed unmixed second-order energies to be upper bounds to the true quantities. The eigenvalues of the matrix $\langle V_{k'}|H_0|V_k\rangle$ in (10) do not correspond to helium energy levels, and some of them could well be smaller than $E_0(\omega)$. In fact, at least one eigenvalue of $\langle V_{k'}|H_0|V_k\rangle$ is close to E_0. This was demonstrated by putting $y_1^{(i)} = 0$ in (10), deleting the first equation, and solving the remaining $N(\omega) - 1$ equations for $y_2^{(i)}, \ldots, y_{N(\omega)}^{(i)}$ as in I. When one inserted the solutions into the left-hand side of the first equation of (10) and compared with the right-hand sides, there was agreement to several digits for the higher values of ω, and the second-order energies obtained this way agreed with the results of Table II to the same number of digits. If one does not divide by $r_1 r_2$ in (9), one would expect the lowest eigenvalue of the matrix of H_0 between such terms to be equal to the $(2p, 3d)\,^3D$ energy level (at −0.559 328 5 a.u.) recently reported by Doyle *et al.*[6]

The results of Table II give directly the perturbation to the $J = 2$ level. Adding up, one gets a shift of $-0.024(1)\times10^{-4}$ cm^{-1}. The J dependence of matrix elements of a contraction of an angular momentum operator of rank K with a spin operator of the same rank between states with angular momenta 1 and 2 and spin 1 on both sides is given by $(-1)^J W(11\,12; JK)$,[10] where W is a Racah coefficient, and K is 1 or 2. Therefore, the perturbation of the $J = 1$ level is given by (as explained in I)

$$\left[\left(\frac{w(11)}{w(21)}\right)^2(4E_2^{(1,1)} + 4E_2^{(1,2)} + E_2^{(2,2)}) + 2\left(\frac{w(11)}{w(22)}\right)(2E_2^{(1,3)} + E_2^{(2,3)}) + \left(\frac{w(12)}{w(22)}\right)^2 E_2^{(3,3)}\right]\tfrac{3}{8}\alpha^4\mathcal{R}$$

$$= \tfrac{5}{24}\left[4E_2^{(1,1)} + 4E_2^{(1,2)} + E_2^{(2,2)} - 6(2E_2^{(1,3)} + E_2^{(2,3)}) + 9E_2^{(3,3)}\right]\alpha^4\mathcal{R}\,,$$

where $w(JK) = w(KJ) \equiv W(11\,12; JK)$. This gives a perturbation of

$$-0.0089(6)\times10^{-4}\ \text{cm}^{-1}$$

for the $J = 1$ level. This is also the contribution to the large fine-structure interval, except for the sign, since the $J = 0$ level does not couple to D states. All of the uncertainties come from $E_2^{(2,2)}$, but the contribution of ^3D intermediate states to the large fine-structure interval is well below the experimental accuracy. It is not surprising that these ^3D contributions should be so much smaller than the ^1P perturbation; if one looks at first terms in the second-order sums and assumes that all matrix elements have the same orders of magnitude, then the order of magnitude of the ratio of the ^3D and ^1P perturbations is given by the inverse ratio of the energy denominators, i.e.,

$$\frac{E(2^3P) - E(2^1P)}{E(2^3P) - E(3(2p, 3d)^3D)} = \frac{-2.133 + 2.123}{-2.133 + 0.559} = 0.006\,,$$

which corresponds to our findings.

The calculations reported here were done in about 20 sec of computer time on the CDC 7600 of the Lawrence Berkeley Laboratory.

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APPENDIX: REDUCTION OF INTEGRALS OF THE TYPE (11) BY ROTATION OF THE COORDINATE SYSTEM AND INTEGRATION

We wish to obtain the function $g(\theta_{12})$ in

$$\int d\Omega_1 \int d\Omega_2 x_1^p y_1^q z_1^r x_2^s y_2^t z_2^u F(\theta_{12}) = \int d\Omega_1 \int d\Omega_2 g_{pqr,stu}(\theta_{12}) F(\theta_{12}) ,$$

where $F(\theta_{12})$ is an arbitrary function. To that effect, first rotate the coordinate system clockwise $\frac{1}{2}\pi - \varphi_1$ about the z axis, so that $\vec{r}_1$ is in the intermediate yz plane. Then rotate θ_1 clockwise about the intermediate x axis. The new unit vectors are now given in terms of the old by

$$\begin{pmatrix} \vec{i}'' \\ \vec{j}'' \\ \vec{k}'' \end{pmatrix} = \begin{pmatrix} \sin\varphi_1 & -\cos\varphi_1 & 0 \\ \cos\theta_1\cos\varphi_1 & \cos\theta_1\sin\varphi_1 & -\sin\theta_1 \\ \sin\theta_1\cos\varphi_1 & \sin\theta_1\sin\varphi_1 & \cos\theta_1 \end{pmatrix} \begin{pmatrix} \vec{i} \\ \vec{j} \\ \vec{k} \end{pmatrix} .$$

In the new system, $\vec{r}_1$ is along the z'' axis, and $\theta_{12} = \theta_2$ and

$$x_2 = \vec{r}_2 \cdot \vec{i} = r_2(\sin\theta\cos\varphi\,\vec{i}'' + \sin\theta\sin\varphi\,\vec{j}'' + \cos\theta\,\vec{k}'')\cdot\vec{i}$$
$$= r_2(\sin\theta\cos\varphi\sin\varphi_1 + \sin\theta\sin\varphi\cos\theta_1\cos\varphi_1 + \cos\theta\sin\theta_1\cos\varphi_1) ,$$

where $\theta = \theta_{12}$ and $\varphi = \varphi_2$. There are similar expressions for y_2 and z_2. We retrieve the usual expressions for x_1, y_1, and z_1 since, for example,

$$x_1 = \vec{r}_1 \cdot \vec{i} = r_1 \vec{k}'' \cdot \vec{i} = r_1 \sin\theta_1 \cos\varphi_1 .$$

In the integration over the polar angles of $\vec{r}_1$ and $\vec{r}_2$,

$$\int d\Omega_1 \int d\Omega_2 = \int_0^{2\pi} d\varphi_1 \int_0^{\pi} d\theta_1 \sin\theta_1 \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta ,$$

φ_1, θ_1, and φ can be integrated. The g functions necessary to derive formulas (13) can now be obtained by elementary integration and some rather lengthy algebra. The results are

$$g_{400,002}(\theta) = 3g_{220,002} = (1 + 2\sin^2\theta)/35 ,$$
$$g_{301,101}(\theta) = 3g_{211,011}(\theta) = (2 - 3\sin^2\theta)/70 ,$$
$$g_{202,200}(\theta) = (3 - \sin^2\theta)/105 ,$$
$$g_{300,102}(\theta) = 3g_{210,012}(\theta) = \cos\theta\,(1 + \sin^2\theta)/35 ,$$
$$g_{111,111}(\theta) = \cos\theta\,(2 - 5\sin^2\theta)/210 ,$$
$$g_{102,102}(\theta) = \cos\theta\,(3 - 4\sin^2\theta)/105 .$$

Formula (13b), for example, is obtained by explicit calculation:

$$\int d\Omega_1 \int d\Omega_2 (\{\{\vec{r}_2\}^{(1)}, \{\vec{r}_2, \vec{r}_1\}^{(1)}\}_2^{(2)} * \{\{\vec{r}_1\}^{(1)}\{\vec{r}_1, \vec{r}_2\}^{(1)}\}_2^{(2)} F(\theta)$$
$$= \tfrac{1}{8} \int d\Omega_1 \int d\Omega_2 (x_2 - iy_2)[(x_2 - iy_2)z_1 - z_2(x_1 - iy_1)](x_1 + iy_1)[(x_1 + iy_1)z_2 - z_1(x_2 + iy_2)]F(\theta)$$
$$= \tfrac{1}{2} \int d\Omega_1 \int d\Omega_2 [g_{201,201}(\theta) + g_{111,111}(\theta) - g_{120,102}(\theta) - g_{300,102}(\theta)]F(\theta)$$
$$= -\tfrac{1}{20} \int d\Omega_1 \int d\Omega_2 r_1^3 r_2^3 \sin^2\theta\cos\theta F(\theta) , \qquad \text{(A1)}$$

where use has been made of the relations $g_{pqr,stu}(\theta) = g_{stu,pqr}(\theta)$, $g_{P(pqr),P(stu)}(\theta) = g_{pqr,stu}(\theta)$, where $P(pqr)$ is a permutation of (pqr). These relations also showed that the imaginary part of the left-hand side of (A1) vanished. The other three formulas (13) can be derived in the same manner.

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