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Singlet-Triplet Mixing in Excited Helium Atoms

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Experiments in collisional transfer of excitation, as well as theoretical considerations, have shown that singlet-triplet mixing occurs for nF states of helium. In this work the helium fine structure has been calculated using polarized orbitals to determine the amount of mixing and its dependence on the state (nl) of the excited electron, and on the polarization of the orbital of the inner electron. Results are presented for $n = 3-10$ and $l = 2(n-1)$. All P states gave poor results because of a large exchange effect involving the polarization term in the wave function. However, the $3\,^3D$ and $4\,^3D$ levels showed improved agreement with experiment for the fine structure. The singlet-triplet mixing is essentially zero for $l = 2$, is significant for $l = 3$, and is virtually complete for $l \geq 4$. It is also found that the mixing decreases slightly with increasing n.

I. INTRODUCTION

For helium-like ions in the lower-energy states, the total spin angular momentum $\vec{S}$ and the total orbital angular momentum $\vec{L}$ are approximately constants of the motion.[1] This is because the spin-orbit interaction which tends to couple the spin and orbital angular momenta of the electrons is small compared to the exchange energy K which tends to couple the two spins.[2] The energy levels for which this approximation (Russell-Saunders coupling) can be applied can be classified according to the spin multiplicity: singlet or triplet for two-electron atoms.[3] As the degree of excitation of the atom increases, the exchange energy decreases much more rapidly than the spin-dependent interactions, and the Russell-Saunders approximation becomes invalid.[2] The wave functions describing these states are not pure singlet or triplet, but must be written as linear combinations, or admixtures, of singlet and triplet states.[3,4] Some fairly recent experiments[5-10] have drawn heavily on the occurrence of singlet-triplet mixing to explain their results. It is the main purpose of this work to calculate the admixture coefficients for the linear combinations of states and in so doing, to study the dependence of the breakdown of Russell-Saunders coupling on the degree of excitation of the helium atom. In another paper the dependence on the nuclear charge Z will be studied.

It is the problem of collisional transfer of excitation in helium which has drawn attention to the breakdown of Russel-Saunders coupling. Lees and Skinner[11] discovered that ^1P excitation seemed to be transferred to ^3D levels and proposed the collision reaction

$$\mathrm{He}(n\,^1P) + \mathrm{He}(1\,^1S) \rightarrow \mathrm{He}(1\,^1S) + \mathrm{He}(n\,^3D) \tag{1}$$

to explain the observations. Although this transfer of excitation was decisively shown to exist by Maruer and Wolfe,[12,13] the reaction above violates the Wigner spin-conservation rule[14] which is expected to hold for states with a low principle quantum number.[15] This is the main objection to the above transfer mechanism, but later experiments revealed more difficulties. Heron, McWhirter, and Rhoderick[16] showed that collisional transfer of excitation for $n = 3$ occurs slowly compared to the mean lifetime of the excited states involved and therefore cannot account for the observed effects. Gabriel and Heddle[17] showed that cascade processes were more important than had been previously supposed. Then, St. John and Fowler[5] proposed a multiple state transfer process which explains the experimental observations and is free from the above objections:

$$\begin{aligned} &\mathrm{He}(n\,^1P) + \mathrm{He}(1\,^1S) \rightarrow \mathrm{He}(nF) + \mathrm{He}(1\,^1S)\,, \\ &\mathrm{He}(nF) \rightarrow \text{cascade} \rightarrow \mathrm{He}(n'\,^3D)\,, \quad n > n'\,. \end{aligned} \tag{2}$$

This mechanism received theoretical support from Lin and Fowler,[2] who showed that the transitions with $\Delta L = \pm 2$ are favored in such collisions. More importantly, they showed that the total spin is not necessarily a constant of the motion for F levels. The combined singlet and triplet nature of the F states allows the transfer to proceed without violating Wigner's rule.[2] The $n\,^1P \rightarrow nF$ transfer model was supported by later experiments.[6-10]

The values of the singlet-triplet admixture coefficients depend on the matrix elements of the spin-dependent interactions and on the exchange energy associated with the spin-independent interactions.[2,4] The coarse structure and the fine structure of the helium spectrum are also determined by these quantities. In the Russell-Saunders approximation, the coarse-structure splitting is determined by the exchange energy and the fine structure by the spin-dependent interactions.[1,4] Therefore, methods of studying the fine structure which are applicable to the problem of singlet-triplet mixing are considered.

Heisenberg[18] was the first to treat the problem of the excited states of two-electron atoms. He used perfectly screened hydrogenic orbitals, incorporating spin effects in an intuitive fashion. Sugiura[19] improved Heisenberg's method by considering imperfect screening. Gaunt[20,21] calculated the triplet separations for the $2\,^3P$, $3\,^3P$, $3\,^3D$, and $4\,^3D$ levels in helium. He incorporated the spin effects more directly into the wave equation. The most accurate of the early calculations were made by Breit[22-24] and by Araki.[25] The most important of several contributions by Breit was the derivation of a wave equation for two-electron atoms.[22] Although it is not Lorentz invariant, it has been verified by several authors[26-28] to be correct to terms of order α^2 in the interaction of the two electrons, where α is Sommerfeld's fine-structure constant. Breit also calculated the fine structure of helium to test the terms in his Hamiltonian, but he did not consider the off-diagonal matrix elements of the spin-dependent terms.[4,24] Araki[25] used Breit's Hamiltonian and allowed for the possible mixing of states. The spatial part of Araki's wave function includes a contribution, derived by Bethe,[29] owing to the polarization of the inner electron orbital by the outer electron. The Coulomb repulsion of one electron polarizes the charge distribution of the other, and Bethe used an approximation, good for excited states, to find the effect on the wave function of the polarization. The secondary purpose of this paper is to study the effects of the polarization correction.

Much more accurate results for the fine structure have been obtained recently by using improved wave functions obtained by variational techniques.[30-36] Unfortunately, these calculations have all been for the lowest excited states[30-35] or for S states.[36] The requirement that each successive variational wave function be orthonormal to those for all lower states leads to an extremely large amount of calculation as well as slow convergence.[4] However, such calculations for singlet-triplet mixing have been made,[37] but only for $2P$ states in the helium sequence.

Araki's method is taken as the starting point for the present calculations, although the method is modified slightly to facilitate the calculation of the admixture coefficients. Also, the energy eigenvalue calculations are extended to states with n as large as 10. Since the polarization is being studied, care is taken to determine the detailed effects of these terms in the wave function.

Breit's Hamiltonian is used, but the spin-independent relativistic corrections are neglected, since they do not contribute to the energy splittings.[4] For the same reason, the direct integrals of the ordinary Schrödinger Hamiltonian terms are not considered. The wave functions used are products of hydrogenic orbitals. The inner orbital is amended by a spherically symmetric correction term and a correction term due to polarization, and for the outer orbital, perfect screening by the inner electron is assumed. In the integrands, only products to first order in these corrections are retained. First-order degenerate perturbation theory[1] is used to find the energy eigenvalues, which determine the level splittings, and to find the admixture coefficients which determine the correct linear combinations of degenerate wave functions that form the correct zeroth-order wave functions corresponding to the split levels.

When the calculations were made, it was found that Araki's results could not be duplicated. It is concluded after careful recalculations and a complete analysis of Araki's paper that errors occur in his work which cannot be accounted for by mistakes in the detailed arithmetic. These errors will be pointed out in Sec. II, as the general theory is presented. By far the most significant effect is that the method does not give the good results for $(1s)(np)$ configurations that Araki had reported. A large exchange effect due to the inclusion of the polarization term in the wave function leads to extremely poor values for the energy splittings for all P states. The remainder of the results are generally satisfactory. The calculations and results are discussed in Sec. III. A summary of the results and the conclusions drawn from them are presented in Sec. IV.

II. THEORY

A. Formulation

The Breit equation[22] is a differential equation for a relativistic wave function for two electrons, interacting with each other and with an external electromagnetic field.[4] It contains an approximation to the relativistic interaction between two electrons, and the field-theoretic treatment of Dirac's pair theory[38] is inexact.[4] In addition, the Pauli approximation[39] involves an expansion in which all terms higher than $(v/c)^2$ are dropped.[4] The Breit equation in Pauli approximation is given by Bethe and Salpeter[4] in position space.

The position vectors of the two electrons are denoted by $\vec{r}_1$ and $\vec{r}_2$, and $\vec{r}_{12}=\vec{r}_1-\vec{r}_2$. The orbital angular momentum operators are given below, where lower-case letters are used for the angular momenta and associated quantum numbers of one electron and capital letters are used for the totals for more than one electron,

$$\vec{1}_j=\vec{r}_j\times\vec{p}_j\ , \qquad j=1,2 \tag{3}$$

$$\vec{1}_{jk}=\vec{r}_{jk}\times\vec{p}_j\ , \qquad j\neq k=1,2 \tag{4}$$

where

$$\vec{\mathrm{p}} = -i\hbar\vec{\nabla} \ . \tag{5}$$

The spin angular momentum operator, s_1 or s_2, has as its components the Pauli spin matrices:

$$s_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \ , \quad s_y = \frac{i\hbar}{2}\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \ , \quad s_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \ . \tag{6}$$

For convenience, the Breit Hamiltonian is written (in atomic units) as

$$H = H_0 + 1/r_{12} + H_{\mathrm{so}}^{(1)} + H_{\mathrm{so}}^{(2)} + H_{\mathrm{ss}} + H_{\mathrm{rel}} \ , \tag{7}$$

where

$$H_0 = -\tfrac{1}{2}\nabla_1{}^2 - Z/r_1 - \tfrac{1}{2}\nabla_2{}^2 - Z/r_2 \ , \tag{8}$$

$$H_{\mathrm{so}}^{(1)} = \tfrac{1}{2}Z\alpha^2(r_1^{-3}\vec{\mathrm{l}}_1 \cdot \vec{\mathrm{s}}_1 + r_2^{-3}\vec{\mathrm{l}}_2 \cdot \vec{\mathrm{s}}_2) \ , \tag{9}$$

$$H_{\mathrm{so}}^{(2)} = -\tfrac{1}{2}\alpha^2 r_{12}{}^{-3}[(\vec{\mathrm{l}}_{12} + 2\vec{\mathrm{l}}_{21}) \cdot \vec{\mathrm{s}}_1 + (\vec{\mathrm{l}}_{21} + 2\vec{\mathrm{l}}_{12}) \cdot \vec{\mathrm{s}}_2] \ , \tag{10}$$

$$H_{\mathrm{ss}} = \alpha^2 r_{12}{}^{-3}[\vec{\mathrm{s}}_1 \cdot \vec{\mathrm{s}}_2 - 3r_{12}{}^{-2}(\vec{\mathrm{r}}_{12} \cdot \vec{\mathrm{s}}_1)(\vec{\mathrm{r}}_{12} \cdot \vec{\mathrm{s}}_2)] \ . \tag{11}$$

H_{rel} includes the spin-independent relativistic interactions, and is neglected since it plays no part in the level splittings and is small compared to the approximations made in obtaining the nonrelativistic eigenvalue.[4] A term in H_{ss} involving the δ-function $\delta(\vec{\mathrm{r}}_{12})$ has been omitted because it does not affect the splittings.[4]

There are three types of corrections for the finite mass of the nucleus,[4] but only one of the three is used in this work. The "elementary" correction for the motion of the nucleus about the center of mass is made by multiplying all energies by $M/(M+m)$, where M is the mass of the nucleus and m is the mass of the electron.[4] This correction is made by using the proper Rydberg constant when the atomic units for energy are converted to cm^{-1}. The mass correction due to electron exchange is applicable only if the electronic states occupied by the two electrons combine optically; that is, only P states are affected, since one electron always remains in the ground state.[4] As stated before, the results for the P states are not good, so this small mass correction is not considered. The correction due to mass polarization is small for excited states[4] and will be neglected.

In Eq. (7), $H_0 + 1/r_{12}$ is the ordinary Schrödinger Hamiltonian for a two-electron atom. $H_{\mathrm{so}}^{(1)}$ is the spin-orbit interaction of one electron, $H_{\mathrm{so}}^{(2)}$ is the spin-orbit interaction of two electrons, and H_{ss} is the spin-spin interaction.

Since all doubly excited states of helium have a higher energy than that of a He^+ ion plus a free electron,[4] the only electron configurations considered here will have one electron in the ground state and one in an excited state. This means that the orbital angular momentum of the atom $\vec{\mathrm{L}}$ is equal to the orbital angular momentum of the outer electron $\vec{\mathrm{l}}$. Also, $M_L = m_l$. The approximations used in obtaining the wave functions further restrict the states to those with nonzero values of l (or L). For the configurations to be considered, the approximate eigenfunctions of the Schrödinger Hamiltonian are

$$\psi_{nlm_l}(1, 2) = (4\pi)^{-1/2}[R_{10}(r_1, Z) + U_0(r_1, r_2) + U_1(r_1, r_2) \times P_1(\cos\theta_{12})]\, R_{nl}(r_2, Z-1)\, Y_{lm_l}^{(2)} \ , \tag{12}$$

where θ_{12} is the angle between $\vec{\mathrm{r}}_1$ and $\vec{\mathrm{r}}_2$, $P_\nu(x)$ is the normalized Legendre polynomial, and Y_{lm_l} is the normalized spherical surface harmonic, with the phase determined by[4, 25]

$$Y_{l,-m} = (-1)^m Y_{lm}^* \ . \tag{13}$$

$R_{nl}(r, Z)$ is the normalized radial eigenfunction of the hydrogenlike atom, given by[1, 4]

$$R_{nl}(r, Z) = -\left[\left(\frac{2Z}{n}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{1/2} \times e^{-2Zr/n}\left(\frac{2Zr}{n}\right)^l L_{n+l}^{(2l+1)}\left(\frac{2Zr}{n}\right) \ , \tag{14}$$

where $L_n^{(m)}(x)$ is the mth derivative of the Laguerre polynomial of degree n. $U_0(r_1, r_2)$ is the spherically symmetric correction to the orbital of the inner electron. It is obtained as an expansion of spherically symmetric hydrogenic radial wave functions:

$$U_0(r_1, r_2) = \sum_{\nu=2}^{\infty} b_\nu(r_2, Z) R_{\nu 0}(r_1, Z) \quad , \tag{15}$$

with

$$b_2(r_2, Z) = -(32/81\sqrt{2})\, e^{-3Zr_2/2}(3r_2 + 2/Z) \ , \tag{16}$$

and

$$b_3(r_2, Z) = (1/64\sqrt{3})\, e^{-4Zr_2/3}(8Zr_2^2 - 36r_2 - 27/Z) \ . \tag{17}$$

These coefficients were given by Araki for the case of $Z = 2$ only.[25] When the generalization to arbitrary Z was made, a discrepancy in the $b_3(r_2, Z)$ coefficient was found. Although the $b_2(r_2, Z)$ coefficients agree for $Z = 2$, the b_3 given by Araki is[25]

$$b_3(r_2) = (1/768\sqrt{3})(1/r_2)\, e^{-8r_2/3}(729 + 1782r_2 + 2160r_2{}^2 + 2712r_2{}^2) \ , \tag{18}$$

which does not agree with Eq. (17) for $Z = 2$. This error is not very significant. The contributions of U_0 to the radial integrals are of the order of 10% of the contribution of the R_{10} term at the very largest, and they are usually much smaller. Furthermore, the b_3 term is smaller than the b_2 term within U_0.

$U_1(r_1, r_2)$ is the coefficient derived by Bethe[29] to approximate the effect of polarization of the (1s) orbital. It is given by[25,29]

$$U_1(r_1, r_2) = \frac{\sqrt{Z}}{Z^2 r_2^{\,2}}\, e^{-Zr_1}\left[Z^2 r_1^{\,2} + 2Zr_1 - \tfrac{3}{2}(1 + 2Zr_2 + Z^2 r_2^{\,2})e^{-2Zr_2}\left(\frac{e^{2Zr_1}}{Z^2 r_1^{\,2}} - \frac{1}{Z^2 r_1^{\,2}} - \frac{2}{Zr_1} - 2\right)\right], \qquad r_1 < r_2 ,$$

$$= \frac{\sqrt{Z}}{Z^2 r_2^{\,2}}\, e^{-Zr_1}\left[2Z^3 r_2^{\,3} - \{Z^3 r_2^{\,3} + \tfrac{3}{2}[1 - Z^2 r_2^{\,2} - e^{-2Zr_2}(1 + 2Zr_2 + Z^2 r_2^{\,2})]\}\left(\frac{1}{Z^2 r_1^{\,2}} + \frac{2}{Zr_1}\right)\right], \quad r_1 > r_2 . \qquad (19)$$

In the derivation of U_1, Bethe used the hydrogenic orbitals with the same sign as given in Eq. (14), but Araki used the orbital of positive sign[25] without making the appropriate correction in U_1. Consequently, all the contributions to the radial integrals from the U_1 term have a minus sign mistake in Araki's paper. The effects of this error will be discussed in Sec. III.

The U_0 and U_1 corrections are equivalent to configuration interactions with the autoionizing states $(2s)(nl)$, $(3s)(nl)$, and $(n'p)(nl)$. It has recently been shown[40] that the lifetimes of the $2p^2\,{}^3P$ and the $2p3p\,{}^1P$ levels are much longer than the lifetimes characteristic of autoionizing states. Thus, the significance of the U_1 term is enhanced.

Four linearly independent, totally antisymmetric basis functions are formed from the spatial eigenfunctions $\psi_{nlm_l}(1, 2)$ and the spin eigenfunctions $S_{SM_S}(1, 2)$:

$$\phi_1^t = [2^{-1/2}(1 - P)\psi_{nlm_j-1}(1, 2)]S_{11}(1, 2) , \qquad (20)$$

$$\phi_0^t = [2^{-1/2}(1 - P)\psi_{nlm_j}(1, 2)]S_{10}(1, 2) , \qquad (21)$$

$$\phi_{-1}^t = [2^{-1/2}(1 - P)\psi_{nlm_j+1}(1, 2)]S_{1-1}(1, 2) , \qquad (22)$$

and

$$\phi_0^s = [2^{-1/2}(1 + P)\psi_{nlm_j}(1, 2)]S_{00}(1, 2) , \qquad (23)$$

where P is a permutation operator which interchanges the electron coordinates. The superscript t indicates triplet character $(S = 1)$, and s indicates singlet $(S = 0)$. The spin eigenfunctions are the usual expressions.[1,4] Since the Hamiltonian H is diagonal in M_J, the total magnetic quantum number, the four basis functions are taken for a given $M_J (= m_j)$; hence, the substitution

$$m_l = M_L = M_J - M_S = m_j - M_S \qquad (24)$$

is made.

In accord with first-order degenerate perturbation theory,[1] the correct zeroth-order eigenfunctions are expanded in terms of the degenerate basis functions as

$$\Psi_k(1, 2) = a_{k,1}^t \phi_1^t + a_{k,0}^t \phi_0^t + a_{k,-1}^t \phi_{-1}^t + a_k^s \phi_0^s , \qquad (25)$$

with $k = 1, 2, 3, 4$. The index k refers to a particular one of the four levels into which the degenerate level is split by the perturbation. The values $k = 1, 2,$ and 3 correspond to the three triplet levels for which $j = l - 1$, $j = l$, and $J = l + 1$, respectively. The index $k = 4$ refers to the singlet level.

The basis functions, Eqs. (20)–(23), are not the same as those used by Araki, who took products of α and β as his spin functions and then antisymmetrized the product of spin and spatial functions. His total wave function is entirely equivalent to Eq. (25), but there is no separation into singlet and triplet parts.[25] Araki's basis functions can be written

$$\phi_1 = (1/\sqrt{2})(1 - P)[\psi_{nlm_j-1}(1, 2)\alpha(1)\alpha(2)] , \qquad (26)$$

$$\phi_2 = (1/\sqrt{2})(1 - P)[\psi_{nlm_j}(1, 2)\alpha(1)\beta(2)] , \qquad (27)$$

$$\phi_3 = (1/\sqrt{2})(1 - P)[\psi_{nlm_j}(1, 2)\alpha(2)\beta(1)] , \qquad (28)$$

and

$$\phi_4 = (1/\sqrt{2})(1 - P)[\psi_{nlm_j}(1, 2)\beta(1)\beta(2)] , \qquad (29)$$

with

$$\Psi_k^A = \sum_{i=1}^{4} b_{ki}\phi_i , \qquad k = 1, 2, 3, 4 \qquad (30)$$

corresponding to Eq. (25). There is a simple transformation from one representation to the other, and the coefficients in Eq. (25) may be obtained from those in Eq. (30) according to

$$a_{k1}^t = b_{k1} , \qquad (31)$$

$$a_{k0}^t = (1/\sqrt{2})(b_{k2} + b_{k3}) , \qquad (32)$$

$$a_{k-1}^t = b_{k4} , \qquad (33)$$

$$a_k^s = (1/\sqrt{2})(b_{k2} - b_{k3}) . \qquad (34)$$

The coefficients in Eq. (25) are found by using Araki's matrix elements to find the coefficients in Eq. (30) and then using the above transformation.

B. Energy Splittings

Taking the perturbation to be

$$H' = 1/r_{12} + H_{\text{so}}^{(1)} + H_{\text{so}}^{(2)} + H_{ss} , \qquad (35)$$

and using Eqs. (26)–(29) as a basis, one obtains a system of four simultaneous homogeneous linear equations in the four unknowns b_{k1}, b_{k2}, b_{k3}, and b_{k4}:

$$\sum_{i=1}^{4} b_{ki}(h_{ji} - \epsilon_k \delta_{ji}) = 0 \,, \quad j = 1, 2, 3, 4 \,. \tag{36}$$

This leads to the secular equation[25]

$$\begin{vmatrix} h_{11}-\epsilon & h_{12} & h_{13} & h_{14} \\ h_{21} & h_{22}-\epsilon & h_{23} & h_{24} \\ h_{31} & h_{32} & h_{33}-\epsilon & h_{34} \\ h_{41} & h_{42} & h_{43} & h_{44}-\epsilon \end{vmatrix} = 0 \,, \tag{37}$$

where

$$h_{11} = -K + (m-1)(\lambda + 2\lambda' - 3\zeta - 6\zeta') - 2[l(l+1) - 3(m-1)^2](\eta + \eta') \,, \tag{38}$$

$$h_{22} = -m(\lambda + \zeta) + 2[l(l+1) - 3m^2](\eta + \eta') \,, \tag{39}$$

$$h_{33} = m(\lambda + \zeta) + 2[l(l+1) - 3m^2](\eta + \eta') \,, \tag{40}$$

$$h_{44} = -K - (m+1)(\lambda + 2\lambda' - 3\zeta - 6\zeta') - 2[l(l+1) - 3(m+1)^2](\eta + \eta') \,, \tag{41}$$

$$h_{12} = h_{21} = -[l(l+1) - m(m-1)]^{1/2}[\lambda + \lambda' - \zeta - 3\zeta' + 3(2m-1)(\eta + \eta')] \,, \tag{42}$$

$$h_{13} = h_{31} = -[l(l+1) - m(m-1)]^{1/2}[\lambda' - 2\zeta - 3\zeta' + 3(2m-1)(\eta + \eta')] \,, \tag{43}$$

$$h_{24} = h_{42} = -[l(l+1) - m(m+1)]^{1/2}[\lambda' - 2\zeta - 3\zeta' - 3(2m+1)(\eta + \eta')] \,, \tag{44}$$

$$h_{34} = h_{43} = -[l(l+1) - m(m+1)]^{1/2}[\lambda + \lambda' - \zeta - 3\zeta' - 3(2m+1)(\eta + \eta')] \,, \tag{45}$$

$$h_{14} = h_{41} = 6[l(l+1) - m(m-1)]^{1/2}[l(l+1) - m(m+1)]^{1/2}(\eta + \eta') \,, \tag{46}$$

and

$$h_{23} = h_{32} = -K + 2[l(l+1) - 3m^2](\eta + \eta') \,. \tag{47}$$

In Eqs. (38)–(47), the substitution $m = m_j$ has been made for convenience. In the evaluation of the matrix elements both direct and exchange integrals occur. The parameters λ, λ', ζ, ζ', η, and η' are radial integrals associated with the spin-dependent interactions. The primes on these parameters indicate exchange integrals. λ and λ' are the direct and exchange integrals due to $H_{so}^{(1)}$, ζ and ζ' are due to $H_{so}^{(2)}$, and η and η' are due to H_{ss}. K is the exchange integral of the spin-independent parts of the Hamiltonian. Araki obtained the solution to Eq. (37) in terms of the radial integrals as

$$\epsilon_1 = -K - (l+1)[\lambda + 2\lambda' - 3\zeta - 6\zeta' - 2(2l+3)(\eta + \eta')] \,, \tag{48}$$

$$\epsilon_2 = -\tfrac{1}{2}\{[2K + \lambda + 2\lambda' - 3\zeta - 6\zeta' + 2(2l-1)(2l+3)(\eta + \eta')]^2 + 4l(l+1)(\lambda + \zeta)^2\}^{1/2} - \tfrac{1}{2}[\lambda + 2\lambda' - 3\zeta - 6\zeta' + 2(2l-1) \times (2l+3)(\eta + \eta')] \,, \tag{49}$$

$$\epsilon_3 = -K + l[\lambda + 2\lambda' - 3\zeta - 6\zeta' + 2(2l-1)(\eta + \eta')] \,, \tag{50}$$

$$\epsilon_4 = \tfrac{1}{2}\{[2K + \lambda + 2\lambda' - 3\zeta - 6\zeta' + 2(2l-1)(2l+3)(\eta + \eta')]^2 + 4l(l+1)(\lambda + \zeta)^2\}^{1/2} - \tfrac{1}{2}[\lambda + 2\lambda' - 3\zeta - 6\zeta' + 2(2l-1) \times (2l+3)(\eta + \eta')]. \tag{51}$$

The analyses of the energy splittings are made from the quantities in Eqs. (48)–(51). The coarse-structure splitting Δ is defined in terms of the eigenvalues as

$$\Delta = \epsilon_4 - [1/3(2l+1)][(2l-1)\epsilon_1 + (2l+1)\epsilon_2 + (2l+3)\epsilon_3] \,. \tag{52}$$

When Russell-Saunders coupling is valid, Δ is equal to $2K$. The second term in the difference is the statistically weighted average of the triplet energy levels. The triplet splittings are defined to be

$$\delta_1 = \epsilon_2 - \epsilon_1 \tag{53}$$

and

$$\delta_2 = \epsilon_3 - \epsilon_2 \,. \tag{54}$$

When Δ is the same order of magnitude as δ_1 and δ_2, one more energy difference is included in the fine structure,

$$\delta_s = \epsilon_4 - \epsilon_3 \,. \tag{55}$$

δ_s is just the difference in the singlet level and the triplet level with $J = l + 1$. This is included in the tabulation when the singlet is not distinctly separated from the triplet levels.

The parameters in the energy equations are given in integral form

$$\lambda = \tfrac{1}{2}\alpha^2 \int_0^\infty [R_{nl}(r_2, Z-1)]^2 r_2^{-3} r_2^2 \, dr_2 \,,$$

and the substitution of $\langle r_2^{-3} \rangle$ from Pauling and Wilson[1] yields

$$\lambda = \alpha^2 / n^3 l(2l+1)(l+1) \,, \tag{56}$$

$$\lambda' = -\frac{1}{2}\frac{\alpha^2}{2l+1}\int_0^\infty\!\!\int_0^\infty r_1^{-3} R_{10}(r_2, Z) U_l(r_1, r_2) R_{nl} \times (r_1, Z-1) R_{nl}(r_2, Z-1) r_1^2 r_2^2 \, dr_1 \, dr_2 \,, \tag{57}$$

and since only the corrections U_0 and U_1 are retained, l is restricted to unity, so that λ' is found for P states only; also,

$$\zeta = -\frac{\alpha^2}{4}\int_0^\infty\!\!\int_0^\infty \left([R_{10}(r_1, Z)]^2 \frac{\partial a_0}{\partial r_2} + 2R_{10}(r_1, Z) \right.$$

$$\times\sum_{\nu=0}^{1}\frac{U_\nu(r_1,r_2)}{2\nu+1}\frac{\partial a_\nu}{\partial r_2}\Big)[R_{nl}(r_2,Z-1)]^2 r_1^2 r_2^2\,dr_1\,dr_2\,, \tag{58}$$

where

$$a_\nu = r_<^\nu / r_>^{\nu+1}\,. \tag{59}$$

Here, $r_<$ is the smaller of r_1 and r_2, $r_>$ the greater of the two. The exchange integral associated with $H_{so}^{(2)}$ is

$$\begin{aligned}\zeta' = -\frac{\alpha^2}{4(2l+1)}\int_0^\infty\int_0^\infty R_{nl}(r_1,Z-1)R_{nl}(r_2,Z-1)\Big\{\frac{a_l}{r_2}R_{10}(r_1,Z)\left[\frac{\partial}{\partial r_2}R_{10}(r_2,Z)\right]+\frac{a_l}{r_2}U_0(r_1,r_2)\left[\frac{\partial}{\partial r_2}R_{10}(r_2,Z)\right]\\ +\frac{a_l}{r_1}R_{10}(r_2,Z)\left[\frac{\partial}{\partial r_1}U_0(r_1,r_2)\right]+U_1(r_1,r_2)\frac{1}{r_2}\left(\frac{l-1}{2l-1}a_{l-1}+\frac{l+2}{2l+3}a_{l+1}\right)\left[\frac{\partial}{\partial r_2}R_{10}(r_2,Z)\right]\\ +\frac{1}{r_1}\left(-\frac{1}{2l-1}\frac{\partial a_{l-1}}{\partial r_1}+\frac{1}{2l+3}\frac{\partial a_{l+1}}{\partial r_1}\right)R_{10}(r_2,Z)\,U_1(r_1,r_2)\\ +\frac{1}{r_1}\left(\frac{l-1}{2l-1}a_{l-1}+\frac{l+2}{2l+3}a_{l+1}\right)R_{10}(r_2,Z)\left[\frac{\partial}{\partial r_1}U_1(r_1,r_2)\right]\Big\}\,r_1^2 r_2^2\,dr_1 dr_2\,.\end{aligned} \tag{60}$$

The terms due to H_{ss} are

$$\begin{aligned}\eta = \frac{\alpha^2}{4}\frac{1}{(2l-1)(2l+3)}\int_0^\infty\int_0^\infty [R_{nl}(r_2,Z-1)]^2 r_1^2(1/r_2)\{[R_{10}(r_1,Z)]^2+2R_{10}(r_1,Z)U_0(r_1,r_2)\\ +2(r_1/r_2)R_{10}(r_1,Z)U_1(r_1,r_2)\}\,dr_1 dr_2\,,\end{aligned} \tag{61}$$

and

$$\eta' = -\frac{\alpha^2}{4}\frac{2}{(2l-1)(2l+1)(2l+3)}\int_0^\infty\int_0^\infty R_{10}(r_1,Z)U_1(r_1,r_2)\frac{a_l}{r_1 r_2}R_{nl}(r_1,Z-1)R_{nl}(r_2,Z-1)r_1^2 r_2^2\,dr_1 dr_2\,. \tag{62}$$

The first terms in (58) and (61) involve the integral

$$\int_0^\infty\int_{r_1}^\infty [R_{10}(r_1,Z)]^2[R_{nl}(r_2,Z-1)]^2(1/r_2^3)\,r_1^2 r_2^2\,dr_1 dr_2\,,$$

which is approximately $\langle r_2^{-3}\rangle$, especially for large l, in which case r_1 is almost always smaller than r_2. Thus, ζ and η are almost directly proportional to λ, particularly for large l.

The direct integral of $1/r_{12}$ is omitted because it does not affect the splittings. The parameter K is the exchange integral of the spin-independent terms in the Hamiltonian H. This is ordinarily just the exchange integral of $1/r_{12}$, unless the accuracy of the wave function makes it practical to include the exchange integrals of H_{rel}. K is due to a coupling between the spins that is produced by the use of antisymmetric wave functions.[41] Araki did not include any expression or present any results for K.[25] One reason for not doing so is that when $K \gg \lambda$, the fine-structure splittings are independent of K. In this case,

$$\delta_1 \simeq l\,[\lambda+2\lambda'-3\zeta-6\zeta'-6(2l+3)(\eta+\eta')]\,, \tag{63}$$

$$\delta_2 \simeq (l+1)[\lambda+2\lambda'-3\zeta-6\zeta'+6(2l-1)(\eta+\eta')]\,. \tag{64}$$

The results of calculations for K using only the hydrogenic term for the (1s) orbital are well known,[18,4] but the contributions from the corrections to the wave function are important and need to be considered.

Another point for the inclusion of an explicit expression for K is that the presence of the polarization term allows the coupling of the spins to H_0 as well as to $1/r_{12}$. As will be shown below, this additional exchange effect is present for only S and P states, so that the usual definition of K as the exchange integral of $1/r_{12}$ will apply for $l \geq 2$.

The first operator to be considered is $1/r_{12}$, which can be written in terms of the spherical surface harmonics as[25]

$$\frac{1}{r_{12}} = \sum_{\nu=0}^{\infty}\frac{4\pi}{2\nu+1}a_\nu\sum_{\mu=-\nu}^{\nu}Y_{\nu\mu}^{(1)}Y_{\nu\mu}^{*(2)}\,, \tag{65}$$

where a_ν is given by Eq. (59). Then,

$$K=\frac{1}{4\pi}\iint[R_{10}(r_1,Z)+U_0(r_1,r_2)+U_1(r_1,r_2)P_1(\cos\theta_{12})]$$

$$\times\sum_{\nu=0}^{\infty}\frac{4\pi}{2\nu+1}\,a_\nu\sum_{\mu=-\nu}^{\nu}Y_{\nu\mu}^{(1)}\,Y_{\nu\mu}^{*(2)}\,[R_{10}(r_2,Z)+U_0(r_1,r_2)$$

$$+U_1(r_2,r_1)P_1^*(\cos\theta_{21})]R_{nl}(r_2,Z-1)Y_{lm}^{(2)}$$

$$\times R_{nl}(r_1,Z-1)Y_{lm}^{*(1)}\,d\tau_1 d\tau_2\;. \qquad (66)$$

Using the approximation that only products to first order in the correction terms are retained in the integrand and performing the angular integration, Eq. (66) reduces to

$$K=K_0+K_1+K_2\;, \qquad (67)$$

where

$$K_0=\frac{2}{2l+1}\int_0^{\infty}\int_{r_1}^{\infty}\frac{r_1{}^{l}}{r_2{}^{l+1}}\,R_{10}(r_1,Z)R_{10}(r_2,Z)$$

$$\times R_{nl}(r_1,Z-1)R_{nl}(r_2,Z-1)r_1{}^2r_2{}^2\,dr_1\,dr_2\;, \qquad (68)$$

$$K_1=\frac{2}{2l+1}\int_0^{\infty}\int_0^{\infty}a_lR_{10}(r_2,Z)\,U_0(r_1,r_2)R_{nl}(r_1,Z-1)$$

$$\times R_{nl}(r_2,Z-1)\,r_1{}^2r_2{}^2\,dr_1dr_2\;, \qquad (69)$$

and

$$K_2=\frac{2}{3}\int^{\infty}\int^{\infty}R_{10}(r_2,Z)U_1(r_1,r_2)R_{nl}(r_1,Z-1)R_{nl}(r_2,Z-1)\left(\frac{3l}{(2l-1)(2l+1)}\,a_{l-1}+\frac{3(l+1)}{(2l+3)(2l+1)}a_{l+1}\right)r_1{}^2r_2{}^2\,dr_1dr_2\;. \qquad (70)$$

If the exchange integral of H_0 is labeled K_h, then

$$K_h=\frac{1}{4\pi}\iint[R_{10}(r_1,Z)+U_0(r_1,r_2)+U_1(r_1,r_2)P_1^*(\cos\theta_{12})]\,R_{nl}(r_2,Z-1)\,Y_{lm}^{*(2)}\left(-\tfrac{1}{2}\nabla_1{}^2-\frac{Z}{r_1}-\tfrac{1}{2}\nabla_2{}^2-\frac{Z}{r_2}\right)$$

$$\times[R_{10}(r_2,Z)+U_0(r_2,r_1)+U_1(r_2,r_1)P_1(\cos\theta_{21})]R_{nl}(r_1,Z-1)\;Y_{lm}^{(1)}\,d\tau_1d\tau_2\;. \qquad (71)$$

Angular integration requires $l=0$ except for the U_1 terms. For these, the angular integral is

$$I=\frac{1}{4\pi}\iint P_1^*(\cos\theta_{12})Y_{lm}^{*(2)}\;Y_{lm}^{(1)}\,d\omega_1d\omega_2=\tfrac{1}{3}\delta_{l1}\;. \qquad (72)$$

Thus,

$$K_h=\frac{1}{3}\int_0^{\infty}\int_0^{\infty}R_{10}(r_1,Z)R_{n1}(r_2,Z-1)R_{n1}(r_1,Z-1)$$

$$\times\left[-\frac{1}{2}\left(\frac{\partial^2}{\partial r_1^2}+\frac{2}{r_1}\frac{\partial}{\partial r_1}-\frac{2}{r_1^2}+Z^2-\frac{2Z}{r_1}\right)-\frac{2Z}{r_1}-\frac{1}{2}\left(\frac{\partial^2}{\partial r_2{}^2}+\frac{2}{r_2}\frac{\partial}{\partial r_2}-\frac{2}{r_2{}^2}+\frac{(Z-1)^2}{n^2}-\frac{2(Z-1)}{r_2}\right)-\frac{2Z}{r_2}\right]$$

$$\times U_1(r_1,r_2)\,r_1{}^2r_2{}^2\,dr_1dr_2\;. \qquad (73)$$

This integral has a relatively large negative value, and when K_h is included along with K in the eigenvalue equations, extremely poor results are obtained for the energy splittings for all P states. The inclusion of the polarization term U_1 has provided a "path" for the coupling of the spins with H_0 through the antisymmetric wave functions. This effect makes this formulation unsuitable for all $(1s)(np)$ configurations of the helium isoelectronic sequence.

The analysis of the results is facilitated somewhat by considering the ratio $B=K/H_s$ where

$$H_s=\lambda-3(\xi+2\xi')+2(2l-1)(2l+3)(\eta+\eta')\;, \qquad (74)$$

is the expectation value with $J=l$ of the spin-dependent term in the Hamiltonian. When K is large compared to H_s, the Russell-Saunders approximation is valid. The decrease of B serves as a convenient measure of the increase of singlet-triplet mixing.

All of the radial integrals may be evaluated in closed form. The formula used in the integration are given in Ref. 42.

C. Admixture Coefficients

There are four sets of four admixture coefficients to be found. Each set corresponds to a particular one of the four energy levels into which the degenerate level is split by the perturbation. In the Russell-Saunders approximation, these coefficients may be obtained as the Clebsch-Gordan coefficients defining the unitary transformation from the LSM_LM_S scheme to the $LSJM$ scheme.[3] The states for which $J=l\pm 1$ have pure triplet character.[4,31] Since the singlet level does not affect these states, the Clebsch-Gordan coefficients tabulated by Condon and Shortley[3] are the same as those obtained by the algebraic solution of Eqs. (36), except for the choice of phase. When the Russell-Saunders approximation is not valid, the coefficients for $k=2$ and for $k=4$ are obtained by substitution of the numerical values for the matrix elements and eigenvalues into Eq. (36) and solving the system of equations. The results for these calculations are given in Sec. III.

Although each of the three triplet basis functions has a separate coefficient (m dependent), an "effective" triplet coefficient can be obtained from the relation

$$a_k^t = [1 - (a_k^s)^2]^{1/2} \; . \tag{75}$$

This allows direct analysis of the amount of single-triplet mixing. Of course, in order to use the wave functions obtained from the authors' basis functions, one must have the individual coefficients of the triplet basis functions.

For the purpose of using a single number to describe the degree of singlet-triplet mixing, the ratio

$$A = \{(a_2^s)^2/[1 - (a_2^s)^2]\}^{1/2} \tag{76}$$

is defined. This is zero in the Russell-Saunders approximation of no mixing and increases to unity for complete mixing.

The qualitative behavior of $B = K/H_s$ should describe the reverse behavior of A, so that one should be able to estimate the qualitative dependence of A on such quantities as n and l by considering the relative properties of K and H_s. Conversely, a study of the properties of A should give information about the coupling constants present in B.

No correction terms are considered in the qualitative analysis. For this purpose

$$\begin{aligned} H_s &\simeq \lambda - 3\zeta + 2(2l-1)(2l+3)\eta \\ &\simeq \tfrac{1}{4}\alpha^2 \langle r_2^{-3} \rangle \; . \end{aligned} \tag{77}$$

From Eqs. (77) and (56), H_s varies with n as n^{-3}. For very large n, K has the same dependence on n,[4] but for small n, K deviates in a small but complicated way from the n^{-3} dependence. Any dependence of the mixing on n should arise from the detailed dependence of K on n when n is not large.

The most dramatic effect is the dependence of the mixing on l. K decreases extremely rapidly with increasing l because of the rapid decrease in overlap of the (1s) and the (nl) hydrogenic orbitals. H_s does not decrease as rapidly, so that the mixing increases with increasing l. The polarization corrections will have a significant effect on the degree of singlet-triplet mixing only if their magnitudes are great enough and their dependence on n and l is significantly different from the uncorrected values.

III. RESULTS

The results of this work depend mainly upon the properties of the radial integrals. For this reason, the radial integrals are presented first, with the energy splittings and admixture coefficients being presented later.

A. Radial Integrals

In Table I, the values of the radial integrals are compared to Araki's calculations. Columns (a) and (c) are the results of Araki and the authors, respectively. The agreement is poor, especially for the (1s)(2p) configuration. Column (b) is an attempt to explain the discrepancies on the basis of the errors in Araki's formulation which were pointed out in Sec. II. Column (b) was obtained by evaluating the radial integrals using Araki's formulation exactly as it was presented in his 1937 paper.

For the (1s)(2p) configuration, all the integrals are significantly smaller than Araki's results and

TABLE I. Comparison of radial integrals. Column (a): Araki's results. Column (b): This work using negative polarization and Araki's b_3 coefficient. Column (c): This work.

	(a)	(b)	(c)
		(1s)(2p)	
λ'	9.084×10^{-8}	5.856×10^{-8}	-5.856×10^{-8}
ζ	5.561×10^{-7}	4.4406×10^{-7}	4.7201×10^{-7}
ζ'	1.412×10^{-7}	0.8509×10^{-7}	1.0493×10^{-7}
η	1.073×10^{-7}	0.8351×10^{-7}	0.9971×10^{-7}
η'	7.046×10^{-9}	5.173×10^{-9}	-5.173×10^{-9}
		(1s)(3p)	
λ'	1.080×10^{-8}	4.826×10^{-8}	-4.826×10^{-8}
ζ	1.171×10^{-7}	1.2686×10^{-7}	1.3512×10^{-7}
ζ'	3.307×10^{-8}	2.4942×10^{-8}	3.4408×10^{-8}
η	2.477×10^{-8}	2.3624×10^{-8}	2.8773×10^{-8}
η'	1.758×10^{-9}	1.735×10^{-9}	-1.735×10^{-9}
		(1s)(3d)	
λ'			
ζ	3.219×10^{-8}	3.2401×10^{-8}	3.3034×10^{-8}
ζ'	2.199×10^{-10}	1.2601×10^{-10}	3.1531×10^{-10}
η	1.506×10^{-9}	1.5533×10^{-9}	1.5830×10^{-9}
η'	2×10^{-12}	2.1043×10^{-12}	-2.1043×10^{-12}
ζ'[a]			2.0691×10^{-10}
		(1s)(4d)	
λ'			
ζ	1.341×10^{-8}	1.3605×10^{-8}	1.3949×10^{-8}
ζ'	1.457×10^{-10}	0.6897×10^{-10}	1.8420×10^{-10}
η	6.411×10^{-10}	6.4236×10^{-10}	6.6971×10^{-10}
η'	1×10^{-12}	1.2377×10^{-12}	-1.2377×10^{-12}
ζ'[a]			1.2095×10^{-10}

[a] Results using no corrections to (1s) orbital for the ζ' integral.

TABLE II. Effect of polarization on radial integrals.

	R_{10}	U_0	U_1
(1s)(3d)			
K	1.2846×10^{-5}	0.10021×10^{-5}	1.0333×10^{-5}
λ	6.57395×10^{-8}		
ζ	3.2709×10^{-8}	-0.00136×10^{-8}	0.03394×10^{-8}
ζ'	2.0691×10^{-10}	0.09512×10^{-10}	0.98891×10^{-10}
η	1.5576×10^{-9}	-0.00065×10^{-9}	0.02606×10^{-9}
η'			-0.00210×10^{-9}
(1s)(4f)			
K	2.5639×10^{-8}	0.1406×10^{-8}	1.8667×10^{-8}
λ	9.9050×10^{-9}		
ζ	4.9523×10^{-9}	-0.1543×10^{-13}	0.0055×10^{-9}
ζ'	3.1416×10^{-13}	0.1190×10^{-13}	1.6967×10^{-13}
η	1.1005×10^{-10}	-3.4300×10^{-16}	0.0018×10^{-10}
η'			-1.1424×10^{-15}
(1s)(10f)			
K	4.4194×10^{-9}	2.4361×10^{-10}	3.2195×10^{-9}
λ	6.3392×10^{-10}		
ζ	3.1691×10^{-10}	-2.7357×10^{-15}	7.0460×10^{-13}
ζ'	5.4554×10^{-14}	2.0674×10^{-15}	2.9452×10^{-14}
η	7.0425×10^{-12}	-6.0793×10^{-17}	2.3717×10^{-14}
η'			-1.9979×10^{-16}

the results in column (b) are disappointing in that these results are farther away. Araki may possibly have corrected for his approximation of perfect screening in some way which was not explicitly stated in his paper. Although he allowed for the inclusion of a general screening function in the orbital of the outer electron,[25] the only explicit correction was the use of Sugiura's value of $\langle r_2^{-3}\rangle$.[19] Araki used the approximation of perfect screening for the higher states.

The results are more satisfactory for the other states. In fact, column (b) exhibits significant improvement in agreement with column (a) except for the value of the integral ζ'. The footnoted values of ζ' in column (c) were found using no corrections to the hydrogenic (1s) orbital. These values are much closer to Araki's results for the D states. The correction terms in ζ' [see Eq. (60)] are extremely tedious, and ζ' is small compared to ζ. It is possible that Araki did not include the correction terms in ζ' because of the amount of tedious calculations required for an apparently small correction. It turns out that while the polarization correction for ζ' is small, it has approximately two-thirds as much effect on the fine structure as the polarization correction for ζ. The integrals λ' and η' depend only on the polarization term U_1, and the change in sign of the hydrogenic orbitals used in calculating column (b) gives agreement in sign for these integrals. These properties indicate that the fundamental differences in columns (a) and (c) are produced by the errors in Araki's work.

The contributions to the radial integrals corresponding to different terms in the (1s) orbital are tabulated for a few configurations in Table II. The correction terms become increasingly negligible with increasing l. While the direct integrals are not affected by the polarization correction very much, the exchange integrals are dramatically increased. When exchange effects are important, the polarization terms are very significant; if the exchange integrals may be neglected, as in the case of large l, the polarization terms are also negligible. The direct integrals depend upon the interaction of the two charge clouds. The change in this interaction produced by polarization is small compared to the uncorrected values. The exchange integrals depend upon the degree of overlap of the two orbitals. Since the original overlap is usually quite small, the small change in the degree of overlap produced by the polarization term produces a very appreciable effect compared to the uncorrected value.

The atom becomes increasingly hydrogenic with increasing excitation, and the neglect of U_0 and U_1 in these cases would be a consistent approximation. If this approximation is desired, care must be taken when l is small even if n is large. For small l, the presence of overlap may cause the exchange effects and the correction terms to be significant.

The occurrence of singlet-triplet mixing depends on the relative sizes of K and H_s, so it is important to look at the rates of change of K and H_s with respect to n. This was done by studying the ratios of K and H_s for nF states to K and H_s for $4F$ states and it was found that H_s has the expected form of being proportional to n^{-3}. For $n\gtrsim 7$, the K ratios exhibit the same type of n dependence, but for the smaller values of n, K decreases more slowly.

B. Coarse Structure

The results for the coarse structure are not satisfactory, especially for (1s)(np) configurations. In Table III, the coarse-structure splittings Δ are presented for the (1s)(np) configurations for $2\leq n\leq 8$ and $Z=2$. The columns refer to the terms included in the calculation of Δ. The zero subscript indicates that no correction terms were used in the calculation of Δ. The U_0 term is included for Δ_1, U_1 is included for Δ_2, and Δ_2' also includes the exchange integral of H_0. It is readily apparent that the inclusion of the polarization correction leads to poor results for P states. Even without the contribution from the H_0 terms, the calculations show serious discrepancies (Δ_2 column). The inclusion of the H_0 exchange effect, which is present only when $U_1(r_1, r_2)$ is included in the orbital

TABLE III. Coarse structure for (1*s*)(*np*) in cm^{-1}.

n	Δ_0	Δ_1	Δ_2	Δ_2'	Expt.[a]
2	1677.899	1827.058	3705.942	457.721	2047.993
3	541.906	587.247	1190.954	112.281	644.777
4	234.312	253.184	513.712	43.910	275.68
5	121.243	130.827	265.521	21.565	141.79
6	70.554	76.073	154.418	12.187	82.13
7	44.576	48.040	97.526	7.563	51.84
8	29.926	32.242	65.457	5.017	34.49

[a] Taken from Ref. 43.

TABLE IV. *nD* and *nF* coarse structure in cm^{-1}.

n	Δ_0	Δ_1	Δ_2	Expt.[a]
		(1*s*)(*nd*)		
3	5.639	6.078	10.613	3.411
4	3.273	3.528	6.160	1.971
5	1.892	2.039	3.561	1.146
6	1.163	1.254	2.189	0.690
7	0.759	0.818	1.428	0.430
8	0.520	0.560	0.978	0.360
9	0.370	0.399	0.697	0.240
10	0.273	0.294	0.514	0.180
		(1*s*)(*nf*)		
4	0.021	0.021	0.027	0.280
5	0.013	0.013	0.019	0.060
6	0.009	0.009	0.013	0.000
7	0.006	0.006	0.009	0.000
8	0.004	0.004	0.006	− 0.010
9	0.003	0.003	0.005	0.016

[a] Taken from Martin's tables, Ref. 43.

of the inner electron, completely disrupts the order of the levels as well as the magnitudes of the splittings. Of course, the fine-structure splittings and the admixture coefficients are similarly affected, so no results for these quantities are presented for *P* states.

In states for which the mixing is almost complete, the separation of singlet and triplet levels is not distinct, and the concept of coarse structure loses its meaning. For this reason, coarse-structure results are given only for the configurations for which the mixing is not predominant. Table IV shows the coarse structure for the (1*s*)(*nd*) and (1*s*)(*nf*) configurations of helium with the columns labeled according to the correction terms included in the inner electron orbital, as done for Table III.

The splittings are all too large for $l=2$ and all too small for $l=3$, when experimental results are available for comparison. The experimental results are taken from Martin's tabulation.[43]

C. Fine Structure

The fine-structure splittings were obtained from all the configurations for which $l \geq 2$ and $3 \leq n \leq 10$. For these configurations, there are very few experimental results available for comparison. The results available are for the $3\,^3D$ and the $4\,^3D$ levels of helium.[44, 45]

The splittings δ_1 and δ_2 for the $n\,^3D$ levels of helium are analyzed in Table V according to the terms included in the wave functions. The results headed by R_{10} are found using no corrections to the hydrogenic orbitals. The other columns refer to various combinations of the contributions made by the different corrections. The term labeled $(U_0)_p$ refers to the $U_0(r_1, r_2)$ formed with the b_3 coefficient determined by the authors. When the b_3 coefficient given by Araki is used, the term is labeled $(U_0)_{\mathrm{A}}$. As expected, there is very little difference in the results obtained with different b_3's. The inclusion of U_1 in the column headings labels the inclusion of the polarization correction. The footnoted results are obtained by changing the sign of the U_1 contribution and using the approximate energy splittings, Eqs. (63) and (64). These values agree very nearly with Araki's calculations, once again indicating the effect of the sign of the radial wave functions used.

It must not be concluded from the first part of Table V that the U_0 term is more important in the fine structure than U_1. If the U_1 contribution is

TABLE V. Fine structure for $n\,^3D$ in cm^{-1}.

	R_{10}			$R_{10}+(U_0)_P$			$R_{10}+(U_0)_{\mathrm{A}}$			$R_{10}+(U_0)_{\mathrm{A}}+U_1$		
n	$-\delta_1$	$-\delta_2$	$\frac{\delta_1}{\delta_2}$	$-\delta_1$	$-\delta_2$	$\frac{\delta_1}{\delta_2}$	$-\delta_1$	$-\delta_2$	$\frac{\delta_1}{\delta_2}$	$-\delta_1$	$-\delta_2$	$\frac{\delta_1}{\delta_2}$
3	0.038	0.0093	4	0.0439	0.0032	13.6	0.0440	0.0034	13.1	0.045	0.0043	10.4
										0.0424[a]	0.0030	14.1
4	0.0159	0.0041	3.9	0.0185	0.0015	12.2	0.0186	0.0016	11.9	0.0191	0.002	9.3
										0.0179[a]	0.00125	14.3
5	0.0082	0.0021	3.8	0.0095	0.0008	11.7	0.0095	0.0008	11.5	0.0098	0.0011	8.9
6	0.0047	0.00123	3.8	0.0055	0.0005	11.5	0.0055	0.00049	11.3	0.0057	0.00066	8.7
7	0.0030	0.00078	3.8	0.0035	0.0003	11.4	0.0035	0.00031	11.2	0.0036	0.00042	8.6
8	0.0020	0.00053	3.8	0.0023	0.00021	11.3	0.0023	0.00021	11.1	0.0024	0.00028	8.5

[a] Calculated using $(-U_1)$ and approximate splitting equations.

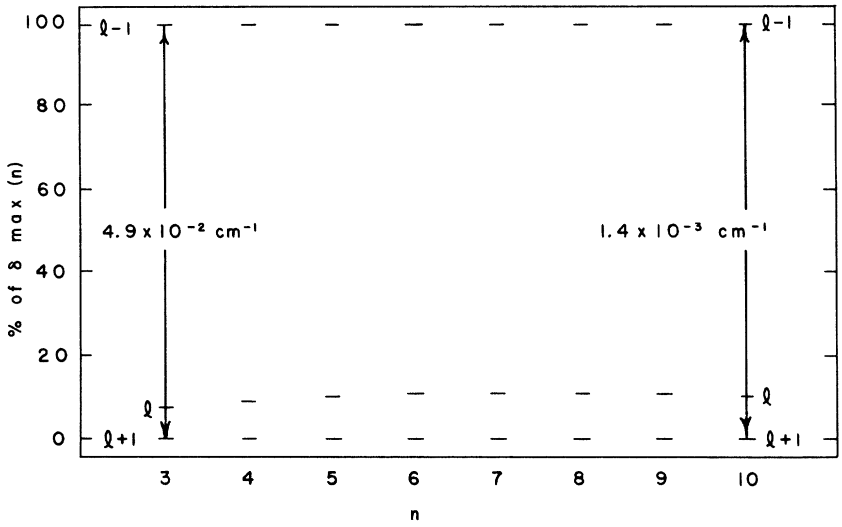

FIG. 1. Schematic triplet separation for (1s) (nd).

considered first, the results are almost the same for δ_1 and δ_2 as when both U_0 and U_1 are included. The fine-structure splittings are quite sensitive to the wave function used, and even the relatively small correction given by U_0 produces significant differences from the uncorrected values.

Table VI compares the theoretical results and the experimental results. The results of Brochard, Chabbal, Chantrel, and Jacquinot[44] were obtained with optical spectroscopy methods, while those of Kaul[45] were obtained with level-crossing spectroscopy. The column under $R_{10}+(U_0)_p+U_1$ contains the results of this work. The results agree well with the experiment for three of the splittings involved. For $4\,{}^3D$, both δ_1 and δ_2 agree with experiment within the range of the experimental error. For $3\,{}^3D$, δ_1 agrees with the measurements of Brochard *et al.*,[44] but it is not within the uncertainty of the precise measurements of Kaul.[45] Although δ_2 for the $3\,{}^3D$ level differs from the most precise experimental value by less than 0.0018 cm^{-1}, it is not within the uncertainty of results of either experiment. The calculations of this work show improvement over Araki's results except for the value of δ_2 for $3\,{}^3D$. To our knowledge, these are the best theoretical results reported for the triplet splittings in the $3\,{}^3D$ and $4\,{}^3D$ levels of helium.

When the separation of the singlet level from the triplet is the same order of magnitude as the triplet separations, the δ_s splitting is included in the fine-structure tabulations. The splittings for the the helium configurations of larger l are given in Table VII. These configurations have δ_2 positive because the $J=l$ and $J=l+1$ states in the triplet structure have exchanged positions relative to the $3\,{}^3D$ structures.

The relative positions of the levels within the triplet structure change with n and l. The schematic diagrams of Figs. 1 and 2 are used to illustrate the relative positions of the states in the fine structure. The value of the energy difference $\delta_{\max}$ be-

TABLE VI. Comparison of theoretical and experimental results. Energy units are cm^{-1}.

	Theoret.						Expt.					
	$R_{10}+(U_0)_P+U_1$			Araki (Ref. 25)			Brochard *et al.* (Ref. 44)			Kaul (Ref. 45)		
n	$-\delta_1$	$-\delta_2$	$\frac{\delta_1}{\delta_2}$	$-\delta_1$	$-\delta_2$	$\frac{\delta_1}{\delta_2}$	$-\delta_1$	$-\delta_2$	$\frac{\delta_1}{\delta_2}$	$-\delta_1$	$-\delta_2$	$\frac{\delta_1}{\delta_2}$
3	0.0449	0.0042	10.8	0.0426	0.0025	17.0	0.0453 ± 0.001	0.0030 ±0.0008	15.1	0.044 271 ±0.000 04	0.002 425 ±0.000 03	18.2
4	0.0191	0.0020	9.6	0.0179	0.000 95	18.8	0.0187 ±0.001	0.0018 ±0.001	10.4			
5	0.0098	0.0011	9.1									
6	0.0057	0.000 64	8.9									
7	0.0036	0.000 41	8.8									
8	0.0024	0.000 28	8.7									
9	0.0017	0.000 20	8.6									
10	0.0012	0.000 14	8.6									

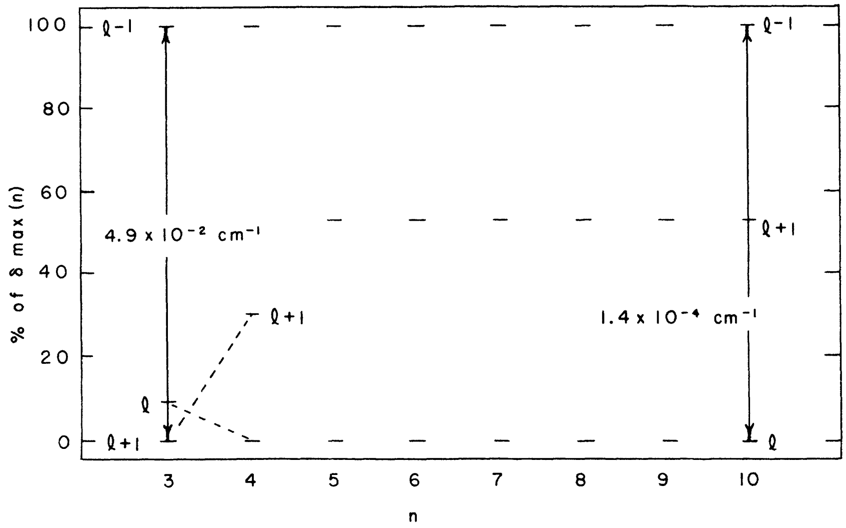

FIG. 2. Schematic triplet separation for (1*s*) (*n*, *n* − 1).

tween the highest and lowest energies of the triplet structure is given in the figures for the extreme values of *n*.

The relative positions of the levels in the triplet structures are almost independent of *n*, as expected.[4] This behavior is shown in Fig. 2. The relative splittings change more with l for $l < 4$, as seen from Fig. 2, in which the levels are shown for the $(1s)(n, n-1)$ configurations of helium. The completely inverted triplet structure of $3\,^3D$ changes for the states of higher angular momentum to one in which the $J = l$ level is lower than the $J = l + 1$ level. The change with l is due to the rapid decrease in K. When K becomes small compared to the spin-dependent interactions, the splitting ratio becomes independent of l and n. As Fig. 2 shows, this occurs for $l = 4$.

D. Admixture Coefficients

The coefficients determined by Eq. (75) for the wave functions corresponding to the $J = l \pm 1$ eigenvalues are not tabulated. The admixture of the singlet does not affect the simple relations of Eq. (75). In the notation of this paper, this corresponds to omitting the tabulation of the a^t_{k,M_S} coefficients for $k = 1$ and $k = 3$. For $k = 2$ and $k = 4$, the coefficients are affected by the admixture of the singlet, and Eq. (76) is no longer correct. The results for $k = 2$ ($J = l$ and $S = 1$) and for $k = 4$ ($J = l$ and $S = 0$) are given in Table VIII for a few typical configurations. Coefficients for configurations not shown may be obtained from the authors. The coefficients are not determined for $m_j = \pm(l+1)$, $\pm l$ because the basis set is not the same for these values of m_j. For example, if $m_j = l + 1$, the only member of the basis set which is defined is ϕ^t_1, Eq. (20). This requires that $\Psi_k(1, 2) = \phi^t_1$ when $m_j = l + 1$. The other values of m_j which are mentioned above also require treatment as special cases, but they are more complicated, since mixing is possible. These special cases are not considered in this work. The interest lies in the linear combinations of the four basis functions, and the cases for which all four states cannot be obtained are omitted. For large enough l, there is very little change in the coefficients with n; consequently, for $l \geq 5$, the coefficients are tabulated for $n = l + 1$, and these values are the same, to at least four decimal places, for the higher values of n. The singlet-triplet mixing parameter A varies very little with m_j over the range tabulated, so only the value calculated for

TABLE VII. Theoretical fine-structure results for larger l. Energy units are 10^{-3} cm^{-1}.

n	δ_1	δ_2	$\frac{\delta_1}{\delta_2}$	δ_1	δ_2	δ_s
	$(1s)\,(nf)$				$(1s)\,(ng)$	
4	−12.10	+3.45	−3.5			
5	−5.43	+0.99	−5.5	−5.276	+2.755	4.364
6	−2.98	+0.41	−7.3	−3.047	+1.588	2.449
7	−1.824	+0.204	−8.9	−1.916	+0.997	1.5455
8	−1.202	+0.116	−10.3	−1.282	+0.666	1.037
9	−0.835	+0.073	−11.5	−0.900	+0.467	0.729
10	−0.605	+0.049	−12.4	−0.655	+0.340	0.532
n	δ_1	δ_2	δ_s			
	$(1s)\,(nh)$				$(1s)\,(ni)$	
6	−1.990	1.042	1.653			
7	−1.253	+0.656	1.041	−0.881	+0.460	0.753
8	−0.840	+0.440	0.697	−0.590	+0.308	0.505
9	−0.590	+0.309	0.490	−0.414	+0.217	0.355
10	−0.430	+0.225	0.357	−0.302	+0.158	0.258
	$(1s)\,(nk)$				$(1s)\,(nl)$	
8	−0.437	+0.228	0.382			
9	−0.307	+0.160	0.268	−0.237	+0.123	0.210
10	−0.224	+0.117	0.196	−0.173	+0.090	0.153
	$(1s)\,(nm)$					
10	−0.137	+0.071	0.123			

TABLE VIII. Admixture coefficients.

k	m_j	a^t_{k1}	a^t_{k0}	a^t_{k-1}	a^s_k	A
			(1*s*) (3*d*)			
2	1	0.709 939	0.404 272	−0.576 650	0.004 998	
	0	0.712 401	0.009 339	−0.701 693	0.004 995	
	−1	0.569 357	−0.389 766	−0.723 802	0.005 009	
						0.0050
4	1	0.003 535	0.002 041	−0.002 886	−0.999 988	
	0	0.003 535	0.000 000	−0.003 535	−0.999 988	
	−1	0.002 886	−0.002 041	−0.003 535	−0.999 988	
			(1*s*) (4*d*)			
2	1	0.709 542	0.404 745	−0.576 817	0.003 635	
	0	0.711 705	−0.008 114	−0.702 422	0.003 633	
	−1	0.570 547	−0.392 866	−0.721 193	0.003 643	
						0.0036
4	1	0.002 571	0.001 484	−0.002 099	−0.999 993	
	0	0.002 571	0.000 000	−0.002 571	−0.999 993	
	−1	0.002 099	−0.001 484	−0.002 571	−0.999 993	
			(1*s*) (10*d*)			
2	1	0.709 216	0.405 131	−0.576 951	0.002 791	
	0	0.711 131	−0.007 111	−0.703 019	0.002 790	
	−1	0.571 487	−0.395 302	−0.719 118	0.002 797	
						0.0028
4	1	0.001 974	0.001 140	−0.001 612	−0.999 996	
	0	0.001 974	−0.000 000	−0.001 974	−0.999 996	
	−1	0.001 612	−0.001 140	−0.001 974	−0.999 996	
			(1*s*) (4*f*)			
2	2	0.591 518	0.529 875	−0.459 354	0.397 822	
	1	0.647 962	0.265 448	−0.592 822	0.397 800	
	0	0.647 803	0.001 256	−0.649 723	0.397 755	
	−1	0.590 912	−0.261 968	−0.651 228	0.397 616	
	−2	0.472 721	−0.596 872	−0.508 376	0.402 284	
						0.4335
4	2	0.256 885	0.229 805	−0.198 669	−0.917 459	
	1	0.281 405	0.114 925	−0.256 653	−0.197 460	
	0	0.281 406	0.000 044	−0.281 205	−0.917 461	
	−1	0.256 888	−0.114 838	−0.281 220	−0.917 462	
	−2	0.198 985	−0.229 721	−0.256 702	−0.917 463	
			(1*s*) (10*f*)			
2	2	0.630 622	0.568 395	−0.491 827	0.193 256	
	1	0.690 257	0.287 133	−0.635 420	0.193 236	
	0	0.688 848	0.007 827	−0.698 647	0.193 183	
	−1	0.619 040	−0.250 812	−0.718 858	0.192 674	
	−2	0.493 650	−0.579 062	−0.619 328	0.193 467	
						0.1969
4	2	0.124 776	0.111 606	−0.096 598	−0.981 144	
	1	0.136 685	0.055 805	−0.124 734	−0.981 144	
	0	0.136 685	0.055 805	−0.136 647	−0.981 145	
	−1	0.124 776	−0.055 797	−0.136 647	−0.981 145	
	−2	0.096 651	−0.111 599	−0.124 734	−0.981 145	
			(1*s*) (5*g*)			
2	3	0.426 670	0.483 933	−0.322 973	0.692 423	
	2	0.483 792	0.322 679	−0.427 062	0.692 416	
	1	0.509 953	0.161 435	−0.484 209	0.692 408	
	0	0.509 939	0.000 209	−0.510 443	0.692 394	
	−1	0.483 750	−0.160 985	−0.510 578	0.692 373	
	−2	0.426 592	−0.322 102	−0.484 713	0.692 331	
	−3	0.322 403	−0.482 950	−0.428 540	0.692 220	
						0.9596

TABLE VIII. *(Continued)*

k	m_j	a^t_{k1}	a^t_{k0}	a^t_{k-1}	a^s_k	A
			(1s) (5g)			
4	3	0.410154	0.465800	−0.306727	−0.721611	
	2	0.464965	0.310513	−0.408328	−0.721566	
	1	0.490068	0.155426	−0.463733	−0.721545	
	0	0.490041	0.000406	−0.489130	−0.721534	
	−1	0.464877	−0.154583	−0.489278	−0.721527	
	−2	0.409973	−0.309555	−0.464225	−0.721521	
	−3	0.309905	−0.464517	−0.409384	−0.721518	
			(1s) (10g)			
2	3	0.42874	0.48628	−0.32454	0.68875	
	2	0.48614	0.32425	−0.42914	0.68875	
	1	0.51243	0.16222	−0.48656	0.68874	
	0	0.51241	0.00021	−0.51293	0.68872	
	−1	0.48610	−0.16176	−0.51306	0.68870	
	−2	0.42866	−0.32366	−0.48708	0.68866	
	−3	0.32396	−0.48526	−0.43067	0.68854	
						0.94993
4	3	0.40796	0.46327	−0.30523	−0.72511	
	2	0.46249	0.30884	−0.40620	−0.72509	
	1	0.48746	0.15458	−0.46129	−0.72505	
	0	0.48743	0.00039	−0.48655	−0.72504	
	−1	0.46240	−0.15377	−0.48669	−0.72503	
	−2	0.40779	−0.30792	−0.46177	−0.72503	
	−3	0.30826	−0.46206	−0.40722	−0.72502	
			(1s) (nh)			
2	4	0.39305	0.52418	−0.29335	0.69620	
	3	0.45385	0.39317	−0.39338	0.69619	
	2	0.4901	0.26217	−0.45419	0.69619	
	1	0.50741	0.13117	−0.49057	0.69618	
	0	0.50740	0.00018	−0.50783	0.69617	
	−1	0.49018	−0.13079	−0.50791	0.69616	
	−2	0.45380	−0.26173	−0.49087	0.69614	
	−3	0.39297	−0.39259	−0.45486	0.69610	
	−4	0.29284	−0.52319	−0.39512	0.69599	
						0.96977
4	4	0.38173	0.50965	−0.28116	−0.71798	
	3	0.44068	0.38212	−0.37995	−0.71793	
	2	0.47595	0.25479	−0.43951	−0.71791	
	1	0.49263	0.12753	−0.47506	−0.71789	
	0	0.49261	0.00031	−0.49191	−0.71788	
	−1	0.47589	−0.12690	−0.49201	−0.71788	
	−2	0.44058	−0.25410	−0.47537	−0.71787	
	−3	0.38155	−0.38129	−0.44011	−0.71787	
	−4	0.28439	−0.50848	−0.38110	−0.71787	

$m_j = 0$ is given. It is A which is analyzed to obtain the n and l dependence of the singlet-triplet mixing.

The l dependence is easily obtained by noting the values of A in Table VIII. The amount of mixing is very small for $l = 2$, but it is significant for $l = 3$. The mixing is practically complete for all $l \geq 4$. These results are not surprising and agree qualitatively with previous work.[2,6–10] The quantitative agreement is not very good, however. Lin and St. John,[6] Kay and Hughes,[9] and Abrams and Wolga[10] all indicate that higher degrees of mixing may be present in the $4F$ states than are indicated by the results of this work. However, St. John and Nee[8] assumed complete singlet-triplet mixing in their work, but their conclusion that the $^3F_2$ and $^3F_4$ states do not actively receive excitation is definitely supported.

The n dependence of A is quite regular and is readily attributed to the relative variations with n of K and the spin-dependent interactions. Since K decreases more slowly than $\langle r_2^{-3} \rangle$ as n increases the degree of mixing decreases. This result is in disagreement with experimental results. Kay and Hughes[9] have found there should be a partial breakdown of Russell-Saunders coupling for $n=4$ and that the breakdown should be complete for $n=6$. The discrepancy cannot be explained by or attributed to the polarization correction, because the contributions from it have the same n dependence as the uncorrected values.

Table IX shows the effect on the admixture coefficients of using no corrections to the wave function. This table indicates that the coefficients are quite sensitive to the wave functions. The degree of mixing is increased, but this is to be expected since the correction terms increase K by a large percentage. The coefficients of the three triplet basis functions should still be approximately the same as the coefficients given by Eq. (76), especially for the $(1s)(3d)$ configuration. The rather abrupt departure from the pattern of Eq. (76) indicates the need for the correction terms in calculating the admixture coefficients.

IV. CONCLUSION

The most disappointing aspect of this work is the failure to obtain good results for the P states. The polarization correction gives large contributions to the exchange integrals, and its angular dependence allows nonvanishing values for P states for the exchange integral of H_0. This relatively large, negative exchange effect leads to very poor results for all P states.

The adiabatic approximation is probably a poor one for the $(1s)(np)$ configurations with small n when the outer electron is near the center of the atom,[46,47] but it can hardly be blamed for the similar failures with larger n. The disruptive effects must be attributed to the exchange terms involving the U_1 part (dipole) of the polarized orbital. This is similar to the conclusion of Oberoi and Callaway[47] that exchange effects due to the monopole part of the polarized orbital lead to poor results for the binding energies of H^-. This is consistent, since they were concerned with S states. Presumably, introduction of each 2^l-multipole term in the polarized orbital would lead to disruptive exchange effects for $(1s)(nl)$ states.

In the states with $l \geq 2$, the results are reasonable and allow comparison with experiment. Very good results are obtained for the triplet separations in the $3\,{}^3D$ and $4\,{}^3D$ levels, which are the only levels with experimental results available for comparison. Correction of some minor errors in an early paper leads to improvement in three of the four triplet separations, but these results seem somewhat fortuitous in view of the poor agreement for K. The poor results obtained for the coarse structure indicate that these wave functions do not give the correct values of K; however, the fine structure does not depend heavily on K for D states, and the good results for the fine structure indicate that the spin-dependent interactions are evaluated relatively accurately by the polarized orbital wave functions.

The results for the admixture coefficients, which determine the degree of singlet-triplet mixing, indicate that the n dependence of K or λ is not correct. While experiment shows that the mixing in-

TABLE IX. Admixture coefficients using no corrections, $Z=2$.

k	m_J	a^t_{k1}	a^t_{k0}	a^t_{k-1}	a^s_k	A
			$(1s)\ (3d)$			
2	1	0.428 22	0.735 95	−0.524 34	0.008 91	0.0063
	0	0.034 36	−0.619 32	0.784 36	−0.006 30	
	−1	0.724 38	−0.670 73	−0.159 24	0.005 97	
4	1	0.005 98	0.002 64	−0.246 80	−0.969 04	
	0	0.005 95	−0.001 07	−0.229 92	−0.973 19	
	−1	0.004 76	−0.004 74	−0.260 68	−0.965 40	
			$(1s)\ (4f)$			
2	2	0.662 63	0.453 12	−0.272 86	0.530 24	0.6151
	1	0.734 87	0.129 19	−0.400 27	0.532 03	
	0	0.736 10	−0.226 76	−0.363 67	0.523 91	
	−1	0.624 78	−0.623 38	−0.657 31	0.465 54	
	−2	0.151 40	−0.631 23	0.755 44	0.089 12	
4	2	0.242 16	0.149 12	−0.606 49	−0.742 49	
	1	0.277 06	0.041 27	−0.564 21	−0.776 66	
	0	0.281 03	−0.073 90	−0.541 81	−0.788 67	
	−1	0.258 09	−0.190 58	−0.516 18	−0.794 12	
	−2	0.200 21	−0.307 10	−0.481 92	−0.795 84	

creases with increasing n for the F states,[9] the results of this work show the opposite trend. The evaluation of the coarse- and fine-structure results would tend to place the responsibility for the faulty n dependence of the singlet-triplet mixing on K, although this has not been explicitly shown.

The qualitative behavior of the breakdown of Russell-Saunders coupling agrees generally with the ideas used in the multiple-state transfer mechanism.[2,5-10] The Russell-Saunders approximation is valid for the D states of helium, but there is significant breakdown for F states. For G states, mixing is almost complete, and the LS coupling scheme is no longer applicable.

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