

Spin Magnetic Effect on the Polarization of the Electron-Atom Impact Radiation

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A new mechanism is proposed to explain the discrepancies between the measured and the expected polarization of the electron-atom impact radiation at threshold energy. The idea is the following: At threshold scattering, the spin of the scattered electron interacts magnetically with the orbital motion of the atomic electrons. The component of this magnetic interaction along the quantization axis, which is perpendicular to the incident electron direction, will split the magnetic sublevels of the atomic excited states. This splitting will cause the coherent interference of the radiation, which originates from two degenerate upper levels and ends on a single lower level, to become ineffective. The polarization of the radiation is thereby affected and in fact decreases. The expected polarization P is modified by a depolarization factor $f = (1 + \langle \omega^2 \rangle_{av} \tau^2)^{-1}$, where ω is the frequency splitting of the excited state, and τ is the lifetime of the transition from the excited upper state to a lower state. By using a simple product wave function for the state, the ω and hence the P for various singlet-singlet transitions and triplet-triplet transitions have been calculated for the helium atom. In general, when the principal quantum number n of the excited state, where the radiation originates, increases, f also increases and approaches unity. Consequently, P increases and approaches the expected value. For example, P for the $3^1P \rightarrow 2^1S$ (5016 Å) line turns out to be 1.2%, whereas for the $4^1D \rightarrow 2^1P$ (4922 Å) line it turns out to be 50%. The expected values are 100% and 60%, respectively. In the case of triplet-triplet transitions, the spin-spin interaction between the scattered electron and the atomic electrons is also included.

1. INTRODUCTION

THERE has been increasing interest in the study of the polarization of light resulting from the excitation of an atom by the electron impact at threshold energy. This interest is specially centered on explaining the discrepancy between the theory^{1,2} and the experimental³⁻⁶ results. When a helium atom in the ground 1^1S state is excited to an n^1P state by electron impact at threshold energy, the outgoing electron, having no linear momentum and hence no angular momentum, can only be an S wave. Because of conservation of the total angular momentum along the incident electron direction (z' axis), only the magnetic sublevel $m_l=0$ of the n^1P state can be excited (see Fig. 1). Here m_l is the component of the electronic angular momentum l along the z' axis. The excited atom can then decay to the ground state by emitting π radiation ($\Delta m_l=0$ transition). The radiation is therefore 100% polarized along the z' axis. If the atom is excited into n^1D state and then decays into lower n'^1P state, the radiation

will be 60% polarized. When the atom has fine and hyperfine structure, the polarization will be further decreased.

Earlier experimental results^{7,8} indicated that the threshold polarization was zero but rose to a maximum within a fraction of a volt. Recent measurements³⁻⁵ on helium with improved techniques showed that except for $\lambda=4922$ Å ($4^1D \rightarrow 2^1P$) and $\lambda=4388$ Å ($5^1D \rightarrow 2^1P$) lines, the observed polarization in the immediate vicinity of threshold is still much too low to be comparable with the theoretical value. The most recent results of McFarland⁶ on $\lambda=4922$ Å line show that the dipping of the polarization to a threshold minimum of approximately 30% (expected value is 60%) is a real effect. The general indication from the experimental observations is that when radiation originates from an upper state of high n (principal quantum number), e.g., 5^1D , the threshold polarization is comparable to the theoretical value, whereas for a low n state, the polarization remains very low.

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¹ W. E. Lamb, *Phys. Rev.* **105**, 562 (1957); W. E. Lamb and T. H. Maiman, *ibid.* **105**, 573 (1957).

² I. C. Percival and M. J. Seaton, *Phil. Trans. Roy. Soc. (London)* **113**, 251 (1958).

³ R. H. McFarland, *Phys. Rev.* **133**, A986 (1964).

⁴ E. A. Soltysik, A. Y. Fournier, and R. L. Gray, *Phys. Rev.*, **153**, 152 (1957).

⁵ D. W. Heddle and R. G. W. Keesing, in *Proceedings of the Fourth International Conference on the Physics of the Electronic and Atomic Collisions, Quebec, 1965* (Science Bookcrafters, Inc., Hastings-on-Hudson, New York, 1965), p. 382; H. Hafner, H. Kleinpopper, and H. Krüger, *ibid.* p. 386.

⁶ R. H. McFarland, *Phys. Rev.* **156**, 55 (1967).

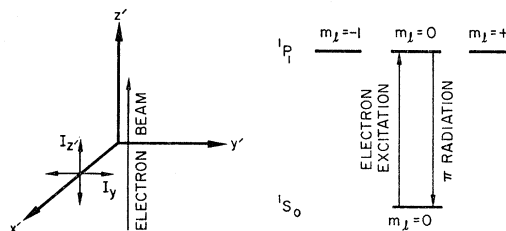


FIG. 1. The electron beam is incident along the z' axis. The polarization of the radiation is observed along the x' direction.

⁷ H. W. B. Skinner, *Proc. Roy. Soc. (London)* **A112**, 642 (1926).

⁸ H. W. B. Skinner and E. T. S. Appleyard, *Proc. Roy. Soc. (London)* **A117**, 224 (1927).

In the present work, a new theory is developed to explain the discrepancies between the expected polarizations, based on the simple conservation of angular momentum, and the experimental results. At threshold scattering, the scattered electron, having no momentum, remains very close to the excited atom, such that its spin can interact magnetically with the orbital motion of the atomic electrons. This interaction is rather similar to the spin-other-orbit interaction in an atomic system. The component of this magnetic interaction along the quantization axis (which is perpendicular to the incoming electron beam direction) will remove the degeneracy among the magnetic sublevels of the excited state, and cause level splittings. The splittings will then affect the interference part of the resonance radiation and hence the polarization of the radiation. In fact, the polarization P , for the case without fine and hyperfine structure, will be shown (in Sec. 2) to be equal to P_0 , which is the polarization from conservation of angular momentum, multiplied by a depolarization factor $f = (1 + \langle \omega^2 \rangle_{av} \tau^2)^{-1}$. The $\langle \omega^2 \rangle_{av}$ here is the square of the frequency separation between two interfering magnetic sublevels ν and $\nu \pm 2$ averaged over the spin orientations of the scattered electron, and τ is the lifetime for the excited state to decay to the lower state considered here. For the high n state of the excited helium, $\langle \omega^2 \rangle_{av}$ is approximately proportional to $[2n(2n-1)(2n-2)]^{-2}$ as will be shown in Sec. 4. Since all of the τ 's are roughly of the same order of magnitude, the depolarization factor f approaches 1 when n becomes large, say, $n \geq 5$, and consequently P approaches P_0 . For states of lower n , e.g., $n=2$ or 3 , $\langle \omega^2 \rangle_{av}$ is considerably larger than 1, so that both f and P are very small. The above conclusion seems to agree well with the general experimental observations.

When the energy of the bombarding electron is slightly above the threshold,⁹ i.e., a fraction of an elec-

tron volt, the selection rule $\Delta m_l = 0$ still holds to a good approximation, and P_0 remains quite close to its threshold value. However, the scattered electron may have gained enough linear momentum to get away from the atom, and hence to make the spin magnetic interaction and the frequency splitting ω insignificantly small. This would naturally cause a rise in P , which will then decrease as P_0 decreases, when the bombarding energy is increased further beyond its threshold value. This rise in P would only occur for cases where P is considerably smaller than P_0 at threshold energy.

The depolarization factor considered above is similar to that derived by Breit¹⁰ and later by Franken,¹¹ in their treatment of the polarization of the resonance fluorescence. There, the depolarization is due to a transverse magnetic field, which is perpendicular to the polarization vector of the incident light. This effect was first observed¹² at the crossing point of two excited fine-structure magnetic sublevels at a certain magnetic field. This level-crossing technique has later been applied to determine the zero-field level structure.¹³ The depolarization effect at the zero-field crossing is also called Hanle effect,¹⁴ which has been used to measure the excited state lifetimes.^{13,15-18}

The depolarization effect of the electron impact radiation at the threshold energy treated here is also magnetic in nature, and it can be looked upon as if due to an effective transverse magnetic field coming from the spin of the scattered electron. The general theory of this treatment will be developed in Sec. 2. The case with the fine and the hyperfine structure will be discussed in Sec. 3. The numerical results on helium will be presented in Sec. 4. In the case of the helium atom in a triplet state, the magnetic interaction between the spin of the scattered electron and the spins of the atomic electrons has also been considered.

2. GENERAL THEORY

First we consider the simple case where the atom has no fine and hyperfine structure, both in the ground and in the excited state. The atom is initially in the ground state a , 1^1S_0 , and is being excited to state b , n^1L_l , by electron impact along the z' axis (shown in Fig. 1). The z' component of the total angular momentum of the initial system is therefore zero, i.e., $M_{z'} = 0$. At threshold collision, the outgoing electron, having lost its linear momentum, has zero angular momentum and becomes a spherical wave centered at the atomic nucleus (origin

⁹ When the energy of the bombarding electron is slightly above the threshold, the scattered electron may still stay for a finite length of time in the vicinity of the excited atom. The depolarization of the collision light will depend on this finite collision time in comparison with the lifetime (due to radiative transition) of the state. The quantitative treatment of the case above threshold is beyond the scope of the present work. In qualitative discussions, there have been attempts to explain the low polarization by assuming that the atom goes into a quasibound (doubly excited) negative-ion state, which is assumed to have a sufficiently long life. However, in the case of helium, so far, all the observed and identified negative-ion states are below the threshold of the excitation of the excited states considered here. [See C. E. Kuyatt, J. A. Simpson, and S. R. Mielczarek, Phys. Rev. **138**, A385 (1965), and U. Fano and J. W. Cooper, *ibid.*, A400 (1965)]. Nevertheless, this idea of quasibound negative ions does not contradict the present theory. The fact that the scattered electrons seem to stay long enough (longer than the lifetime $\sim 10^{-8}$ sec of the excited states) to give rise to the magnetic effect to cause the observed low polarization suggests that they might be quasibound. At or immediately above the threshold of excitation, the scattered electron is or still approximates an S wave (with zero or very small linear momentum), which remains close to the excited atom and can be considered as a quasibound n 's electron of the atom. Since the excited helium atom has the configuration $(1s)(np)$ or $(1s)(nd)$, the whole system can then be looked upon as a doubly excited negative ion of configuration $(1s)(np)(n's)$ or $(1s)(nd)(n's)$.

¹⁰ G. Breit, Rev. Mod. Phys. **5**, 117 (1933).

¹¹ P. A. Franken, Phys. Rev. **121**, 508 (1961).

¹² F. D. Colegrove, P. A. Franken, R. R. Lewis, and R. H. Sands, Phys. Rev. Letters **3**, 420 (1959).

¹³ A. Lurio and R. Novick, Phys. Rev. **134**, A608 (1964).

¹⁴ W. Hanle, Z. Physik **30**, 93 (1924).

¹⁵ A. Landman and R. Novick, Phys. Rev. **134**, A56 (1964).

¹⁶ A. Lurio, R. L. deZafra, and R. J. Goshen, Phys. Rev. **134**, A1198 (1964).

¹⁷ D. K. Anderson, Phys. Rev. **137**, A21 (1965).

¹⁸ H. Henry Stoke, Phys. Today **19**, No. 10, 55 (1966).

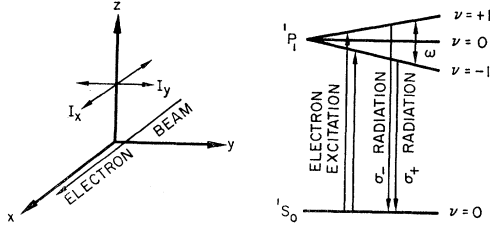


FIG. 2. The electron beam is incident along the x axis. The polarization of the radiation is observed along the z axis. When $\omega=0$, σ_- and σ_+ interfere coherently to give polarized I_x radiation. When ω increases, the above coherent interference between σ_+ and σ_- becomes ineffective.

of the system). Because of the conservation of $M_{z'}$, the atom can be excited to the magnetic sublevel $\phi_{l,0}(\mathbf{r}')$ only. The subscript 0 means $m_l=0$ and m_l is the z' component of the atomic angular momentum \mathbf{l} . Now we transform the coordinate system (\mathbf{r}') into the system (\mathbf{r}) by rotating (clockwise) $\frac{1}{2}\pi$ around the y' axis (see Fig. 2). The wave function $\phi_{l,0}(\mathbf{r}')$ is then transformed linearly into a set of wave functions $\phi_{l\nu}(\mathbf{r})$ as follows:

$$\begin{aligned} \phi_{l,0}(\mathbf{r}') &= \sum_{\nu} D_{\nu,0}^l(0, \frac{1}{2}\pi, 0) \phi_{l\nu}(\mathbf{r}) \\ &= [4\pi/(2l+1)]^{1/2} \sum_{\nu} Y_{l\nu}^*(\frac{1}{2}\pi, 0) \phi_{l\nu}(\mathbf{r}). \end{aligned} \quad (2.1)$$

In this rotated (\mathbf{r}) system, the electron is incident along the x axis. The subscript ν here is the projection of \mathbf{l} along the new z axis, and the magnetic sublevels $\phi_{l\nu}(\mathbf{r})$ with $\nu \neq 0$ as well as with $\nu=0$ can be populated. Including a time-dependent factor into (2.1), the time-dependent wave function of the excited state b is as follows:

$$(4\pi/2l+1)^{1/2} \sum_{\nu} Y_{l\nu}^*(\frac{1}{2}\pi, 0) \phi_{l\nu}(\mathbf{r}) \times \exp(-iE_{\nu}/\hbar - \frac{1}{2}\Gamma_{nl}t), \quad (2.2)$$

where E_{ν} is the energy of the sublevel ν . The quantity Γ_{nl} is the decay constant of state b , and is the reciprocal of the lifetime τ_{nl} , i.e., $\Gamma_{nl}=1/\tau_{nl}$. The state b then decays via electric-dipole transition into a lower state $c(n'l')$, which has a decay constant $\Gamma_{n'l'}$ and a set of magnetic sublevels μ . The instantaneous rate at which the radiation of polarization \mathbf{q} is emitted during the transition process is

$$\begin{aligned} R(\mathbf{q}, t) &= A \sum_{\mu} |\langle \sum_{\nu} Y_{l\nu}^*(\frac{1}{2}\pi, 0) \phi_{l\nu}(\mathbf{r}) e^{-i(E_{\nu}/\hbar + \Gamma_{nl}/2)t} \\ &\quad \times |\mathbf{q} \cdot \mathbf{r}| \phi_{l\nu\mu}(\mathbf{r}) e^{-i(E_{\mu}/\hbar + \Gamma_{n'l'}/2)t} \rangle|^2, \end{aligned} \quad (2.3)$$

where the proportionality constant A absorbs all the factors which are independent of the summation indices. Using the expression

$$q_{\nu\mu} = \langle \phi_{l\nu}(\mathbf{r}) | \mathbf{q} \cdot \mathbf{r} | \phi_{l\nu\mu}(\mathbf{r}) \rangle \quad (2.4)$$

for the electric-dipole transition matrix, (2.3) now reads

$$\begin{aligned} R(\mathbf{q}, t) &= A \sum_{\mu} \sum_{\nu} \sum_{\bar{\nu}} Y_{l\nu}(\frac{1}{2}\pi, 0) \\ &\quad \times Y_{l\bar{\nu}}^*(\frac{1}{2}\pi, 0) q_{\nu\mu} q_{\bar{\nu}\mu}^* e^{i(\omega_{\nu\bar{\nu}} - \Gamma_{ll'})t}, \end{aligned} \quad (2.5)$$

where

$$\omega_{\nu\bar{\nu}} = (E_{\nu} - E_{\bar{\nu}})/\hbar \quad \text{and} \quad \Gamma_{ll'} = \Gamma_{nl} + \Gamma_{n'l'}.$$

The indices $n, l, \nu, \bar{\nu}$ refer to the upper state b , and n', l', μ refer to the lower state c . Since the decay constant $\Gamma_{ll'}$ usually is large enough ($10^7 \sim 10^{10} \text{ sec}^{-1}$), an atom is excited to state b and then decays to lower state c by emitting a photon all in a time short compared with the time for this atom to be reexcited. We can then integrate Eq. (2.5) over time to obtain the rate $R(\mathbf{q})$:

$$\begin{aligned} R(\mathbf{q}) &= \int_0^{\infty} R(\mathbf{q}, t) dt \\ &= A\tau \sum_{\mu} \sum_{\nu} \sum_{\bar{\nu}} Y_{l\nu}(\frac{1}{2}\pi, 0) \\ &\quad \times Y_{l\bar{\nu}}^*(\frac{1}{2}\pi, 0) q_{\nu\mu} q_{\bar{\nu}\mu}^* (1 - i\tau\omega_{\nu\bar{\nu}})^{-1}, \end{aligned} \quad (2.6)$$

where

$$\tau = 1/\Gamma_{ll'} \quad (2.7)$$

is the lifetime of transition from state b to state c . Each term on the right-hand side of (2.6) will be nonvanishing only when

$$\nu = \bar{\nu}, \quad \bar{\nu} \pm 2. \quad (2.8)$$

Since

$$x_{\nu\mu} x_{\bar{\nu}\mu}^* = y_{\nu\mu} y_{\bar{\nu}\mu}^* \quad \text{when} \quad \nu = \bar{\nu}, \quad (2.9a)$$

and

$$x_{\nu\mu} x_{\bar{\nu}\mu}^* = -y_{\nu\mu} y_{\bar{\nu}\mu}^* \quad \text{when} \quad \nu = \bar{\nu} \pm 2, \quad (2.9b)$$

we can express $R(\mathbf{x})$ and $R(\mathbf{y})$ as follows:

$$R(\mathbf{x}) = R_0 + R_1, \quad (2.10a)$$

and

$$R(\mathbf{y}) = R_0 - R_1, \quad (2.10b)$$

where

$$R_0 = A\tau \sum_{\mu} \sum_{\nu} |Y_{l\nu}(\frac{1}{2}\pi, 0)|^2 |x_{\nu\mu}|^2, \quad (2.11)$$

and

$$\begin{aligned} R_1 &= 2A\tau \sum_{\mu} \sum_{\nu > \bar{\nu}} Y_{l\nu}(\frac{1}{2}\pi, 0) \\ &\quad \times Y_{l\bar{\nu}}^*(\frac{1}{2}\pi, 0) x_{\nu\mu} x_{\bar{\nu}\mu}^* (1 + \tau^2 \omega_{\nu\bar{\nu}}^2)^{-1}. \end{aligned} \quad (2.12a)$$

The Zeeman level splitting $\hbar\omega_{\nu\bar{\nu}} = E_{\nu} - E_{\bar{\nu}-2}$ is independent of the subscripts ν and $\bar{\nu}$; $\omega_{\nu\bar{\nu}}$ can therefore be replaced by ω , and (2.12a) becomes

$$R_1 = 2A\tau (1 + \tau^2 \omega^2)^{-1} \sum_{\mu} \sum_{\nu > \bar{\nu}} Y_{l\nu}(\frac{1}{2}\pi, 0) Y_{l\bar{\nu}}^*(\frac{1}{2}\pi, 0) x_{\nu\mu} x_{\bar{\nu}\mu}^*. \quad (2.12b)$$

The polarization, P , of the emitted radiation (observed along z axis) is as follows:

$$P = R(\mathbf{x}) - R(\mathbf{y}) / R(\mathbf{x}) + R(\mathbf{y}) = \frac{R_1}{R_0} = P_0 f, \quad (2.13)$$

where

$$P_0 = 2 \sum_{\mu} \sum_{\nu > \bar{\nu}} Y_{l\nu}(\frac{1}{2}\pi, 0) Y_{l\bar{\nu}}^*(\frac{1}{2}\pi, 0) x_{\nu\mu} x_{\bar{\nu}\mu}^* / \sum_{\mu} \sum_{\nu} |Y_{l\nu}(\frac{1}{2}\pi, 0)|^2 |x_{\nu\mu}|^2 \quad (2.14)$$

is the expected polarization by considering the conservation of angular momentum only, and

$$f = (1 + \tau^2 \omega^2)^{-1} \quad (2.15)$$

is the depolarization factor. When the state b is degenerate, i.e., $\omega = 0$, P is equal to its maximum value P_0 . It decreases because of the factor f when the Zeeman splitting (with respect to the new z axis), ω , becomes nonzero. If $\tau^2 \omega^2 \gg 1$, then $P \rightarrow 0$, and the emitted radiation is unpolarized. The above electric-dipole matrix element $x_{\nu\mu}$ need not be evaluated. Since¹⁹

$$r_{\pm} = \mp (1/\sqrt{2})(x \pm iy) \quad \text{or} \quad x = -(1/\sqrt{2})(r_{+} - r_{-}), \quad (2.16)$$

we have²⁰

$$x_{\nu\mu} = -(1/\sqrt{2})[(l'1l; \mu 1\nu) - (l'1l; \mu, -1, \nu)](l||r||l'). \quad (2.17)$$

The reduced matrix element $(l||r||l')$ will be cancelled in (2.14), and only Clebsch-Gordan coefficients $(l'1l; \mu, \pm 1, \nu)$ will remain in the expression for P_0 and P .

R_1 as shown in (2.12), arising from the decay of two upper Zeeman levels ν and $\bar{\nu}$ into a single lower level μ , represents the interference part of the radiation, and which appears to be most effective when ν and $\bar{\nu}$ are degenerate (interfering coherently). But in the case of degeneracy, this interference cannot be regarded as the true interference. The magnetic sublevels $\phi_{l,\nu}(\mathbf{r})$ in this case can always be combined linearly and transformed back into a single level $\phi_{l,0}(\mathbf{r}')$ [for this was the only populated level in the original (\mathbf{r}') system] by rotating the coordinate system (\mathbf{r}) back to (\mathbf{r}'). Naturally, no interference can arise when only a single upper level is populated.

Let us concentrate our attention again on this rotated (\mathbf{r}) system, which is assumed free from the external transverse magnetic field (which is parallel to the z axis and perpendicular to the incident electron beam), that causes Zeeman splitting. A field which is parallel to the electron beam direction (x axis) will obviously have no effect on the polarization P , because it does not remove the degeneracy among the magnetic sublevels ν (which are quantized with respect to the z axis). The energy separation $\Delta E_{\nu\bar{\nu}} = \hbar\omega_{\nu\bar{\nu}}$, here is considered to raise out of the magnetic interaction between the spin of the scattered electron and the orbital motion of the atomic

electron. (The spin-spin interaction will be considered in Sec. 4.) At threshold scattering, the outgoing electron, having lost its momentum, becomes a stationary spherical wave about the origin which is also the center of the atom. The excited atom consists of a shielded nuclear core and an outer electron in the atomic shell (nl). The scattered electron is electron 1 with coordinate \mathbf{r}_1 and spin \mathbf{s}_1 . The excited atomic electron is electron 2 with coordinate \mathbf{r}_2 , and its linear and angular momenta are \mathbf{p}_2 and $\mathbf{l}_2 (= \mathbf{l})$, respectively. The vector potential \mathbf{A} at electron 2 due to the spin magnetic moment, \mathbf{u}_s , of the electron 1 is

$$\mathbf{A} = (\mathbf{u}_s \times \mathbf{r}_{12}) / r_{12}^3, \quad (2.18)$$

where $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$. The interaction Hamiltonian of \mathbf{p}_2 with potential \mathbf{A} is,

$$H = (e/mc) \mathbf{A} \cdot \mathbf{p}_2 = (e/mc) (\mathbf{u}_s \cdot \mathbf{r}_{12} \times \mathbf{p}_2) / r_{12}^3, \quad (2.19)$$

where e and m are the electron charge and the electron mass respectively, and c is the velocity of light. Since

$$\mathbf{u}_s = g_s \mu_0 \mathbf{s}_1 = 2\mu_0 \mathbf{s}_1, \quad (2.20)$$

where $\mu_0 = e\hbar/2mc$ is the Bohr magneton, we express (2.19) in atomic units as follows:

$$\mathcal{H}C = \alpha^2 (\mathbf{s}_1 \cdot \mathbf{r}_{12} \times \mathbf{p}_2) / r_{12}^3. \quad (2.21)$$

The fine-structure constant $\alpha = e^2/\hbar c$ is a dimensionless quantity. Equation (2.21) resembles the spin-other-orbit interaction between two electrons. The difference is that the interaction between \mathbf{s}_2 and \mathbf{p}_1 is not present here. Now we take the expectation value of $\mathcal{H}C$ over the product wave function of electron 1 and electron 2 where s_{1z} and l_{2z} are quantized with eigenvalues σ and ν , respectively.

$$\langle \mathcal{H}C \rangle = \alpha^2 \sigma \langle u(\mathbf{r}_1) \phi(\mathbf{r}_2) | (\mathbf{r}_{12} \times \mathbf{p}_2)_z / r_{12}^3 | u(\mathbf{r}_1) \phi(\mathbf{r}_2) \rangle. \quad (2.22)$$

$u(\mathbf{r}_1)$ and $\phi(\mathbf{r}_2)$ are the electronic wave functions of electrons 1 and 2. $u(\mathbf{r}_1)$ is a radial wave function only, because the scattered electron is an S wave (at threshold scattering).

Using the relation $\mathbf{p} = -i\nabla$, we express the operator in (2.22) as follows:

$$\frac{1}{r_{12}^3} (\mathbf{r}_{12} \times \mathbf{p}_2)_z = \left(\frac{4}{3}\pi\right)^{1/2} \times \left[\frac{Y_{1,-1}(\mathbf{r}_{12})}{r_{12}^2} \nabla_2^{(1)} - \frac{Y_{1,1}(\mathbf{r}_{12})}{r_{12}^2} \nabla_2^{(-1)} \right], \quad (2.23)$$

where

$$\nabla_2^{(\pm 1)} = \mp \frac{1}{\sqrt{2}} \left(\frac{\partial}{\partial x_2} \pm i \frac{\partial}{\partial y_2} \right) \quad \text{and} \quad \nabla_2^{(0)} = \partial / \partial z_2 \quad (2.24)$$

are the spherical components of a gradient operator, and $Y_{1,\pm 1}(\mathbf{r}_{12})/r_{12}^2$ is the irregular solid spherical harmonics of the first order and it can be expanded as

¹⁹ r_{+1} , r_{-1} , and r_0 are the components of an unitary spherical vector \mathbf{r} .

²⁰ M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1961).

follows^{21,22}:

For $r_2 > r_1$,

$$\frac{Y_{1\pm 1}(\mathbf{r}_{12})}{r_{12}^2} = \sum_{l=1}^{\infty} \sum_{m=-l}^l (-)^l \left[\frac{4\pi(2l)!}{2(2l-1)!} \right]^{1/2} \times (l-1, l, 1; \pm 1-m, m, \pm 1) \frac{r_1^{l-1}}{r_2^{l+1}} \times Y_{l-1, \pm 1-m}(\mathbf{r}_1) Y_{l,m}(\mathbf{r}_2), \quad (2.25a)$$

$$\frac{Y_{1\pm 1}(\mathbf{r}_{12})}{r_{12}^2} = \sum_{l=1}^{\infty} \sum_{m=-l}^l (-)^{l+1} \left[\frac{4\pi(2l)!}{2(2l-1)!} \right]^{1/2} \times (l-1, l, 1; \pm 1-m, m, \pm 1) \frac{r_2^{l-1}}{r_1^{l+1}} \times Y_{l-1, \pm 1-m}(\mathbf{r}_2) Y_{l,m}(\mathbf{r}_1). \quad (2.25b)$$

Now we use (2.25) to expand the operator in (2.23), which is then multiplied by $|u(\mathbf{r}_1)|^2$ and integrated over the volume element $d\mathbf{r}_1$ of electron 1. Since $u(\mathbf{r}_1)$ is independent of angle, only the $l=1$ term in the expansion (2.25a) for the case of $r_1 < r_2$ will contribute to the integral. We therefore have

$$\int |u(\mathbf{r}_1)|^2 \frac{(\mathbf{r}_{12} \times \mathbf{p}_2)_z}{r_{12}^3} d\mathbf{r}_1 = \left(\frac{4}{3}\pi \right)^{1/2} f(r_2) \left[\frac{Y_{1,-1}(\mathbf{r}_2)}{r_2^2} \nabla_2^{(1)} - \frac{Y_{1,+1}(\mathbf{r}_2)}{r_2^2} \nabla_2^{(-1)} \right] = f(r_2) (1/r_2^3) (\mathbf{r}_2 \times \mathbf{p}_2)_z = f(r_2) (1/r_2^3) l_{2z}, \quad (2.26)$$

where

$$f(r_2) = -4\pi \int_0^{r_2} |u(\mathbf{r}_1)|^2 r_1^2 dr_1. \quad (2.27)$$

Using (2.26), the two-electron integral,

$$I = \langle \phi(\mathbf{r}_2) u(\mathbf{r}_1) | (\mathbf{r}_{12} \times \mathbf{p}_2)_z / r_{12}^3 | \phi(\mathbf{r}_2) u(\mathbf{r}_1) \rangle = \langle \phi(\mathbf{r}_2) | f(r_2) (1/r_2^3) l_{2z} | \phi(\mathbf{r}_2) \rangle = \nu Q, \quad (2.28)$$

becomes a one-electron integral,²³ where ν is the eigenvalue of l_{2z} , and

$$Q = \langle \phi(\mathbf{r}_2) | f(r_2) (1/r_2^3) | \phi(\mathbf{r}_2) \rangle. \quad (2.29)$$

The expectation value of \mathcal{H} now becomes,

$$\langle \mathcal{H} \rangle = \alpha^2 \sigma \nu Q. \quad (2.30)$$

²¹ L. Y. Chow Chiu, Phys. Rev. **137**, A385 (1965).

²² Y. N. Chiu, J. Math. Phys. **5**, 283 (1964).

and for $r_1 > r_2$

²³ The operator, $\alpha^2 \sigma f(r_2) (1/r_2^3) l_{2z}$, which appears in (2.28), can be considered as an effective perturbation, on the electronic orbital motion of the atom, by the scattered electron. The perturbation on the electron spin of the atom (spin-spin interaction) is zero for the atom in the singlet state. When the helium atom is in the triplet state, this spin-spin interaction will be considered in Sec. 4.

The frequency separation (in atomic units) between sublevels ν and $\nu' (= \nu - 2)$ is

$$\omega = \Delta E_{\nu, \nu-2} = 2\alpha^2 \sigma Q. \quad (2.31)$$

Since σ is the eigenvalue of s_{1z} , it can take the value of $+\frac{1}{2}$ or $-\frac{1}{2}$, depending on the orientation of \mathbf{s}_1 with respect to the z axis. However, $\sigma^2 (= \frac{1}{4})$ is the same for both cases, which then stands for the average values, $\langle \sigma^2 \rangle_{av}$, over the orientations. Using $\langle \sigma^2 \rangle_{av} = \frac{1}{4}$, we have

$$\langle \omega^2 \rangle_{av} \tau^2 = \alpha^4 Q^2 \tau^2 \quad (2.32)$$

and

$$P = P_0 (1 + \alpha^4 Q^2 \tau^2)^{-1}. \quad (2.33)$$

Now the remaining job is to evaluate Q which is defined in (2.29). Q can be readily integrated when

$$f(r_2) = -4\pi \int_0^{r_2} |u(\mathbf{r}_1)|^2 r_1^2 dr_1 \quad (2.27)$$

is known. Here $|u(\mathbf{r}_1)|^2$, the density of the scattered electron 1, is fortunately needed only in the region $0 \leq r_1 \leq r_2$. In this region, $u(\mathbf{r}_1)$ is an S wave (stationary, with zero linear momentum) outside a shielded nuclear core of $+1$ charge, and to a good approximation it can be written as,⁹

$$u(\mathbf{r}_1) = (1/\sqrt{\pi}) e^{-r_1}, \quad (2.34)$$

where $1/\sqrt{\pi}$ is the normalization constant. Substituting (2.34) into (2.27) we have

$$f(r_2) = e^{-2r_2} (2r_2^2 + 2r_2 + 1) - 1. \quad (2.35)$$

The above equation, of course, would not be valid in region $r_1 > r_2$.

3. EFFECT OF FINE AND HYPERFINE STRUCTURE

Following the discussion in the last section, the atom, which is initially in the ground state a with zero orbital angular momentum (S state), can only be excited to $m_l=0$ sublevel of the excited state b (which has principal quantum number n and orbital angular momentum l) by electron impact along the quantization z' axis at threshold energy. Now the state b has a total electronic spin \mathbf{s} , hence there exists fine-structure interaction. The good quantum numbers in this case are j and m_j , where $\mathbf{j} (= \mathbf{l} + \mathbf{s})$ is the total electronic angular momentum and m_j is the projection of \mathbf{j} along the z' axis. In (j, m_j) representation, state b is as follows²⁴:

$$\begin{aligned} \phi_b(\mathbf{r}') &= \sum_{m_s} \phi_{l,0}(\mathbf{r}') \chi_{sm_s} \\ &= \sum_{j m_j} (l s j; 0 m_s m_j) \phi_{j m_j}(\mathbf{r}'), \end{aligned} \quad (3.1)$$

where the Clebsch-Gordan coefficient $(l s j; 0 m_s m_j)$ is the weighting factor for each fine-structure sublevel

²⁴ The states with $m_s = 1, 0, -1$ are taken to be of the same amplitude and phase.

ϕ_{jm_j} , m_s is the projection of \mathbf{s} along the z' axis, and the relation δ_{m_s, m_j} is implied. We again rotate (clockwise) the coordinate system (\mathbf{r}') $\frac{1}{2}\pi$ around the y' axis into the new system (\mathbf{r}) , and $\phi_{jm_j}(\mathbf{r}')$ is transformed into a linear combination of $\phi_{j\nu}(\mathbf{r})$. The subscript ν is the projection of \mathbf{j} along the new z axis. Equation (3.1) now becomes

$$\phi_b(\mathbf{r}') = \sum_{j\nu} G(j\nu)\phi_{j\nu}(\mathbf{r}), \quad (3.2)$$

where²⁵

$$G(j\nu) = \sum_{m_s} (lsj; 0m_s m_s) D_{\nu m_s}^j(0, \frac{1}{2}\pi, 0). \quad (3.3)$$

The time-dependent wave function of state b is

$$\phi_b(\mathbf{r}, t) = \sum_{j\nu} G(j\nu)\phi_{j\nu}(\mathbf{r}) \exp[-(iE_{j\nu}/\hbar + \Gamma_{nl}/2)t], \quad (3.4)$$

and the rate of transition from state b to a lower state c [which has principal quantum number n , orbital angular momentum l' and fine-structure sublevels $(j'\mu)$] by emitting radiation of polarization \mathbf{q} is [c.f. Eq. (2.6)]

$$R(\mathbf{q}) = A\tau \sum_{jj'} \sum_{\nu\bar{\nu}} \sum_{j'\mu} G^*(j\nu)G(j\bar{\nu}) \times q(j\nu; j'\mu)q^*(j\bar{\nu}; j'\mu)[1 - i\tau\omega(j\nu; j\bar{\nu})]^{-1}, \quad (3.5)$$

where

$$q(j\nu; j'\mu) = \langle \phi_{j\nu}(\mathbf{r}) | \mathbf{q} \cdot \mathbf{r} | \phi_{j'\mu}(\mathbf{r}) \rangle, \quad (3.6)$$

and

$$\omega(j\nu; j\bar{\nu}) = (E_{j\nu} - E_{j\bar{\nu}})/\hbar. \quad (3.7)$$

The lifetime τ of transition between states l and l' [which is defined in (2.7)] is independent of j and j' . A is a proportionality constant which is independent of all the summation indices. Here the quantum numbers $l, j, \nu, \bar{j}, \bar{\nu}$ belong to the upper state b , and l', j', μ belong to the lower state c . We again split $R(\mathbf{q})$ into a linear combination of an interfering part R_1 and a noninterfering part R_0 such that

$$R(\mathbf{x}) = R_0 + R_1 \quad \text{and} \quad R(\mathbf{y}) = R_0 - R_1. \quad (3.8)$$

R_0 and R_1 have the following expressions:

$$R_0 = A\tau \sum_{jj'} R_0(jj'), \quad (3.9)$$

where

$$R_0(jj') = \sum_{\nu\mu} |G(j\nu)|^2 |x(j\nu; j'\mu)|^2 \quad (3.10)$$

²⁵ The rotation matrix $D_{m_s m_j}^j(0, \beta, 0)$ equals the reduced matrix $d_{m_s m_j}^j(\beta)$ which is real. Wigner's general expression for $d_{m_s m_j}^j(\beta)$ can be found in page 52 of Ref. 20. However, the simple formulas for $j=1$ and 2 can be found in D. M. Brink and G. R. Satchler, *Angular Momentum* (Clarendon Press, Oxford, 1962), p. 24. The formulas for $j=3$ has just been listed in Y. N. Chiu, *J. Chem. Phys.* 45, 2985 (1966).

and

$$R_1 = 2A\tau \sum_{j'\mu} \sum_{j\nu > j\bar{\nu}} G^*(j\nu)G(j\bar{\nu})x(j\nu; j'\mu) \times x^*(j\bar{\nu}; j'\mu)[1 + \tau^2\omega^2(j\nu; j\bar{\nu})]^{-1}. \quad (3.11)$$

Since the fine-structure separations are usually large enough that

$$\tau^2\omega^2(j\nu; j\bar{\nu}) \gg 1 \quad \text{for } j \neq \bar{j}, \quad (3.12)$$

we can neglect the terms of $j \neq \bar{j}$ in (3.11) and rewrite R_1 as follows:

$$R_1 \approx A\tau \sum_{jj'} R_1(jj') \quad (3.13)$$

and

$$R_1(jj') = 2(1 + \tau^2\omega_j^2)^{-1} \sum_{\mu} \sum_{\nu > \bar{\nu}} G^*(j\nu)G(j\bar{\nu}) \times x(j\nu; j'\mu)x^*(j\bar{\nu}; j'\mu), \quad (3.14)$$

where

$$\omega_j = (E_{j\nu} - E_{j\bar{\nu}})/\hbar \quad (3.15)$$

is independent of ν . The polarization of the radiation is therefore

$$P = [R(\mathbf{x}) - R(\mathbf{y})]/[R(\mathbf{x}) + R(\mathbf{y})] = R_1/R_0 = \sum_{jj'} R_1(jj')/\sum_{jj'} R_0(jj'). \quad (3.16)$$

In the above expression for P , we have included the radiation arising from all of the allowed transitions between the fine-structure levels j of the upper state b and the levels j' of the lower state c . When each fine-structure line, e.g., radiation due to a single upper level j to a single lower level j' can be resolved, the polarization $P(jj')$ of each line is expressed as follows:

$$P(jj') = R_1(jj')/R_0(jj') = P_0(jj')f_j, \quad (3.17)$$

where

$$f_j = (1 + \tau^2\omega_j^2)^{-1} \quad (3.18)$$

and

$$P_0(jj') = 2[R_0(jj')]^{-1} \sum_{\mu} \sum_{\nu > \bar{\nu}} G^*(j\nu)G(j\bar{\nu}) \times x(j\nu; j'\mu)x^*(j\bar{\nu}; j'\mu). \quad (3.19)$$

$R_0(jj')$ is defined in (3.10).

When the nuclear spin of the atom is nonzero, $\mathbf{i} \neq 0$, a hyperfine-structure interaction exists. The excited state b is then a linear combination of eigenstates $\phi_{f m_f}(\mathbf{r}')$, where $\mathbf{f} (= \mathbf{i} + \mathbf{j})$ is the total angular momentum of the atom and m_f is the projection of \mathbf{f} along the z' axis. After the coordinate system (\mathbf{r}') has been rotated into the (\mathbf{r}) system by a rotation of $\frac{1}{2}\pi$ around the y' axis, we have

$$\phi_b(\mathbf{r}') = \sum_{j'f\nu} G(j'f\nu)\phi_{j'f\nu}(\mathbf{r}), \quad (3.20)$$

where

$$G(jf\nu) = \sum_{m_f} \sum_{m_s} (jif; m_s m_i m_f) \times (lsj; 0 m_s m_a) D_{vmf'}(0, \frac{1}{2}\pi, 0). \quad (3.21)$$

ν here now is the projection of the \mathbf{f} along the new z axis. The rate of radiation $R(\mathbf{q})$ is again split into a linear combination of R_0 and R_1 , such that

$$R(\mathbf{x}) = R_0 + R_1 \quad \text{and} \quad R(\mathbf{y}) = R_0 - R_1 \quad (3.22)$$

and

$$\text{polarization } P = R_1/R_0. \quad (3.23)$$

R_0 and R_1 are expressed as follows:

$$R_0 = A\tau \sum_{jj'} \sum_{ff'} \sum_{\nu\mu} |G(jf\nu)|^2 |x(jf\nu; j'f'\mu)|^2 \quad (3.24)$$

and

$$R_1 = A\tau \sum_{jj'} \sum_{ff'} \sum_{\nu>\bar{\nu}} 2G^*(jf\nu)G(j\bar{j}\bar{\nu})x(jf\nu; j'f'\mu) \times x^*(j\bar{j}\bar{\nu}; j'f'\mu) [1 + \tau^2 \omega_j^2(f\nu; \bar{j}\bar{\nu})]^{-1}, \quad (3.25)$$

where

$$x(jf\nu; j'f'\mu) = \langle \phi_{jf\nu}(\mathbf{r}) | x | \phi_{j'f'\mu}(\mathbf{r}) \rangle \quad (3.26)$$

and

$$\omega_j(f\nu; \bar{j}\bar{\nu}) = (E_{jf\nu} - E_{j\bar{j}\bar{\nu}})/\hbar. \quad (3.27)$$

In the above equations, the quantum numbers $j, f, \bar{j}, \nu, \bar{\nu}$ belong to the upper state b and the quantum numbers j', f', μ belong to the lower state c . The lifetime τ is the same as defined in (2.7). In writing down the expression for R_1 in (3.25), we have assumed that the frequency splitting between the fine-structure level j and the level $\bar{j} \neq j$ is large, so that the terms of $j \neq \bar{j}$ have been neglected. If the hyperfine splitting is also large that

$$\tau^2 \omega_j^2(f\nu; \bar{j}\bar{\nu}) \gg 1 \quad \text{for } f \neq \bar{j}, \quad (3.28)$$

then

$$R_1 = A\tau \sum_{if} 2(1 + \tau^2 \omega_{if}^2) \left[\sum_{j'f'\mu} \sum_{\nu>\bar{\nu}} G^*(jf\nu)G(j\bar{j}\bar{\nu}) \times x(jf\nu; j'f'\mu)x^*(j\bar{j}\bar{\nu}; j'f'\mu) \right], \quad (3.29)$$

where

$$\omega_{if} = (E_{if\nu} - E_{i\bar{j}\bar{\nu}})/\hbar. \quad (3.30)$$

Similar to the dipole matrix element $x_{\nu\mu}$ in the last section (Eq. 2.17), the matrix elements $x(j\nu; j'\mu)$ and $x(jf\nu; j'f'\mu)$ can also be expressed in terms of the reduced matrix element ($l||\mathbf{r}||l'$) as follows²⁰:

$$x(j\nu; j'\mu) = (1/\sqrt{2})(-)^{s-l-j} [(j'1j; \mu 1\nu) - (j'1j; \mu, -1, \nu)] [(2l+1)(2j'+1)]^{1/2} \times W(l'j'lj; s1)(l||\mathbf{r}||l') \quad (3.31)$$

and

$$x(jf\nu; j'f'\mu) = -(1/\sqrt{2})(-)^{i+s-l'-j-i-f} \times [(f'1f; \mu 1\nu) - (f'1f; \mu, -1, \nu)] \times [(2l+1)(2j+1)(2j'+1)(2f'+1)]^{1/2} \times W(j'f'jf; i1)W(l'j'lj; s1)(l||\mathbf{r}||l'), \quad (3.32)$$

where $W(abcd; ef)$ is the Racah coefficient,²⁶ \mathbf{l} and \mathbf{l}' are the orbital angular momenta of the excited upper state b and the lower state c , respectively. The reduced matrix element will be cancelled in the ratio in evaluating the polarization P , and only the Racah and Clebsch-Gordan coefficients will remain.

4. NUMERICAL VALUES FOR He ATOM

A helium atom at the ground 1^1S_0 state can be excited into either a singlet excited state n^1L_l or a triplet excited state n^3L_j . In the case of a singlet state,²⁷ we need to calculate the frequency splitting $\omega = 2\alpha^2\sigma Q$ of Eq. (2.31). The integral Q which is defined in (2.29) has the following expression:

$$Q_n = \langle \phi_{nl}(\mathbf{r}_2) | f(\mathbf{r}_2)(1/r_2^3) | \phi_{nl}(\mathbf{r}_2) \rangle, \quad (4.1)$$

where $f(\mathbf{r}_2)$ is shown in (2.35), and $\phi_{nl}(\mathbf{r}_2)$ is the wave function for the outer excited electron 2 of the helium. The inner (unexcited) electron, which remains in the $1s$ orbital, does not contribute to the frequency splitting ω . We use the following approximate wave function for $\phi_{nl}(\mathbf{r}_2)$:

$$\phi_{nl}(\mathbf{r}_2) = (2n!)^{-1/2} (2\zeta)^{n+1/2} r_2^{n-1} e^{-\zeta r_2} Y_{lm}(\theta_2, \varphi_2). \quad (4.2)$$

The ζ values are chosen by Slater's rules.²⁸ We will calculate the polarization of the following transitions:

$$\begin{aligned} 2^1P \rightarrow 1^1S, \quad 3^1P \rightarrow 2^1S, \quad 3^1D \rightarrow 2^1P, \\ 4^1D \rightarrow 2^1P, \quad \text{and} \quad 5^1D \rightarrow 2^1P. \end{aligned} \quad (4.3)$$

The chosen ζ values for the corresponding upper state of the above transitions are, for He,

$$\begin{aligned} \zeta(2p) = 0.575, \quad \zeta(3p) = 0.333, \quad \zeta(3d) = 0.333, \\ \zeta(4d) = 0.270, \quad \text{and} \quad \zeta(5d) = 0.250. \end{aligned} \quad (4.4)$$

Using the wave function in (4.2) and the expression in (2.35) for $f(\mathbf{r}_2)$, integral Q_n in (4.1) is integrated to give the following:

$$Q_n = - \frac{(2\zeta)^{2n+1}}{2n(2n-1)(2n-2)} \left\{ \frac{1}{(2\zeta)^{2n-2}} \frac{2(2n-1)(2n-2)}{(2\zeta+2)^{2n}} - \frac{2(2n-2)}{(2\zeta+2)^{2n-1}} \frac{1}{(2\zeta+2)^{2n-2}} \right\}. \quad (4.5)$$

The values of Q_n for all the above-mentioned excited states are calculated and listed in Table I. The depolar-

²⁶ L. C. Biedenharn, J. M. Blatt, and M. E. Rose, Rev. Mod. Phys. **24**, 249 (1952); A. Simon, J. H. Vandersluij, and L. C. Biedenharn, Oak Ridge National Laboratory Report No. ORNL-1679, 1954 (unpublished).

²⁷ If we use a symmetrical wave function, $(\frac{1}{2})^{1/2} [\phi_{nl}(\mathbf{r}_2)\phi_{1s}(\mathbf{r}_3) + \phi_{nl}(\mathbf{r}_3)\phi_{1s}(\mathbf{r}_2)]$, for the singlet state of the helium atom (which has electrons 2 and 3), the effective operator $\alpha^2\sigma f(\mathbf{r}_2)(1/r_2^3)l_{2z}$ (see Ref. 23) should be replaced by $\alpha^2\sigma [f(\mathbf{r}_2)(1/r_2^3)l_{2z} + f(\mathbf{r}_3)(1/r_3^3)l_{3z}]$, but the final results will be the same.

²⁸ J. C. Slater, Phys. Rev. **36**, 57 (1930).

TABLE I. Polarization of the e -He impact radiation at threshold energy, singlet-singlet transitions.^a

Transition	Wavelength (Å)	$\tau(10^{-9}$ sec)	$-Q_n(10^{-3}$ a.u.)	$\langle\omega^2\rangle_{\text{av}}\tau^2$	$f=(1+\langle\omega^2\rangle_{\text{av}}\tau^2)^{-1}$	P_0 (%)	P (%)
$2^1P \rightarrow 1^1S$	584	0.427	63.4	3.54×10^3	2.8×10^{-4}	100	0.03
$3^1P \rightarrow 2^1S$	5016	1.739	2.37	8.23×10	1.2×10^{-2}	100	1.2
$3^1D \rightarrow 2^1P$	6678	0.415	2.37	4.69	1.7×10^{-1}	60	10.5
$4^1D \rightarrow 2^1P$	4922	0.424	0.468	1.91×10^{-1}	8.4×10^{-1}	60	50
$5^1D \rightarrow 2^1P$	4388	0.426	0.174	2.65×10^{-2}	9.7×10^{-1}	60	58

^a τ (sec) here is to be converted into τ (a.u.). In computing f , ω and τ both should be in atomic units. Unit of time (τ) = \hbar^3/me^4 and unit of frequency (ω) = me^4/\hbar^3 . $\langle\omega^2\rangle_{\text{av}} = \alpha^4 Q_n^2$. The values for τ here are those of Ref. 27.

ization factor f ,

$$f = (1 + \langle\omega^2\rangle_{\text{av}}\tau^2)^{-1} = (1 + \alpha^4 Q_n^2 \tau^2)^{-1} \quad (4.6)$$

as well as the polarization P from (2.33),

$$P = P_0 f = P_0 (1 + \alpha^4 Q_n^2 \tau^2)^{-1} \quad (4.7)$$

are thus obtained and listed in Table I. P_0 , which is the threshold polarization by conservation of angular momentum, is calculated by (2.14) and is also listed in Table I. The lifetime τ used here are those calculated by Goldberg.²⁹

When the principal quantum number n becomes large, say $n \geq 3$, the last three terms in the curly bracket of (4.5) becomes negligibly small comparing to the first term. If we neglect these three terms, Q_n becomes

$$Q_n \approx - (2\xi)^3 / [2n(2n-1)(2n-2)] \quad \text{when } n \geq 3. \quad (4.8)$$

The above approximate expression for Q_n indicates that $|Q_n|$ decreases as n increases. Since the lifetimes τ of the excited singlet states are of the same order of magnitude, the depolarization factor f increases as n increases (see Table I). When $n \geq 5$, $f \rightarrow 1$ and hence $P \rightarrow P_0$. In fact, this general conclusion on the n dependent of the polarization agrees very well with the experimental observations.^{3,4} The present calculation on the individual transitions is by no means exact considering the approximations included, and it will be improved when better wave functions are used. Nevertheless, this new mechanism with a simple minded calculation does seem to explain satisfactorily the discrepancies between the expected threshold polarizations P_0 's and the observed values.

When the helium atom is excited into a triplet state, n^3L , and then decays into a lower triplet state, n'^3L' , by electric-dipole transition, the total polarization of the radiation shown in (3.16) cannot be written in a form similar to that in (4.7) for singlet transitions. However, when fine-structure lines are resolved, the polarization between a pair of fine-structure levels j (of the upper state) and j' (of the lower state) can be measured. This polarization, which is shown in (3.17),

$$P(j, j') = P_0(j, j') f_j = P_0(j, j') / [1 + \tau^2 \langle\omega^2\rangle_{\text{av}}] \quad (4.9)$$

is quite similar to the expression in (4.7). Here we need

to know $\langle\omega_j^2\rangle_{\text{av}}$. Instead of evaluating the integral I as shown in (2.28) for the singlet states, we now evaluate $\langle\mathcal{H}\mathcal{C}\rangle$ in the $(j\nu)$ representation

$$\langle\mathcal{H}\mathcal{C}\rangle = \alpha^2 \sigma \langle\phi_{j\nu}(\mathbf{r}_2, \mathbf{r}_3) | \sum_{i=2}^3 f(r_i) (1/r_i^3) l_{iz} | \phi_{j\nu}(\mathbf{r}_2, \mathbf{r}_3)\rangle, \quad (4.10)$$

where \mathbf{r}_2 and \mathbf{r}_3 are the coordinates of the two atomic electrons. The operator^{23,27}

$$\mathcal{H}\mathcal{C}(\text{eff}) = \alpha^2 \sigma \sum_{i=2}^3 f(r_i) (1/r_i^3) l_{iz} \quad (4.11)$$

is the effective perturbation on the atomic electronic orbital motion by the scattered electron. By the Wigner-Eckart theorem,²⁰ (4.10) may be expressed as a product of a reduced matrix element in the l representation, and a coefficient which contains the quantum numbers ν , j , l , and s ,

$$\langle\mathcal{H}\mathcal{C}\rangle = \frac{\nu \alpha^2 \sigma [j(j+1) + l(l+1) - s(s+1)]}{2j(j+1)[l(l+1)]^{1/2}} \times [l | \sum_{i=2}^3 f(r_i) (1/r_i^3) l_i | l]. \quad (4.12)$$

The orbital wave function $\phi_{nl}(\mathbf{r}_2, \mathbf{r}_3)$ of the excited helium atom is again approximated by an antisymmetrized product wave function, $(1/\sqrt{2})[\phi_{nl}(\mathbf{r}_2)\phi_{1s}(\mathbf{r}_3) - \phi_{nl}(\mathbf{r}_3)\phi_{1s}(\mathbf{r}_2)]$, and the reduced matrix element becomes

$$[l | \sum_i f(r_i) (1/r_i^3) l_i | l] = [l(l+1)]^{1/2} Q_n, \quad (4.13)$$

where

$$Q_n = \langle\phi_{nl}(\mathbf{x}) | f(r) (1/r^3) | \phi_{nl}(\mathbf{x})\rangle$$

is the same as that in (4.1) for the singlet states. The expectation value of $\mathcal{H}\mathcal{C}$ now reads

$$\langle\mathcal{H}\mathcal{C}\rangle = \nu \alpha^2 \sigma g_j Q_n, \quad (4.14)$$

where

$$g_j = [j(j+1) + l(l+1) - s(s+1)] / 2j(j+1) \quad (4.15)$$

and σ is the projection of the spin of the scattered electron along the z axis, and which can take values $+\frac{1}{2}$ or $-\frac{1}{2}$.

Since the total electron spin of the helium atom in a triplet state is nonzero, there are magnetic interactions,

²⁹ L. Goldberg, *Astrophys. J.* **90**, 414 (1939).

\mathcal{H}_{ss} , between the spin of the scattered electron 1 and the spins of the atomic electrons 2 and 3, in addition to the interaction \mathcal{H} considered above. It is expressed (in atomic units) as follows³⁰:

$$\mathcal{H}_{ss} = \sum_{i=2}^3 (\alpha^2/r_{1i}^3) \left[(\mathbf{s}_1 \cdot \mathbf{s}_i) - \frac{3(\mathbf{s}_1 \cdot \mathbf{r}_{1i})(\mathbf{s}_i \cdot \mathbf{r}_{1i})}{r_{1i}^2} \right]. \quad (4.16)$$

We take the expectation value of \mathcal{H}_{ss} over the product wave function of electron 1 and the electrons of the helium atom (in the excited state n^3L_j). Here s_{1z} and j_z are quantized with eigenvalues σ and ν , respectively.

$$\langle \mathcal{H}_{ss} \rangle = \alpha^2 \sigma \langle u(r_1) \phi_{j\nu}(\mathbf{r}_2, \mathbf{r}_3) | \sum_{i=2}^3 (1/r_{1i}^3) \times \left[s_{iz} - \frac{3z_{1i}(\mathbf{s}_i \cdot \mathbf{r}_{1i})}{r_{1i}^2} \right] | u(r_1) \phi_{j\nu}(\mathbf{r}_2, \mathbf{r}_3) \rangle. \quad (4.17)$$

The vector operator in (4.17) can be expressed as a contraction of a tensor, $Y_2(\mathbf{r}_{1i})$, and a vector, \mathbf{s}_i ;

$$\begin{aligned} & (1/r_{1i}^3) [s_{iz} - 3z_{1i}(\mathbf{s}_i \cdot \mathbf{r}_{1i})/r_{1i}^2] \\ &= (8\pi)^{1/2} \sum_{\mu} (211; \mu, -\mu, 0) (1/r_{1i}^3) \\ & \quad \times Y_{2,\mu}(\mathbf{r}_{1i}) s_{-\mu}(i). \end{aligned} \quad (4.18)$$

Furthermore, we can expand the two-electron operator, $Y_{2,\mu}(\mathbf{r}_{1i})/r_{1i}^3$, as follows^{21,22}:

For $r_i > r_1$

$$\begin{aligned} \frac{Y_{2,\mu}(\mathbf{r}_{1i})}{r_{1i}^3} &= \sum_{l=2}^{\infty} \sum_{m=-l}^l (-)^l \left[\frac{4\pi(2l)!}{4!(2l-3)!} \right]^{1/2} \\ & \quad \times (l-2, l, 2; \mu-m, m, \mu) (r_1^{l-2}/r_i^{l+1}) \\ & \quad \times Y_{l-2,\mu-m}(\mathbf{r}_1) Y_{lm}(\mathbf{r}_i), \end{aligned} \quad (4.19)$$

for $r_i < r_1$

$$\begin{aligned} \frac{Y_{2,\mu}(\mathbf{r}_{1i})}{r_{1i}^3} &= \sum_{l=2}^{\infty} \sum_{m=-l}^l (-)^l \left[\frac{4\pi(2l)!}{4!(2l-3)!} \right]^{1/2} \\ & \quad \times (l-2, l, 2; \mu-m, m, \mu) (r_i^{l-2}/r_1^{l+1}) \\ & \quad \times Y_{l-2,\mu-m}(\mathbf{r}_i) Y_{lm}(\mathbf{r}_1), \end{aligned} \quad (4.20)$$

and for $r_i = r_1$,

$$\frac{Y_{2,\mu}(\mathbf{r}_{1i})}{r_{1i}^3} = -\frac{4}{3}\pi Y_{2,\mu}(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_i). \quad (4.21)$$

Substituting the above expansions into (4.18) and integrating over the spherically symmetric wave function $u(r_1)$ of electron 1, we obtain the effective perturbation, $\mathcal{H}_{ss}(\text{eff})$, on the electron spins of the triplet helium atom,

by the scattered electron.

$$\begin{aligned} \mathcal{H}_{ss}(\text{eff}) &= \alpha^2 \sigma \langle u(r_1) | \sum_{i=2}^3 (1/r_{1i}^3) \\ & \quad \times [s_{iz} - 3z_{1i}(\mathbf{s}_i \cdot \mathbf{r}_{1i})/r_{1i}^2] | u(r_1) \rangle \\ &= -\alpha^2 \sigma \sum_{i=2}^3 [h(r_i)/r_i^3] [s_{iz} - 3z_i(\mathbf{s}_i \cdot \mathbf{r}_i)/r_i^2], \end{aligned} \quad (4.22)$$

where

$$h(r_i) = \frac{4}{3} r_i^3 e^{-2r_i} + f(r_i) \quad (4.23)$$

and $f(r_i)$ is defined in (2.27). The expectation value of \mathcal{H}_{ss} is as follows³¹:

$$\begin{aligned} \langle \mathcal{H}_{ss} \rangle &= \langle \phi_{j\nu}(2,3) | \mathcal{H}_{ss}(\text{eff}) | \phi_{j\nu}(2,3) \rangle \\ &= -\alpha^2 \sigma (j_1 j; \nu 0 \nu) (j l s) \left\| \sum_{i=2}^3 [h(r_i)/r_i^3] \right. \\ & \quad \left. \times [\mathbf{s}_i - 3\mathbf{r}_i(\mathbf{s}_i \cdot \mathbf{r}_i)/r_i^2] \right\| j l s = \nu \alpha^2 \sigma \bar{Q}_n \bar{g}_j, \end{aligned} \quad (4.24)$$

where

$$\bar{g}_j = \{ [4 + l(l+1) - j(j+1)] [3j(j+1) + l(l+1)] - 12 \} / [4j(j+1)(2l-1)(2l+3)], \quad (4.25)$$

$$\bar{Q}_n = Q_n + Q_n', \quad (4.26)$$

and

$$Q_n' = \frac{4}{3} \langle \phi_{nl}(\mathbf{r}) | e^{-2r} | \phi_{nl}(\mathbf{r}) \rangle. \quad (4.27)$$

The total interaction energy is

$$E_{j\nu} = \langle \mathcal{H} + \mathcal{H}_{ss} \rangle = \nu \alpha^2 \sigma (Q_n g_j + \bar{Q}_n \bar{g}_j). \quad (4.28)$$

The frequency separation (in atomic units), ω_j , between the levels ($j\nu$) and ($j\nu-2$) is

$$\omega_j = E_{j\nu} - E_{j\nu-2} = 2\alpha^2 \sigma (Q_n g_j + \bar{Q}_n \bar{g}_j). \quad (4.29)$$

Since

$$\langle \sigma^2 \rangle_{\text{av}} = \frac{1}{4} \quad (4.30)$$

we have

$$\langle \omega_j^2 \rangle_{\text{av}} = \alpha^4 (Q_n g_j + \bar{Q}_n \bar{g}_j)^2. \quad (4.31)$$

Substituting (4.31) into (4.9), the polarization of the line $n^3L_j \rightarrow n'^3L_{j'}$ becomes

$$P(jj') = P_0(jj') f_j$$

and

$$f_j = (1 + \tau^2 \langle \omega_j^2 \rangle_{\text{av}})^{-1} = [1 + \tau^2 \alpha^4 (Q_n g_j + \bar{Q}_n \bar{g}_j)^2]^{-1}. \quad (4.32)$$

When the fine structure lines are not resolved, the total polarization for the transition $n^3L \rightarrow n'^3L'$ is [by (3.16)]

$$P = \sum_{jj'} f_j R_1^0(jj') / \sum_{jj'} R_0(jj'), \quad (4.33)$$

³⁰ H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One and Two Electron Atoms* (Academic Press Inc., New York, 1957), p. 181.

³¹ For detailed steps to evaluate the (diagonal and off-diagonal) reduced matrix elements of this type, see: (a) A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1960), p. 110; (b) L. Y. C. Chiu, *Phys. Rev.* **145**, 4 (1966).

TABLE II. Polarization of the e -He impact radiation at threshold energy, triplet-triplet transitions.*

Transition	Wave-length (Å)	τ (10^{-8} sec)	$-Q_n$ (10^{-3} a.u.)	g_j	$-\bar{Q}_n$ (10^{-3} a.u.)	\bar{g}_j	$\langle \omega_j^2 \rangle_{av}$ (10^{-16} a.u.)	$10^4 f_j$	P_0 (%)	P (%)	P_{corr} (%)
$3^3P_2 \rightarrow 2^3S_1$	3889	9.43	2.37	$\frac{1}{2}$	2.29	$-\frac{1}{10}$	2.59	0.254	21.4	0.54×10^{-3}	0.54×10^{-3}
$3^3P_1 \rightarrow 2^3S_1$	3889	9.43	2.37	$\frac{1}{2}$	2.29	$\frac{1}{2}$	15.4	0.043	0	0	0
$3^3P_0 \rightarrow 2^3S_1$	3889	9.43	2.37	...	2.29	1	0	0	0
$3^3P \rightarrow 2^3S$	3889	9.43	2.37	...	2.29	12	0.30×10^{-3}	0.30×10^{-3}
$4^3D_3 \rightarrow 2^3P_2$	4472	2.76	0.468	$\frac{2}{5}$	0.467	$-2/21$	0.202	37.9	25.5	0.10	0.09
$4^3D_2 \rightarrow 2^3P_2$	4472	2.76	0.468	$\frac{5}{6}$	0.467	$\frac{1}{6}$	0.621	12.4	-60	-0.07	-0.07
$4^3D_2 \rightarrow 2^3P_1$	4472	2.76	0.468	$\frac{5}{6}$	0.467	$\frac{1}{6}$	0.621	12.4	100	0.12	0.12
$4^3D_1 \rightarrow 2^3P_2$	4472	2.76	0.468	$\frac{3}{2}$	0.467	$\frac{1}{2}$	2.48	3.10	4.76	1.5×10^{-3}	1.5×10^{-3}
$4^3D_1 \rightarrow 2^3P_1$	4472	2.76	0.468	$\frac{3}{2}$	0.467	$\frac{1}{2}$	2.48	3.10	-33.3	-0.01	-0.01
$4^3D_1 \rightarrow 2^3P_0$	4472	2.76	0.468	$\frac{3}{2}$	0.467	$\frac{1}{2}$	2.48	3.10	33.3	0.01	0.01
$4^3D \rightarrow 2^3P$	4472	2.76	0.468	...	0.467	27.8	0.067	0.066

* To compute $f_j = (1 + (\omega_j^2)_{av} \tau^2)^{-1}$, ω and τ both should be in atomic units. The unit of frequency ($\omega = m e^4 / \hbar^3$) and the unit of time ($\tau = \hbar^3 / m e^4$). $\langle \omega_j^2 \rangle_{av} = \alpha^4 (Q_n g_j + \bar{Q}_n \bar{g}_j)^2$. For transition between two fine-structure lines, $n^3L_j \rightarrow n'^3L_{j'}$, the values in column P_0 and P are those for $P_0(jj')$ and $P(jj')$, which are defined in (3.19) and (3.17) respectively. The values in column P_{corr} are computed directly from (4.43) and (3.16) (where off-diagonal matrix elements in j have been considered). The values for τ are from Ref. 27.

where

$$R_1^0(jj') = R_1(jj') f_j^{-1} \quad (4.34)$$

and $R_1(jj')$ and $R_0(jj')$ are defined in (3.14) and (3.10) respectively. The P_0 in this case is defined as

$$P_0 = \lim_{\text{all } j_j \rightarrow 1} P = \sum_{jj'} R_1^0(jj') / \sum_{jj'} R_0(jj'), \quad (4.35)$$

which has the same meaning as before, namely, it is the threshold polarization when only the simple conservation law of angular momentum is considered.

In Table II is listed the polarization for the transitions $3^3P \rightarrow 2^3S$ and $4^3D \rightarrow 2^3P$. The depolarization factors f_j 's and consequently the polarization P 's here of the triplet transitions are considerably smaller than those of the singlet transitions. This is due to the fact that the lifetimes of the triplet transitions are nearly two orders of magnitude longer than those of the singlet transitions. In addition, the fine-structure effect would also decrease the P_0 's and hence the P 's. The P_0 's in Table I for singlet transitions agree with those previously calculated.^{1,2} However, the P_0 's in Table II for triplet transitions do not agree with all the previous values. For example, the P_0 for $3^3P \rightarrow 2^3S$ transition was shown^{1,2} to be 36.6%, whereas our value is 12%. The reason is that we have included the interference effect in the present treatment while it has been neglected previously. For singlet transitions and for the case of complete degeneracy, this interference is not a true effect as has been discussed in Sec. 2. Since P_0 corresponds to the value of P when magnetic sublevels are degenerate, i.e., $\omega = 0$, it will be the same whether the interference effect has been included or not in computing P_0 for the singlet transitions. The situations, of course, will be different for the triplet transitions, because the interference remains effective even when the sublevels are degenerate, i.e., $\omega_j = 0$.

So far we have neglected the nonlinear effect on the energy separation, $\omega_j = E_{j\nu} - E_{j\nu-2}$ ($E_{j\nu}$ may have terms

which are nonlinear in ν). Since the fine-structure splittings of helium are not too large, j is not a good quantum number and the off-diagonal matrix elements in j should also be considered. For perturbation up to the second order, the interaction energy is as follows:

$$E_{j\nu} = E_{j\nu}^{(1)} + E_{j\nu}^{(2)}, \quad (4.36)$$

where

$$E_{j\nu}^{(1)} = \langle j\nu | \mathcal{H}(\text{eff}) + \mathcal{H}_{ss}(\text{eff}) | j\nu \rangle = \nu \alpha^2 \sigma (Q_n g_j + \bar{Q}_n \bar{g}_j) \quad (4.37)$$

is the same as that in (4.28) and is linear in ν , and

$$E_{j\nu}^{(2)} = \sum_{j' \neq j} \frac{|\langle j'\nu | \mathcal{H}(\text{eff}) + \mathcal{H}_{ss}(\text{eff}) | j\nu \rangle|^2}{E_j - E_{j'}}. \quad (4.38)$$

The off-diagonal matrix element has the following expression (detailed steps are shown in the Appendix):

$$\begin{aligned} \langle j+1, \nu | \mathcal{H}(\text{eff}) + \mathcal{H}_{ss}(\text{eff}) | j\nu \rangle &= \alpha^2 \sigma \frac{[(j+1)^2 - \nu^2]^{1/2}}{2(j+1)} \\ &\times \left[\frac{(j+l+3)(l-j+1)(j-l+2)(l+j)}{(2j+3)(2j+1)} \right]^{1/2} \\ &\times \left\{ Q_n \frac{[3(j+1)^2 - l(l+1) - 6] \bar{Q}_n}{2(2l-1)(2l+3)} \right\}. \end{aligned} \quad (4.39)$$

The energy splitting is then

$$\begin{aligned} \omega(j\nu; j\nu-2) &= E_{j\nu} - E_{j\nu-2} \\ &= \omega_j + E_{j\nu}^{(2)} - E_{j\nu-2}^{(2)}, \end{aligned} \quad (4.40)$$

where

$$\begin{aligned} \omega_j &= E_{j\nu}^{(1)} - E_{j\nu-2}^{(1)} \\ &= 2\alpha^2 \sigma (Q_n g_j + \bar{Q}_n \bar{g}_j) \end{aligned} \quad (4.41)$$

is the same as (4.29). Since ω_j is linear in σ which can take the values $+\frac{1}{2}$ of $-\frac{1}{2}$, we have

$$\langle \omega_j \rangle_{av} = 0,$$

and hence

$$\langle \omega^2(j\nu; j\nu-2) \rangle_{\text{av}} = \langle \omega_j^2 \rangle_{\text{av}} + \langle (E_{j\nu}^{(2)} - E_{j\nu-2}^{(2)})^2 \rangle_{\text{av}}. \quad (4.42)$$

To compute the polarization $P(jj')$, we use the original formula

$$P(jj') = R_1(jj')/R_0(jj'), \quad (4.43)$$

where $R_0(jj')$, the radiation without interference, is the same as defined in (3.10) and $R_1(jj')$, the interfering part is now as follows:

$$R_1(jj') = 2A\tau \sum_{\mu, \nu} G^*(j\nu)G(j\nu-2)x(j\nu; j'\mu) \times x^*(j\nu-2; j'\mu)[1 + \tau^2 \langle \omega^2(j\nu; j\nu-2) \rangle_{\text{av}}]^{-1}. \quad (4.44)$$

Since the off-diagonal matrix element depends on ν^2 , we have

$$E_{j\nu}^{(2)} = E_{j, -\nu}^{(2)}$$

and

$$\omega(j, 1; j, -1) = \omega_j. \quad (4.45)$$

The second-order perturbation, therefore, has no effect on the energy separation between $(j, \nu=1)$ and $(j, \nu=-1)$. For transitions $4^3D_2 \rightarrow 2^3P_{j'}$, $4^3D_1 \rightarrow 2^3P_{j'}$, and $3^3P_1 \rightarrow 2^3S_1$ considered here, only the interference between $(j, \nu=1)$ and $(j, \nu=-1)$ contributes to the $R_1(jj')$ in (4.44). The polarizations, $P(jj')$, for those transitions are therefore the same whether they are computed by (4.43) or by the previous formula (4.32), where the nonlinear effect has been neglected. For transition $4^3D_3 \rightarrow 2^3P_2$, $R_1(jj')$ has contributions from terms which contain $\langle \omega^2(3, 3; 3, 1) \rangle_{\text{av}}$, $\langle \omega^2(3, -1; 3, -3) \rangle_{\text{av}}$, and $\langle \omega^2(3, 1; 3, -1) \rangle_{\text{av}}$. To compute $\langle \omega^2(3, 3; 3, 1) \rangle_{\text{av}}$ [$= \langle \omega^2(3, -1; 3, -3) \rangle_{\text{av}}$], we need the second-order energy correction $E_{j=3, \nu=1}^{(2)}$, ($E_{j=3, \nu=3}^{(2)}=0$), and the fine-structure splitting $E(4^3D_2) - E(4^3D_3) = 8.9 \times 10^{-9}$ a.u.²² is used. Similarly for transition $3^3P_2 \rightarrow 2^3S_1$, $R_1(jj')$ has contributions from the interference between $(j=2, \nu=2)$ and $(j=2, \nu=0)$. To compute $\langle \omega^2(2, 2; 2, 0) \rangle_{\text{av}}$ we need the second-order energy correction $E_{j=2, \nu=0}^{(2)}$, ($E_{j=2, \nu=2}^{(2)}=0$), and the fine-structure splitting $E(3^3P_1) - E(3^3P_2) = 1.0 \times 10^{-7}$ a.u.³¹ is used. Because of the smallness of the off-diagonal matrix element, both $(E_{3,1}^{(2)})^2 (= 6.5 \times 10^{-18}$ a.u.) and $(E_{2,0}^{(2)})^2 (= 2.5 \times 10^{-17}$ a.u.) contributes less than 5% in computing $\langle \omega^2(j\nu; j\nu-2) \rangle_{\text{av}}$. The $\langle \omega^2(j\nu; j\nu-2) \rangle_{\text{av}}$'s are used to compute $R_1(jj')$ and $P(jj')$. The polarizations thus computed are listed in the last column of the Table II under the heading " P_{corr} " which differs very little from the values in the previous column, where the second-order corrections are neglected.

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²² See Ref. 30, p. 188, $E(3^3P_1) - E(3^3P_2) = 1.0 \times 10^{-7}$ a.u. is the experimental value. $E(4^3D_2) - E(4^3D_3) = 8.9 \times 10^{-9}$ a.u. is the

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APPENDIX

OFF-DIAGONAL MATRIX ELEMENT

We evaluate the following off-diagonal matrix element which appears in (4.38):

$$\langle \phi_{j+1, \nu}(\mathbf{r}_2, \mathbf{r}_3) | \mathcal{H}(\text{eff}) + \mathcal{H}_{ss}(\text{eff}) | \phi_{j, \nu}(\mathbf{r}_2, \mathbf{r}_3) \rangle, \quad (A1)$$

where

$$\mathcal{H}(\text{eff}) = \alpha^2 \sigma \sum_{i=2}^3 f(r_i) (1/r_i^3) l_{iz} \quad (A2)$$

and

$$\mathcal{H}_{ss}(\text{eff}) = -\alpha^2 \sigma \sum_{i=2}^3 h(r_i) (1/r_i^3) [s_{iz} - 3z_i(\mathbf{s}_i \cdot \mathbf{r}_i)/r_i^2] \quad (A3)$$

are defined in (4.11) and (4.22), respectively. For the matrix element of $\mathcal{H}(\text{eff})$, we have²⁰

$$\begin{aligned} \langle j+1, \nu l s | \mathcal{H}(\text{eff}) | j \nu l s \rangle \\ = (-)^{s-l-j} \alpha^2 \sigma [(2l+1)(2j+1)]^{1/2} \\ \times (j1, j+1; \nu 0 \nu) W(lj, j+1; s1) \\ \times [l \|\sum_{i=2}^3 f(r_i) (1/r_i^3) \mathbf{l}_i\| l]. \quad (A4) \end{aligned}$$

By writing the Clebsch-Gordan coefficient and the Racah coefficient²⁶ explicitly ($s=1$), and using (4.13) for the reduced matrix element, we have

$$\begin{aligned} \langle \phi_{j+1, \nu}(\mathbf{r}_2, \mathbf{r}_3) | \mathcal{H}(\text{eff}) | \phi_{j, \nu}(\mathbf{r}_2, \mathbf{r}_3) \rangle = \alpha^2 \sigma Q_n \frac{[(j+1)^2 - \nu^2]^{1/2}}{2(j+1)} \\ \times \left[\frac{(l+j+3)(l-j+1)(j-l+2)(l+j)}{(2j+3)(2j+1)} \right]^{1/2}. \quad (A5) \end{aligned}$$

Since the matrix element is diagonal in s ($\mathbf{s} = \mathbf{s}_1 + \mathbf{s}_2$), for the matrix element of $\mathcal{H}_{ss}(\text{eff})$ we have²⁰

$$\begin{aligned} \langle j+1, \nu l s | \mathcal{H}_{ss}(\text{eff}) | j \nu l s \rangle = (-\alpha^2 \sigma / 2) (j1, j+1; \nu 0 \nu) \\ \times \{ j+1, l s \|\sum_{i=2}^3 h(r_i) (1/r_i^3) \\ \times [\mathbf{s} - 3\mathbf{r}_i(\mathbf{s} \cdot \mathbf{r}_i)/r_i^2] \| j l s \}. \quad (A6) \end{aligned}$$

Since the vector operator $[h(r_i)/r_i^3][\mathbf{s} - 3\mathbf{r}_i(\mathbf{s} \cdot \mathbf{r}_i)/r_i^2]$ is a contraction of a vector \mathbf{s} and a tensor $[h(r_i)/r_i^3]\mathbf{C}^{(2)}(\mathbf{r}_i)$ [where $C_m^{(2)}(\mathbf{r}_i) = (4\pi/5)^{1/2} Y_{2,m}(\mathbf{r}_i)$], the reduced matrix element can be expressed as a product of $(s \| \mathbf{r} \| s)$,

$$[l \|\sum_i (h(r_i)/r_i^3) \mathbf{C}^{(2)}(\mathbf{r}_i) \| l]$$

value from the approximate formula (40.12), which has been corrected for estimated experimental deviation.

and some coefficient.³¹ After evaluating all of the reduced matrix elements and writing out all of the coefficients we have

$$\begin{aligned} & \langle \phi_{j+1,\nu}(\mathbf{r}_2, \mathbf{r}_3) | \mathcal{H}C_{ss}(\text{eff}) | \phi_{j\nu}(\mathbf{r}_2, \mathbf{r}_3) \rangle \\ &= -\alpha^2 \sigma \bar{Q}_n [(j+1)^2 - \nu^2]^{1/2} \frac{3(j+1)^2 - l(l+1) - 6}{4(j+1)(2l-1)(2l+3)} \\ & \quad \times \left[\frac{(j+l+3)(l+j)(j-l+2)(l-j+1)}{(2j+1)(2j+3)} \right]^{1/2}. \quad (\text{A7}) \end{aligned}$$

To compute the second-order energy correction, the

needed off-diagonal matrix elements have the following simple expressions:

$$\begin{aligned} & \langle \phi_{2,\nu}({}^3P_2) | \mathcal{H}C(\text{eff}) + \mathcal{H}C_{ss}(\text{eff}) | \phi_{1,\nu}({}^3P_1) \rangle \\ &= \frac{1}{2} \alpha^2 \sigma \left(\frac{4-\nu^2}{3} \right)^{1/2} (Q_n - \frac{2}{5} \bar{Q}_n) \quad (\text{A8}) \end{aligned}$$

and

$$\begin{aligned} & \langle \phi_{3,\nu}({}^3D_3) | \mathcal{H}C(\text{eff}) + \mathcal{H}C_{ss}(\text{eff}) | \phi_{2,\nu}({}^3D_2) \rangle \\ &= \frac{1}{3} \alpha^2 \sigma \left[\frac{2}{5} (9-\nu^2) \right]^{1/2} \left(Q_n - \frac{5}{14} \bar{Q}_n \right). \quad (\text{A9}) \end{aligned}$$

Nonorthogonal Formulation of Hartree-Fock Perturbation Theory*

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Perturbation theory, up to first order in the wave function and second order in the energy, is formulated for a many-electron system without requiring the perturbed one-electron states to be orthogonal. The most general self-consistent coupled equations, referred to as Method 1, form the counterpart of Langhoff, Karplus, and Hurst's (LKH) Method *a* for orthogonal orbitals. The uncoupling of the perturbations $\delta\psi_i$, $\delta\psi_j$ to the zero order wave functions ψ_i^0 and ψ_j^0 produces equations referred to as Method 2. Further approximation in the Method-2 equations yields a set of equations called Method 3. Methods 2 and 3 are counterparts of LKH's Method *b*, but have computational advantages over Method *b* in that normalization and orthogonalization are accomplished in a particularly simple fashion. In comparing the uncoupled Method-3 equations with Dalgarno's equations, an additional difference is found involving the overlap integral between perturbed states, besides the difficulty pointed out by LKH. Application of the Method-2 and -3 equations is made to the spin-polarization problem of the Fe^{+3} ion, leading to a hyperfine constant in reasonable agreement with earlier unrestricted Hartree-Fock (UHF) calculations. A comparison between results obtained by Methods 2 and 3 and Dalgarno's equations permits a relative evaluation of these methods. We have also studied the effect of indirect spin polarization of the *s* electrons through the action of the *p* electrons which are in turn polarized by the unpaired *d* electrons. This contribution is found to be about 10% of the direct effect.

I. INTRODUCTION

IN a recent paper, Langhoff, Karplus, and Hurst¹ (LKH) have examined some methods of applying perturbation theory to Hartree-Fock systems. In particular they showed that some important terms were omitted in the perturbation equations derived by Dalgarno² which led to inconsistencies. Thus, in the Hartree-Fock equation for the zero-order wave function, the Coulomb and exchange terms can be written in

either of two equivalent forms:

$$\begin{aligned} h_i^{\text{ce}}(1)u_i^0(1) &= \sum_{j=1, j \neq i}^N [\langle u_j^0(2) | r_{12}^{-1} | u_j^0(2) \rangle u_i^0(1) \\ & \quad - \langle u_j^0(2) | r_{12}^{-1} | u_i^0(2) \rangle u_j^0(1)] \quad (1) \\ &= \sum_{j=1}^N [\langle u_j^0(2) | r_{12}^{-1} | u_j^0(2) \rangle u_i^0(1) \\ & \quad - \langle u_j^0(2) | r_{12}^{-1} | u_i^0(2) \rangle u_j^0(1)] = h(1)^{\text{ce}}u_i^0(1). \quad (2) \end{aligned}$$

However, this is only true if the one-electron Hamiltonian acts on the zero-order wave function u_i^0 , since in this case the self-Coulomb and self-exchange terms cancel. When the Hamiltonian acts on a first-order correction to the wave function, there is no such can-

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¹ P. W. Langhoff, M. Karplus, and R. P. Hurst, *J. Chem. Phys.* **44**, 505 (1966).

² A. Dalgarno, *Proc. Roy. Soc. (London)* **A251**, 282 (1959).