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Stark and Zeeman Effects on Neutral-Helium Lines

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The effect of a static electromagnetic field on the $2P$-nS and $2S$-nP He I isolated lines is systematically investigated. Exact expressions are given for the shift of the allowed component, and the behavior of the corresponding transition probability under static perturbation is considered in detail. The usual hydrogenic approximations for the Stark constants are discussed with reference to the most recent values for the oscillator strengths available. They are found to be consistent, expecially for the 2^1P-n^1S and 2^1S-n^1P lines with $n \geq 3$, when accurate data are used for the unperturbed excitation energies. The shifts determined with either nondegenerate or degenerate perturbation theory are critically compared, and the greatest difference is found for the magnetic sublevels in the presence of crossed fields. The fourth-order Stark effect is also considered. Calculated shifts are compared with the existing experimental data, and attention is also given to the methods used in plasma spectroscopy for the evaluation of the static Stark effect.

I. INTRODUCTION

Usually, the Stark broadening of lines whose shape conforms to a static pattern consisting of an allowed transition with a neighborhood of weakly excitable forbidden ones is studied within the isolated-line approximation.[1] This consists of a dynamic treatment of the free-electron contribution to the line core and a hydrogenic (or Coulomb) evaluation of the statically perturbed atomic parameters, which in practice reduces to a Stark-constant calculation.[2]

The aim of the present work is twofold: first, to examine in detail the effect of a static electromagnetic (electric + magnetic) field on the static pattern of a line usually assumed isolated; and second, to estimate quantitatively the various static approximations made in the isolated-line concept, which consist mainly of the unperturbed-wave-function assumption and of the hydrogenic approximation for the transition probabilities in the Stark-constant calculation. In particular, we pay special attention to the $2P$-nS and $2S$-nP (with $n \geq 3$) transitions of He I.

The corresponding lines are very often encountered in plasma diagnostics, and their atomic parameters [mainly the averaged Stark constant used in the reduced expression (1) for the isolated-line profile] can now be computed with a very good accuracy, a fact which allows us to draw quantitative conclusions.

Recently, there have been many efforts[3-7] devoted to the partially degenerate $2P$-nQ ($n \geq 4$, $Q = P$, D, $F, \ldots$) lines emitted with or without magnetic field present. The corresponding profiles show the interesting feature that their spectroscopic character, isolated or quasihydrogenic, depends strongly on the electron density. A quantitative evaluation of this effect needs a careful investigation of the approximations used for the statically perturbed atomic quantities. Therefore we give critical attention to the various perturbation methods of calculation for the Stark shift. Our investigation being mainly limited to sublevels (n, l) with $n \leq 10$, we may safely consider the Zeeman perturbation within a first-order treatment.

II. GENERAL EXPRESSIONS FOR SHIFT AND TRANSITION PROBABILITY

The electromagnetic perturbation we consider is taken to be always far greater than any relativistic effect of fine (*a fortiori* hyperfine) structure. This approximation is necessary in order to define easily the perturbed eigenstates in the LS-coupling scheme. When the magnetic (or electric) perturbation is comparable to the fine structure, one is faced with a very complicated situation, which has been recently cleared up by Descoubes.[8] For the problem of Stark broadening in plasmas, we may limit ourselves to a situation where the separation $L e\hbar H/2m_e c$ (m_e being the electron mass) between the outer components of a line remains much larger than the most important fine-structure splitting encountered in the group of sublevels involved in the broadening process. More precisely, we have to be able to neglect the energy difference[8,9]

$$E(^3L_{L-1}) - E(^3L_{L+1}) \gg E(^3L_L) - E(^3L_{L+1}) \ ,$$

where $E(^3L_J)$ represents the energy of a level with orbital number L and total angular momentum J. If we restrict our considerations to the n^3P states which are the most affected by the fine-structure splitting, and are very often used in line measurements, we have to consider a magnetic intensity given by the relation

$$\frac{H(\mathrm{G})}{107\,10} \gg E(^3L_{L-1}) - E(^3L_{L+1}) \ , \tag{1}$$

the energy difference being evaluated in cm^{-1}. The minimum magnetic intensity is given in Table I.

A. Static Shift of Allowed Component $nlm \rightarrow 2l'm'$

Thus we see that the presence of a moderate magnetic intensity allows us to work with the spherically symmetric wave functions of the LS-coupling scheme, labeling the quantum numbers (n, l, m) independently of the spin multiplicity. The geometry of the applied static perturbation is that used previously[10] (see Fig. 1) with the magnetic intensity taken along the $0z$ axis and the electric intensity orientated at θ with $\alpha = \cos\theta$.

The shift of the allowed component $nlm \rightarrow n'l'm'$, located at the line center, is given then by a straightforward generalization of the usual second-order expression for the electric-field-perturbed energy of a nondegenerate level,[7] i.e.,

$$\Delta E_{nlm} - \Delta E_{n'l'm'} = (m - m')\,\frac{e\hbar H}{2m_e c} + (eFa_0)^2 \sum_{n'',l'',m''} (E_{nlm} - E_{n''l''m''})^{-1} \times \left[\alpha^2 \left|\langle nlm|\, z/a_0 |n''l''m''\rangle\right|^2 + (1-\alpha^2)\left|\langle nlm|x/a_0|n''l''m''\rangle\right|^2\right] \ , \tag{2}$$

where $\vec{r}(x, y, z)$ is the optical-electron position vector. The spin part of the Zeeman effect is canceled in the foregoing difference. The dipole selection rules show[11] that the cross-term contribution in x and z vanishes. The ket $|nlm\rangle$ refers to the spherical quantum numbers of the optical electron, the inner electron being considered in the He^+ ground state. E_{nlm} and $E_{n'l'm'}$ represent the energy of the corresponding sublevels in the presence of a magnetic field. ΔE_i gives the electromagnetic shift of the i states. Hence Eq. (2) may be given the form (with $\Delta\lambda$ and λ in Å, H in kG, and F in kV/cm)

$$\Delta\lambda = -\frac{\lambda^2(\Delta E_{nlm} - \Delta E_{n'l'm'})}{hc} = \Bigg(46.28\,(m-m')H + 1.82 \sum_{n'',l'',m''} (E_{nlm} - E_{n'',l'',m''})^{-1} \times \left[\alpha^2\left|\langle nlm|\, z/a_0|n''l''m''\rangle\right|^2 + (1-\alpha^2)\left|\langle nlm|x/a_0|n''l''m''\rangle\right|^2 F^2\right]\Bigg) \times 10^{-11}\lambda^2 \ , \tag{3}$$

which is very suitable for numerical applications. Equation (3) is a direct extension of the Kirkwood formula[12] which is valid for the pure Stark effect. In the above expressions, the Stark shift of the lower sublevel $(2, l', m')$ which is not greater than $10^{-3}\ \mathrm{cm}^{-1}$ for 10 kV/cm has been neglected (in this work we consider only the lines with $n' = 2$, the most interesting ones in plasma diagnostics).

B. Transition Probability of Component $nlm \rightarrow 2l'm'$

The Stark perturbation of the $(2, l', m')$ wave function is again omitted. The magnetic field introduces no modification in the wave-function expression. If $|nlm\rangle$ labels the (n, l, m) wave function, then the first-order-perturbation contribution is[13]

$$|nlm\rangle_1 = e\,Fa_0 \sum_{n'',l'',m''} \left[\alpha\langle n''l''m''|\, z/a_0 |nlm\rangle + (1-\alpha^2)^{1/2}\langle n''l''m''|x/a_0|nlm\rangle\right] \times \frac{|n''l''m''\rangle}{E_{nlm} - E_{n''l''m''}} \ , \tag{4}$$

where $(n'', l'', m'') \neq (n, l, m)$. The unperturbed wave functions have a definite parity, so that

$$\langle n'l'm'|\vec{r}/a_0|nlm\rangle_1 = 0 \ ,$$

showing that there is no first-order Stark contribution to the transition probability. Let us consider the quantity

TABLE I. H values (kG) necessary for the use of LS coupling.

$n\,^3P$	$2\,^3P$	$3\,^3P$	$4\,^3P$	$5\,^3P$	$6\,^3P$
H_{min}	10.7	3	1.5	0.7	0.5

$$V_{n''l''m'',nlm}=eFa_0[\alpha\langle n''l''m''|z/a_0|nlm\rangle+(1-\alpha^2)^{1/2}\langle n''l''m''|x/a_0|nlm\rangle] \quad . \tag{5}$$

Then, the second-order contribution may be given the form[14]

$$|nlm\rangle_2=\sum_{\substack{n'',l'',m''\\ n''',l''',m'''}}\frac{V_{n'''l'''m''',n''l''m''}V_{n''l''m'',nlm}}{(E_{nlm}-E_{n''l''m''})(E_{nlm}-E_{n'''l'''m'''})}|n'''l'''m'''\rangle-\frac{1}{2}\sum_{n'',l'',m''}\frac{|V_{n''l''m'',nlm}|^2}{(E_{nlm}-E_{n''l''m''})^2}|nlm\rangle , \tag{6}$$

with $(n,l,m)\neq(n'',l'',m'')$, (n''',l''',m'''). Now, the selection rules[11] allow a second-order contribution to be added to the unperturbed transition probability.

The sum $|nlm\rangle+|nlm\rangle_2$ is normalized to unity. Therefore, expression (6) shows that the unperturbed wave function will be depleted to the benefit of $(n, l\pm 2, m''')$, with $|m'''|\leq|m+2|$ under the influence of a static electric perturbation. In the presence of partial degeneracy for the upper levels (n,l,m) and small F values, this process is responsible for the disintegration of the allowed and isolated $nlm\rightarrow n'l\pm 1m$ components into $nl\pm 2m\rightarrow n'l\pm 1m$ for a pure Stark effect. In the presence of a nonparallel magnetic intensity $(\alpha\neq 1)$, there also appears $nl\pm 2m\pm 1\rightarrow n'l\pm 1m\pm 1$, $nl\pm 2m\pm 1\rightarrow n'l\pm 1m$, and $nl\pm 2m\pm 2\rightarrow n'l\pm 1m\pm 1$, polarized parallel $(\Delta m=0)$ or perpendicular $(\Delta m=|1|)$ to $\vec{H}$. An accurate estimate for the Stark depletion of the upper (n,l,m) level may be obtained with $n'=n$ and the aid of the symmetrized (singlet) or antisymmetrized (triplet) product

$$U=2^{-1/2}[u_1(1)u_{nlm}(2)\pm u_{nlm}(1)u_1(2)] \tag{7}$$

of hydrogenic wave functions. If we specialize to the case $\vec{F}\parallel\vec{H}$ $(\alpha=1)$ and sublevels $(n,0,0)$ [mainly perturbed by $(n,1,0)$] and $(n,1,0)$ [perturbed by $(n,2,0)$], then the depletion considered will be measured by the ratios

$$\frac{|\langle n00|\,Z/a_0|n10\rangle|^2}{(E_{n00}-E_{n10})^2}\simeq\frac{(R_{n0}^{n1})^2}{3(E_{n00}-E_{n10})^2} , \tag{8a}$$

$$\frac{|\langle n10|\,Z/a_0|n20\rangle|^2}{(E_{n10}-E_{n20})^2}\simeq\frac{4(R_{n1}^{n2})^2}{15(E_{n10}-E_{n20})^2} , \tag{8b}$$

where R_{nl}^{nl+1} may be given the hydrogenic values $1.5n[n^2-(l+1)^2]^{1/2}$.

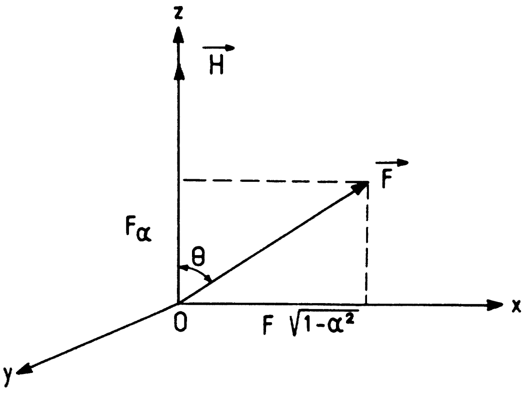

FIG. 1. Geometry of the static electromagnetic perturbation.

For instance, in Table II, we have plotted F values such that the (n,l) wave functions with $3\leq n\leq 6$ be reduced by an amount of 0.5%. It then appears that for $n\geq 5$ and the usual discharges in plasma spectroscopy with $N_e\geq 10^{15}e$ cm^{-3}, the unperturbed-wave-function approximation becomes of questionable accuracy for the isolated levels $(n,0)$ and $(n,1)$. Furthermore, it must be noticed that the population of (n,l,m) due to other perturbed levels should also be taken into account, and degenerate perturbation theory with linear Stark effects has to be used for the determination of perturbed wave functions in those cases ($n\geq 5$ with $F\geq 10^4$ V/cm).

When the unperturbed-wave-function assumption remains valid, it is possible to obtain accurate values for the transition probabilities

$$|\langle nlm|\vec{r}/a_0|n'l'm'\rangle|^2$$

with the aid of the absorption oscillator strengths recently given for He I by Green *et al.*[15] So, it remains necessary to discuss the electromagnetic static shift of isolated lines.

III. STATIC SHIFT OF 2*P*-*nS* LINES

The scalar nature of the nS wave functions allows us to write

$$|\langle n00|Z/a_0|n''10\rangle|^2=\sum_{m''}|\langle n00|x/a_0|n''1m''\rangle|^2$$
$$=f_{nS\text{-}n''P}/2(E_{n''10}-E_{n00}) , \tag{9}$$

where $f_{nS\text{-}n''P}$ denotes the absorption oscillator strength of the given transition. With the accurate f values recently obtained for He I by Green *et al.*[15] and the above relation, Eq. (2) becomes

$$\Delta E_{n00}-\Delta E_{21m'}=-\frac{m'e\hbar H}{2m_e c}$$

TABLE II. Electric intensity (V/cm) needed to deplete nQ states by 0.5%.

n	^1S	^3S	^1P	^3P
3	4.28×10^5	8.15×10^6	5.24×10^4	8.85×10^4
4	9.70×10^4	1.61×10^5	1.11×10^4	5.71×10^4
5	3.11×10^4	5.03×10^4	3.54×10^3	1.88×10^4
6	1.22×10^4	1.96×10^4	1.39×10^3	6.94×10^3

TABLE III. F_0 values (kV/cm) needed to shift the nS states by 1 cm^{-1}.

	^3S		^1S	
n	Hydrogenic (Ref. 7)	Eq. (12)	Hydrogenic (Ref. 7)	Eq. (12)
2	735	896	535	546.54
3	151	173.34	115	119.61
4	52	59.12	40	42
5	23	29.4	18	19.01
6	12	13.4	9.5	9.88

$$-(eFa_0)^2 \sum_{n''} \frac{f_{nS-n''P}}{2(E_{n''10}-E_{n00})^2}\,, \qquad (10)$$

an α-independent expression in accord with the spherical symmetry of the nS state. The magnetic dependence of $E_{n'',1,m''}$ is negligible with respect to the difference $E_{n''10}-E_{n00}$ for $H \le 10^5$ G and $n \le 10$ (the main values we consider in this work).

A. Stark Constants ($H=0, \alpha=1$)

The Stark shift produces a lowering of E_{n00}, a feature which already appears in the hydrogenic Unsöld treatment.[16] In order to get quantitative estimates, it appears of interest[9] to introduce the electric intensity F_0 which is necessary to shift $(n, 0, 0)$ by 1 cm^{-1}, so that

$$E_{n00}^{\text{electr}} = (F/F_0)^2 \text{ cm}^{-1} \qquad (11)$$

gives the Stark shift of $(n, 0, 0)$ with the aid of

$$F_0 = \frac{4.9206\times10^{7/2}}{[\sum_{n''} f_{nS-n''P}/(E_{n00}-E_{n''10})^2]^{1/2}} \qquad (12)$$

in kV/cm.

In Table III, the F_0 values are given for $2 \le n \le 6$ and $2 \le n'' \le 8$, and compared with those obtained by using the hydrogenic wave functions (11).

It may be easily seen that the introduction of more sophisticated wave functions, such as those used in the oscillator-strength calculations,[15] does not produce results differing very much from the hydrogenic ones for the singlet (para) states, when accurate unperturbed energies[17] are taken. Therefore, it is *a fortiori* possible to compute Stark constants for the sublevels (n, l, m) with expression (7) for $n \ge 3$ and $l \ge 1$. The hydrogenic approximation appears less suited for the triplet states $n\,^3S$. Nevertheless, it is to be noticed that we have included eight sublevels $(n'', 1, 0)$ in our calculation, while the hydrogenic values[11] are given with only one perturbing level $(n, 1, 0)$, so that the inclusion of four additional states would give hydrogenic data significantly weaker than the

TABLE IV. Comparison of the nS shifts (cm^{-1}) as given, respectively, by the degenerate and the nondegenerate methods. An over-all minus sign ($2P$-nS lines are shifted toward the red) has been omitted. Upper nondegenerate values (in parentheses) havebeen obtained from the hydrogenic data given in Table III.

	$4\,^1S$		$5\,^1S$		$6\,^3S$	
F (kV/cm)	Degenerate [Eq. (13)]	Nondegenerate [Eq. (12)]	Degenerate	Nondegenerate	Degenerate	Nondegenerate
1	6×10^{-4}	(6.25×10^{-4}) 5.66×10^{-4}	2.9×10^{-3}	(3.086×10^{-3}) 2.74×10^{-3}	1.08×10^{-2}	(1.11×10^{-2}) 1.024×10^{-2}
10	0.059	0.0566	0.294	0.274	1.07	1.024
50	1.49	(1.56) 1.41	7.34	(77.15) 6.85	26.09	(27.05) 25.6
100	5.92	5.66	28.66	27.4	92.64	102.4
200	23.34	22.64	81.21	109.6	267.78	409.6
500	137.08	141	449.47	685	839.87	2560
	$4\,^3S$		$5\,^3S$		$6\,^1S$	
1	4×10^{-4}	(3.69×10^{-4}) 2.86×10^{-4}	1.8×10^{-3}	(1.89×10^{-3}) 1.15×10^{-3}	6.7×10^{-3}	(6.94×10^{-3}) 5.57×10^{-3}
10	0.036	0.0286	0.175	0.115	0.66	0.56
50	0.896	(0.92) 0.715	4.42	(4.725) 2.875	16.42	(17.36) 13.92
100	3.56	2.86	17.17	11.5	61.01	55.7
200	14.11	11.44	67.51	46.0	200.4	222.8
500	87.97	71.5	338.71	287.5	739.97	1392.5

present ones. As a by-product, the hydrogenic-nonhydrogenic energy difference would become smaller, especially for the $n\,^3S$ state.

B. Degenerate and Nondegenerate Stark Shifts

It is also of interest to make a connection with previous work[10,18] and compare the nS shift values obtained from Eqs. (11) and (12) with the results of the degenerate perturbation calculation obtained through the diagonalization in the subspace of quantum number n of

$$(H_0+H_2+Az/a_0-\xi)|\psi\rangle=0\quad,\tag{13}$$

with $A=0.0427$ (F in kV/cm). H_2 is a diagonal operator (in the LS scheme) accounting for the distortion correction of the unperturbed eigenvalues from those given by the hydrogenic Hamiltonian $H_0=P^2/2m-e^2/r$. This comparison is detailed in Table IV.

The degenerate values (taken from the Pfennig-Trefftz tabulation[18]) are, of course, expected to be inaccurate for the nS sublevels. Nevertheless, a quantitative estimate of this inaccuracy would be of value in order to determine an upper bound for the error made in the matrix-diagonalization method, the only technique of practical use for profile calculation of degenerate lines[4,17] in the presence of a magnetic field.

For the singlet states the agreement between the degenerate and the nondegenerate values appears quite good with $F\leq 100$ kV/cm. Of course, as F increases, the shifts diverge. The nondegenerate triplet values, excepting $6\,^3S$ with $F\geq 200$ kV/cm, are situated significantly below the degenerate ones. The hydrogenic nondegenerate values (given in parentheses) are computed with the F_0 values given in Table II. They lie above the accurate ones and close (even very close for the $n\,^3S$ states) to the degenerate ones. This feature is explained by the use of hydrogenic wave functions and the large central distortion correction of the nS (greatest for $n\,^3S$) states in the degenerate matrices.[10,18] More precisely, when $F\leq 200$ kV/cm, the nS states interact very weakly with the others, nQ ($Q=P, D, D, \ldots$), and the degenerate method is expected to give nondegenerate results,[19] if the same atomic parameters are used in both cases.

IV. STATIC SHIFT OF $2S$-nP LINES

Now, Eq. (2) specializes to the form

$$\Delta E_{n1m}-\Delta E_{200}=\frac{me\hbar H}{2m_ec}+(eFa_0)^2\left[\alpha^2\sum_{n''}\left(\frac{|\langle n1m|z/a_0|n''0m\rangle|^2}{E_{n10}-E_{n''00}}+\frac{|\langle n1m|z/a_0|n''2m\rangle|^2}{E_{n10}-E_{n''20}}\right)\right.$$
$$\left.+(1-\alpha^2)\sum_{n'',m''}\left(\frac{|\langle n1m|x/a_0|n''2m''\rangle|^2}{E_{n10}-E_{n''20}}+\frac{|\langle n1m|x/a_0|n''0m''\rangle|^2}{E_{n10}-E_{n''00}}\right)\right]\quad,\tag{14}$$

with $m''=m\pm 1$, and neglecting the magnetic dependence of the denominator.

The level scheme of He I (see, for instance, Ref. 9, p. 127) shows that the above expression is essentially negative for the $n\,^3P$ states and strictly positive and greater (in absolute value) for $n\,^1P$.

The interaction of level $(n, 1, m)$ with level $(n'', 0, 0)$ is described by the relations

$$\frac{|\langle n10|z/a_0|n''00\rangle|^2}{E_{n10}-E_{n''00}}=\frac{f_{n''S\text{-}nP}}{2(E_{n10}-E_{n''00})^2}\quad,\tag{15a}$$

$$\frac{|\langle n1m|x/a_0|n''00\rangle|^2}{E_{n10}-E_{n''00}}=\frac{f_{n''S\text{-}nP}}{4(E_{n10}-E_{n''00})^2}\quad,\tag{15b}$$

obtained, respectively, by using Eq. (9) and the equalities

$$|\langle n10|z/a_0|n''00\rangle|^2=2|\langle n1m|x/a_0|n''00\rangle|^2\;,$$

$$|\langle n1-1|x/a_0|n''00\rangle|^2=|\langle n11|x/a_0|n''00\rangle|^2\;.$$

The interaction between $(n, 1, m)$ and $(n'', 2, m'')$ could be expressed in an analogous way with the aid of the absorption oscillator strengths $f_{nP\text{-}n''D}$. Unfortunately, the data of Green *et al.*,[15] which are the most accurate now available, still maintain a 5% uncertainty. So, as is shown in the Appendix, it is sufficient to work with hydrogenic values for the radial integrals

$$R_{n1}^{n''2}=\int_0^\infty R_{n1}(r)\,R_{n''2}(r)\,r^3dr\tag{16}$$

and to neglect the singlet-triplet difference in the matrix elements.

The introduction of Eq. (15) and the use of the one-electron angular dependence (see, for instance, Ref. 11, p. 253) for the matrix elements in Eq. (14) give, respectively,

$$\Delta E_{n10}-\Delta E_{200}=(eFa_0)^2\left(\alpha^2\sum_{n''}\frac{f_{n''S\text{-}nP}}{2(E_{n10}-E_{n''00})^2}+\frac{4(R_{n1}^{n''2})^2}{15(E_{n10}-E_{n''20})}+(1-\alpha^2)\sum_{n''}\frac{(R_{n1}^{n''2})^2}{5(E_{n10}-E_{n''20})}\right)\tag{17}$$

for the central Zeeman component, and

$$\Delta E_{n1m}-\Delta E_{200}=\frac{me\hbar H}{2m_e c}+\frac{(eFa_0)^2}{3}\left[\alpha^2\sum_{n''}\frac{(R_{n1}^{n''2})^2}{5}\,\frac{4-m^2}{E_{n1m}-E_{n''2m}}+(1-\alpha^2)\sum_{n''}\left(\frac{3f_{n''S\text{-}nP}}{4\,(E_{n10}-E_{n''00})^2}+\frac{(R_{n1}^{n''2})^2\,(6+m^2)}{10\,(E_{n1m}-E_{n''20})}\right)\right] \tag{18}$$

for the outer ($m=\pm 1$) components. Of course, the accuracy of expressions (17) and (18) would increase with more refined radial integrals (or oscillator strengths). In the general case, the introduction of a magnetic field produces two Stark constants: a longitudinal one, specialized for $\alpha = 1$, and having a maximum at $m = 0$, like the usual Stark constant,[9,16] and a transverse one, specialized for $\alpha = 0$, which is not a straightforward extension of the pure Stark constant.

A. Longitudinal Stark Constants ($H = 0, \alpha = 1$)

The previous F_0 comparison is repeated in Table V. The most accurate nondegenerate values are given, respectively, by Eqs. (17) and (18) for the $m = 0$ and $m = |1|$ components (in parentheses), with the use of a F_0 expression analogous to Eq. (12). The relative agreement of the nondegenerate data with the hydrogenic ones taken from Bethe and Salpeter[11] appears quite good for the singlet states with $n \geq 3$. Also, it is of interest to comment on the huge and nondegenerate $2\,^3P$ value. This level is shown to be more difficult to shift than any other excited levels (see Table III) of He I. In fact, this result is only true for second-order perturbation theory, because the $2\,^3S$-$2\,^3P$ interaction is then nearly canceled by the sum of all the $2\,^3P$-$n\,^3S$, D $(3 \leq n \leq 8)$ interactions. In this case, a more significant result would certainly be obtained by including higher-order corrections, as considered later. Nevertheless, for the purpose of using optical lines in plasma diagnostics, the present calculation is more than sufficiently accurate, and makes clear that the $2\,^3P$ shifts are unobservable in practice.

The change of sign (and of absolute magnitude) for the $F_0(m=0)$-$F_0(m=|1|)$ difference from singlet to triplet is due to the unperturbed He I level scheme, which produces a partial cancellation of the $m = 0$ shift for the $n\,^3P$ state localized between $n\,^3S$ and $n\,^3D$, if one remembers that a Hermitian perturbation has a tendency to make close levels repel each other. The same effect is absent for the $m = |1|$ $n\,^3P$ levels, which are not coupled with $n\,^3S$ (as long as $\alpha = 1$), and for the $n\,^1P$ states situated above all the $n\,^1Q$ other levels. In the latter case $n\,^1S$ and $n\,^1D$ perturbations add their contribution.

B. Degenerate and Nondegenerate Stark Shifts

The pure Stark shifts ($H = 0$, $\alpha = 1$) are given in Table VI. In contradistinction to the nS case (see Table IV), the accurate nondegenerate values are now situated always higher than the degenerate ones. This feature is the immediate consequence of the non-negligible interaction of nP with nQ ($Q = D, F$, etc.) in the degenerate method.[10,18] It is worthwhile to note that the degenerate-nondegenerate difference is systematically enhanced in Table VI, because the $n''S$ and $n''D$ states $(2 \leq n'' \leq 8)$ are included as perturbers in the nondegenerate expressions (17) and (18).

Nevertheless, the foregoing remark remains valid, because the accurate nS shifts where evaluated under the same conditions. An identical conclusion may be deduced from the nondegenerate hydrogenic shifts ($m = 0$) given in upper parentheses. These latter (except $4\,^3P$ with $F \leq 100$ kV/cm which is little influenced by $4\,^3D$) lie above the degenerate shifts. The hydrogenic data, taken from Table V, included only the nP-nS and nP-nD perturbations in the subspace spanned by the (n, l) sublevels. Moreover, the degenerate-nondegenerate difference appears very small for $4\,^1P$ and $n\,^3P$ with $F \leq 100$ kV/cm. In the presence of higher field strengths ($F \geq 100$ kV/cm) the electric shift becomes comparable with the nP-nD distance, and the degenerate results are to be preferred against the nondegenerate ones. These features, as well as those previously noticed for nS, allow us to understand completely the meaning of degenerate perturbation theory when it is applied to well-separated levels and isolated lines.

C. Combined Stark and Zeeman Shifts

The combined Stark and Zeeman effect of the $4P$ sublevels is illustrated, with a few parameters, in Table VII. The degenerate shifts are those pre-

TABLE V. F_0 values (kV/cm) needed to shift by $|1\ \text{cm}^{-1}|$ the $m = 0$ and $m = |1|$ (this latter in parentheses) sublevels. Hydrogenic values are given only for $m = 0$.

	^3P			^1P		
n	Hydrogenic (Ref. 7)	Eqs. (17) and (18)		Hydrogenic (Ref. 7)	Eqs. (17) and (18)	
2	735	1629	(1313)	535	636	(1213)
3	157	116.12	(112.12)	42	40.88	(50.51)
4	42	37.16	(34.56)	13.8	13.66	(16.73)
5	17.5	16	(15.6)	6	5.95	(7.41
6	9	8.18	(8.05)	3.1	3.05	(3.61)

TABLE VI. Comparison of the nS shifts (cm^{-1}) as given, respectively, by the degenerate and nondegenerate methods for the $m = 0$ and $m = |1|$ sublevels (the latter in lower parentheses). Upper nondegenerate values (upper parentheses) have been obtained from the hydrogenic data ($m = 0$) given in Table V. The $n\,^1P$ shifts are to be considered with a plus sign ($2\,^1S$-$n\,^1P$ line shifted toward the blue). The $n\,^3P$ shifts are to be taken with a minus sign ($2\,^3S$-$n\,^3P$ line shifted toward the red).

F	$4\,^1P$		$5\,^1P$		$6\,^1P$	
(kV/cm)	Degenerate	Nondegenerate	Degenerate	Nondegenerate	Degenerate	Nondegenerate
1		(5.25×10^{-3})		(2.78×10^{-2})		(0.104)
	5.1×10^{-3}	5.36×10^{-3}	2.67×10^{-2}	2.82×10^{-2}	0.1	0.11
	$(3.4\times10^{-3}$	(3.57×10^{-3})	(1.78×10^{-2})	(1.82×10^{-2})	(0.066)	(0.077)
10	0.51	0.54	2.59	2.82	8.57	10.75
	(0.34)	(0.36)	(1.78)	(1.82)	(8.53)	(7.67)
50		(13.12)		69.50		260
	11.57	13.40	39.80	70.60	77.83	268.75
	(8.08)	(8.92)	(31.91)	(45.52)	(66.15)	(191.82)
100	36.63	53.60	96.30	282.40	169.48	1075.01
	(27.17)	(35.70)	(78.76)	(182.11)	(142.67)	(767.3)
200	96.87	214.40	214.95	1129.6	356.85	6718.75
	(74.37)	(142.80)	(178.92)	(728.4)	(295.59)	(4795.62)
500	300.12	1340	590.19	7060	933	26.875
	(226.80)	892.5	(463.49)	(4552)	(759)	(19.183)
	$4\,^3P$		$5\,^3P$		$6\,^3P$	
1		(5.66×10^{-3})		(3.20×10^{-3})		(1.23×10^{-2})
	6×10^{-4}	7.24×10^{-4}	3.1×10^{-3}	3.91×10^{-3}	1.2×10^{-2}	1.49×10^{-2}
	(7×10^{-4})	(8.37×10^{-4})	(3.7×10^{-3})	(4.11×10^{-3})	(1.4×10^{-2})	(1.54×10^{-2})
10	0.056	0.072	0.31	0.39	1.21	1.49
	(0.069)	(0.084)	(0.37)	(0.41)	(1.40)	(1.54)
50		(1.42)		8.16		30.75
	1.42	1.81	7.84	9.76	29.97	37.35
	(1.73)	(2.10)	(9.16)	(10.27)	(32.72)	(38.57)
100	5.61	7.24	30.30	39.06	92.24	149.4
	(6.85)	(8.3)	(34.60)	(41.09)	(100.72)	(154.3)
200	21.67	28.96	98.57	156.24	217.28	597.60
	(26.37)	(33.50)	(112.41)	(164.36)	(250.29)	(617.12)
500	109.07	181	315.35	976.50	571.34	3735
	(135.59)	(209)	(392.04)	(1027.25)	(712.34)	(3857)

viously derived in Ref. 10 with the aid of the diagonalization of the operator

$$H_0+H_2+\frac{L_z}{\hbar}+1+A\left(\frac{x}{a_0}\,(1-\alpha^2)^{1/2}+\frac{z}{a_0}\,\alpha\right)\ ,$$

$$A=0.9143F/H\quad(F \text{ in kV/cm},\ H \text{ in kG})\qquad(19)$$

in the (n, l) subspace. For the case of parallel fields ($\alpha = 1$), the degenerate values may equally be obtained from Eq. (13) and addition of the magnetic shift $me\hbar\,H/2m_ec$. The corresponding data may be seen within the parentheses of Table VII and are localized a little higher (in absolute value) than the degenerate ones. This fact is due to the nonfactorization into smaller submatrices of the Stark and Zeeman degenerate perturbation matrix. Therefore, the interaction between partially degenerate (n, l, m) sublevels is made stronger, and the corresponding shifts become weaker. The same remark is true for the $m = \pm 1$ states and nonparallel fields ($\alpha \neq 1$). The relative degenerate-nondegenerate distance increases from its parallel value and accounts for a stronger off-diagonal interaction in the degenerate treatment. In the presence of crossed fields, the three m components are influenced (especially the $m = |1|$ ones), even in the presence of a weak perturbation, as may be deduced from $4\,^1P$ data.

This behavior confirms the results of the degenerate perturbation theory obtained previously[10] for the $2P$-nQ ($Q = D, F$ and $n \geq 4$) components with $\alpha = 0$.

V. FOURTH-ORDER STARK EFFECT

Until now, the nondegenerate electric perturbation

TABLE VII. Shifts of the $4P$ states in presence of a magnetic intensity. Some Stark ($H=0$) values are reproduced for the purpose of comparison. Degenerate values are obtained from Eq. (19) or from Eq. (13) with addition of the magnetic shift for $\alpha=1$. The latter are given in parentheses.

m \ $4\,^1P$	Singlet		m \ $4\,^3P$	Triplet	
	Nondegenerate	Degenerate		Nondegenerate	Degenerate
	$H=0$	$F=5$ kV/cm		$H=0$	$F=100$ kV/cm
0	0.134	0.129	0	−7.24	−5.61
|1|	0.089	0.086	|1|	−8.37	−6.85
	$H=0.2$ kG	F = 5 V/cm, $\alpha=0$		$H=40$ kG	$F=100$ V/cm, $\alpha=1$
−1	0.121	0.083	−1	−10.24	−8.677 (−8.715)
0	0.089	0.085	0	−7.24	−5.582 (−5.613)
1	0.1215	0.130	1	−6.51	−4.942 (−4.985)
	$H=0$	$F=100$ kV/cm			
0	53.60	36.63			
|1|	35.70	27.17			
	$H=40$ kG	$F=100$ kV/cm, $\alpha=1$		$H=40$ kG	$F=100$ kV/cm, $\alpha=1/\sqrt{2}$
−1	33.84	25.27 (25.30)	−1	−12.465	−8.48
0	53.60	36.57 (36.63)	0	−7.35	−6.266
1	37.57	29.00 (29.04)	1	−8.735	−4.453

has been discussed only within the second-order approximation. This procedure is valid as long as higher-order corrections remain negligible. In this section, we intend to evaluate these latter contributions. It is to be pointed out that from a rigorous point of view this procedure is questionable because the explicit F nondegenerate series is only an asymptotic expansion[20] of the true result and could diverge with the inclusion of higher-order terms. Nevertheless, it is possible to skip in the present situation this point of rigor with the aid of the following argument: The foregoing evaluations show that for a sufficiently high electric intensity producing a shift comparable with the intersublevels distance, the degenerate method is to be preferred. Hence, in practice the nondegenerate calculation is limited to a domain where the considered series is converging[21] and higher-order corrections to the second-order term are meaningful for sublevels (n, l) with $n \geq 3$.

First, we note that for the given range of F values the electric perturbation of the wave functions[19] may be, as before, neglected. Therefore, following Dalgarno's presentation of nondegenerate perturbation theory,[19] we consider, respectively, the third-order,

$$E_i^{(3)} = \sum_{s,t}{}' \frac{\langle i|h|s\rangle\langle s|\bar{h}|t\rangle\langle t|h|i\rangle}{(E_s-E_i)(E_t-E_i)} , \tag{20}$$

and the fourth-order,

$$E_i^{(4)} = -\sum_{r,t,s}{}' \frac{\langle i|h|r\rangle\langle r|\bar{h}|s\rangle\langle s|\bar{h}|t\rangle\langle t|h|i\rangle}{(E_r-E_i)(E_s-E_i)(E_t-E_i)} - E_i^{(2)}\sum_t{}' \frac{|\langle i|h|t\rangle|^2}{(E_t-E_i)^2} , \tag{21}$$

contributions to the shift to the excited level i. The index i is excluded from the various summations, and $E_i^{(2)}$ represents the second-order shift considered above. As before, the various excitation energies E_i, E_r, etc., are to be taken unperturbed, or with a first-order magnetic perturbation. The operator h is defined by

$$\bar{h} \equiv h - \langle i|h|i\rangle \tag{22}$$

for an arbitrary perturbation and simplifies $\bar{h} \equiv h$ with the Stark operator $h \equiv e\vec{F}\cdot\vec{r}$. It may be seen immediately that $E_i^{(3)}$, and any odd contribution, vanishes for such a vectorial interaction. A complete evaluation of Eq. (21) would be rather tedious in the general case ($\alpha \neq 1$), and so we restrict our considerations to a situation with parallel fields ($\alpha=1$) and obtain

$$E_{nm}^{(4)}(\alpha=1) = -(eFa_0)^4 \sum_{\substack{n',l'\\ n'',l''}}{}' \frac{|\langle nlm|z/a_0|n'l'm\rangle|^2 |\langle n'l'm|z/a_0|n''l''m\rangle|^2}{(E_{n'l'm}-E_{nlm})^2(E_{n''l''m}-E_{nlm})} - (eFa_0)^2 E_{nlm}^{(2)} \sum_{n',l'}{}' \frac{|\langle nlm|z/a_0|n'l'm\rangle|^2}{(E_{n'l'm}-E_{nlm})^2} , \tag{23}$$

where (n', l'), $(n'', l'') \neq (n, l)$.

Moreover, for sublevels (n, l) with $3 \leq n \leq 6$ and $l = 0, 1$, the He I level scheme[9] makes it obvious that the most important contribution to Eq. (23) is given by the first term with $n = n''$, schematized in Fig. 2. As a consequence, Eq. (23) is well approximated by

$$E^{(4)}_{nlm}\ (\alpha = 1) \simeq -E^{(2)}_{nlm}\left(\frac{E^{(2)}_{nl+1m}}{E_{nl+2m} - E_{nlm}} + \frac{E^{(2)}_{nlm}}{E_{nl+1m} - E_{nlm}}\right), \tag{24}$$

providing an estimate for $E^{(4)}_{nlm}$ in terms of second-order shifts. It appears of interest to plot the $E^{(4)}/E^{(2)}$ ratio, as is shown in Table VIII, for some nS levels and $F = 100$ kV/cm. It is then worthwhile to notice that $E^{(4)}_{nlm} \simeq E^{(2)}_{nlm}$ if $E^{(2)}_{nl+1m} \simeq E_{nl+2m} - E_{nlm}$. Hence, the foregoing estimates for the fourth-order Stark effect could provide a numerical prescription for the use of the degenerate perturbation theory. For instance, the given ratio is equal to one for $6\,^1S$ at 20 kV/cm and for $6\,^1P$ at 10 kV/cm.

VI. COMPARISON WITH EXPERIMENTAL DATA

A. Pure Stark Effect

It is also of interest to get a quantitative understanding of the absolute accuracy of the computed shifts with the aid of the available experimental results. For $F \leq 100$ kV/cm and nL levels with $n = 4, 5$ and $L \geq 1$, a systematic confrontation between experience and the results of the degenerate theory has been achieved by Foster,[22] who has shown that for the considered shifts, the theoretical results reproduce the experimental ones within the accuracy (0.5 cm^{-1}) of the latter. Moreover, the new degenerate computed values established by Pfennig and Trefftz,[18] with the aid of more accurate unperturbed energies, remain within Foster's experimental uncertainty.

On the other hand, the agreement between the Sjögren experimental results and the Foster (or Pfennig-Trefftz) shifts is not so good for $F > 100$ kV/cm, as pointed out by Minnhagen.[23] Therefore, it is worthwhile to resume the corresponding confrontation with new computed values, as may be seen in Table IX(a) for $4\,^3S$ and in Table IX(b) for $4\,^3P$.

TABLE VIII. Approximate ratio of fourth- to second-order Stark shift for some nS levels with $F = 100$ kV/cm.

n	$E^{(4)}/E^{(2)}$ Triplet	 Singlet
4	9.44×10^{-3}	0.12
5	9.47×10^{-2}	2.22
6	0.68	7.7

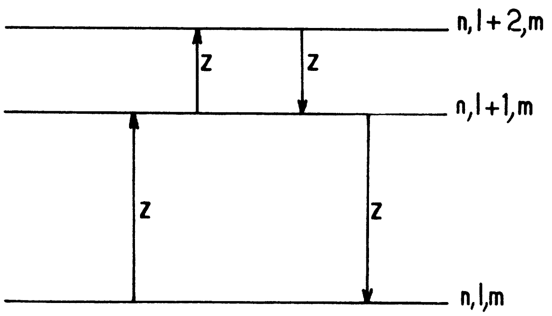

FIG. 2. Graph of the first and most important contribution to the fourth-order Stark effect.

It clearly appears that even in the presence of a very high electric perturbation ($F > 400$ kV/cm), the $4\,^3S$ shift is well accounted for by the quadratic result. The degenerate method is to be preferred for the $4\,^3P$ shifts, however.

B. Combined Stark and Zeeman Effects ($\vec{F} \perp \vec{H}$)

In Table X a comparison between the results of Eq. (19) (degenerate method), Eqs. (17) and (18) (nondegenerate method), and the measurements performed by Foster and Pounder[24] and by Lebowsky and Steubing[25] is presented for $5\,^3P$ and $5\,^1P$, respectively, in the presence of crossed fields ($\alpha = 0$).

The more recent Lebowsky-Steubing data appear well reproduced by the degenerate results, a fact already pointed out in Ref. 10. In the presence of strong magnetic fields, and even moderate electric fields, there appears a rather important discrepancy between the degenerate values and those given by Eqs. (17) and (18), especially for $m = 0, 1$, the quadratic shifts being then larger (in absolute value) than the experimental ones.

TABLE IX. Comparison of calculated and measured shifts (cm^{-1}) for the pure Stark effect of 4^3S and 4^3P.

(a) $4\,^3S$

F (kV/cm)	Nondegenerate calculation [Eq. (10)]	Sjögren measurements (Ref. 25)	Degenerate calculation [Eq. (13)]
110	−3.468	−3.7	−4.796
217	−13.472	−13.0	−16.832
319	−29.114	−30.1	−35.778
403	−46.466	−44.8	−56.257

(b) $4\,^3P$

F (kV/cm)	Nondegenerate calculation[a] [Eqs. (17) and (18)]	Sjögren measurements (Ref. 25)	Degenerate calculation[a] [Eq. (13)]
110	− 8.762 (−10.13)	−6.55	−6.906 (− 8.424)
217	− 34.100 (−39.42)	−30.05	−25.597 (−31.148)
319	− 73.68 (−85.19)	−65.55	−51.822 (− 63.122)
403	−117.72 (−135.95)	−96.25	−76.830 (−94.364)

[a] The $|m| = 1$ values are given in the parentheses.

TABLE X. Comparison of calculated and measured shifts (cm^{-1}) for combined Stark and Zeeman effects of $5\,^3P$ and $5\,^1P$, respectively, in the presence of crossed fields ($\alpha = 0$).

(a) $5\,^3P$ ($H = 25.8$ kG, $F = 64$ kV/cm, $\alpha = 0$)

m	Nondegenerate calculation [Eqs. (17) and (18)]	Foster-Pounder measurements (Ref. 26)	Degenerate calculation [Eq. (19)]
−1	−133.294	−123.0	−128.52
0	−164.495	−125.3	−130.00
1	−166.895	−139.8	−132.41

(b) $5\,^1P$ ($H = 32$ kG, $F = 13.9$ kV/cm, $\alpha = 0$)

m	Nondegenerate calculation [Eqs. (17) and (18)]	Lebowsky-Staubing measurements (Ref. 27)	Degenerate calculation [Eq. (19)]
−1	27.697	25.6	25.01
0	36.144	27.9	28.56
1	39.128	28.8	29.09

VII. APPLICATION TO STARK BROADENING

A. Stark Constants for Isolated Lines

Although we have discussed at length the approximations on which the isolated-line concept is based, it still remains to evaluate with the aid of accurate atomic data the quadratic Stark constants which appear explicitly in the reduced profile expression [see Eq. (4.14) of Ref. 1]. In order to get a connection with the hydrogenic results already given in Ref. 1, we consider the quadratic constant $\overline{C}$ averaged over the magnetic quantum numbers of the upper level of the considered transition. Then, we obtain

$$\overline{C} = C^{(0)} \qquad (25)$$

for lines with upper nS levels, and

$$\overline{C} = \tfrac{1}{3}(C^{(0)} + 2C^{(1)}) \qquad (26)$$

for lines with upper nP levels. $C^{(m)}$ represents the quadratic shift of the sublevel (n, l, m) referred to the lower level (n', l') and averaged over the magnetic number m' (see Table XI).

$\overline{C}$ data then deduced from Eqs. (10), (17), and (18) for singlet lines appear nearly equal to or a little higher (in absolute value) than the results given in Ref. 1. The triplet values show much larger discrepancies, and their hydrogenic estimates lie systematically higher than ours. The comparison with the available experimental material shown in Ref. 1 suggests fair agreement between computed and measured values for the $2P$-nS lines (especially the important 4713-Å) with $n = 3, 4$. On the contrary, it is bad for the $2S$-nP lines with $n = 3, 4$. This fact may be easily explained by the non-negligible nP-nQ interactions, which are at present not taken into account in the nondegenerate definition of the Stark constant.

TABLE XI. Averaged Stark constant $\overline{C}$ in cm^{-1} per (100 kV/cm)^2.

Line	Nondegenerate [Eqs. (10), (17), and (18)]	Hydrogenic (Ref. 1)	Landolt-Börnstein experimental (Ref. 1)
$1\,^1S$-$4\,^1P$ 522.2	41.58	39.4	
$1\,^1S$-$3\,^1P$ 537.1 Å	4.606	4.10	
1^1S-$2\,^1P$ 584.4 Å	0.0127	0.0046	
$2\,^3S$-$4\,^3P$ 3188 Å	−7.98	−6.83	−6.2
$2\,^3S$-$3\,^3P$ 3889 Å	−0.657	−0.67	−0.71
$2\,^1S$-$4\,^1P$ 3965 Å	41.61	39.4	37.3
$2\,^3P$-$5\,^3S$ 4121 Å	−11.564	−15.6	
$2\,^1P$-$5\,^1S$ 4438 Å	−27.80	−28.10	
$2\,^3P$-$4\,^3S$ 4713 Å	−2.85	−3.14	−2.9
2^1S-$3\,^1P$ 5016 Å	4.639	4.14	4.3
$2\,^1P$-$4\,^1S$ 5048 Å	−5.681	−5.79	−5.2
2^3P-$3\,^3S$ 7065 Å	−0.328	−0.37	−0.25
$2\,^1P$-$3\,^1S$ 7281 Å	−0.712	−0.72	
$3\,^3P$-$5\,^3S$ 12 850 Å	−10.792	−15.0	
$3\,^1P$-$5\,^1S$ 13 477 Å	−32.28	−32.2	
$3\,^1S$-$4\,^1P$ 15 088 Å	42.28	40.1	
$3\,^3P$-$4\,^3S$ 21 127 Å	−2.06	−2.48	
$3\,^1P$-$4\,^1S$ 21 138 Å	−10.662	−9.9	
$4\,^1P$-$5\,^1S$ 46 066 Å	−69.25	−67.5	
$4\,^3P$-$5\,^3S$ 46 950 Å	−3.576	−8.9	

B. Static Splitting of Partially Overlapping Lines

For the quantitative evaluation of partially overlapping lines such as $2P$-nQ ($Q = P, D, F, \ldots$), with $n \geq 4$, one has to compute simultaneously the static shifts of all the sublevels (n, l, m) pertaining to a main quantum number n. This procedure, performed with the aid of the diagonalization of Eq. (13) [or Eq. (19)], leads to cumbersome algebraic manipulations for degenerate eigenquantities, which are unavoidable in the presence of a magnetic perturbation.[7] Happily, for a pure Stark effect, the above-mentioned partition of the perturbation matrix into smaller submatrices allows us, as pointed out by Griem,[3] to write the complete profile

$$L(\omega) = \textstyle\sum_m g_m L_m(\omega) \tag{27}$$

as a sum of magnetic profiles indexed by the upper magnetic quantum number. For instance, the line centered at 4471 Å ($n = 4$) may be given the form (27) with[3] $m = 0, 1, 2$, $g_0 = 5^{-1}$, and $g_1 = g_2 = \frac{2}{5}$.

Therefore, the evaluation of static quantities may be obtained by solving algebraic equations of low order. Using that method, Griem[3] and also Gieske and Griem[5] have computed the $2\,^3P$-$n\,^3D$, ^3F profiles with the aid of degenerate perturbation theory, and corrected them with a quadratic interaction arising from the $n\,^3P$ level. Actually, the results derived in the present work show that for all field strengths, the static nP shifts, with $n \geq 4$, have to be calculated within degenerate perturbation theory. This amounts to a lowering by 20–25% (for $F \leq 100$ kV/cm) of the k_m Stark constant used in Ref. 3, and to reducing only by 2 and 3% the $4\,^3P$ contribution to the L_0 and $L \pm 1$ profiles, respectively, of the 4471-Å line.

Indeed, these remarks give additional support to Griem's procedure[3] of treating apart the relatively isolated $2\,^3P$-$n\,^3P$ components, if the remaining Stark interaction is considered with the degenerate theory.

On the other hand, the quadratic calculation seems well suited to include the contribution of the $n\,^3S$-$n\,^3Q$ ($n \leq 6$) interactions as long as $F \leq 100$ kV/cm.

VIII. THEORETICAL REMARKS

A detailed evaluation of the Stark effect for the excited He I levels appears interesting not only in providing more accurate atomic parameters needed in optical spectroscopy. It is also of value in order to get a deeper insight into the various time-dependent perturbation methods of calculation. Usually, great theoretical attention is devoted to the discussion of the validity of the perturbation approach for the electric shift of well-isolated levels, (see, for instance, Refs. 19 and 20), such as the ground state or the first excited ones. Indeed, our estimates of the $2S$ and $2P$ shifts confirm the usefulness of such investigations. But this work also shows the need for a better understanding of the behavior of upper excited levels in the presence of an electric field. Particularly, the case of the nS shifts that are more influenced by the Stark interaction with the distant $n'P$ states ($n' \neq n$) than by the degenerate coupling with the nQ ($Q = D, F, \ldots$) levels lying in the same subspace has to be examined with a special attention. The foregoing calculations then confirm the difficulty, previously emphasized by Dalgarno,[19] of establishing standard prescriptions for the choice of a given perturbation method of partially degenerate levels. At first sight, it appears possible to consider a very large perturbation matrix including all the levels of interest with various main quantum numbers, so that the distant nS-$n'P$ interaction would be included, and the corresponding shifts could be taken as the most accurate ones. Moreover, it is likely that these values would not differ very much from the quadratic ones, because for small electric perturbation (relative to the nS-$n'P$ distance) degenerate theory (see Tables IV and VI) is expected to reproduce the nondegenerate results. Numerically, the problem still remains, in view of the inaccuracy (increasing with the size of the perturbation matrix) of the diagonalization techniques. Nevertheless, it is likely that extensive machine calculations could lead to practical rules.

Moreover, in the presence of a nonparallel magnetic field, the electric perturbation may introduce strong interactions between the magnetic sublevels, thus adding to the inaccuracy of the diagonalization procedure,[10] a fact which tends to obscure the physical meaning of the eigenvalues.

In conclusion, it is possible to state that the electric properties of excited levels cannot be well understood within the one-level approximation used for the first excited states, and that it is necessary to solve the eigenvalue problem for the whole spectrum [or at least the most excited part of it, i.e., all (n, l, m) sublevels with $n \geq 4$] simultaneously.

APPENDIX

We briefly outline the method for extracting the radial integral from the absorption oscillator strength. The desired relation is provided by the Rohrlich expression written with Griem notation,[26]

$$f_{JJ'} = 2(E_J - E_{J'})(2J'+1)(2L+1)(2L'+1) \times W(LJL'J';S1)^2\, W(LLL'L';01)^2 L_>(R_{nL}^{n'L'})^2 , \tag{A1}$$

where $L_> = \sup(L, L')$ and W is a Racah coefficient. $f_{JJ'}$ represents the absorption oscillator strength of the J-J' transition with

$$|L-S| \leq J \leq L+S, \quad |L'-S'| \leq J' \leq L'+S' .$$

The $f_{JJ'}$ are themselves linearly connected to the usually tabulated orbital oscillator strengths

$$f_{LL'} = [(2S+1)(2L+1)]^{-1} \sum_{JJ'} (2J+1) f_{JJ'} . \qquad \text{(A2)}$$

For example, let us consider the singlet line $2\,^1S$-$3\,^1P$ ($S=0$). The coefficient $W(1122;01) = 0.2582$ and $f_{LL'} = f_{JJ'}$ give

$$(R_{31}^{32})^2_{\mathrm{Green}} = 100.6,$$

with the $f_{3\,^1P-3\,^1D}$ value due to Green *et al.*[15] These data differ very little from the hydrogenic data,

$$(R_{nl}^{nl+1}) = 1.5\,[n^2-(l+1)^2]^{1/2} \quad ,$$

$$(R_{31}^{32})^2_{\mathrm{hydr}} = 101.25 .$$

(The same procedure could be repeated for $n\,^1P$ with $n \geq 4$.) But the difference between the data of Green *et al.* and the hydrogenic data remains much smaller than the 5% uncertainty of Green *et al.* in the $f_{n\,^1P-n''\,^1D}$.

Moreover, the same argument is even more valid for the $n\,^3P$ states with $n \geq 3$, in view of greater uncertainties appearing in the corresponding oscillator strength values. Therefore, in practice, it is sufficient to work with hydrogenic radial integrals (given on p. 255 of Ref. 9 or tabulated by Green *et al.*[27]) and to neglect the singlet-triplet difference in expression (16).

Also, the Bates-Damgaard Coulomb results[28] for He do not appear more accurate than the results of Green *et al.* These remarks suggest strongly that new and more accurate $f_{nP-n''D}$ data should be calculated with the aid of the configurational method of Green *et al.*[17]

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