# Electron Broadening and Shift of Spectral Lines of Helium*

BENNETT KIVEL†
*Sloane Physics Laboratory, Yale University, New Haven, Connecticut, AND University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico*

(Received December 9, 1954)

The quantum mechanical treatment of electron broadening as used by Kivel, Bloom, and Margenau is extended to include line shifts and is applied to the He I spectrum. The $3d \rightarrow 2p$ line is anomalous, since it has a small Stark shift and consequently a small Holtsmark broadening. For it the electron effects dominate. Comparison of this line's width and shape with others in the He I spectrum provides a simple experimental check on the theory.

## I. THEORY

THE methods for treating electron broadening developed by Kivel, Bloom, and Margenau (KBM)[1] are here extended to include line shifts and applied to He I spectrum. In KBM the broadened line was shown to have a Lorentz shape $1/[(\gamma+\gamma_P+\gamma_U)^2+\omega^2]$, the half-width being the sum of natural ($\gamma$), universal ($\gamma_U$) and polarization ($\gamma_P$) contributions. For practical applications the polarization term dominates the broadening. It corresponds to the lack of rigid quantization in the perturbed atom which, shocked out of its initial state by the passing electron, has a shortened lifetime and more uncertain energy.

In this paper we treat the interaction between atom and free electron as a perturbation and expand the Schrödinger $\Psi$ function with plane wave factors for the free electron. This will give $\gamma_U$ incorrectly, a shortcoming which is not urgent, since in our applications we neglect $\gamma_U$, which was shown to be small compared to $\gamma_P$ in KBM.

The time rate of change of the expansion amplitude of an initially excited state of the atom, state 2, with no photons present and a free electron with wave number vector $\mathbf{k}_\lambda$, is

$$i\hbar\dot{d}_\lambda=\sum_r J_r e^{i\omega t}b_{r\lambda}+\sum_\mu C_{2\lambda,\,2\mu}e^{i\Omega_{\lambda\mu}t}d_\mu + \sum_{n\neq 2}'\sum_\mu C_{2\lambda,\,n\mu}e^{i(\omega_{2n}+\Omega_{\lambda\mu})t}n_\mu. \quad (1)$$

The first sum of matrix elements ($J_r$), of the interaction between radiation field and atom, coupling atomic state 2 to the ground state 1 and a single photon with energy $\hbar\omega_r$, leads in the usual way to spontaneous emission ($\gamma$). The second sum over the diagonal collision matrix elements contributes to $\gamma_U$. Although the atomic state is undistorted, an energy exchange between electron and the emitted photon is introduced. The last sum couples state 2 to all others ($n$), giving rise to polarization broadening (which also includes quenching). Several amplitudes appear on the right side of Eq. (1): $b_{r\lambda}$—atom in state 1, photon with energy $\hbar\omega_r$, free electron in state $\mathbf{k}_\lambda$ (with energy $\epsilon_\lambda=\hbar^2k_\lambda^2/2m$); $d_\mu$—atom in state 2, no photons, electron state $\mathbf{k}_\mu$; and $n_\mu$—atom in state $n$, no photons, electron state $\mathbf{k}_\mu$. The energies involved are

$$\hbar\omega=E_2-E_1-\hbar\omega_r;\quad \hbar\Omega_{\lambda\mu}=\epsilon_\lambda-\epsilon_\mu;\quad \text{and}\quad \hbar\omega_{2n}=E_2-E_n,$$

where $E_n$ is the energy of the atom in state $n$.

Similar equations exist for each of the amplitudes. They can be used to reduce Eq. (1) to the form

$$i\hbar\dot{d}_\lambda=\sum_\mu C_{2\lambda,\,2\mu}e^{i\Omega_{\lambda\mu}t}\sum_\nu\int_0^t\frac{1}{i\hbar}C_{2\mu,\,2\nu}e^{i\Omega_{\mu\nu}\tau}d_\nu d\tau+\cdots. \quad (2)$$

The solution of these coupled differential equations is more easily obtained if all terms on the right of Eq. (2) with amplitudes other than the one on the left ($d_\lambda$) can be neglected. This is a valid procedure if one can average over arbitrary phases associated with these amplitudes. Since the electrons come from different sources (i.e., are incoherent), the $d_\nu$ have factors $\exp(i\phi_\nu)$ containing unrelated arbitrary phases $\phi_\nu$. An average over these phases leads to the cancellation of all terms on the right of Eq. (2) except the one with $d_\lambda$. To see this, consider the simpler example of a similar differential equation:

$$\dot{a}e^{i\phi}=Ae^{i\phi}+Be^{i\phi'}.$$

Assuming this to be true when averaged over $\phi$ and $\phi'$, one obtains $\dot{a}=A$.

Thus Eq. (1) becomes

$$\dot{d}_\lambda=-\frac{1}{\hbar^2}\Big\{\sum_r|J_r|^2\int_0^t e^{i\omega(t-\tau)}d_\lambda(\tau)d\tau + \sum_\mu|C_{2\lambda,\,2\mu}|^2\int_0^t e^{i\Omega_{\lambda\mu}(t-\tau)}d_\lambda(\tau)d\tau + \sum_n'\sum_\mu|C_{2\lambda,\,n\mu}|^2\int_0^t e^{i(\omega_{2n}+\Omega_{\lambda\mu})(t-\tau)}d_\lambda(\tau)d\tau\Big\}. \quad (3)$$

The solution,

$$d_\lambda=a_\lambda\exp(-\gamma_2+i\delta_2)t, \quad (4)$$

* Supported under the auspices of the U. S. Atomic Energy Commission. Part II of this paper is contained in a dissertation presented for the degree of Doctor of Philosophy in Yale University.

† Now at the Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

[1] Kivel, Bloom, and Margenau, Phys. Rev. 98, 495 (1955).

of Eq. (3) is sought. The quantity $\gamma_2$ contributes to the spectral line width and $\delta_2$ shifts the line center.

The summations over $r$ and $\mu$ on the right side of Eq. (3) can be replaced by an integral over energy and a sum over degenerate states. Then using Eq. (4), one obtains the equation for $d_\lambda$ in the form,

$$\dot{d}_\lambda=\left\{\int_{-\infty}^{+\infty}f(y)\left[\int_0^t e^{[i(y-\delta_2)+\gamma_2](t-\tau)}d\tau\right]dy\right\}d_\lambda$$
$$=\left\{\int_{-\infty}^{+\infty}f(y)\left[\frac{e^{[i(y-\delta_2)+\gamma_2]t}-1}{i(y-\delta_2)+\gamma_2}\right]dy\right\}d_\lambda; \quad (5)$$

$f(y)$ is a sum over degenerate states; e.g., see Eq. (7) where

$$\sum_\mu|C_{2\lambda,n\mu}|^2=\int_{-\infty}^{+\infty}f(y)dy \quad \text{and} \quad y=\omega_{2n}+\Omega_{\lambda\mu}.$$

It is usually assumed that $|J_r|^2$ varies slowly with the photon energy, and that the corresponding $f(y)$ in Eq. (5) can be given its resonance value,[2] i.e.,

$$f_J(\delta_2)\int_{-\infty}^{+\infty}\left\{\frac{e^{[i(y-\delta_2)+\gamma_2]t}-1}{i(y-\delta_2)+\gamma_2}\right\}dyd_\lambda$$
$$=\pi f_J(\delta_2)d_\lambda=-\gamma d_\lambda. \quad (6)$$

Here the factor $\gamma$ is real, since $f_J(y)$ is real; and radiative decay contributes the natural width $\gamma$ to $\gamma_2$.

In KBM, this same approximation was used for the collision matrix elements. However, it was seen that some matrix elements had logarithmic variations. For these matrix elements a resonance approximation is not strictly valid. The more detailed analysis below shows that in addition to a real part $\gamma_P$, there is an imaginary term $i\delta_2$.

Following KBM, we write

$$\sum_\mu|C_{2\lambda,n\mu}|^2=\int\frac{V}{(2\pi)^3}d\mathbf{k}_\mu$$
$$\times\left|\int\int\frac{e^{i\mathbf{K}\cdot\mathbf{R}}}{V}\psi_2^*\psi_n\left(\frac{e^2}{|\mathbf{R}-\mathbf{r}|}-\frac{e^2}{|\mathbf{R}|}\right)d\mathbf{r}d\mathbf{R}\right|^2$$
$$=\frac{V}{(2\pi)^2}\frac{m}{2\hbar k_\lambda}\int_{-\infty}^{+\infty}dy\int_{(k_\lambda-k_\mu)^2}^{(k_\lambda+k_\mu)^2}dK^2$$
$$\times\left|\frac{4\pi e^2}{VK^2}\int(e^{i\mathbf{K}\cdot\mathbf{r}}-1)\psi_2^*\psi_n d\mathbf{r}\right|^2, \quad (7)$$

where $\mathbf{k}_\mu$=final wave number vector of electron, $\mathbf{K}=\mathbf{k}_\mu-\mathbf{k}_\lambda$=momentum transfer vector, $V$=reciprocal of electron density $n$, $\psi$=atomic function, $\mathbf{r}(\mathbf{R})$=position vector of atomic (free) electron from nucleus, and $y=\omega_{2n}+\Omega_{\lambda\mu}$.

[2] G. Wentzel, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), second edition, Vol. 24.1, p. 753.

For small $\mathbf{K}$, we expand

$$e^{i\mathbf{K}\cdot\mathbf{r}}=1+i\mathbf{K}\cdot\mathbf{r}+\cdots.$$

Since the $\psi$ are orthogonal, the leading term survives only in the diagonal elements where it is canceled by the nuclear interaction term. The next term leads to polarization broadening. Retaining this term only, since the $K^{-4}$ factor weights small $K$ heavily,

$$\frac{\sum_\mu|C_{2\lambda,n\mu}|^2}{\hbar^2}\cong\frac{2}{V}\frac{me^4}{\hbar^3k_\lambda}\frac{1}{3}\left|\int\psi_2^*\psi_n r\right.$$
$$\left.\times\cos\theta d\mathbf{r}\right|^2\int_{-\infty}^{+\infty}2\ln\left|\frac{k_\lambda+k_\mu}{k_\lambda-k_\mu}\right|dy$$
$$=\frac{2nv_\lambda\sigma_\lambda}{3\pi}\left(\frac{z_{2n}}{a}\right)^2\int_{-\infty}^{+\infty}2\ln\left|\frac{k_\lambda+k_\mu}{k_\lambda-k_\mu}\right|dy,$$

where

$$z_{2n}\equiv\int\psi_2^*\psi_n r\cos\theta d\mathbf{r},$$

$$\sigma_\lambda=\pi/k_\lambda^2.$$

The factor $\frac{1}{3}$ enters when an average is taken over the random orientation of the atom with respect to the direction of the incident electron.

The coefficient of $d_\lambda$ on the right side of Eq. (5) is

$$\frac{-2nv_\lambda\sigma_\lambda}{3\pi}\left(\frac{z_{2n}}{a}\right)^2\int_{-\infty}^{+\infty}2\ln\left|\frac{k_\lambda+k_\mu}{k_\lambda-k_\mu}\right|$$
$$\times\left\{\frac{e^{[i(y-\delta_2)+\gamma_2]t}-1}{i(y-\delta_2)+\gamma_2}\right\}dy. \quad (8)$$

We introduce a new variable of integration,

$$Y=(y-\delta_2)/|\omega_{2n}-\delta_2|.$$

Our treatment will be restricted to nondegenerate states where $\omega_{2n}\gg\delta_2$. Then,

$$\frac{k_\lambda+k_\mu}{k_\lambda-k_\mu}=\frac{\hbar(k_\lambda+k_\mu)^2}{2m(Y\mp1)(|\omega_{2n}-\delta_2|)},$$

where the $-(+)$ sign corresponds to $\omega_{2n}-\delta_2>0$ ($\omega_{2n}-\delta_2<0$). The integral in Eq. (8) is simplified by use of a resonance approximation for the slowly varying part of the logarithm, namely,

$$2\pi\ln\left[\frac{\hbar(k_\lambda+k_{\mu'})^2}{2m(|\omega_{2n}-\delta_2|)}\right]$$
$$-\int_{-\infty}^{+\infty}2\left[\frac{e^{[iY+\Gamma]T}-1}{iY+\Gamma}\right]\ln|Y\mp1|dY, \quad (9)$$

provided $k_{\mu'}$ is the resonance value

$$k_{\mu'}^2=(2m/\hbar)(\omega_{2n}-\delta_2)+k_\lambda^2,$$

and, by definition,

$$\Gamma \equiv \gamma_2/|\omega_{2n}-\delta_2|$$
$$T \equiv t(|\omega_{2n}-\delta_2|).$$

The resonance approximation is not satisfactory for $2\ln|Y\mp1|$ which diverges at $Y=\pm1$. With this factor the integral in Eq. (9) has an imaginary part. First we evaluate the imaginary part of the first term in the integrand, which is on the order of $\Gamma\ll1$; i.e.,

$$-\mathrm{Im}\int_{-\infty}^{+\infty}\{2\ln|Y\mp1|\exp[(iY+\Gamma)T]\}/(iY+\Gamma)dY=O(\Gamma).$$

To show this we define

$$I(a)\equiv\int_{-\infty}^{+\infty}\{2\ln|Y+a|\exp(iY+\Gamma)T\}/(iY+\Gamma)dY,$$

and use

$$I(a)=\int_{-a}^{+a}\left(\frac{dI}{da}\right)_x dx+I(-a).$$

Since

$$I(a)=[I(-a)]^*,$$

$$2\,\mathrm{Im}I(a)=\int_{-a}^{+a}\left(\frac{dI}{da}\right)_x dx.$$

Now using the semi-circle contour in the positive half of the imaginary plane, we find

$$\frac{dI}{da}=2\int_{-\infty}^{+\infty}\{[e^{(iY+\Gamma)T}]/(Y+a)(iY+\Gamma)\}dY=2\left[\frac{2\pi}{(i\Gamma+a)}+\frac{\pi i e^{(-ia+\Gamma)T}}{-ia+\Gamma}\right];$$

and

$$2\,\mathrm{Im}I(a)\cong-8\pi i\tan^{-1}(a/\Gamma)+4\pi^2 i,$$

since

$$\int_0^{a/\Gamma}\frac{\cos(\Gamma Tx)}{1+x^2}dx\cong\int_0^{\infty}\frac{\cos(\Gamma Tx)}{1+x^2}dx=\frac{\pi}{2}e^{-\Gamma T},$$

and

$$-\frac{d}{d\Gamma T}\int_0^{\infty}\frac{\cos(\Gamma Tx)}{1+x^2}dx=\int_0^{\infty}\frac{x\sin(\Gamma Tx)}{1+x^2}dx=\frac{\pi}{2}e^{-\Gamma T}.$$

Consequently, for $\Gamma\ll1$, we can expand $\tan^{-1}(1/\Gamma)=\frac{1}{2}\pi+O(\Gamma)$, and

$$2\,\mathrm{Im}I(\pm1)\cong O(\Gamma).$$

For the real part of $I(\pm1)$,

$$\mathrm{Re}I(\pm1)=e^{\Gamma T}\int_{-\infty}^{+\infty}2\ln|Y\pm1|\left[\frac{\Gamma\cos(YT)+Y\sin(YT)}{Y^2+\Gamma^2}\right]dY,$$

we lack as neat an evaluation procedure. It is assumed that the resonance approximation of KBM gives $\gamma_P$ correctly. The method is analogous to Eq. (6) for the radiation field perturbation. To demonstrate its validity we expand $2\ln|Y\pm1|$ in a Taylor series about the resonance value $Y=0$, obtaining $2\ln|Y\pm1|\cong\pm2Y-Y^2$. The slowest variation is the constant resonance value zero, which gives no correction to the term already removed in Eq. (9). The next term in the expansion has an odd integrand and also contributes nothing. The contribution from the neighborhood of the resonance for the $Y^2$ term is $O(\Gamma^2)$. Hence, the resonance approximation appears to be reasonable in this case and we neglect the real part of $I(\pm1)$.

Second, we write the remaining term in the integral of Eq. (9) as a real and an imaginary part,

$$+\int_{-\infty}^{+\infty}\frac{2\ln|Y\mp1|}{iY+\Gamma}dY=\Gamma\int_{-\infty}^{+\infty}\frac{2\ln|Y\mp1|}{\Gamma^2+Y^2}dY-i\int_{-\infty}^{+\infty}\frac{2Y\ln|Y\mp1|}{\Gamma^2+Y^2}dY.$$

The real part is of the order of $\Gamma^2$. To show this we define

$$\Gamma\int_{-\infty}^{+\infty}\frac{2\ln|Y\mp1|}{\Gamma^2+Y^2}dY\equiv\Gamma I_1(\mp1),$$

where

$$I_1(a)\equiv\int_{-\infty}^{+\infty}\frac{2\ln|Y+a|}{\Gamma^2+Y^2}dY=\int_0^a\left(\frac{dI_1}{da}\right)_x dx+I_1(0).$$

Thus,

$$\frac{dI_1}{da}=\frac{2a\pi}{\Gamma(\Gamma^2+a^2)},$$

and

$$I_1(0)=(\pi/\Gamma)\ln(\Gamma^2).$$

Therefore,

$$I_1(a)=(\pi/\Gamma)\ln(\Gamma^2+a^2),$$

and

$$\Gamma I_1(\mp1)=\pi\ln(\Gamma^2+1)\cong\pi\Gamma^2.$$

In a similar manner we evaluate the imaginary part, which leads to the line shift. We define

$$-iI_2(\mp1)\equiv-i\int_{-\infty}^{+\infty}\frac{2Y\ln|Y\mp1|}{\Gamma^2+Y^2}dY,$$

where

$$I_2(a)=\int_{-\infty}^{+\infty}\frac{2Y\ln|Y+a|}{\Gamma^2+Y^2}dY=\int_0^a\left(\frac{dI_2(a)}{da}\right)_x dx+I_2(0).$$

As before,

$$\frac{dI_2}{da}=\frac{2\pi}{\Gamma}-\frac{2a^2\pi}{\Gamma(\Gamma^2+a^2)},$$

and

$$I_2(0)=0,$$

the integrand being an odd function of $Y$. Finally, we obtain a contribution to $\delta$ which is large compared to $\Gamma$:

$$-iI_2(\mp1)=-i2\pi\tan^{-1}(\mp1/\Gamma)=\pm i\pi^2+O(\Gamma)\quad\text{for}\quad\Gamma\ll1.\qquad(11)$$

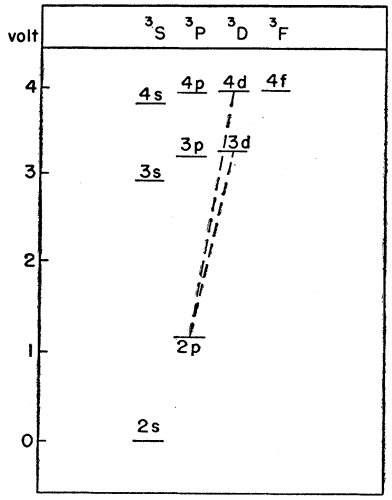


FIG. 1. Partial term scheme for orthohelium. Since broadening depends on near neighbors, the $4d$ level has different properties than $3d$, which lacks a partner corresponding to $4f$.

Collecting the results, we rewrite expression (8), with neglect of terms of order $\Gamma$,

$$\frac{-2nv_\lambda\sigma_\lambda}{3\pi}\left(\frac{z_{2n}}{a}\right)^2\left\{2\pi\ln\left[\frac{\hbar(k_\lambda+k_{\mu'})^2}{2m|\omega_{2n}-\delta_2|}\right]\pm i\pi^2\right\} \tag{12}$$
$$\equiv-\gamma_P(2n)+i\delta_{2n},$$

where the $\pm$ sign corresponds to $\omega_{2n}-\delta_2\gtrless 0$.

Consequently,

$$\delta_2=-\left(\frac{2nv_\lambda\sigma_\lambda\pi}{3}\right)\sum_n{}'\left(\frac{z_{2n}}{a}\right)^2\frac{(\omega_{2n}-\delta_2)}{|\omega_{2n}-\delta_2|}=\sum_n{}'\delta_{2n}, \tag{13}$$

where the sum over $n$ includes all states that can be excited by the free electron. Provided $\omega_{2n}$ is large in comparison with $\delta_2$, the contributions to the shift are independent of the magnitude of the level separation $\omega_{2n}$ and many levels must be considered. The shift $\delta_{2n}$, however, depends on the sign of $\omega_{2n}$. If $\omega_{2n}>0$, then by Eq. (13) $\delta_{2n}<0$ and according to Eq. (14) below $\omega_r>\omega_{21}$. This is consistent with perturbation theory in which coupled levels are mutually repelled. Inversely, if $\omega_{2n}<0$, then $\omega_r<\omega_{21}$, which is also expected. Although for broadening only the near levels need be considered, $\gamma_2$ contains the same sum and[3]

$$\gamma_2=\sum_n{}'\gamma_P(2n)+\gamma.$$

This result is the same as KBM under these circumstances.

Since polarization broadening depends on near atomic levels, it is in general smaller for the ground state. Hence, it is reasonable to neglect this broadening contribution. The level shift is not correspondingly small and must be considered. Consequently, we return to Eq. (1) and write

$$i\hbar\dot{b}_{r\lambda}=J_r^*e^{-i\omega t}d_\lambda-(\textstyle\sum_n{}'\hbar\delta_{1n})b_{r\lambda}.$$

Defining $\delta_1\equiv\sum_n{}'\delta_{1n}$ corresponding to $\delta_2$ in Eq. (13), and substituting $B_{r\lambda}e^{i\delta_1 t}$ for $b_{r\lambda}$, one obtains for an initially excited atom ($d_\lambda=1$ at $t=0$):

$$i\hbar\dot{B}_{r\lambda}=J_r^*e^{[i(\delta_2-\delta_1-\omega)-\gamma_2]t};$$

and the emitted line intensity becomes

$$I(\omega)=\rho_r|b_{r\lambda}(\infty)|^2=\frac{\rho_r|J_r/\hbar|^2}{\gamma_2^2+(\omega+\delta_1-\delta_2)^2}, \tag{14}$$

where $\rho_r$ symbolizes the sum over polarizations and angles of emission as well as the density of final states at $\omega_r$.

## II. EXPERIMENTAL VERIFICATION—BROADENING[4]

It is not easy to obtain knowledge of electron or ion densities and temperatures which determine the line broadening. Consequently, an experiment which is independent of these parameters is desired. The comparison of different line widths in a spectrum, of radiators in the same plasma, where all the atoms emit in a given though perhaps uncertain temperature and density, has this property. An especially interesting case is presented by the relative widths of the $nd\,^3D\rightarrow 2p\,^3P$ lines in the helium spectrum (Fig. 1). For example, we will show that the width ratio for lines from the principal quantum levels $n=4$ and $n=3$ is $\sim$150 for Holtsmark ion broadening while it is only $\sim$10 for electron collision broadening. This difference stems from the fact that there is no $3f\,^3F$ level. For the higher principal quantum numbers, the $F$ level is the nearest neighbor of the $D$ level and leads to much larger Stark shifts and consequent Holtsmark broadening than occurs for $n=3$. On the other hand, the collision width receiving a contribution from the more distant $P$ level which is comparable to that from $F$, remains relatively unchanged with $n$.

The energy separations of interest are given in Table I (see also reference 5).

TABLE I. Experimental energy separations of some $(1s)(nl)$ and $(1s)(nl+1)$ configurations in triplet helium.[a]

| $n$ | $\bar{\nu}_{nf}-\bar{\nu}_{nd}$ (cm$^{-1}$) | $\bar{\nu}_{nd}-\bar{\nu}_{np}$ (cm$^{-1}$) |
|---|---|---|
| 3 | | 536.8 |
| 4 | 7.78 | 227.4 |
| 5 | 4.31 | 116.4 |
| 6 | 2.45 | 67.16 |

[a] See reference 5.

[3] This agrees with the results given in an earlier unpublished report by R. Sternheimer.

[4] The author is indebted to Professor G. Breit for the suggestion to consider broadening in the nondegenerate case and to Dr. L. B. Seely for the choice of spectral levels.

[5] C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular 467 (U. S. Government Printing Office, Washington, D. C., 1948), Vol. 1.

The matrix elements which enter both Stark broadening and electron collision broadening are[6]

$$(z_{n,l,0;n,l-1,0})^2=\frac{9n^2}{4}\left[\frac{(n^2-l^2)l^2}{4l^2-1}\right]a^2\equiv z_{nl}{}^2,$$

when hydrogen wave functions are used for the radiating electron. Table II gives values of $z_{nl}{}^2$ for $l=2$ and 3.

### A. Estimate of Holtsmark Broadening (Ion Effect)

The component with $m=0$ has the largest Stark shift in a uniform electric field ($F$). Because the levels of helium are nondegenerate, one obtains in weak fields the quadratic Stark shift. For the $D$ levels with $m=0$ this shift is

$$E_{nd0}{}^{(2)}=e^2F^2\left(\frac{z_{n3}{}^2}{E_{nd}-E_{nf}}+\frac{z_{n2}{}^2}{E_{nd}-E_{np}}\right). \quad (15)$$

With the values in Tables I and II, we find $E_{nd0}{}^{(2)}$ (Table III). The very small shift for $n=3$ reflects the nonexistence of a $3f\,{}^3F$ level. The shift of the ground state $(1s)(2p)$ can be neglected, since $E_{2p0}{}^{(2)}/(e^2F^2a^2/hc)=0.000975$. To estimate the width we follow Holtsmark

TABLE II. $(z_{n,l,0;n,l-1,0})^2\equiv z_{nl}{}^2$.

| $n$ | $z_{n2}{}^2/a^2$ | $z_{n3}{}^2/a^2$ |
|---|---|---|
| 3 | 0 | 27.0 |
| 4 | 64.8 | 115.2 |
| 5 | 231.4 | 315.0 |
| 6 | 562.4 | 691.2 |

and take

$$F=3.26en^{\frac{2}{3}},$$

and for the ion broadening width (Table IV)

$$\hbar(\gamma_{\text{ion}})_{nd}=4(3.26)^2(e^2/2a)^2n^{4/3}a^4\times\left|\frac{(z_{n3}{}^2/a^2)}{E_{nd}-E_{nf}}+\frac{(z_{n2}{}^2/a^2)}{E_{nd}-E_{np}}\right|. \quad (16)$$

### B. Electron Collision Broadening

Neglecting the natural width and considering only the nearest neighbors, one obtains, according to Eq. (12),

$$\gamma_{nl}\cong(2nv_\lambda\sigma_\lambda/3)\sum_{l=l,l+1}\frac{z_{nl}{}^2}{a^2}2\ln\left|\frac{4\epsilon_\lambda}{E_{nl}-E_{n\,l-1}}\right|, \quad (17)$$

provided we approximate

$$\frac{\hbar^2}{2m}(k_\lambda+k_{\mu'})^2\cong 4\epsilon_\lambda,$$

and

$$\hbar(\omega_{2n}-\delta_n)\cong\hbar\omega_{2n}.$$

Since the broadening depends logarithmically on the energy separation, it is not as sensitive to the principal quantum number as ion broadening.

TABLE III. Stark shifts.

| $n$ | 3 | 4 | 5 | 6 |
|---|---|---|---|---|
| $\frac{E_{nd0}{}^{(2)}}{(e^2F^2a^2/hc)}$ | 0.0503 | −7.82 | −51.0 | −219.3 |

Table V contains contributions to $\gamma_{nl}$ from the two near levels, their sum, their successive ratios, and for comparison the corresponding ion ratios (see Table IV). Also included are the wavelengths of the $nd\,{}^3D\rightarrow 2p\,{}^3P$ lines. Since the theory used does not correct for the fact that distant electrons are shielded and do not exert a Coulomb field at the atom (plasma cutoff —KBM), the broadening given will be too large. At the density considered, this correction is not serious.

Unlike hydrogen, where there is a large linear Stark effect, helium exhibits an electron broadening that is larger than or comparable to ion broadening. Another advantage in the use of helium is the possible appearance of the forbidden transitions as $4f\,{}^3F\rightarrow 2p\,{}^3P$ and $4p\,{}^3P\rightarrow 2p\,{}^3P$. Since the uniform field intensity for their appearance is known, this may serve as an indicator of the ion density.

It is likely that our calculation overestimates $\gamma_P$. The electrons have been assumed monoenergetic and are represented by plane waves. Actually, the electrons are distributed in energy and our calculation is poor for the slower ones (failure of the Born approximation). If the very slow electrons produce ion-like (Stark) effects, then we may expect that the electron density to be used in $\gamma_P$ is less than the actual density. This diminution of our calculated $\gamma_P$ may mean that electron effects are actually less important than ion effects for the lines $nd\,{}^3D\rightarrow 2p\,{}^3P$ where $n>3$. Hence, these lines would have contours predictable from Stark shifts.[7] On the other hand, $3d\,{}^3D\rightarrow 2p\,{}^3P$ can still have the anomalous electron broadening shape, i.e., the Lorentz shape $[(\gamma+\gamma_P)^2+\omega^2]^{-1}$. Also this line should be broader than expected on comparison with the other members of the series when only ion effects are con-

TABLE IV. Ion broadening width and width ratios for $n=10^{15}$.

| $n$ | $(\gamma_{\text{ion}})_{nd}$ $(\text{sec}^{-1})$[a] | $\frac{(\gamma_{\text{ion}})_{n+1,d}}{(\gamma_{\text{ion}})_{n,d}}$ |
|---|---|---|
| 3 | $+3.80\times10^{8}$ | 155. |
| 4 | $-5.91\times10^{10}$ | 6.5 |
| 5 | $-3.85\times10^{11}$ | 4.3 |
| 6 | $-1.65\times10^{12}$ | |

[a] + indicates blue asymmetry; −, red.

[6] In this section, we use several results given by H. Bethe, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), second edition, Vol. 24, Part 1.

[7] Toshio Takamine, Sci. Papers Inst. Phys. Chem. Research (Tokyo) 5, 55 (1926).

TABLE V. Electron broadening widths for $n=10^{15}$ and $\epsilon_\lambda=e^2/50a$.

| $n$ | $nd\,^3D \rightarrow 2p\,^3P$ Wavelength (A) | Contributions to $\gamma_{nd}$ from $p$ level ($\sec^{-1}$) | $f$ level ($\sec^{-1}$) | $\gamma_{nd}$ Sum ($\sec^{-1}$) | $\frac{\gamma_{n+1,d}}{\gamma_{n,d}}$ | $\frac{(\gamma_{\text{ion}})_{n+1,d}}{(\gamma_{\text{ion}})_{n,d}}$ |
|---|---|---|---|---|---|---|
| 3 | 5877 | $1.21\times10^{10}$ | 0. | $1.21\times10^{10}$ | 10.6 | 155 |
| 4 | 4473 | $6.43\times10^{10}$ | $6.42\times10^{10}$ | $1.28\times10^{11}$ | 3.50 | 6.5 |
| 5 | 4027 | $2.03\times10^{11}$ | $2.46\times10^{11}$ | $4.49\times10^{11}$ | 2.52 | 4.3 |
| 6 | 3821 | $4.93\times10^{11}$ | $6.40\times10^{11}$ | $1.13\times10^{12}$ | | |

sidered. The ions present may still superpose a slight asymmetry toward the violet. The corresponding singlet line $3d\,^1D \rightarrow 2p\,^1P$ would have the asymmetry to the red side, since unlike the triplet case the energy level $3p$ is greater than $3d$. Thus, electron broadening effects as treated in this report may find a fairly simple experimental verification.

The experimenter must overcome difficulties imposed by the Doppler width,[8] which for the $3d \rightarrow 2p$ line at $\frac{1}{2}$ ev, and $n=10^{15}$ is comparable with the electron broadening. By going to the wings of the line where the Doppler effect is small, the electron "dispersion" width can be determined. This complication in the measurement of the line shape can be avoided by working at higher electron densities. If $n$ is increased by a factor 10 without change in temperature, then electron broadening dominates. Hence, it is suggested that the helium spectrum be studied in an atmosphere of a more easily ionized element, for example, argon for which densities of $10^{17}$ at 1 ev have been obtained in shock tubes.

## III. EXPERIMENTAL VERIFICATION—SPECTRAL LINE SHIFT

Laporte[9] and Kantrowitz[10] have observed large shifts of spectral lines from atoms radiating in shock tubes. Baranger[11] has proposed that these shifts are the result of collisions with electrons. According to the quantum mechanical calculation previously given, there is a line shift. In order to make the result more quantitative, we consider two He I lines: $3d\,^3D \rightarrow 2p\,^3P$ and $4d\,^3D \rightarrow 2p\,^3P$.

For the metastable ground state $2p\,^3P$, only coupling to $2s\,^3S$ shifts the levels. This is because the matrix element to the $1s$ level vanishes (since we have neglected exchange collisions), and the free electrons lack sufficient energy to excite the atom. Thus, for $\epsilon=e^2/50a$ and $n=10^{15}$, $2nv\sigma\pi/3=2.015\times10^8$ $\sec^{-1}$; and the level is shifted according to Eq. (13) by $\delta_{2p}=-1.814\times10^9$ $\sec^{-1}$. The shift of the $3d$ level is found by considering only coupling to $3p$ and $2p$ levels; $\delta_{3d}=-6.650\times10^9$ $\sec^{-1}$. For $4d$, since the atom can be excited, we include $2p$, $3p$, $\cdots$, $6p$ and $4f$, $5f$, $6f$ (a total of 8 levels); $\delta_{4d}=-1.163\times10^9$ $\sec^{-1}$. Consequently, $3d\,^3D \rightarrow 2p\,^3P$ is shifted to the violet $4.836\times10^9$ $\sec^{-1}$ (0.056 A) whereas $4d\,^3D \rightarrow 2p\,^3P$ is shifted to the red by $0.651\times10^9$ $\sec^{-1}$ (0.0043 A). Although these are small shifts, it should be remembered that they are in proportion to the free electron density. If, as reported by Kantrowitz, $n=10^{18}$, then these shifts are increased by a factor $10^3$. Thus, sufficiently high electron densities can introduce measurable line shifts.

## IV. ACKNOWLEDGMENTS

The author is happy to acknowledge continued guidance and critical suggestions received from Professor Henry Margenau. Thanks are also due to M. M. Gordon (University of Florida), H. Mayer (Los Alamos Scientific Laboratory), and G. Breit (Yale University) for stimulating discussions.

[8] This Doppler complication was brought to our attention by Dr. R. E. Meyerott.
[9] O. Laporte (private communication).
[10] A. Kantrowitz, Phys. Rev. **90**, 368 (1953).
[11] M. Baranger, Phys. Rev. **91**, 436 (1953).