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ON THE WIDTH AND DENSITY OF HIGHLY EXCITED ATOMIC LEVELS IN GASES

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The broadening of excited atomic levels in a gas owing to electron scattering by neighboring atoms is considered. The density of highly excited levels is determined. It is shown that no bound electron states exist at energies $|E| \lesssim \epsilon_0$, where ϵ_0 is a characteristic parameter of the problem [see formula (34)]. The change of the level density of the free electrons is determined in the region $E \lesssim \epsilon_0$. It is shown that for small values of ϵ_0 the contribution of the excited states to the partition function should be taken into account, while at large values of ϵ_0 the change of the level density of the free electrons becomes important.

BEGINNING with a paper by Fermi,[1] a rather large number of articles have appeared in which the shift and the broadening of highly excited levels of the atoms of a gas have been investigated. Firsov[2,3] studied in detail the shift of highly excited levels owing to the scattering of the excited electrons on neighboring atoms of the gas and to the polarization of these atoms by the electron and the remainder of the atom. He considered the case where one can restrict oneself to s scattering. The same problem was treated in [4] with account of the scattering contribution of all partial waves. The calculation was based on the assumption $\gamma_n \ll |E_n - E_{n+1}|$, where γ_n is the width and E_n is the energy of the n-th level; in the derivation of the formulas for the level width the degeneracy of the levels was in fact neglected [cf., for example, formula (2) in [4]].

If $\gamma_n \approx |E_n - E_{n+1}|$, the spectroscopic analysis of such levels becomes impossible since the spectrum does not by itself imply that we are dealing with free electrons. As will be seen in the following, the electron becomes free (by this we mean its ability to move over the whole volume) for $\gamma_n \approx |E_n|$. Thus there exists a range of frequencies where the radiation spectrum is continuous but the radiation itself is caused by transitions of electrons between bound states. The spectral density of such excited atomic states is clearly of interest since it determines the contribution of these states to the partition function of the gas and hence, to the thermodynamic properties of the gas.

In our view, the most natural approach is to consider this problem by calculating the Green's function of the excited electron moving in the field of the ion and the neutral atoms of the gas. The temperature is assumed to be sufficiently low that one may assume that the gas atoms near an atom in an excited state are only in the ground state, i.e., the concentration of excited atoms is very low. In order to exclude resonant energy transfer from atom to atom, we shall assume that the excited atoms are different from the scattering atoms. This model can be applied with good accuracy to a gas with an admixture of alkali atoms. The concentration of the admixture must be sufficiently low so that we can neglect the resonant transfer of the excitation [a quantitative criterion is given below, see formula (47)]. The atomic scatterers are assumed at rest; we average over all possible configurations of the scatterers.[1] The assumption that the scatterers are immovable is justified as long as one can neglect the energy transfer between the atom and the excited electron. An excited electron (which is hence weakly bound to the ion) receives as a result of the collision with an atom an average energy transfer $\Delta E \approx kTm/M$, where m and M are the masses of the electron and the atom, and T is the temperature. This energy transfer must be taken into account only if

$$\Delta E_n = E_{n+1} - E_n \approx kTm/M. \tag{1}$$

The highly excited levels of any atom are hydrogen-like, and we therefore obtain from (1) that the heat motion of the atoms can be neglected for all levels with

$$n \lesssim (Me^4/\hbar^2 kT)^{1/3}. \tag{1a}$$

Thus the problem consists in finding the Green's function of an electron moving in the field of the remainder of the atom and of the atomic scatterers which are randomly distributed in space. Then the equation for the Green's function is

$$\left[i\hbar \frac{\partial}{\partial t} + \frac{\hbar^2}{2m}\Delta - V(\mathbf{r}) - \sum_i U(\mathbf{r}-\mathbf{R}_i) \mp i\varepsilon \right] \times G_\pm(\mathbf{r}, \mathbf{r}'; t-t') = 2\pi\hbar\,\delta(\mathbf{r}-\mathbf{r}')\,\delta(t-t'). \tag{2}$$

Here $G_\pm$ are the retarded (+) and advanced (−) Green's functions of the electron, $V(\mathbf{r})$ is the potential energy of the interaction between the electron and the ion, and $U(\mathbf{r}-\mathbf{R}_i)$ is the potential energy of the electron in the field of an atomic scatterer located at the point $\mathbf{R}_i$ (the origin of the coordinate system is taken at the nucleus of the ion). Let us introduce the Fourier transform of the Green's function:

$$G_\pm(\mathbf{r}, \mathbf{r}'; E) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{iE\tau/\hbar} G_\pm(\mathbf{r}, \mathbf{r}'; \tau)\, d\tau, \tag{3}$$

and expand $G_\pm(\mathbf{r}, \mathbf{r}'; E)$ in a complete orthonormal set of hydrogen-like functions $\psi_\nu(\mathbf{r})$, $\psi^*_{\nu'}(\mathbf{r}')$:

$$G_\pm(\mathbf{r}, \mathbf{r}'; E) = \sum_{\nu, \nu'} G_\pm(\nu, \nu'; E)\, \psi_\nu(\mathbf{r})\, \psi_{\nu'}^*(\mathbf{r}'); \tag{4}$$

ν, ν' are the quantum numbers (nlm) in the case of a discrete spectrum or a complete set of quantum numbers in the case of a continuous spectrum. Then we obtain from (2) the following equation for $G_\pm(\nu, \nu'; E)$:

$$\{E - E_\nu \mp i\varepsilon\}\, G_\pm(\nu, \nu'; E) - \sum_{\nu''} \langle \nu | U(\mathbf{r}) | \nu'' \rangle G_\pm(\nu'', \nu'; E) = \delta_{\nu\nu'}. \tag{5}$$

Here

$$U(\mathbf{r}) = \sum_i U(\mathbf{r}-\mathbf{R}_i) - \bar{U}, \quad \bar{U} = \frac{N}{V} \int U(\mathbf{r}-\mathbf{R}_i)\, dV, \tag{6}$$

where $\bar{U}$ is the average interaction energy between the electrons and the atoms, and E_ν is the eigenvalue of the electron energy in the Coulomb field but with an energy scale shifted by $\bar{U}$. The density matrix is expressed through the Green's function by:[5]

$$\rho(\mathbf{r}, \mathbf{r}'; E) = (2\pi i)^{-1}[G_+(\mathbf{r}, \mathbf{r}'; E) - G_-(\mathbf{r}, \mathbf{r}'; E)], \tag{7}$$

and the level density by

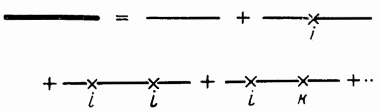
$$N(E) = 2 \int \rho(\mathbf{r}, \mathbf{r}; E)\, d\mathbf{r}. \tag{8}$$

The factor 2 in front of the integral in (8) comes from the spin of the electron.

We shall solve (5) by iteration taking into account that we must average over all possible positions of the atomic scatterers. The method for obtaining from (5) a closed equation for the average Green's function G_+ is analogous to that used in [6, 7]. The zeroth iteration for $G_+(\nu, \nu'; E)$ of (5) [without account of $U(\mathbf{r})$] gives

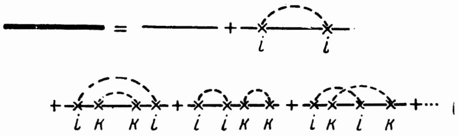
$$G_+^0(\nu, \nu'; E) = \frac{1}{E - E_{\nu'} - i\varepsilon}\, \delta_{\nu\nu'}. \tag{9}$$

It is convenient to apply the graph technique for the solution of (5). Let us symbolize $G_+^0(\nu, \nu'; E)$ by a thin line and $\langle \nu | U(\mathbf{r}-\mathbf{R}_i) | \nu' \rangle$ by a cross ×. Drawing a heavy line for $G_+(\nu, \nu'; E)$, we then obtain the graphical equation



(10)

When we average over all possible positions of each atom and sum over all indices i, k, ... (each of these takes the values from 1 to N, where N is the total number of gas atoms in the volume V), then, because of (6), all graphs drop out which contain any index only once. Joining the crosses with identical indices (over which the average and sum is taken) by dotted lines, we obtain



(11)

$\bar{G}_+(\nu, \nu'; E)$ thus retains the same graphical form as $G_+(\nu, \nu'; E)$.

Let us consider the graph

which is equal to

$$\frac{N}{V} \sum_{\nu'} \int d\mathbf{R}_i \int d\mathbf{r}\, \psi_\nu^*(\mathbf{r})\, U(\mathbf{r}-\mathbf{R}_i) \times \psi_{\nu'}(\mathbf{r}) \frac{1}{E - E_{\nu'} - i\varepsilon} \int d\mathbf{r}' \psi_{\nu'}^*(\mathbf{r}')\, U(\mathbf{r}'-\mathbf{R}_i)\, \psi_{\nu''}(\mathbf{r}'). \tag{12}$$

The wave functions $\psi_\nu(\mathbf{r})$ are evidently quasiclassical, where the deBroglie wave length is

$$\lambda \gg a, \tag{13}$$

with a the scattering length for electron-atom scattering. Then (13) is violated only near the ion, but this region makes a small contribution to (12). It follows from (12) and (13) that

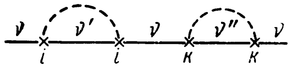
$$\sim \int d\mathbf{R}_i \psi_\nu(\mathbf{R}_i)\,|\psi_{\nu'}(\mathbf{R}_i)|^2 \psi_{\nu''}(\mathbf{R}_i). \quad (14)$$

It is easy to see that (14) has a sharp maximum for $\nu = \nu''$ [for free particles, the expression (14) $\sim \delta_{\nu\nu''}$[7]]. We may assume with good accuracy that

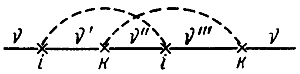
$$\sim \delta_{\nu\nu''} \quad (14a)$$

Let us now show that the graphs with non-intersecting dotted lines are larger than graphs with intersecting dotted lines. To this end let us compare, for example, the two graphs

a)



b)



In graph a) the sum goes over ν' and ν'', whereas in graph b) we must have either $\nu' = \nu''$, $\nu''' = \nu$ or $\nu' = \nu$, $\nu'' = \nu'''$, i.e., we have one summation less. In the continuous electron spectrum b) is smaller than a) in the ratio $\approx E^{-1}$ Im G^{-1}.[7] Since the wave functions of the excited states in the region where most of the electron-atom collisions occur differ little from the wave functions of free electrons, this criterion should hardly change.

Indeed, by direct calculation of a) and b) with the help of quasiclassical wave functions we obtain for b) the condition

$$p_{nl} - p_{n'l'} + p_{n''l''} - p_{n'''l'''} \approx 0, \quad (15)$$

where p_{nl} is the radial momentum of the electron in a state with principal quantum number n and angular momentum l. All principal quantum numbers n, n′, n″, n‴ must be assumed to be about equal, so that the corresponding E_n, $E_{n'}$, etc., differ by no more than Im G^{-1}. Otherwise the energy denominators in b) and in a) are very large and the contributions of such states is small. It then follows from (15) that l, l', l'', and l''' are subject to the two conditions

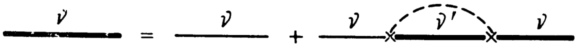
$$l^2 + l''^2 = l'^2 + l'''^2, \qquad l^2 l''^2 = l'^2 l'''^2, \quad (16)$$

i.e., the summation goes practically only over one of the three numbers l', l'', l''', for example, l', whereas in case a) the summation goes over l' and l''. However, condition (16) fixes l'' (for arbitrary l') since n′, n″, n‴ are fixed, i.e., $\Delta l'' \approx \Delta n''$. But since $n'' \sim |E|^{-1/2}$ we have $\Delta l'' \sim |E|^{-3/2}$ Im G^{-1}. In case a) the total number of possible l'' is $\approx n'' \sim |E|^{-1/2}$. This implies

$$\frac{|\,b)\,|}{|\,a)\,|} \approx \frac{\Delta l''}{l''} \approx \frac{\operatorname{Im} G^{-1}}{|E|}, \quad (17)$$

i.e., the same criterion as in the case of the continuous spectrum. As long as E^{-1} Im $G^{-1} \ll 1$, we can therefore neglect in (11) all graphs of type b) with intersecting dotted lines; this involves an error of $\approx E^{-1}$ Im G^{-1}. For an isolated level Im G^{-1} determines the width of the level. One may say that our approximation—including only graphs with non-intersecting dotted lines—is valid so long as the level width is smaller than the energy of the level itself.

Neglecting the correlation between the positions of the different atoms, we can average (11) independently over the position of each atom. Using (14a) we thus transform (11) into the integral equation



(18)

or

$$\bar{G}_+(\nu; E) = G_+^0(\nu; E) + G_+^0(\nu; E) \sum_{\nu', i} \overline{|\langle\nu|U(\mathbf{r}-\mathbf{R}_i)|\nu'\rangle|^2} \bar{G}_+(\nu'; E)\,\bar{G}_+(\nu; E). \quad (18')$$

Equation (18) has been obtained under the assumption that each scatterer enters only twice in (11). In this case the square of the matrix element $|\langle\nu|U(\mathbf{r}-\mathbf{R}_i)|\nu'\rangle|^2 \equiv U^2_{\nu\nu'}(\mathbf{R}_i)$ appearing in (18′) is expressed through the Born scattering amplitude. It can be shown that the Born amplitude in (18) must be replaced by the full scattering amplitude if all terms of the perturbation series for one and the same scatterer are taken into account [as before, we discard graphs of type b)].[6]

Equation (18) can be rewritten in the form

$$\bar{G}_+(\nu; E) = \frac{G_+^0(\nu; E)}{1 - G_+^0(\nu; E) \sum_{\nu', i} \overline{U_{\nu\nu'}^2(\mathbf{R}_i)}\,\bar{G}_+(\nu'; E)}. \quad (19)$$

Let us introduce

$$C_+(\nu; E) = \sum_{\nu', i} \overline{U_{\nu\nu'}^2(\mathbf{R}_i)}\,\bar{G}_+(\nu'; E). \quad (20)$$

Then $\bar{G}_+(\nu; E)$ is expressed through $C_+(\nu; E)$:

$$\bar{G}_+(\nu; E) = \frac{1}{E - E_\nu - i\varepsilon - C_+(\nu; E)}. \quad (21)$$

Thus Im $C_+(\nu; E)$ = Im $\bar{G}^{-1}(\nu; E)$. Substituting (21) in (20), we obtain an integral equation for $C_+(\nu; E)$, whose solution will now be obtained:

$$C_+(\nu; E) = \sum_{\nu', i} \overline{U_{\nu\nu'}^2(\mathbf{R}_i)} \frac{1}{E - E_{\nu'} - i\varepsilon - C_+(\nu'; E)}. \quad (22)$$

Let us consider $\sum\limits_i \overline{U^2_{\nu\nu'}(\mathbf{R}_i)}$ in various regions of the energy spectrum.

Let us assume that ν' and ν belong to the continuous spectrum, where we choose as basis functions the functions $\overset{+}{\psi}_{\mathbf{k}}(\mathbf{r})$,[8] normalized to unity in the volume V:

$$\sum_i \overline{U_{\nu\nu'}{}^2(\mathbf{R}_i)} = \frac{N}{V}\int d\mathbf{R}_i\,|U_{\mathbf{k}\mathbf{k}'}(\mathbf{R}_i)|^2, \tag{23}$$

here N is the total number of atomic scatterers. Since the probability that the atomic scatterer lies in a region close to the ion, i.e., where $\overset{+}{\psi}_{\mathbf{k}}$ is appreciably different from a plane wave, is very small, we may assume that the wave functions with which the matrix element in (23) is calculated are plane waves normalized to unity in the volume V. Replacing the matrix element by the scattering amplitude $f_{\mathbf{k}\mathbf{k}'}$, we obtain

$$\sum_i \overline{|U_{\mathbf{k}\mathbf{k}'}(\mathbf{R}_i)|^2} = n_0\frac{1}{V}\left(\frac{2\pi\hbar^2}{m}\right)^2 f_{\mathbf{k}\mathbf{k}'}{}^2, \tag{24}$$

where n_0 is the density of the gas.

For transitions between the discrete and continuous spectra we use the expansion

$$\psi_{nlm}(\mathbf{r}) = \int d^3k'\,\Phi(nlm\,|\,\mathbf{k}')\,e^{i\mathbf{k}'\mathbf{r}}, \tag{25}$$

and $\overset{+}{\psi}_{\mathbf{k}}(\mathbf{r})$ of the continuous spectrum is replaced by the plane wave $V^{-1/2}\,e^{i\mathbf{r}\cdot\mathbf{k}}$. Here we incur a much larger error than in the derivation of (24), since in this case the average is taken over the volume of the excited atom, where $\overset{+}{\psi}_{\mathbf{k}}(\mathbf{r})$ can differ appreciably from a plane wave. However, the exact value of $|U_{nlm,\mathbf{k}}(\mathbf{R}_i)|^2$ will not be needed in the following, so that it is sufficient to have an estimate for it. Using (25), we obtain

$$\begin{aligned} U_{nlm,\,\mathbf{k}}(\mathbf{R}_i) &= \frac{1}{\sqrt{V}}\int d^3k' \\ &\times\int d\mathbf{r}\,\Phi^*(nlm\,|\,\mathbf{k}')e^{-i\mathbf{k}'\mathbf{r}}U(\mathbf{r}-\mathbf{R}_i)e^{i\mathbf{k}\mathbf{r}} \\ &= \frac{1}{\sqrt{V}}\int d^3k'\,\Phi^*(nlm\,|\,\mathbf{k}')\,e^{-i\mathbf{k}'\mathbf{R}_i}\int d^3\rho\,U(\rho)\,e^{i(\mathbf{k}-\mathbf{k}')\rho}e^{i\mathbf{k}\mathbf{R}_i}. \end{aligned} \tag{26}$$

If we assume that the s scattering plays the main role (this is generally the case for highly excited levels, since **k** and **k**′ have a small absolute value) then

$$\sum_i \overline{|U_{nlm,\,\mathbf{k}}(\mathbf{R}_i)|^2} \approx n_0\frac{1}{V}\left(\frac{2\pi\hbar^2}{m}\right)^2 f^2. \tag{27}$$

Comparing (27) and (24), we see that the averaged square of the matrix element is about the same for the continuum-continuum and the continuum-discrete transitions.

For the calculation of a discrete-discrete transition we use the expansion (25):

$$\begin{aligned} U_{nlm}^{n'l'm'}(\mathbf{R}_i) &= \iint d^3k\,d^3k'\,\Phi^*(nlm\,|\,\mathbf{k})\,e^{-i\mathbf{k}\mathbf{R}_i} \\ &\times\Phi(n'l'm'\,|\,\mathbf{k}')\,e^{i\mathbf{k}'\mathbf{R}_i}\int d^3\rho\,e^{i(\mathbf{k}'-\mathbf{k})\rho}U(\rho). \end{aligned} \tag{28}$$

Let us replace the matrix element $U_{\mathbf{k}\mathbf{k}'}$ in (28) by the scattering amplitude. We assume that the main contribution comes from s scattering. This does not impair the generality of our subsequent considerations but simplifies the numerical calculations and permits us to solve (22) in analytic form. With the assumption of s scattering we obtain

$$\begin{aligned} \sum_i |U_{nlm}^{n'l'm'}(\mathbf{R}_i)|^2 &= n_0\left(\frac{2\pi\hbar^2}{m}\right)^2 f^2 \\ &\times\int d\mathbf{r}\,|\psi_{nlm}(\mathbf{r})|^2|\psi_{n'l'm'}(\mathbf{r})|^2. \end{aligned} \tag{29}$$

The integral in (29) can be found in analytic form using the fact that the wave functions of highly excited states are quasiclassical:

$$\begin{aligned} I_{nlm}^{n'l'm'} &\equiv \int d\mathbf{r}\,|\psi_{nlm}(\mathbf{r})|^2|\psi_{n'l'm'}(\mathbf{r})|^2 \\ &= \left(\frac{\hbar^2}{me^2}\right)^3\frac{1}{\pi^5}\,\frac{ll'}{n^2n'^2}\,\frac{1}{a_0+b_0}\,\frac{1}{\sqrt{(a-c)(b-d)}} \\ &\times K\left(\frac{2\sqrt{a_0b_0}}{a_0+b_0}\right)K\left(\frac{(b-c)(a-d)}{(a-c)(b-d)}\right)^{1/2}, \end{aligned} \tag{30}$$

where

$$a_0 = l^2\sqrt{1-m^2/l^2}, \qquad h_0 = l'^2\sqrt{1-m'^2/l'^2},$$

$$\begin{aligned} b &= \min \\ a &= \max \end{aligned}\left\{\begin{aligned} &n^2(1+\sqrt{1-l^2/n^2}) \\ &n'^2(1+\sqrt{1-l'^2/n'^2}) \end{aligned}\right.$$

$$\begin{aligned} d &= \min \\ c &= \max \end{aligned}\left\{\begin{aligned} &n^2(1-\sqrt{1-l^2/n^2}) \\ &n'^2(1-\sqrt{1-l'^2/n'^2}). \end{aligned}\right.$$

The quantity K is the complete elliptic integral of the first kind; it diverges logarithmically for $n = n'$, $l = l'$. However, since we sum over n' and l' in (22) (this summation will be replaced by an integration), this divergence does not affect the result.

Let us rewrite (22), separating the continuous and discrete spectra, and let us go from the summation over k to an integral over dk according to the rule

$$\sum_k \longrightarrow \frac{V}{(2\pi)^3}\int d^3k.$$

Taking account of (24), (26), (29), and (30) and assuming s scattering, we obtain

$$C(\mathbf{k};E)=n_0\left(\frac{2\pi\hbar^2}{m}\right)^2 f^2\frac{1}{(2\pi)^3}\times\int d^3k'\frac{1}{E-\hbar^2k'^2/2m-i\varepsilon-C(\mathbf{k}';E)}+n_0\frac{1}{V}\left(\frac{2\pi\hbar^2}{m}\right)^2 f^2\sum_{nlm}{}'\frac{1}{E-E_n-i\varepsilon-C(nlm;E)},\tag{31a}$$

$$C(nlm;E)=n_0\left(\frac{2\pi\hbar^2}{m}\right)^2 f^2\frac{1}{(2\pi)^3}\times\int d^3k\frac{1}{E-\hbar^2k^2/2m-i\varepsilon-C(\mathbf{k};E)}+n_0\left(\frac{2\pi\hbar^2}{m}\right)^2 f^2\sum_{n'l'm'}I_{nlm}^{n'l'm'}\frac{1}{E-E_{n'}-i\varepsilon-C(n'l'm';E)}.\tag{31b}$$

The second term in (31a) is smaller than the first in the ratio V_{nlm}/V, where V_{nlm} is the volume of the excited atom; it can therefore be neglected. This is easy to understand: transitions between levels of the continuous spectrum due to scattering occur over the whole volume of the system, whereas transitions between the continuous and discrete spectra occur only within the volume of the excited atom. Then we obtain from (31a) an equation for $\operatorname{Im} C(\mathbf{k};E)\equiv b(\mathbf{k};E)$:

$$b(\mathbf{k};E)=n_0\sigma\frac{\hbar^4}{8\pi^2m^2}\int d^3k'\frac{b(\mathbf{k}';E)}{(\tilde{E}-\hbar^2k'^2/2m)^2+b^2(\mathbf{k}';E)},\tag{32}$$

where $\sigma=4\pi f^2$ is the cross section for the electron–atom scattering and $\tilde{E}=E-\operatorname{Re}C(\mathbf{k}';E)$. The right-hand side of (32) is independent of **k**. Hence $b(\mathbf{k};E)=b(E)$. This equality is a consequence of the independence of σ of **k**.

For $b(E)$ we obtain from (32) the algebraic equation

$$1=\sqrt{\varepsilon_0}\int_0^\infty\frac{\sqrt{x}\,dx}{(\tilde{E}-x)^2+b^2(E)}.\tag{33}$$

Here

$$\varepsilon_0=\frac{1}{(2\pi)^2}(\sigma n_0)^2\frac{\hbar^2}{m},\tag{34}$$

$\operatorname{Re}C(\mathbf{k};E)$ is independent of **k**, just as $b(\mathbf{k};E)$ is. Using $b(E)/E\ll 1$ we can extend the integration in (33) to $-\infty$. Then (33) leads to

$$b(E)=\pi\varepsilon_0^{1/2}(\tilde{E}+\pi^2\varepsilon_0/4)^{1/2}.\tag{35}$$

Since we have considered the case $b(E)/E\ll 1$, (35) implies $\tilde{E}\gg\epsilon_0$, i.e.,

$$b(E)\approx\pi\sqrt{E\varepsilon_0}.\tag{36}$$

In (36) we have replaced $\tilde{E}$ by E, because $\operatorname{Re}C(\mathbf{k};E)$ is in general of the same order as $b(E)$, and taking account of the difference between $\tilde{E}$ and E is equivalent to including higher powers of ϵ_0 than was done in (36).

Let us now consider the solution of (31b). For $E<0$ and $|E|\gg\epsilon_0$ we can neglect the first term on the right-hand side of (31b), since it gives a relative contribution $\sim\epsilon_0/E$ to the imaginary part. Thus the quantity $\operatorname{Im}G^{-1}$ is independent of the character of the positive energy spectrum, if $-E\gg\epsilon_0$. From (31b) we obtain

$$C(nlm;E)=n_0\left(\frac{2\pi\hbar^2}{m}\right)^2 f^2\times\sum_{n'l'm'}I_{nlm}^{n'l'm'}\frac{1}{E-E_{n'}-C(n'l'm';E)},\tag{37}$$

where the expression (30) must be substituted for $I_{nlm}^{n'l'm'}$.

Let us first consider the case of overlapping levels $\epsilon_0\gg\Delta E_{n,n+1}$. In this energy region it is only meaningful to calculate the level density, using (8). Since we will sum over l in the following, we introduce

$$\tilde{C}(n;E)=\frac{1}{n^2}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}C(nlm;E).\tag{38}$$

After replacing $C(n'l'm';E)$ by $\tilde{C}(n';E)$ and the sum over n' by an integration over the energy, Eq. (37) becomes up to a factor of order unity,

$$\tilde{C}(x;E)=\sqrt{\varepsilon_0}\,x\int_0^\infty\frac{1}{\sqrt{x'}}\frac{1}{x'+E-\tilde{C}(x';E)}y\left(\frac{x'}{x}\right)dx'.\tag{39}$$

Here $x=|E_n|$, $x'=|E_{n'}|$, and the function $y(x'/x)$ is shown in Fig. 1. The asymptotic values of $y(z)$ are

$$y(z)=\begin{cases}3.7z^{1/2}, & z\longrightarrow 0\\ 0.3z^{-3/2} & z\longrightarrow\infty\end{cases}.\tag{40}$$

The replacement of $C(nlm;E)$ by $\tilde{C}(n;E)$ does not introduce a large error since $I_{nl_1m_1}^{n'l'm'}\approx I_{nl_2m_2}^{n'l'm'}$ up to factor of order unity, i.e., the right-hand side of (37) is almost independent of l and m (for given n). The integral in (39) converges rapidly at the upper limit; therefore, we do not incur a large error if we replace the sum over n' for small n' by an integration over x' for large x' $=|E_{n'}|$.

In solving (39) as before, we assume $|\tilde{C}(x;E)/E|\ll 1$, which corresponds to $|\epsilon_0/E|\ll 1$. Let us introduce

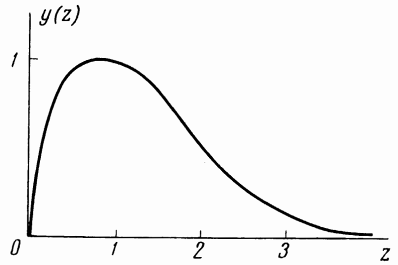


FIG. 1

$$b(x'; E) \equiv \operatorname{Im} \bar{C}(x'; E). \tag{41}$$

Up to terms $\sim\epsilon_0/|E| \ll 1$, we may set b(x′; E) constant in the interval (x′, x′ ± |C(x′; E)|), i.e.,

$$\frac{db(x'; E)}{dx'} b \approx \frac{\varepsilon_0}{|E|} \ll 1. \tag{42}$$

Using (42) and the fact that the region $x' \approx |E|$ makes the most important contribution to the integral in (39), we obtain

$$b(E_n; E) = \pi\left(\frac{\varepsilon_0}{|E|}\right)^{1/2} |E_n| y\left(\frac{E}{E_n}\right). \tag{43}$$

It is seen from (43) and Fig. 1 that for a given energy E, the imaginary part of the Green's function is nonvanishing for all n such that

$$1/2 \lesssim E_n / E \lesssim 2. \tag{44}$$

Recalling the definition of $b(E_n; E)$, we find

$$G_\pm(nlm; E) = \frac{1}{E - E_n \mp ib(E_n; E)}. \tag{45}$$

The level density calculated by (7), (8), and (45) is equal to

$$N(E) = m^{3/2} e^6 \hbar^{-3} |E|^{-5/2}. \tag{46}$$

Formula (46) holds for energies at which resonant transfer of the excitation from one alkali atom to another is not yet important. Taking for the average radius of the orbit of the excited electron $r \approx e^2/|E_n|$, we find that (46) is valid if

$$|E| > e^2 \rho_0^{1/3}, \tag{47}$$

where ρ_0 is the density of the alkali atoms.

The calculation of the number of levels enclosed in the unit energy interval with the help of (46) leads to the same result as the calculation by the formula $N(n) = 2n^2$, where n^2 is the principal quantum number of the level.

Formula (46) has been derived under the assumption $-E \gg \epsilon_0$. In the region of negative energies with $-E \lesssim \epsilon_0$, Eq. (31b) does not reduce to (37). We see from (31a) and (31b) and from $|C| \approx \epsilon_0$, that at these energies the contribution of the unbound states of the electron must also be included. Then the level density in this energy region $|E| \lesssim \epsilon_0$ is proportional to the volume, i.e., at these energies the electron should be regarded as unbound. The electron is in a bound state only for negative energies $-E \gg \epsilon_0$. Indeed, the probability density for the presence of an electron with energy E at the point $\mathbf{r}_0$,

$$\rho(\mathbf{r}_0, \mathbf{r}_0; E) = \sum_{\nu,\nu'} [\bar{G}_+(\nu, \nu'; E) - \bar{G}_-(\nu, \nu'; E)] \psi_\nu(\mathbf{r}_0) \psi_{\nu'}^*(\mathbf{r}_0) \tag{48}$$

decreases exponentially with increasing $\mathbf{r}_0$:

$$\rho(\mathbf{r}_0, \mathbf{r}_0; E) \sim \exp\{-c\sqrt{m}\sqrt{E} r_0 / \hbar\},$$

where c is a number of order unity, since the summation over ν, ν' for $-E \gg \epsilon_0$ is restricted by an inequality of the type (44). For $E > -\epsilon_0$ the electron can be regarded as free, since the sum in (48) includes the $\psi_\nu(\mathbf{r}_0)$ of the continuous spectrum and $\rho(\mathbf{r}_0, \mathbf{r}_0; E)$ does not drop off to zero with increasing r_0.

It is easy to see that $\operatorname{Im} G^{-1} \approx \operatorname{Re} G^{-1}$ for $|E| \lesssim \epsilon_0$, i.e., the poles of the Green's function do not even approximately correspond to energy levels of the system. Indeed, the indeterminacy of the energy of the unperturbed state is $\Delta E \approx \hbar/\tau$, where τ is the time between two collisions, $\tau = [\sigma n_0 \sqrt{2E/m}]^{-1}$. Then

$$\frac{\Delta E}{E} \approx \frac{\hbar}{\sqrt{m}} \frac{\sigma n_0}{\sqrt{E}} \approx \left(\frac{\varepsilon_0}{E}\right)^{1/2},$$

i.e., $\Delta E/E \approx 1$ for $E \approx \epsilon_0$. At such energies the scattering of the electron by the atoms of the gas leads to a strong mixing of unperturbed states, and the density of states is probably constant over the whole energy interval $|E| \lesssim \epsilon_0$.

The calculation of the level density of the states of the unbound electron with the help of (35) gives

$$N(E) = \frac{V}{\pi^2} \left(\frac{m}{\hbar^2}\right)^{3/2} b(E) (\sqrt{E^2 + b^2} - E)^{-1/2}. \tag{49}$$

For $E \gg \epsilon_0$ it follows from (49) that

$$N_0(E) = \frac{V\sqrt{2}}{\pi^2} \left(\frac{m}{\hbar^2}\right)^{3/2} \sqrt{E} \tag{49a}$$

the usual expression for the density of unperturbed states of the continuous spectrum. But for E = 0 we obtain from (49)

$$N(0) = \frac{V}{\pi\sqrt{2}} \left(\frac{m}{\hbar^2}\right)^{3/2} \sqrt{\varepsilon_0}. \tag{49b}$$

Expression (49b) cannot be regarded as exact, since (31a), (31b), and hence also (49) were derived under the assumption $\epsilon_0/E \ll 1$. However, it follows from the general considerations above that the density of states is almost constant for $|E| \lesssim \epsilon_0$ and should naturally be determined by the parameter ϵ_0.

An interpolation formula can be given, which is simpler than (49), gives the exact result (49a) for $E \gg \epsilon_0$ and in general reproduces approximately the heuristic quantity N(0):

$$N(E) = \frac{V\sqrt{2}}{\pi^2}\left(\frac{m}{\hbar^2}\right)^{3/2}\sqrt{|E| + \varepsilon_0}, \tag{50}$$

where (50) is valid for $E < 0$ but $|E| < \epsilon_0$ (see Fig. 2).

Thus we see that ϵ_0 is the characteristic parameter which determines the spectrum of highly excited atomic levels in a gas. In the calculation of the statistical sums of gases one usually does not include the contribution of the excited levels of the atoms (cf. [9], Sec. 106). This is not always justified. It has been shown by Larkin[10] how many levels must be included if one wants to take account of the Debye screening of the ion. Here the number of levels is finite, and the energy $|E_n|$ of the last level is given by

$$E_n \approx e^2 / R_d, \tag{51}$$

where R_d is the Debye screening radius.

The quantity ϵ_0 is another competing limiting boundary of the spectrum of atomic levels in the calculation of the collision broadening. For the usual density $n_0 \approx 3 \times 10^{19}$ cm^{-3} and $\sigma \approx 3 \times 10^{-15}$ cm^2 we have $\epsilon_0 \approx 10^{-18}$ erg, i.e., in such cases the spectrum of bound states is bounded by E_n of (51) or (1a). But the level density for the calculation of the statistical sum must as before be taken from (46). We call attention to the fact that ϵ_0 increases rapidly with $n_0\sigma$. If a weakly bound state of the electron and the atomic scatterer is possible, then σ may be very large: $\sigma \approx 10^{-13}$ cm^2 (cf. [8], Sec. 131). Then $\epsilon_0 \approx 10^{-13}$ erg for a density $n_0 \approx 3 \times 10^{20}$ cm^{-3}, i.e., the number of bound states is indeed small. But in taking account of the spectrum of the free electrons one must use formula (50). In the calculation of the statistical sum this corresponds to an effective lowering of the ionization potential by ϵ_0. This correction can become appreciable at high gas densities. In the case of small ϵ_0 it is necessary to include the excited levels in the statistical sum, since their number is of order 10^6 for $\epsilon_0 \approx 10^{-15}$ erg, and the statistical sum over the excited states may be of the same order of magnitude as the statistical sum over the free electrons.

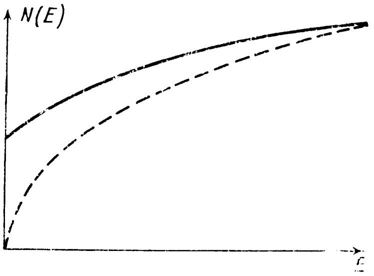


FIG. 2. Dependence of the level density of free electrons on the energy. Solid curve: according to (50), dotted curve: N(E) without account of scattering.

Let us now briefly consider the situation for $\epsilon_0 \ll \Delta E_{n,\,n+1}$. In this case one may, with an accuracy $\sim \epsilon_0/\Delta E_{n,\,n+1}$, retain on the right-hand side of (37) only the terms corresponding to a single energy level:

$$C(nlm; E) = n_0\left(\frac{2\pi\hbar^2}{m}\right)^2 f^2 \sum_{l'm'} I_{nlm}^{n'l'm'} \frac{1}{E - E_n - C(nl'm'; E)} \tag{52}$$

Thus the presence of gas atoms leads to an effective removal of the degeneracy in l, where the broadening of the level with given l depends on the broadening of the levels with other l'. Equation (52) can be solved only numerically. A calculation of the broadening of an isolated degenerate atomic level in a gas is in progress and will be published.

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