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The Negative Ions of Hydrogen and Oxygen in Stellar Atmospheres

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I. THE NEGATIVE ION OF HYDROGEN

THE discussion of a variety of astrophysical problems relating to the continuous spectrum of the sun and the stars has shown that they radiate approximately like gray bodies; i.e., with an absorption coefficient independent of wave-length, and that moreover, the departure from grayness must be in the sense of a gradual decrease of the absorption coefficient from λ12000 to λ4000 and then an increase as we go further into the violet. The evidence for this behavior of the continuous absorption coefficient in stellar atmospheres is so conclusive as to constitute a major problem of theoretical astrophysics.

For many years it was believed that the principal contributions to continuous opacity in stellar atmospheres must arise from the absorption beyond the various series limits of hydrogen and the commoner elements like Na, Mg, Ca, Fe, and Si (which we shall collectively refer to as the "metals"). However, it was soon found that such an assumption concerning the source of continuous absorption leads to many contradictions between theory and observation, the most serious of which was the following: At the temperatures of the solar and the near solar types ($T=4500°$–$6500°$K) the ionization of hydrogen is so little advanced that the absorption must arise from the metals only, in which case we must expect to observe discontinuities in the form of absorption edges at the heads of at least some of the series limits. But such absorption edges except in the case of hydrogen (and the negative ion of oxygen for which we shall present evidence) have never been detected. Of course, the absence of a measurable discontinuity at a particular series limit can be explained on the supposition that the element responsible for the series under consideration is of low abundance. But such an explanation cannot clearly be advanced for the absence of absorption edges for all the elements if we are to maintain at the same time that it is the absorption beyond the series limits of these same elements that constitutes general opacity. In addition to this principal difficulty, it was also found that the dependence on wave-length of the derived continuous absorption coefficient was quite inadequate to account for many of the features of the continuous spectrum of the sun and the stars. The clue to an understanding of this entire complex of questions was provided by R. Wildt who pointed out in 1938[1] that in view of the enormous abundance of hydrogen and the ample supply of free electrons made available by the ionization of the metals, there must be a sufficient amount of the negative ions of hydrogen in stellar atmospheres to provide an important, if not the main, source of continuous absorption. Wildt's further considerations[2] relating to a number of specific astrophysical questions, though of a provisional character, were sufficiently successful to carry the conviction that no theory of the stellar atmospheres can be satisfactory which did not properly incorporate the part played by the negative ions of hydrogen. Therefore in view of the central position thus gained by the negative ions of hydrogen in theoretical astrophysics, it may be of interest to review here particularly the physical studies which have been carried out relating to this ion.

Though the negative ion of hydrogen has long been suspected in canal ray tubes and its stability expected from physico-chemical studies relating to the alkali hydrides, a reliable estimate of the *electron affinity* of hydrogen was not forthcoming before its first theoretical evaluation by H. A. Bethe[3] and E. A. Hylleraas.[4] Indeed, the only reliable means of determining this quantity still remains theoretical. The method by which Bethe and Hylleraas derived the electron affinity of hydrogen was based on the latter's investigations on the theoretical evaluation of the energy of the ground state of helium.

As is well known, Hylleraas's evaluation of the energy of the ground state of helium was the

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[1] R. Wildt, Astrophys. J. **89**, 295 (1939).
[2] R. Wildt, Astrophys. J. **93**, 47 (1941); also A. Wheeler and R. Wildt, Astrophys. J. **95**, 281 (1942).
[3] H. A. Bethe, Zeits. f. Physik **57**, 815 (1930).
[4] E. A. Hylleraas, Zeits. f. Physik **60**, 624 (1930).

result of a successful application of the Ritz method for solving the wave equation.[5] As applied to the lowest eigenstate, this method is based on the fact that the corresponding wave function makes E a minimum where

$$E=\int\psi^*H\psi d\tau\Big/\int\psi^*\psi d\tau. \tag{1}$$

In Eq. (1), the integrations are to be extended over the entire configuration space. In practice, a form for the wave function is assumed which involves a certain number of parameters. The "best" function of the assumed form is then obtained by assigning to the parameters, values which would make the right hand side of Eq. (1) a minimum. The success of this method clearly depends on how "well" the initial form for the wave function has been chosen. But Hylleraas showed that the value of E for the ground state of helium can be predicted to one part in several thousands by assuming wave functions of the form

$$\Psi=e^{-\alpha s}\sum c_{l,m,n}s^lt^mu^n, \tag{2}$$

where s, t, and u are related to the distances r_1, r_2, and r_{12} of the two electrons from the nucleus and one another respectively, according to the relations

$$s=r_1+r_2;\quad t=-r_1+r_2;\quad u=r_{12}. \tag{3}$$

Further, in Eq. (2), α and the $c_{l,m,n}$'s are the parameters chosen under the minimal requirement of E.

In Table I, we have listed the various particular forms for Ψ which Hylleraas chose and the values of E to which they led. It is seen that with a wave function of the form 6 (Table I) the energy of the ground state of helium is predicted to within one part in 5000. With the success thus achieved in the case of helium, it was natural that attempts should be made to extend the method to other two-electron systems, and in particular, to the determination of the electron affinity of hydrogen. And with a wave function of the form 4 (see Table I), Bethe and Hylleraas found an energy of -0.5253 atomic unit leading to an electron affinity of 0.0253 atomic unit or 0.70 ev. By certain extrapolations of an essentially *ad hoc* nature, Hylleraas estimated that the true electron affinity must have the value 0.02642 atomic unit of energy.

As we have already indicated, it is of prime importance for astrophysics that the continuous absorption coefficient of H^- be determined as accurately as possible. However, it soon became clear[6] that in order that we may achieve this, it is necessary that the utmost accuracy of the wave function representing the ground state of H^- be demanded. Accordingly, the writer and his students at the Yerkes Observatory have concerned themselves with the improvement of the original wave function of Bethe and Hylleraas and the results of these attempts are summarized in Table I.

First, it will be noticed that the electron affinity of hydrogen has now been increased to 0.02756 atomic unit (or 0.747 electron volt) which is substantially more than the value 0.02642 atomic unit estimated by Hylleraas. This result has, among other things, the effect of modifying Hylleraas's formula[7] giving the energies for the ground states of the various two electron systems. With the new value for the electron affinity, the formula becomes

$$E=-2Z^2+1.25Z-0.31488+\frac{0.01980}{Z}-\frac{0.01004}{Z^2}\ \text{Rydberg}. \tag{4}$$

Second, it is seen that the functions 3, 5, and 8, which allow for different amounts of screening for the two electrons, are uniformly better than the similar ones which do not. Thus, the function $e^{-\alpha s}$ does not even make H^- stable, while the function $e^{-\alpha s}\cosh\beta t$ does. Similarly, the function 5 is better than the Bethe-Hylleraas function 4, and the function 7 yields a lower value for E than does function 6, which is the form which provides for helium the best value. And finally, the function 8, with eleven parameters does the best of all.

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[5] E. A. Hylleraas, Zeits. f. Physik **54**, 347 (1929). For an account of these and related matters, see Bethe, *Handbuch der Physik* (1933), Vol. 24; Pt I, pp. 353–368.

[6] Cf. S. Chandrasekhar and M. K. Krogdahl, Astrophys. J. **98**, 205 (1943); also S. Chandrasekhar, Astrophys. J. **100**, 176 (1944).

[7] Cf. Bethe, reference 5, p. 363, Eq. (18.34).

TABLE I. Energies of the ground state of the negative ion of hydrogen and helium by the Ritz method.

Form of wave function	$-E$ (atomic units) H$^-$	He
1. $e^{-\alpha s}$	0.473	2.84765
2. $e^{-\alpha s}(1+\beta u)$	0.509	2.8912
3. $e^{-\alpha s}\cosh \beta t$	0.5133*	
4. $e^{-\alpha s}(1+\beta u+\gamma t^2)$	0.5253†	2.90244††
5. $e^{-\alpha s}\cosh \beta t(1+\gamma u)$	0.52592*	
6. $e^{-\alpha s}(1+\beta u+\gamma t^2+\delta s+\epsilon s^2+\zeta u^2)$	0.52646**	2.90324††
7. $e^{-\alpha s}\cosh \beta t(1+\gamma_2 s+\gamma_4 u+\gamma_5 us)+te^{-\alpha s}\sinh \beta t(\gamma_3+\gamma_6 u)$	0.526904*	2.14490†††
8. $e^{-\alpha s}(1+\beta u+\gamma t^2+\delta s+\epsilon s^2+\zeta u^2+\chi_6 t^4+\chi_7 t^6+\chi_8 t^4 u^2+\chi_9 t^2 u^2+\chi_{10} t^2 u^4)$	0.52756#	
Experimental		2.90368

* Chandrasekhar; † Bethe and Hylleraas; ** Williamson; # Henrich; †† Hylleraas; ††† Hylleraas and Undheim (for the 2^1s state.)

We now turn to the question of the continuous absorption coefficient of H$^-$. The calculations of the absorption cross sections which have been carried out so far[8–11] are based on two approximations. The first consists in the use of the wave function for describing the bound state the ones derived from the minimal calculations, and the second in the use of a plane-wave representation of the ejected outgoing electron. The validity, or otherwise, of these approximations will depend upon whether the principal contributions to the matrix element,

$$\mathfrak{p}=\int \Psi_d(\mathbf{r}_1+\mathbf{r}_2)\Psi_c d\tau, \qquad (5)$$

come from those regions of the configuration space in which the two approximations may be expected to be satisfactory. In Eq. (5) Ψ_d denotes the normalized wave function for the ground state of H$^-$, and Ψ_c, the wave function of the continuous state normalized to correspond to an outgoing electron of unit density.

It appears that the use of the plane-wave representation for the free electron will not introduce any very serious error, since, as we shall show presently, only parts of the configuration space which are only relatively far from the hydrogenic core, are relevant for the absorption process.

In any event, it might prove to be an adequate approximation to use for the continuous wave function one of an electron moving in the Hartree field of a hydrogen atom. In other words, it might be sufficient to use for Ψ_c the expression

$$\Psi_c=1/(2\pi)^{\frac{1}{2}}\{e^{-r_2}\phi(\mathbf{r}_1)+e^{-r_1}\phi(\mathbf{r}_2)\}, \qquad (6)$$

where $\phi(\mathbf{r})$ satisfies the wave equation

$$\nabla^2\phi+[k^2+2[1+(1/r)]e^{-2r}]\phi=0, \qquad (7)$$

and tends asymptotically at infinity to a plane wave of unit amplitude along some chosen direction. If this direction in which the ejected electron moves at infinity be chosen as the polar axis of a spherical system of co-ordinates, it is readily shown that the appropriate solution for ϕ can be expressed in the form

$$\phi=\sum_{l=0}^{\infty}\frac{1}{kr}(2l+1)P_l(\cos\vartheta)\chi_l(r), \qquad (8)$$

where the radial function χ_l is a solution of the equation

$$\frac{d^2\chi_l}{dr^2}+\left\{k^2-\frac{l(l+1)}{r^2}+2\left(1+\frac{1}{r}\right)e^{-2r}\right\}\chi_l=0, \qquad (9)$$

which tends to a pure sinusoidal wave of unit amplitude at infinity. Thus, on our present approximation Ψ_c can be written in the form

$$\Psi_c=\frac{1}{(2\pi)^{\frac{1}{2}}}\left\{e^{-r_2}\sum_{l=0}^{\infty}\frac{1}{kr_1}(2l+1)P_l(\cos\vartheta_1)\chi_l(r_1;k)\right.$$
$$\left.+e^{-r_1}\sum_{l=0}^{\infty}\frac{1}{kr_2}(2l+1)P_l(\cos\vartheta_2)\chi_l(r_2;k)\right\}. \qquad (10)$$

By use of the foregoing form for Ψ_c, the standard formula for the absorption cross section for a process in which a photoelectron with k atomic

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[8] H. S. W. Massey and D. R. Bates, Astrophys. J. **91**, 202 (1940).

[9] R. E. Williamson, Astrophys. J. **96**, 438 (1942).

[10] L. R. Henrich, Astrophys. J. **99**, 59 (1943).

[11] S. Chandrasekhar, unpublished.

TABLE II. The weight function $W(r)$.

r	$W(r)$	r	$W(r)$	r	$W(r)$	r	$W(r)$
0	0	4.0	1.597	11.0	0.833	19.0	0.131
0.5	0.210	4.5	1.623	12.0	0.703	20.0	0.096
1.0	0.553	5.0	1.620	13.0	0.585	21.0	0.069
1.5	0.861	6.0	1.548	14.0	0.478	22.0	0.049
2.0	1.108	7.0	1.422	15.0	0.383	23.0	0.034
2.5	1.298	8.0	1.273	16.0	0.301	24.0	0.024
3.0	1.439	9.0	1.120	17.0	0.233	25.0	0.016
3.5	1.538	10.0	0.972	18.0	0.177	∞	0

units of momentum is ejected can be reduced to the form

$$\kappa = 9.27\times 10^{-19}\frac{k^2+0.05512}{k}\times\left|\int_0^\infty W(r)\chi_1(r)dr\right|^2 \text{cm}^2. \tag{11}$$

where $W(r)$ is a certain weight function which can be derived from, and only depends on, the wave function for the bound state. It is seen that according to Eq. (11), the absorption cross section depends only on the single radial function χ_1. This is to be expected since the ground state (being an s-state) transitions can take place only to a p-state. It may be noted here, that on the plane-wave representation of the free electron the appropriate form for χ_1 is

$$\chi_1 \text{ (plane wave)} = \frac{\sin kr}{kr} - \cos kr. \tag{12}$$

The function $W(r)$ corresponding to wave function 8 has been computed and is tabulated in Table II.

An examination of the values given in Table II discloses that substantial contributions to the integral

$$\int_0^\infty W(r)\chi_1(r)dr, \tag{13}$$

arise from values of r up to 25, while as much as 30–40 percent of the entire value comes from $r \geqslant 10$. This result has two consequences. The first is that the use of the p-spherical wave (12) instead of the solution derived from (cf. Eq. [9]),

$$\frac{d^2\chi_1}{dr^2} + \left\{k^2 - \frac{2}{r^2} + 2\left(1+\frac{1}{r}\right)e^{-2r}\right\}\chi_1 = 0, \tag{14}$$

will not lead to any serious error, for the solution of Eq. (14) which tends to a sine wave of unit amplitude at infinity, has the behavior

$$\chi_1 \rightarrow (\sin(kr+\delta)/kr) - \cos(kr+\delta), \quad (r\rightarrow\infty), \tag{15}$$

and the phase shift δ may be taken as a measure of the distortion of the p-spherical wave by the hydrogen atom at the origin. And it is found that for the values of $k^2 < 1$ which are of astrophysical interest, the phase shifts are less than a tenth of a radian. The second consequence of the run of the function $W(r)$ is not so satisfactory, for an examination of the energy integral minimized in the Ritz principle reveals that over 95 percent of the contribution to the integral arises from regions of the configuration space which correspond to $r<10$. Accordingly, it would appear that the choice of the wave function in accordance only with the Ritz principle cannot be expected to lead to values of $W(r)$ which are necessarily trustworthy for $r>10$. Under these circumstances, the best hope for improving the current wave functions would consist in first determining the true asymptotic forms of the wave function for large distances and in later choosing functions which will lead not only to the best value for the energy, but also to the correct asymptotic forms. However, such calculations are likely to be extremely laborious, and we may have to content ourselves, for the present at any rate, with the results obtained with the functions listed in Table I. The absorption cross sections derived on the basis of the different wave functions for the ground state are illustrated in Fig. 1. It is seen how important it is to have a really good wave function to describe the ground state. Moreover, it would appear from the results obtained so far, that a sufficiently rigorous evaluation of the absorption coefficient would place the maximum of the absorption curve in the region of λ10,000A in accordance with the astrophysical requirements.

It is not possible to review here the various astrophysical problems which have found their solutions by properly incorporating the role which the negative hydrogen ions play in the theory of stellar atmospheres. But reference might be made to an important contribution by B.

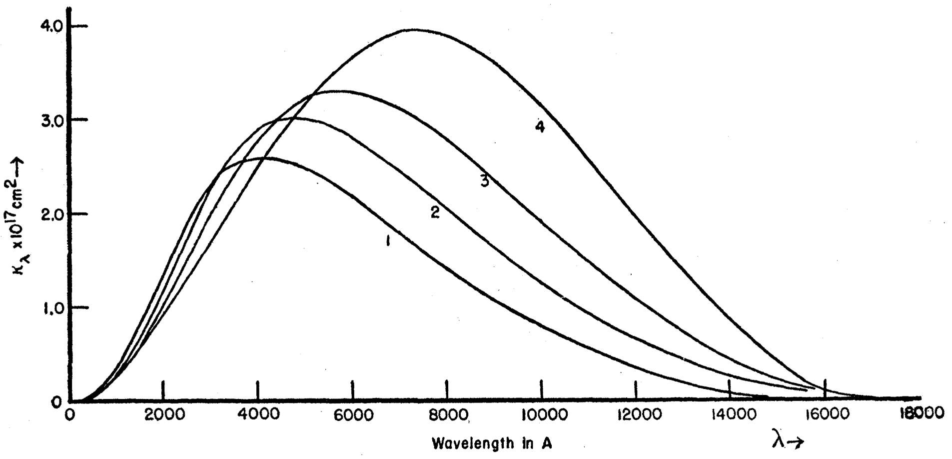

FIG. 1. The continuous absorption coefficient of H^- derived on the basis of different wave functions for the ground state. 1. Massey and Bates, using wave function 4; 2. Williamson, using wave function 6; 3. Chandrasekhar, using wave function 7; 4. Henrich, using wave function 8.

Strömgren in which a first quantitative analysis of the solar atmosphere has been made.[12]

II. THE NEGATIVE ION OF OXYGEN

Recently Wildt and Chandrasekhar[13] have identified the presence of the negative ion of oxygen in the atmospheres of the late type stars. We shall briefly review here the considerations which have led to this identification.

The stability of the negative ion of oxygen has long been known from its frequent appearance in the mass spectrograph. Moreover, from an analysis of certain experiments on electron collisions in molecular oxygen, W. W. Lozier[14] assigned to oxygen an electron affinity of $2.2+0.2$ ev. However, more recently, D. T. Vier and J. E. Mayer[15] have announced a much higher value for the electron affinity of oxygen, namely 3.07 ± 0.08 ev. Though this new value differs considerably from the earlier determinations, Vier and Mayer express confidence in their value in view of the proved reliability of their method as demonstrated by the determinations of the electron affinities of the halogens by Mayer and his collaborators. In our further considerations, we shall accept Vier and Mayer's value of 3.07 ev., as the correct one.

On the theoretical side, the structure of the negative ion of oxygen has been the subject of investigations by D. R. Hartree, W. Hartree, and B. Swirles[16] and D. R. Bates and H. S. W. Massey.[17] Hartree, Hartree, and Swirles calculated the energy of the normal state of O^- by the method of the self-consistent field taking electron exchange into account. They found that the ion is stable, but the calculated value (0.5 ev) of the electron affinity came out rather low. However, the inherent uncertainties of the theoretical method, particularly as applied to negative ions, are such as not to be incompatible with the experimental determinations.

Bates and Massey have discussed the structure of O^- in considerable detail and have evaluated the various cross sections for absorption, capture, and so on. It is not possible to review this extensive paper here, but attention may be drawn to one important point.

Lozier's experiments, to which we have already made reference, indicated that O^- may have an excited state with an energy near that of the continuum. Further evidence in the same direction has been furnished by the collision experi-

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[12] B. Strömgren, *Festschrift für Elis Stromgren* (Copenhagen, 1940), pp. 218–257.

[13] R. Wildt and S. Chandrasekhar, Astrophys. J. **100**, 87 (1944).

[14] W. W. Lozier, Phys. Rev. **46**, 268 (1932).

[15] D. T. Vier and J. E. Mayer, J. Chem. Phys. **12**, 28 (1944).

[16] D. R. Hartree, W. Hartree, and B. Swirles, Proc. Roy. Soc. **A150**, 9 (1935).

[17] D. R. Bates and H. S. W. Massey, Phil. Trans. Roy. Soc. **A239**, 33 (1943).

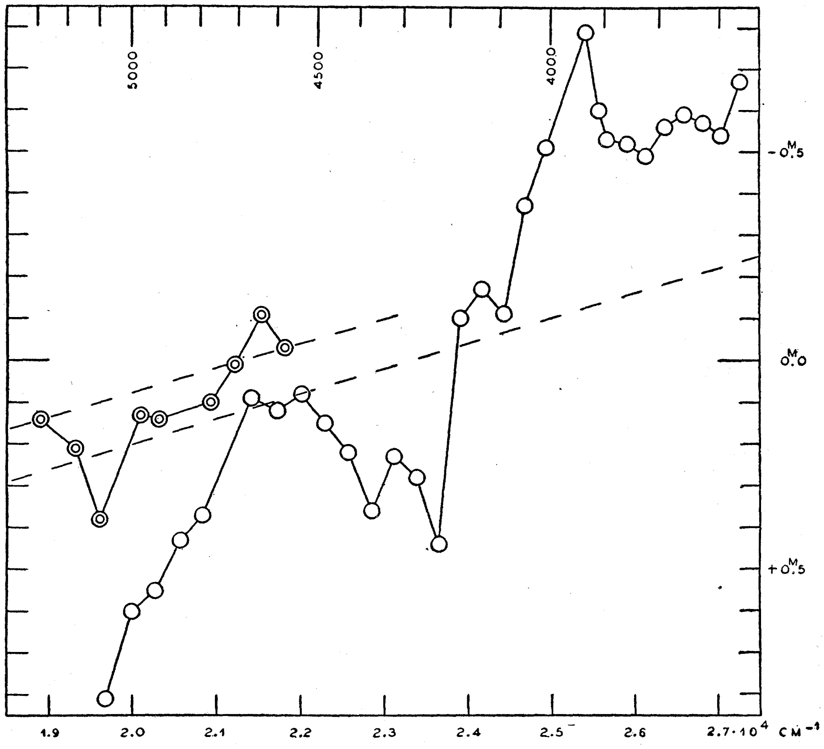

FIG. 2. Ordinates: magnitude differences ($dM2-gM2$) according to Lindblad (single circles) and Öhman (double circles). Abscissas: wave numbers (cm^{-1}). Because of certain systematic differences between the measures of Lindblad and Öhman, the latter's values should be depressed by the amount indicated by the dotted lines to reduce them to the same system.

ments of Hagstrum and Tate.[18] Now the ground state of O^- has the configuration $(1s)^2(2s)^2(2p)^5$ and is a $^2P^0$ term. But it appears difficult to decide the nature of the excited state. There are two possibilities; namely $(1s)^2(2s)(2p)^6$ or $(1s)^2(2s)^2(2p)^4 3s$. After considerable discussion, Bates and Massey decide on the second possibility. This is important since the cross sections for attachment and detachment are sensitive to the assumption made regarding the excited state.

Turning to the astrophysical side, the relevant data are those of B. Lindblad[19] and Y. Öhman[20] who have made spectrophotometric comparisons between two stars, a giant and a dwarf belonging to the class $M2$ ($T \sim 3200°\text{K}$). The results of this comparison are shown in Fig. 2. It is evident from this comparison that there is a discontinuity to the extent of half a magnitude near λ4000 in the sense that the intensity of the continuous spectrum in the giant relative to the dwarf decreases sharply by a factor of about 1.8. This must mean that in the atmosphere of the giant, a new source of absorption sets in as we pass to the violet of λ4000, and which is absent in the dwarf. It is the suggestion of Wildt and Chandrasekhar that this new source of absorption is owing to the negative ion of oxygen beyond its absorption edge at λ4050. Since the temperature of the two atmospheres are the same, the validity of the identification requires that the relative abundance of atomic oxygen to atomic hydrogen is greater by a factor of the order 2 in the atmosphere of the giant, as compared to that of the dwarf. This is not impossible, since it has been known for some time[21] that more of the oxygen atoms in the atmosphere of a dwarf star are "locked" up in the form of compounds (oxides of Ti and Zr) than they are in the atmosphere of a giant. In addition to this effect, it may, of course, be that oxygen is intrinsically more abundant in the giant stars than they are in the dwarf stars.

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[18] H. D. Hagstrum and J. T. Tate, Phys. Rev. **59**, 354 (1941).

[19] B. Lindblad, *Stockholm Obs. Ann.* **12**, No. 2 (1935).

[20] Y. Öhman, *Stockholm Obs. Ann.* **12**, No. 8 (1936).

[21] Cf. H. N. Russell, Astrophys. J. **79**, 281 (1934).