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ON THE HIGH PRESSURE BEHAVIOUR OF HYDROGEN AND HELIUM

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The purpose of this paper is to obtain an exact equation of state for hydrogen and helium at $T = 0$ °K. For the derivation of the energy-molar volume function a cellular method is applied using the boundary condition $(\partial\varrho/\partial r)_{r=r_s} = 0$, where ϱ and r_s are the electron density and the radius of the elementar sphere, respectively. This condition may be satisfied by $(\partial\psi/\partial r)_{r=r_s} = 0$ or $\psi(r_s) = 0$. Both cases are examined. The modification of the Balmer series as a function of density is derived, and a qualitative indication suggesting the presence of a pressure ionization obtained, which may be of interest for geophysics too.

1. INTRODUCTION

One of the most important problems of astrophysics is the satisfactory description of hydrogen and helium under very high pressures: an adequate equation of state should be given for this case. Considering the relationship $p = -(\partial G/\partial v)_T$ the task is to give the free energy G as a function of molar volume v.

In this paper first the behaviour of hydrogen under high pressure is discussed, then the examination of helium follows. In the considerations on hydrogen the method developed by J. de Boer, J. Korringa and R. Kronig [1] is adopted, yet owing to a different numerical solution, not only the variation of ground-state energy as a function of density, but the whole energy spectrum of hydrogen i.e. the analogue of the Balmer series at high pressures is obtained.

E. Wigner and H. B. Hunington [2] were the first to prove that metallic hydrogen may exist at high pressures. They have also calculated the internal energy of metallic hydrogen. The essence of their method was, that the boundary condition

$$\left.\frac{d\psi}{dr}\right|_{r=r_s} = 0 \tag{1}$$

that has stood the test in the description of monovalent metals, applies also to hydrogen under high pressure. (In the formula ψ is the wave function of an electron, and r_s the radius of the elementary sphere for a hydrogen atom.)

In connection with the Kuhn–Rittman Earth model the behaviour of hydrogen under high pressure has come to the foreground again. De Boer and others have solved the Schrödinger equation by taking boundary condition (1) into consideration: they have determined the function $\varepsilon_0(r_s)$. (ε_0 is the energy of the first stationary orbit, which means that for $T = 0°$ K the calculation can be assumed to be exact). From this, they calculated the critical pressure of the formation of the metallic phase; for the molecular phase they used the Lennard–Jones potential, also called as 6–12 potential. This

has a greater significance for the discussion of giant planets; considering the excessive pressures and temperatures, in astrophysical applications molecular hydrogen may occur only exceptionally.

With respect to the internal consitution of Jupiter and Saturn, W. C. DeMarcus [4, 5] repeatedly determined the function $\varepsilon_0(r_s)$ for atomic hydrogen. DeMarcus has not given the details of his calculations, he only mentions having followed the Wigner and Hunington method and used a variation wave function of three parameters. Above 300 000 atmospheres his results are in fair agreement with those of de Boer and others.

To calculate the internal energy of electron gas in divalent metals S. Raimes [6] has described a method. His results are fairly consistent with the high-pressure test results of Bridgman. DeMarcus mentions that he applied the same method for the determination of the equation of state of helium. Raimes' results are reliable up to about 10^5 atmospheres for metals. Therefore DeMarcus' extrapolation should be regarded with some reserve, as in the centre of Jupiter a pressure of about 10^8 atmospheres predominates. (The electrostatic interaction of helium electrons cannot be taken into account by this method quantum mechanically as the Hamiltonian operator does not contain any terms including the relative position vector r_{12} of two electrons.)

2. SPECTRUM OF HYDROGEN AT HIGH PRESSURES

First of all it should be made clear that in what follows by high pressures we mean 10^8 to 10^{10} atmospheres. Under such conditions the problem may still be treated in a non-relativistic approach; the Schrödinger equation must be solved, subject to boundary condition (1) in addition to regularity at the origin. This gives the following picture of the material under compression: individual hydrogen atoms come closer as pressure goes increasing and the regularity of the wave function can be ensured only by boundary condition (1).

Calculations are made in the usual atomic units, i.e.

$$\hbar = m_e = e = 1 \tag{2}$$

and energy is measured in ry units.

Then the Schrödinger equation becomes

$$\left(\Delta + \frac{2Z}{r} + \varepsilon\right)\psi = 0. \tag{3}$$

Since the boundary condition (1) preserves spherical symmetry, the radial part of the wave function can be separated in the same way, as in the case of a free hydrogen atom; thus the equation of the radial part of the wave function is:

$$\varphi'' + \frac{2}{r}\varphi' + \left(\varepsilon + \frac{2Z}{r} - \frac{l(l+1)}{r^2}\right)\varphi = 0. \tag{4}$$

The boundary condition is

$$\left.\frac{d\varphi}{dr}\right|_{r=r_s} = 0. \tag{5}$$

In what follows we limit our considerations to the s states, i.e. we take $l = 0$. (In ground state, there is no other possibility, and only excitations of state s will be examined. In addition the results will show that above certain pressures electrons may exist only in the state $1s$).

Thus the problem is to solve the differential equation

$$\varphi'' + \frac{2}{r}\varphi' + \left(\varepsilon + \frac{2Z}{r}\right)\varphi = 0 \tag{6}$$

by taking (5) into consideration. With the transformation

$$\varphi(r) = e^{-t/2} F(t) \tag{7}$$

where

$$t = 2r\sqrt{|\varepsilon|} \tag{8}$$

equation (6) becomes a confluent hypergeometric differential equation of index $c = 2$, namely

$$tF'' + (2 - t)F' - \alpha F = 0. \tag{9}$$

The parameter α includes the energy eigenvalue

$$\alpha = 1 - \frac{Z}{\sqrt{|\varepsilon|}} \tag{10a}$$

$$\varepsilon = -\frac{Z^2}{(1-\alpha)^2}. \tag{10b}$$

It can be seen that the stationary states with the $n = 1, 2, 3 \ldots$ main quantum numbers belong to the values $\alpha = 0, -1, -2, \ldots$ The solution of equation (9) is a confluent hypergeometric function

$$F_\alpha(t) = \sum_{k=0}^{\infty} \frac{(\alpha)_k}{(k+1)!}\frac{t^k}{k!} \tag{11}$$

where

$$(\alpha)_k = \alpha(\alpha+1)\ldots(\alpha+k-1)$$

and

$$(\alpha)_0 = 1.$$

As it could be expected, for not positive integer values of α Equ. (11) is a polinom of order $k \geqq 0$ and for other values of α it is a uniformly convergent infinite series.

Consider the boundary condition

$$\left.\frac{d\varphi}{dr}\right|_{r=r_s} = 2\sqrt{|\varepsilon|}\, e^{-t/2}\left[F'(t) - \frac{1}{2}F(t)\right]\Bigg|_{t=t_s} = 0. \tag{12}$$

As

$$t = \frac{2Zr}{1-\alpha} \tag{13}$$

after the transposition of the form of the $F(t)$ series Equ. (12) is transformed into

$$\frac{1}{2}+\sum_{k=1}^{\infty}\left[\frac{(2Z)^k}{(k-1)!\,(k+1)!}\,\frac{(\alpha)_k}{(1-\alpha)^k}\,r_s^k\left(\frac{1}{2k}-\frac{1-\alpha}{2Zr_s}\right)\right]=0. \tag{14}$$

It only α occurs in (14) and after solution for various r_s values, on the basis of (10b) the required $\varepsilon(r_s)$ function may be written down. The equation is of infinite degree, but the term $[(k-1)!(k+1)!]^{-1}$ ensures convergency for any finite value of r_s.
Therefore, in the numerical solution the equation

$$H_n(\alpha)=\frac{1}{2}+\sum_{k=1}^{n}\left[\frac{(2Z)^k}{(k-1)!\,(k+1)!}\,\frac{(\alpha)_k}{(1-\alpha)^k}\,r_s^k\left(\frac{1}{2k}-\frac{1-\alpha}{2Zr_s}\right)\right]=0 \tag{15}$$

will be solved for a finite value of n great enough to comply with the required accuracy of α (one-thousandth part in this paper). The solution thus obtained is represented in Figure 1 and 2; for large r_s values $\varepsilon(r_s)$ gives the Balmer series again.

The mathematical reason of the different behaviour of the states $n=1$ and $n>1$ is that the eigenfunction of the state $n=1$ is an exponential function, whereas in case of $n>1$ it is the product of a polynomial of order $k\geq 1$ and of an exponential function. Following from the uncertainty principle in the course of compression the drop of potential energy is at first more rapid than the increase of the kinetic energy coming from localisation, because

$$V_{\text{pot}}\sim-\frac{1}{r_s}\qquad E_{\text{kin}}\sim\frac{1}{r_s^2}\,. \tag{16}$$

This means that with the decrease of r_s, at first α must go increasing, that is to say, for $n=1$ $0<\alpha<1$, for $n=2$ $-1<\alpha<0$, $n=3$ $-2<\alpha<-1$.

$$F_0(t)\equiv 1 \tag{17}$$

which is consistent with the fact that the eigenfunction of $n=1$ is exponential. So that the energy eigenvalue of the ground state with decreasing r_s should likewise converge to zero, the condition

$$\lim_{r_s\to 0}\alpha=-\infty$$

should be fulfilled. ($\lim\alpha=+\infty$ is eliminated by the singularity in $\alpha=1$). Considering those discussed above, $\alpha=0$ will occur at some finite value of r_s. Then the eigenfunction becomes exponential again because of (17): on the other hand, its slope in finite is zero. This is an apparent contradiction. Yet the slope of the eigenfunction of the states $n>1$ is zero not only in the infinite, and thus it is no contradiction that the relationship

$$\alpha=-(n-1) \tag{18}$$

must be fulfilled at least for two values of r_s. (One of them is $r_s=\infty$).

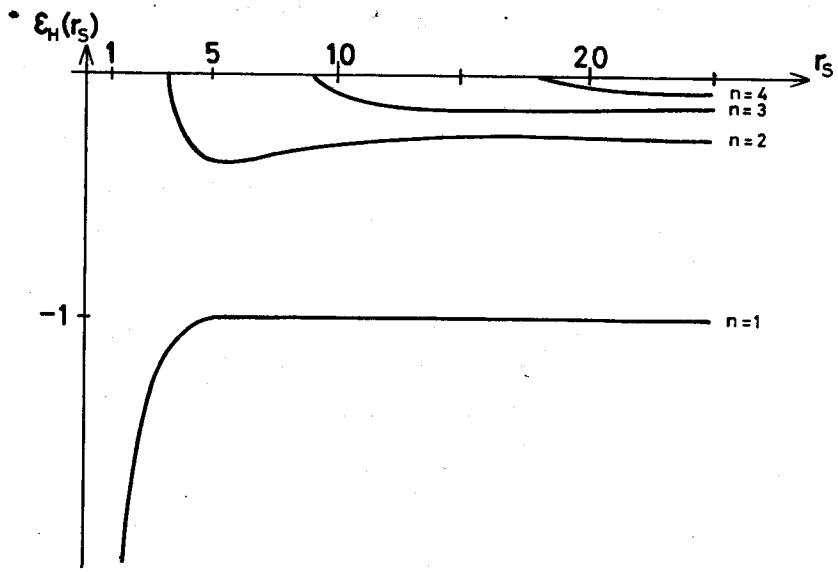

Figure 1

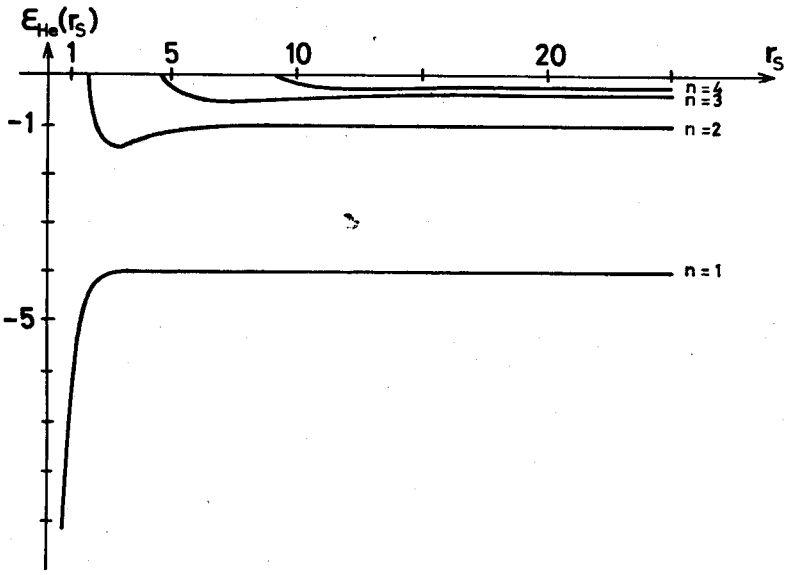

Figure 2

The Figures represent the course of the energy eigenvalues of various stationary states. The horizontal axis carries r_s in units of a_0 the vertical axis $\varepsilon(r_s)$ in ry units (a_0 is the first Bohr radius)

3. APPLICATIONS

a) The equation of state of atomic hydrogen may be derived from the well-known relationship

$$p = -\left(\frac{\partial G}{\partial v}\right)_T. \tag{19}$$

(At $T = 0$ °K we may take $G = E$.) It goes without saying that the overall energy, E, belonging to a single atom, which is composed of the sum of the Fermi, exchange, correlation and Coulomb energies [1, 4]

$$E_H(r_s) = \frac{2.21}{r_s^2} + \frac{1.20}{r_s} - \frac{0.916}{r_s} - \frac{0.88}{r_s + 7.8} + \varepsilon(r_s) \tag{20}$$

monotonously increases with the dropping of r_s. If (20) had a local minimum, this would correspond to the forming of some crystal structure. Transpose (20) into (19) and consider that mass density expressed in terms of cgs is

$$\varrho = \frac{2.679}{r_s^3} \tag{19a}$$

then the equation of state may be written as

$$p(\varrho) = 1.175 \times 10^{13} \left[0.855\, \varrho^{5/3} + 0.0763\, \varrho^{4/3} - \frac{0.236\, \varrho^{4/3}}{(1 + 5.61\, \varrho^{1/3})^2} + \right.$$
$$\left. + 1.118\, \varrho^2 \frac{d\varepsilon}{d\varrho}\right] \frac{\text{dyn}}{\text{cm}^2}\,. \tag{19b}$$

Substituting numerical values into (19b) for the case of $n = 1$ the equation of state given in Table 1 is obtained, in fair agreement with the DeMarcus equation of state. Discrepancies come among others, from the zero point energy neglected. Another source of discrepancy is the use of a three-parameter wave function instead of the exact formula, (7). The critical pressure of 1.93×10^6 atmospheres for the formation of the metallic phase is in very good accordance with DeMarcus' results. (For the molecular phase the "6—12" potential was used.)

b) For the case of n = 2, $E_H(r_s)$ is reptesented in Figure 3.

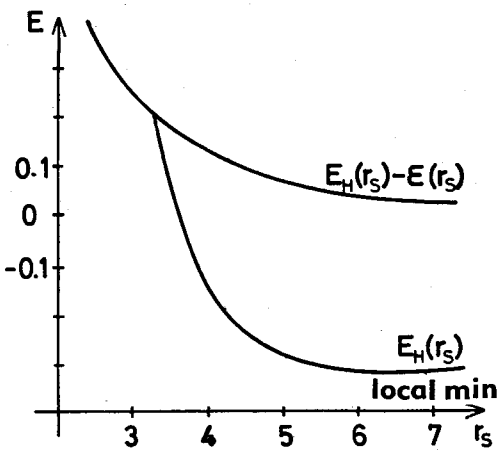

Figure 3

The unit for E is ry, that for r_s is a_0

Figures 1, 2, 3 imply a conclusion much more interesting for geophysics as regards pressure ionization. It is seen that above a certain pressure (or density) only a single s bound state is found. This means that, if an atom, considered as spherically symmetrical for the sake of approximation, for which $Z > 2$, is compressed, $2s$, $3s$, . . . electrons leave the atom bonds. (They become free as $E > 0$ for the stationary

Table 1

(The equation of state of the metallic hydrogen at 0 °K)

r_s (a_0)	ϱ (cgs)	p (cgs 10^{-12})	r_s	ϱ	p
			1.00	2.680	22.2
0.15	794.0	6.20×10^5	1.05	2.314	14.3
0.20	335.0	1.37×10^5	1.10	2.013	10.7
0.25	171.5	3.79×10^4	1.15	1.762	7.57
0.30	99.55	1.36×10^4	1.20	1.551	5.51
0.35	62.50	6.04×10^3	1.25	1.372	4.00
0.40	41.87	3.04×10^3	1.30	1.220	2.92
0.45	29.41	1.56×10^3	1.35	1.089	2.10
0.50	21.44	964	1.40	0.9766	1.47
0.55	16.11	446	1.45	0.8789	0.955
0.60	12.40	327	1.50	0.7940	0.646
0.65	9.758	195	1.55	0.7196	0.419
0.70	7.812	127	1.60	0.6542	0.233
0.88	3.930	42.0	1.65	0.5965	0.125

state.) As seen in Figure 3, such phase transformation is accompanied by a density jump as pressure is in proportion to the slope of the curve. Setting Figures 1, 2 side-by-side it is seen that the higher the atomic number the higher the density (pressure) at which this phenomenon takes place. By a further development of this train of ideas the density jumps in the interior of the Earth could be explained supposing that different metallic phases of the chemically homogeneous material of the Earth, produced in the way outlined above, form mantle, core and inner core.

4. EQUATION OF STATE OF HELIUM IN CASE OF $T = 0$ °K

In the first part of this paper the eigenfunction of hydrogen for various r_s values was obtained, so to speak, "incidentally". It is reasonable to try to determine the ground-state energy of a helium atom as a function of r_s, too, as for the first approximation of the perturbation theory: to the calculation of $(\varphi_0, H_1 \varphi_0)$ everything is at hand. By this, as a matter of fact, the Wigner–Seitz cellular method has been applied to helium, considering the interaction within the elementary cell quantum-mechanically. The eigenfunction of helium will be constructed as a product of eigenfunctions of the type of Equation (7) and, considering that because of $T = 0$ °K the space-dependent part is symmetrical:

$$\varphi_0 = e^{-2\frac{r_1 + r_2}{1-\alpha}} F\left(\frac{4r_1}{1-\alpha}\right) F\left(\frac{4r_2}{1-\alpha}\right). \tag{21}$$

The boundary condition imposed on the wave function will be determined so that the slope of electron density is zero at the surface of the elementary cell. As the electrons are in the state $1s$, the density of electrons at place r is:

$$\varrho(r) = \varphi_0^2(r). \tag{22}$$

Differentiating and taking it at the boundary of the cell

$$\left.\frac{d\varrho}{dr}\right|_{r=r_s} = 2\,\varphi_0'(r_s)\,\varphi_0(r_s) = 0. \tag{22a}$$

Expression (22a) may be zero when $\varphi_0'(r_s)$ or $\varphi_0(r_s)$ are equal to zero. In the first case the solution of (14) and (15) gives the function $\alpha(r_s)$ wanted, as, because of symmetry

$$\operatorname{grad}_1 \varphi_0|_{r=r_s} = \operatorname{grad}_2 \varphi_0|_{r=r_s} = 0 \tag{22b}$$

where grad_1 is derivation with respect to the coordinate of the first, and grad_2 derivation with respect to the coordinate of the second electron.

The energy becomes

$$\varepsilon^1_{He} = \frac{(\varphi_0, H\varphi_0)}{(\varphi_0, \varphi_0)} \tag{23}$$

where

$$H = -\Delta_1 - \Delta_2 - 2\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right) + \frac{2}{r_{12}} = H_0 + H_1. \tag{24}$$

The contribution of the non-perturbed Hamiltonian operator H_0 to (23) is $2\,\varepsilon_{He^+}(r_s)$. i.e.

$$\varepsilon^1_{He}(r_s) = 2\,\varepsilon_{He^+}(r_s) + \frac{(\varphi_0, H_1\varphi_0)}{(\varphi_0, \varphi_0)}. \tag{25}$$

Thus the problem is reduced to the determination of the increment due to the operator H_1. To calculate this the following relationships are needed.

$$F^2(t) = \sum_{k=0}^{\infty} c_k' t^k = \sum_{k=0}^{\infty}\left(\sum_{l=0}^{k} c_l\, c_{k-l}\right) t^k \tag{26}$$

where

$$c_k = \frac{(\alpha)_k}{k!(k+1)!}$$

$$\int_0^{t_s} e^{-t}\, t^n\, dt = -\sum_{m=0}^{n} \frac{n!}{(n-m)!}\left[e^{-t}\, t^{n-m}\right]_{t=0}^{t=t_s}. \tag{27}$$

As nothing can depend on the position in space of the helium atom, and the electrons are in state s, after integration with respect to one, respectively to two polar angles of six-dimension elementary volume position vectors r_1 and r_2 we may write

$$dV = 8\pi^2 r_1^2 r_2^2 \sin\vartheta\, d\vartheta\, dr_1\, dr_2 \tag{28a}$$

or, r_{12} having been introduced it takes the form

$$dV = 8\pi^2 r_1 r_2 r_{12}\, dr_{12}\, dr_1\, dr_2. \tag{28b}$$

As $r_{12} = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\vartheta}$ integration with respect to r_{12} is carried out between the limits $|r_1 - r_2|$ and $r_1 + r_2$.

Considering the above, the normalization factor is

$$N = (\varphi_0, \varphi_0) = 16\pi^2 \int_0^{r_s} dr_1 \int_0^{r_s} dr_2\, r_1^2 r_2^2 \varphi_0^2. \tag{29}$$

As r_1 and r_2 are independent variables, the double integral becomes a product of single ones. Thus

$$N = 16\pi^2 \int_0^{r_s} e^{-\frac{4r_1}{1-\alpha}} F^2\left(\frac{4r_1}{1-\alpha}\right) r_1^2 dr_1 \int_0^{r_s} e^{-\frac{4r_2}{1-\alpha}} F^2\left(\frac{4r_2}{1-\alpha}\right) r_2^2 dr_2. \tag{30}$$

Introducing the notation

$$G_2(r_s, \alpha) = \int_0^{r_s} e^{-\frac{4r}{1-\alpha}} F^2\left(\frac{4r}{1-\alpha}\right) r^2 dr \tag{31}$$

and using Eqs (13), (27) we can perform the integration:

$$G_2(r_s, \alpha) = \left(\frac{1-\alpha}{4}\right)^3 \sum_{k=0}^{\infty} c'_k \left[(k+2)! - e^{-t_s} \sum_{m=0}^{k+2} \frac{(k+2)!}{(k+2-m)!} t^{k+2-m}\right]$$

$$= \left(\frac{1-\alpha}{4}\right)^3 e^{-\frac{4r_s}{1-\alpha}} \sum_{m=0}^{\infty} c'_k p^{k+2} \tag{31a}$$

where

$$p^k = k!\left[1 - e^{-t_s} \sum_{m=0}^{k} \frac{t_s^k}{(k-m)!}\right] = \sum_{m=k+1}^{\infty} \frac{k!}{m!} \left(\frac{4r_s}{1-\alpha}\right)^m. \tag{31b}$$

Thus

$$N = 16\pi^2 [G_2(r_s, \alpha)]^2. \tag{32}$$

The potential energy correction for repulsion between two electrons is

$$L_p = (\varphi_0, H_1 \varphi_0) = 16\pi^2 \int_0^{r_s} dr_1 \int_0^{r_s} dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} dr_{12}\, r_1 r_2 \varphi_0^2$$

$$= 32\pi^2 \int_0^{r_s} dr_1 \left(\int_0^{r_1} dr_2\, r_1 r_2^2 \varphi_0^2 + \int_{r_1}^{r_s} dr_2\, r_1^2 r_2 \varphi_0^2\right). \tag{33}$$

Using form (21) for φ_0 and integrating with respect to r_2 we get

$$L_p = 32\pi^2 \left(\frac{1-\alpha}{4}\right)^5 \left\{\int_0^{t_s} e^{-t} \left(\sum_{l=0}^{\infty} c'_l t^{l+1}\right) \left[\sum_{k=0}^{\infty} c'_k (k+2)! \left(1 - e^{-t} \sum_{m=0}^{k+2} \frac{t^m}{m!}\right)\right] dt \right.$$

$$\left. + \int_0^{t_s} e^{-t} \left(\sum_{l=0}^{\infty} c'_l t^{l+2}\right) \left[\sum_{k=0}^{\infty} c'_k (k+1)! \left(\sum_{m=0}^{\infty} \frac{e^{-t} t^m}{m!} - \frac{e^{-t_s} t_s^m}{m!}\right)\right] dt \right\}. \tag{34}$$

Apply the Cauchy rule for the multiplication of infinite series and use (27) again to obtain

$$L_p = 32\pi^2 \left(\frac{1-\alpha}{4}\right)^5 \sum_{l=0}^{j} c'_l \left\{ e^{-t_s} \left[\sum_{k=0}^{l+k=j} c'_k (k+1)! \left((k+2) p^{l+1} - e^{-t_s} p^{l+2} \sum_{m=0}^{k+1} \frac{t_s^m}{m!} \right) \right] \right.$$

$$+ \sum_{k=0}^{l+k=j} c'_k (k+1)! \left[\sum_{m=0}^{k+1} \frac{(m+l+2)!}{2^{m+l+3}\, m!} \left(1 - e^{-2t_s} \sum_{p=0}^{m+l+2} \frac{(2t_s)^p}{p!} \right) \right. \tag{35}$$

$$\left. \left. -(k+2) \sum_{m=0}^{k+2} \frac{(m+l+1)!}{2^{m+l+2}\, m!} \left(1 - e^{-2t_s} \sum_{p=0}^{m+l+1} \frac{(2t_s)^p}{p!} \right) \right] \right\} .$$

Equation (35) was computed on an Ural-2 type computer. The numerical results are listed in Table 2. In the range of $0.1 \leq r_s \leq 3.5$ for L_p/N $j \leq 20$ they are reliable one part in thousandth.

The total energy for each helium electron can be set up on the analogy of (20); considering, that a sphere of radius r_s now contains two electrons:

$$E_{He}(r_s) = \frac{3.51}{r_s^2} + \frac{2.40}{r_s} - \frac{1.154}{r_s} - \frac{1.109}{r_s + 9.38} + \frac{1}{2} \varepsilon^1_{He}(r_s). \tag{36}$$

Using Eq. (19) the equation of state for $T = 0$ °K can be derived

$$p = \frac{1.475 \times 10^{14}}{4\pi r_s^2} \left[\frac{14.04}{r_s^3} + \frac{2.492}{r_s^2} - \frac{2.21}{(r_s + 9.83)^2} - \frac{d\varepsilon^1_{He}}{dr_s} \right] \frac{\text{dyn}}{\text{cm}^2} . \tag{37}$$

Table 2 lists the numerical values of (25) and of interaction energy, (37) as functions of density. ($\varrho = 10.85\ r_s^{-3}$ cgs)

Table 2

(The helium at 0 °K)

r_s (a_0)	$\varepsilon_{He}(r_s)$ (ry)	L_p/N (ry)	p (cgs $\times 10^{-12}$)	r_s	$\varepsilon_{He}(r_s)$	L_p/N	p
0.15	−64.67	16.13	2.22×10^6	1.50	−7.638	2.110	7.33
0.20	−48.67	12.13	4.60×10^5	1.60	−7.288	2.084	5.61
0.25	−39.13	9.746	1.69×10^5	1.70	−6.995	2.077	3.76
0.30	−32.71	8.152	6.62×10^4	1.80	−6.727	2.090	2.76
0.35	−28.16	7.017	2.56×10^4	1.90	−6.509	2.115	2.16
0.40	−24.77	6.165	1.29×10^4	2.00	−6.309	2.157	1.81
0.45	−22.11	5.505	6.86×10^3	2.10	−6.153	2.197	1.50
0.50	−20.00	4.976	3.94×10^3	2.20	−6.013	2.245	1.31
0.60	−16.85	4.191	1.49×10^3	2.30	−5.893	2.293	1.23
0.70	−14.58	3.639	637	2.40	−5.802	2.334	1.26
0.80	−12.91	3.228	307	2.50	−5.726	2.370	1.29
0.90	−11.61	2.917	156	2.60	−5.677	2.395	1.22
1.00	−10.55	2.678	83.6	2.70	−5.635	2.417	1.08
1.10	− 9.769	2.488	53.4	2.80	−5.590	2.444	0.972
1.20	− 9.093	2.349	29.0	2.90	−5.577	2.451	0.869
1.30	− 8.525	2.237	19.0	3.00	−5.561	2.459	0.788
1.40	− 8.050	2.160	11.8	3.20	−5.527	2.481	0.633
				3.50	−5.507	2.493	0.466

The values obtained for pressures do not agree with the empirical values at low densities. This is by no means surprising, as the Fermi gas model of the material does not give a correct description here. Non-metallic helium was described as if its behaviour under high pressures were dependent on an elec-

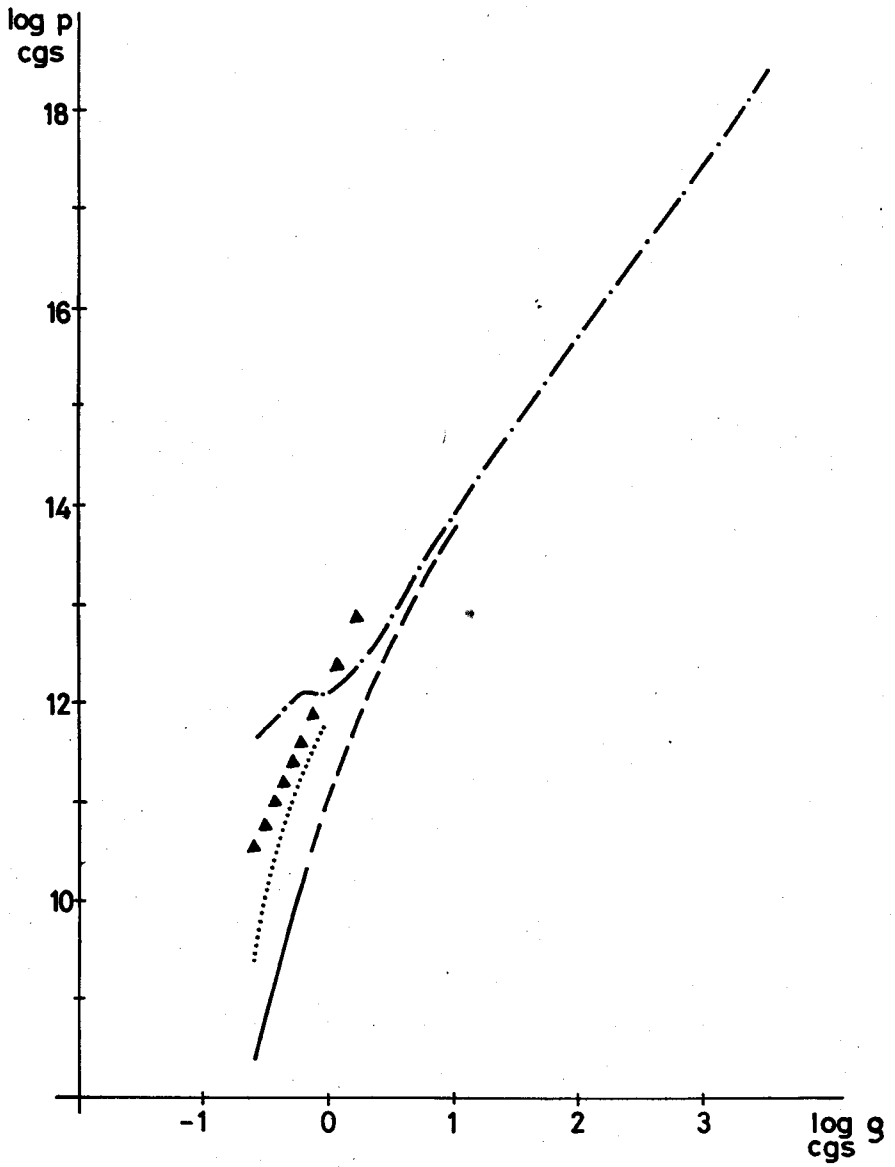

Figure 4

——————— Experimental curve of Stewart
— — — — — Extrapolation of equation of state of DeMarcus
—·—·—·—·— Numerical values of (37)

The comment for the two other curves can be found on the next page.

tron gas similar in some respects to that found in divalent metals. As, however, pressure goes increasing, (37) should become of ever better reliability. As the paper of Raimes indicates and a numerical comparison shows, the part falling into the 10^6–10^7 atmosphere range of the DeMarcus' equation of state corresponds to $L_p(r_s) = 0$ which makes the matter under compression softer than in reality it is. DeMarcus selected the low-pressure section apparently in order to get a good interpolation between experimental and high-pressure sections.

Only in the possession of an equation of state of better reliability one could judge the question, how close the phase transformation represented in Figure 4 comes to reality. It should take place at about one million atmospheres, and the density jump that occurs is of about 0.3 gcm^{-3}. This result, provided it is confirmed by further calculations, may be of outstanding importance in the discussion of giant planets, and may give a new basis for looking for the origins of discontinuities in the core of the Earth in the formation of the electron structure of a homogeneous silicate material as outlined above.

For a better agreement at low pressures the fulfillment of boundary condition (22a) was examined also in the case when the wave function itself is zero. Then, of course, electron density on the surface of the elementary sphere is likewise zero, which corresponds to a most strict localization of the helium electrons — the case of an ideal insulator of infinitely high potential barrier. Expressed by the terms of mathematics, this means, that instead of (14) the equation

$$F_\alpha(t_s) = \sum_{k=0}^{\infty} \frac{(\alpha)_k}{k!(k+1)!} \left(\frac{4r_s}{1-\alpha}\right)^k = 0 \tag{38}$$

must be solved. It is seen that Equ. (38) can be fulfilled, even at ground state, only when α is negative which means, that $\varepsilon_0(r_s)$ is a function increasing monotonously. The "one electron spectrum" obtained from (38) — the analogy of Figures 1, 2 — is represented in Figure 5. In this case, only the last term of (36) is preserved, to which correction of the attraction of the Van der Waals forces should be applied. (It is negligible. [8])

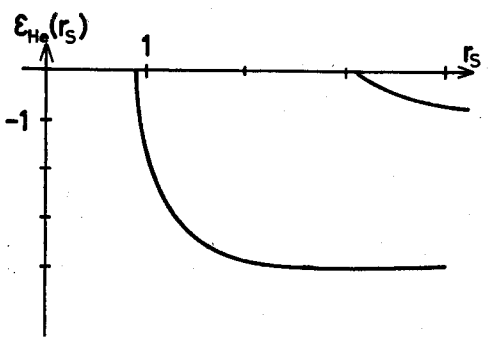

Figure 5

The quantities ε and r_s are given in ry and a_0 respectively. The curves represent the energy eigenvalue of the $1s$ and $2s$ states

Figure 4 includes the equation of state determined from (38), computed on the basis of $\varepsilon^1_{He}(r_s)$ as derived from $\alpha(r_s)$ of (38). The data of the dotted curve were calculated by the introduction of effective nuclear charge Z^* which account for the fact that one of the electrons screens the charge from the other [7]. At high densities, instead of Z^*/r the Yukawa potential should be used, and for this reason, at about 10^6 atmospheres the curve cannot be considered as reliable any more. The curve marked with triangles was

derived from (25). (With the function $\alpha(r_s)$ obtained from (38) Equ. (35) was computed and in the place of $\varepsilon_{He^+}(r_s)$ the numerical values of Figure 5 have been transposed.)

5. SUMMARY AND DISCUSSION

The results may be summerized as follows:

a) The modification of the spectra of hydrogen and He^+ ion at high pressures has been obtained. The equation of state of hydrogen for the temperature of $T = 0$ °K as well as the critical pressure of the evolution of metallic phase have been determined.

b) The equation of state of helium has been obtained for $T = 0$ °K. For astrophysical application the accuracy of the equation of state is satisfactory, as only the use of first order perturbation theory includes an error. The error in correlation energy is neglected, because it is only significant at low densities, where the Fermi gas model cannot be used anyway. At low pressures the equation of state resulting from the boundary condition $\varphi_0(r_s) = 0$ is apparently more realistic, though the condition that electron density is zero at the boundaries, applies only to free atoms. For more accurate calculations the boundary condition $\varphi_0(r_s) = \text{const}$ might be applied; the constant dependent on r_s would be close to zero, and much smaller than the value of $\varphi_0(r_s)$ in the case when boundary condition (22b) was applied. This means that inside the matter electron density $\varrho(r)$ is continuous, but it cannot be differentiated at point r_s.

c) Indications significant for geophysics have been gained relatively to pressure ionization and density jumps taking place in compressed matter.

The measurement of the modification of the hydrogen spectrum represented in Figures 1, 2 does not seem impracticable. Through a pressure of a few hundred atmospheres the region of $r_s \approx 10a_0$ can be reached. Here the gas must be kept at a temperature high enough to permit the observation of the spectrum of the hydrogen atom. A test performed to this effect would give precious information as regards the legitimacy of boundary condition (1).

Another possibility for the experimental verification is to measure the ionization energy of helium as a function of density; the theoretical value can be obtained from Fig. 2 and (25). (Then the value of (25) has to be calculated with $\alpha(r_s)$ from (38).)

The calculations of band width that would prove the well-foundedness of assumptions (22a) and (36) pass the frames of this paper, but their holding true at high pressures can hardly be contested.

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