NUMERICAL SOLUTION OF STATISTICAL EQUATION WITH EXCHANGE

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An alternative derivation of the quantum-statistical equation with exchange is presented and details concerning the procedure of its numerical solution are given. The solutions are tabulated for the cases of the free neutral Kr atom, one free positive Kr ion and one neutral Kr atom in a crystal under pressure.

§ 1. *Introduction*

The author (1963, henceforth denoted by [I]) recently derived a statistical equation with exchange where the local density correction due to the existence of the finite volume of exchange holes in the electron gas of statistical atom has been taken into account. Different solutions of this statistical equation with exchange are possible, depending on the various conditions imposed on the boundary of the atomic system. We obtain in this way solutions corresponding respectively to free atoms, free positive ions, atoms (ions) in crystals and crystal atoms (ions) under pressure. The purpose of the present note is to give details concerning the numerical solution for each of these atomic cases.

On the other hand, we find it desirable to derive our statistical equation along a somewhat different path than in [I]. The calculation is carried out by variation of the energy E of the statistical atom where a simple form of Slater's (1951) average exchange potential used formerly and given by

$$V_e^a = \frac{2\varkappa_a}{e}\varrho^{1/3} \tag{1}$$

(ϱ being the density of particles (electrons), $\varkappa_a = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} e^2$ and e — the positive elementary charge) is replaced by a more developed form of the exchange potential. Here, no simplifying integration is applied previous to the calculation of δE. The treatment is presented below.

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§ 2. Derivation of statistical equation with exchange

We have the average exchange electron density represented by

$$\varrho_a(\boldsymbol{r},\boldsymbol{r}') = -\frac{\varrho(\boldsymbol{r}')}{2}\left[3\frac{\sin\{[3\pi^2\varrho(\boldsymbol{r}')]^{1/3}|\boldsymbol{r}-\boldsymbol{r}'|\}-[3\pi^2\varrho(\boldsymbol{r}')]^{1/3}|\boldsymbol{r}-\boldsymbol{r}'|\cos\{[3\pi^2\varrho(\boldsymbol{r}')]^{1/3}|\boldsymbol{r}-\boldsymbol{r}'|\}}{\{[3\pi^2\varrho(\boldsymbol{r}')]^{1/3}|\boldsymbol{r}-\boldsymbol{r}'|\}^3}\right]^2 \tag{2}$$

(*cf. e.g.* Wigner and Seitz 1933, Slater 1951). The corresponding expressions for the exchange potential and exchange energy are, respectively,

$$V_e^a = -e\int\frac{\varrho_a(\boldsymbol{r},\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,dv', \tag{3}$$

$$E_a = -\frac{1}{2}e\int V_e^a\varrho(\boldsymbol{r})dv. \tag{4}$$

It is convenient to denote

$$\varrho_a(\boldsymbol{r},\boldsymbol{r}') \equiv \varrho(\boldsymbol{r}')h[\varrho(\boldsymbol{r}'),[\boldsymbol{r}-\boldsymbol{r}'|]. \tag{5}$$

Thus, we have

$$E_a = \frac{1}{2}e^2\int\int\frac{\varrho(\boldsymbol{r})\varrho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}h[\varrho(\boldsymbol{r}'),|\boldsymbol{r}-\boldsymbol{r}'|]\,dvdv' \tag{6}$$

and the corresponding expression for V_e^a with h from (5) is obtained.

The relation between the electron density ϱ and the total potential V acting in the statistical model is established from the equation

$$\delta(E+V_0Ne) = 0, \tag{7}$$

where E is the total energy, V_0 the Lagrangian multiplier and N the number of electrons in the statistical system. We compute here only δE_a, since the other components of E are the same as in the book by Gombás (1949). Thus,

$$\begin{aligned}\delta E_a &= \frac{1}{2}e^2\int\int\frac{\varrho(\boldsymbol{r}')\,\delta\varrho(\boldsymbol{r})+\delta\varrho(\boldsymbol{r}')\,\varrho(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}h[\varrho(\boldsymbol{r}'),|\boldsymbol{r}-\boldsymbol{r}'|]\,dvdv'+\\ &+\frac{1}{2}e^2\int\int\frac{\varrho(\boldsymbol{r})\varrho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\frac{\partial h[\varrho(\boldsymbol{r}'),|\boldsymbol{r}-\boldsymbol{r}'|]}{\partial\varrho(\boldsymbol{r}')}\delta\varrho(\boldsymbol{r}')\,dvdv'\\ &\approx -e\int V_e^a\delta\varrho(\boldsymbol{r})dv+\frac{1}{2}e^2\int\int\frac{\varrho(\boldsymbol{r})\varrho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\frac{\partial h[\varrho(\boldsymbol{r}'),|\boldsymbol{r}-\boldsymbol{r}'|]}{\partial\varrho(\boldsymbol{r}')}\delta\varrho(\boldsymbol{r})\,dvdv'\\ &= \int\left(-eV_e^a+\frac{1}{2}e^2\varrho\int\frac{\varrho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\frac{\partial h}{\partial\varrho(\boldsymbol{r}')}\,dv'\right)\delta\varrho dv,\end{aligned} \tag{8}$$

where in the one but last transformation of (8) use has been made of the fact that

$$\frac{\varrho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}h[\varrho(\boldsymbol{r}),|\boldsymbol{r}-\boldsymbol{r}'|] \quad\text{and}\quad \frac{\varrho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\frac{\partial h[\varrho(\boldsymbol{r}),|\boldsymbol{r}-\boldsymbol{r}'|]}{\partial\varrho(\boldsymbol{r})} \tag{9}$$

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tend to zero unless $\boldsymbol{r}\to\boldsymbol{r}'$. Introducting δE_a into Eq. (7), where E_a is one of the components of E, we have

$$\int\left\{\frac{5}{3}\,\varkappa_k\,\varrho^{2/3}-V_e^k e-V_e^e e-V_e^a e+\frac{1}{2}\,e^2\varrho\int\frac{\varrho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\frac{\partial h}{\partial\varrho(\boldsymbol{r}')}\,dv'+V_0 e\right\}\delta\varrho dv=0, \tag{10}$$

where $\varkappa_k=\dfrac{3}{10}\,(3\pi^2)^{2/3}e^2a_0$, $e\delta N=e\int\delta\varrho\,dv$ and V_e^e, V_e^k are respectively the electron--electron and electron-nucleus potentials. Thus we obtain the equation

$$(V-V_0)e-\frac{5}{3}\,\varkappa_k\,\varrho^{2/3}-\frac{1}{2}\,e^2\varrho\int\frac{\varrho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\frac{\partial h}{\partial\varrho(\boldsymbol{r}')}\,dv'=0, \tag{11}$$

where the total potential V is put — following the reasoning of [I] — equal to:

$$V_e^k+V_e^e+V_e^a. \tag{12}$$

Calculation of the integral entering into (11) can be effected according to Flügge (1952): (I) Instead of integrating over dv' we integrate over $dv_{|\boldsymbol{r}-\boldsymbol{r}'|}$; (II) The integration limits tend to infinity; (III) We put $\varrho(\boldsymbol{r}')=\varrho(\boldsymbol{r})=\varrho$, where ϱ is now a constant. Introducing the variable $u=(3\pi^2)^{1/3}\varrho^{1/3}|\boldsymbol{r}-\boldsymbol{r}'|$ and denoting the last term on the left side of (11) by $-I$, we have

$$I=-2e^2\varrho^{1/3}\left(\frac{3}{\pi}\right)^{1/3}\int_0^\infty\frac{\sin u-u\cos u}{u^5}\{(u^2-3)\sin u+3u\cos u\}\,du. \tag{13}$$

Integration in (13) yields $-\frac{1}{4}$, thus

$$I=\frac{2}{3}\,\varkappa_a\varrho^{1/3}. \tag{14}$$

Substituting I into Eq. (11) and applying it locally we arrive at

$$(V-V_0)e-\frac{5}{3}\,\varkappa_k\,\varrho^{2/3}-\frac{2}{3}\,\varkappa_a\,\varrho^{1/3}=0; \tag{15}$$

thus, we have an expression identical to Eq. (15) of [I]. Substituting ϱ as a function of V in Poisson's equation we obtain the statistical equation with exchange

$$\Delta V=4\pi e\left(\frac{2}{ea_0}\right)^{3/2}\frac{1}{3\pi^2}\left[\left(V-V_0+\frac{e}{8\pi^2a_0}\right)^{1/2}-\left(\frac{e}{8\pi^2a_0}\right)^{1/2}\right]^3 \tag{16}$$

(*cf.* [I], Eq. (16)).

§ 3. Numerical solution of statistical equation with exchange

The statistical equation with exchange of Section 2 can be represented in a reduced form analogous to that of the Thomas-Fermi and Thomas-Fermi-Dirac models. This reduced form is (see also [I])

$$\varphi''=x\left[\left(\frac{\varphi}{x}\right)^{1/2}-\gamma\right]^3, \tag{17}$$

where

$$\varphi = \frac{r}{Ze}\left[V - V_0 + \frac{e}{8\pi^2 a_0}\right] \tag{18}$$

and

$$x = \frac{r}{\mu} \tag{19}$$

$$\mu = \frac{1}{4}\left(\frac{9\pi^2}{2}\right)^{1/3}\frac{a_0}{Z^{1/3}} \quad \text{and} \quad \gamma = \left(\frac{\mu}{8\pi^2 a_0 Z}\right)^{1/2} = \frac{0.105936}{Z^{2/3}}.$$

Z is the atomic number, and r the distance from the atomic centre (spherical symmetry).

The set of boundary conditions corresponding to the free neutral atom ($Z = N$) or to the free positive ion ($Z > N$) is[1]

$$\varphi(0) = 1 \tag{20}$$

$$\varphi(x_0) = \gamma^2 x_0 \tag{21}$$

$$x_0\varphi'(x_0) - \varphi(x_0) = -\frac{Z-N}{Z}; \tag{22}$$

x_0 is the reduced atomic (ionic) radius. ($x_0 = r_0/\mu$ where r_0 is the atomic (ionic) radius). We found elsewhere (see [I]) that for the free neutral atom with exchange x_0 tends to infinity. In the case of an atom (ion) in a crystal we have instead of (21)

$$\varphi(x_0) = \frac{49}{4}\gamma^2 x_0. \tag{23}$$

Then, x_0 is finite. The case of

$$\varphi(x_0) > \frac{49}{4}\gamma^2 x_0 \tag{24}$$

corresponds to an atom (ion) in a crystal under positive pressure, and

$$\gamma^2 x_0 < \varphi(x_0) < \frac{49}{4}\gamma^2 x_0 \tag{25}$$

represents the atom (ion) under negative pressure, *i.e.* a situation intermediate between the free atom and the atom in a crystal. The remaining boundary conditions in each of the cases represented by (23), (24), and (25) are the same as for the free atom (ion) *i.e.* identical with (20) and (22). The electron density ϱ of the atom (ion) at the distance $r = \mu x$ from the atomic (ionic) center is in all cases equal to

$$\varrho = \left(\frac{2}{ea_0}\right)^{3/2}\frac{1}{3\pi^2}\left[\left(V(r) - V_0 + \frac{e}{8\pi^2 a_0}\right)^{1/2} - \left(\frac{e}{8\pi^2 a_0}\right)^{1/2}\right]^3$$

$$= \frac{Z}{4\pi\mu^3}\frac{\varphi''(x)}{x} = \frac{Z}{4\pi\mu^3}\left[\left\{\frac{\varphi(x)}{x}\right\}^{1/2} - \gamma\right]^3, \tag{25a}$$

where $V(r)$, V_0, $\varphi(x)$ change from case to case.

[1] For a discussion on the negative ions, see the end of the present section

Practically, in solving our statistical Eq. (17) we apply a procedure fully analogous to that applied by Feynman, Metropolis and Teller (1949), and Metropolis and Reitz (1951) in solving the TF and TFD equations. We replace the variable x by w

$$x = \frac{w^2}{2} \tag{26}$$

and expand φ (and φ') for small w (or x) in series taking into account (17) and (20) and considering $\varphi'(0)$ as a parameter of known value. It is easily verified that in calculating the coefficients in the expansions we are justified in using the corresponding formulae of Feynman, Metropolis and Teller (1949), completed by Metropolis and Reitz (1951) and Kobayashi (1955), and given for the case of the TFD equation, if the constant ε of the reduced form of the TFD equation entering in the formulae is replaced by $-\gamma$. Between the values of ε and γ the simple relation exists

$$\gamma = \frac{\varepsilon}{2}\,. \tag{27}$$

We take the Kr atom as object of our solution ($\gamma = 0.00972$). In calculating the values of φ and φ' for the set of small w (up to $w = 0.48$) we include eleven terms in the series, in order to obtain the accuracy of Feynman, Metropolis and Teller and of Metropolis and Reitz. The ordinary procedure of step-by-step integration is now applied, beginning from $w = 0.48$. The interval is $\Delta w = 0.04$.

We arrive at a value of $\varphi_0'(0)$ corresponding to initial slope of the free neutral Kr atom by considering the behaviour of the φ solutions of (17) (with $\varphi(0) = 1$) for the different $\varphi'(0)$. In general, we obtain two sets of solutions:

The first set is when fulfillment of condition (21) is attained. We have then generally a negative value for (22). This corresponds to $Z>N$, *i.e.* to positive free ions, if by an ion we understand any object with $Z>N$.

The second set of solutions are those where fulfillment of condition (21) is never attained. In this case the curves change in character from descending to ascending at some point; they rise, however, more steeply than $\gamma^2 x$ and never come in touch with the $\varphi = \gamma^2 x$ axis. For solutions of this type we always attain $\varphi'(x_0) - \varphi(x_0)/x_0 = 0$ after the minimum point, but then $\varphi(x_0)/x_0 > \gamma^2$. Thus, the solutions correspond to an atom having a finite electron density at the boundary and, consequently, a finite radius. A particular case of such an atom is the atom in a crystal (*cf.* Eq. (23)). The other atoms with finite electron density at the boundary are those at positive and negative pressures (of Eqs (24) and (25), respectively).

The values of $\varphi'(0)$ corresponding to each of the two sets of solutions approach one another and in the limit we obtain $\varphi_0'(0)$ — the value of the slope corresponding to the neutral free atom. The φ solution now exhibits asymptotical behaviour tending to the $\varphi = \gamma^2 x$ axis. In the case of the Thomas-Fermi model of a free neutral atom the reduced φ_{TF} solution tends asymptotically to the $\varphi = 0$ axis. Thus the whole situation presented above is well-known from the Thomas-Fermi atom with the only difference that the classification of the φ solutions as to their behaviour with regard to the $\varphi = 0$ axis is replaced by an investigation of their behaviour towards $\varphi = \gamma^2 x$ axis.

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TABLE I

Solution of Eq. (17) in the w variable for the initial slope from Eq. (28); *i.e.* φ approaches the solution for the neutral Kr atom

w	$\varphi(w)$	$-\varphi'(w)$	w	$\varphi(w)$	$-\varphi'(w)$
0.52	0.84998	0.46826	4.04	0.04654	0.03215
0.60	0.81160	0.48953	4.12	0.04406	0.02985
0.68	0.77191	0.50139	4.20	0.04176	0.02772
0.76	0.73159	0.50528	4.28	0.03962	0.00075
0.84	0.69124	0.50254	4.36	0.03763	0.02395
0.92	0.65133	0,49441	4.44	0.03579	0.02228
1.00	0.61225	0.48200	4.52	0.03407	0.02074
1.08	0.57430	0.46627	4.60	0.03246	0.01932
1.16	0.53771	0.44808	4.68	0.03097	0.01800
1.24	0.50265	0.42814	4.76	0.02958	0.01678
1.32	0.46924	0.40708	4.84	0.02829	0 01565
1.40	0.43753	0.38540	4.92	0.02708	0.01460
1.48	0.40758	0.36351	5.00	0.02595	0.01363
1.56	0.37937	0.34175	5.08	0.02489	0.01274
1.64	0.35289	0.32039	5.16	0.02391	0.01190
1.72	0.32809	0.29962	5.24	0.02299	0.01113
1.80	0.30493	0.27960	5.32	0.02213	0.01041
1.88	0.28333	0.26043	5.40	0.02132	0.00974
1.96	0.26323	0.24219	5.48	0.02057	0.00912
2.04	0.24456	0.22491	5:56	0.01986	0.00854
2.12	0.22722	0.20862	5.64	0.01920	0.00800
2.20	0.21115	0.19331	5.72	0.01858	0.00750
2.28	0.19627	0.17898	5.80	0.01800	0.00703
2.36	0.18249	0.16560	5.88	0.01745	0.00659
2.44	0.16975	0.15313	5.96	0.01694	0.00618
2.52	0.15797	0.14154	6.04	0.01646	0.00580
2.60	0.14708	0.13078	6.12	0.01601	0.00544
2.68	0.13702	0.12081	6.20	0.01559	0.00510
2.76	0.12773	0.11159	6.28	0.01520	0.00479
2.84	0.11915	0.10306	6.36	0.01483	0.00450
2.92	0.11122	0.09519	6.44	0.01448	0.00422
3.00	0.10390	0.08792	6.52	0.01415	0.00396
3.08	0.09714	0.08122	6.60	0.01384	0.00371
3.16	0,09089	0.07504	6.68	0.01356	0.00348
3.24	0.08512	0.06935	6.76	0.01329	0.00327
3.32	0.07978	0.06411	6.84	0.01303	0.00306
3.40	0.07485	0.05928	6.92	0.01280	0.00287
3.48	0.07029	0.05483	7.00	0.01257	0.00269
3.56	0.06607	0.05074	7.08	0.01237	0.00252
3.64	0.06216	0.04697	7.16	0.01217	0.00125
3.72	0.05855	0.04350	7.24	0.01199	0.00220
3.80	0.05520	0.04031	7.32	0.01182	0.00205
3.88	0.05209	0.03736	7.40	0.01166	0.00191
3.96	0.04921	0.03465	7.48	0.01151	0.00178

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TABLE I (continued)

w	$\varphi(w)$	$-\varphi'(w)$	w	$\varphi(w)$	$-\varphi'(w)$
7.56	0.01138	0.00166	9.32	0.01023	—0.00011
7.64	0.01125	0.00154	9.40	0.01024	—0.00016
7.72	0.01113	0.00142	9.48	0.01025	—0.00022
7.80	0.01102	0.00131	9.56	0.01027	—0.00027
7.88	0.01092	0.00121	9.64	0.01029	—0.00032
7.96	0.01083	0.00111	9.72	0.01032	—0.00037
8.04	0.01074	0.00102	9.80	0.01035	—0.00042
8.12	0.01066	0.00092	9.88	0.01039	—0.00046
8.20	0.01059	0.00084	9.96	0.01043	—0.00051
8.28	0.01053	0.00075	10.04	0.01047	—0.00056
8.36	0.01047	0.00067	10.12	0.01052	—0.00061
8.44	0.01042	0.00060	10.20	0.01057	—0.00065
8.52	0.01038	0.00052	10.28	0.01062	—0.00070
8.60	0.01034	0.00045	10.36	0.01068	—0.00074
8.68	0.01031	0.00038	10.44	0.01074	—0.00079
8.76	0.01028	0.00031	10.52	0.01080	—0.00083
8.84	0.01026	0.00025	10.60	0.01087	—0.00087
8.92	0.01024	0.00018	10.68	0.01094	—0.00092
9.00	0.01023	0.00012	10.76	0.01102	—0.00096
9.08	0.01022	0.00006	10.84	0.01110	—0.00100
9.16	0.01022	0.00000	10.92	0.01118	—0.00105
9.24	0.01022	—0.00005	11.00	0.01127	—0.00109

TABLE II

Solution of Eq. (17) in the w variable for the initial slope $\varphi'(x)_{x=0} = -1.5730990$; *i.e.* φ corresponds to the solution for Kr's positive ion with $(Z-N)/Z = 0.0299$

w	$\varphi(w)$	$-\varphi'(w)$	w	$\varphi(w)$	$-\varphi'(w)$
1.56	0.37937	0.34176	2.84	0.11912	0.10310
1.64	0.35288	0.32040	2.92	0.11119	0.09532
1.72	0.32809	0.29963	3.00	0.10387	0.08797
1.80	0.30492	0.27961	3.08	0.09710	0.08128
1.88	0.28333	0.26044	3.16	0.09085	0.07511
1.96	0.26323	0.24220	3.24	0.08507	0.06942
2.04	0.24455	0.22492	3.32	0.07973	0.06419
2.12	0.22722	0.20863	3.40	0.07479	0.05937
2.20	0.21114	0.19333	3.48	0.07022	0.05494
2.28	0.19626	0.17900	3.56	0.06599	0.05086
2.36	0.18248	0.16562	3.64	0.06207	0.04710
2.44	0.16973	0.15315	3.72	0.05845	0.04364
2.52	0.15795	0.14157	3.80	0.05508	0.04046
2.60	0.14706	0.13081	3.88	0.05197	0.03754
2.68	0.13700	0.12085	3.96	0.04907	0.03485
2.76	0.12771	0.11163	4.04	0.04639	0.03237

TABLE II (continued)

w	$\varphi(w)$	$-\varphi'(w)$	w	$\varphi(w)$	$-\varphi'(w)$
4.12	0.04389	0.03009	6.20	0.01355	0.00715
4.20	0.04157	0.02799	6.28	0.01299	0.00697
4.28	0.03941	0.02605	6.36	0.01244	0.00682
4.36	0.03739	0.02427	6.44	0.01189	0.00669
4.44	0.03552	0.02263	6.52	0.01136	0.00659
4.52	0.03377	0.02113	6.60	0.01084	0.00651
4.60	0.03214	0.01974	6.68	0.01032	0.00644
4.68	0.03061	0.01846	6.76	0.00981	0.00640
4.76	0.02918	0.01728	6.84	0.00930	0.00637
4.84	0.02784	0.01620	6.92	0.00879	0.00639
4.92	0.02658	0.01521	7.00	0.00828	0.00637
5.00	0.02541	0.01429	7.08	0.00777	0.00638
5.08	0.02430	0.01345	7.16	0.00726	0.00641
5.16	0.02325	0.01268	7.24	0.00674	0.00645
5.24	0.02227	0.01197	7.32	0.00622	0.00650
5.32	0.02133	0.01132	7.40	0.00570	0.00655
5.40	0.02045	0.01073	7.48	0.00518	0.00661
5.48	0.01962	0.01019	7.56	0.00464	0.00668
5.56	0.01882	0.00969	7.64	0.00411	0.00675
5.64	0.01806	0.00925	7.72	0.00356	0.00682
5.72	0.01734	0.00884	7.80	0.00302	0.00689
5.80	0.01665	0.00847	7.88	0.00246	0.00696
5.88	0.01598	0.00814	7.96	0.00190	0.00703
5.96	0.01535	0.00785	8.04	0.00134	0.00710
6.04	0.01473	0.00758	8.12	0.00077	0.00719
6.12	0.01413	0.00735	8.20	0.00019	0.00730

TABLE III

Solution of Eq. (17) in the w variable for the initial slope $\varphi'(x)_{x=0} = -1.5728125$; *i.e.* φ correrponds to the case of Kr atom under the pressure

w	$\varphi(w)$	$-\varphi'(w)$	w	$\varphi(w)$	$-\varphi'(w)$
0.52	0.85002	0.46811	1.56	0.37988	0.34079
0.60	0.81165	0.48935	1.64	0.35348	0.31928
0.68	0.77197	0.50117	1.72	0.32878	0.29836
0.76	0.73168	0.50503	1.80	0.30572	0.27815
0.84	0.69135	0.50226	1.88	0.28425	0.25878
0.92	0.65146	0.49409	1.96	0.26430	0.24030
1.00	0.61241	0.48162	2.04	0.24578	0.22276
1.08	0.57449	0.46584	2.12	0.22863	0.20617
1.16	0.53794	0.44758	2.20	0.21277	0.19052
1.24	0.50292	0.42758	2.28	0.19812	0.17581
1 32	0.46956	0.40643	2.36	0.18461	0.16199
1.40	0.43791	0.38466	2.44	0.17218	0.14904
1.48	0.40802	0.36266	2.52	0.16075	0.13690

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TABLE III (continued)

w	$\varphi(w)$	$-\varphi'(w)$	w	$\varphi(w)$	$-\varphi'(w)$
2.60	0.15026	0.12552	3.64	0.07842	0.02275
2.68	0.14064	0.11486	3.72	0.07685	0.01641
2.76	0.13186	0.10486	3.80	0.07580	0.01002
2.84	0.12385	0.09547	3.88	0.07525	0.00351
2.92	0.11657	0.08663	3.96	0.07524	−0.00320
3.00	0.10998	0.07827	4.04	0.07577	−0.01017
3.08	0.10404	0.07035	4.12	0.07688	−0.01749
3.15	0.09871	0.06283	4.20	0.07858	−0.02526
3.24	0.09398	0.05563	4.28	0.08093	−0.03360
3.32	0.08980	0.04871	4.36	0.08398	−0.04264
3.40	0.08618	0.04202	4.44	0.08778	−0.05253
3.48	0.08308	0.03550	4.52	0.09241	−0.06346
3.56	0.08049	0.02909			

We obtain in the case of the free neutral Kr atom an initial slope equal to

$$\varphi_0'(0) = -1.5730975. \tag{28}$$

The initial slope corresponding to a neutral Kr atom in a crystal lies between

$$-1.5730950 < \varphi'_{\text{cryst}}(0) < -1.5730900. \tag{29}$$

The figure to the left in (29) corresponds to the initial slope of the neutral atom at small negative pressure, that to the right to an atom at small positive pressure. Positive ions in a crystal (boundary coditions (20), (23) and (22) where $Z>N$) can be obtained in a manner completely analogous to that applied for neutral crystal atoms.

It is readily seen that in our model there is no place for solutions corresponding to free negative ions, because the solutions for those ions are only possible when φ will intersect the line $\varphi = \gamma^2 x$ with $\varphi' > \gamma^2$. This can never happen: the curve intersecting first with $\varphi = \gamma^2 x$ has $\varphi' < \gamma^2$ and at the same time has its inflection point where φ'' changes its sign from plus to minus. Thus φ' at this point is the maximum value of the derivative of φ and farther φ is never bent towards $\varphi = \gamma^2 x$. The problem of the existence of negative ions in crystals lies beyond the scope of the present note.

In Tables I, II and III we present as numerical examples of the solution of (17) solutions with initial slopes equal respectively to (28),

$$-1.5730990 \tag{30}$$

and

$$-1.5728125 \tag{31}$$

(30) corresponds to the free positive ion: $(Z-N)/Z \approx 0.03$, the reduced radius of the ion being equal to 30.5, whereas (31) corresponds to the initial slope of the neutral Kr atom at pressure of *ca* 7.1×10^{12} dyn cm^{-2}. This pressure of the electron gas of the statistical

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atom (ion) exerted at the boundary can be obtained from the value of the solution of (17) at the boundary. We follow here the equation:

$$P = \frac{2}{3} \varkappa_k \varrho^{5/3}(r_0) \left[1 - \frac{\varkappa_k}{2\varkappa_a} \frac{1}{\varrho^{1/3}(r_0)} \right] \tag{32}$$

established by Jensen (1939), which is valid in our case too (see [I]). r_0 is here the radius of the present atom (ion) under pressure, P the pressure at the atomic (ionic) boundary and $\varrho(r_0)$ is the boundary electron density equal to

$$\varrho(r_0) = \frac{Z}{4\pi\mu^3} \frac{\varphi''(x_0)}{x_0} = \frac{Z}{4\pi\mu^3} \left[\left\{ \frac{\varphi(x_0)}{x_0} \right\}^{1/2} - \gamma \right]^3 . \tag{33}$$

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