

ON THE GROUND STATE OF A MODEL FOR  
COMPRESSED HELIUM

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**Synopsis**

In the problem of the "compressed helium atom", the boundary condition that the wave function  $\psi$  must vanish at infinity ( $r = \infty$ ), is replaced by:  $\psi = 0$  at a finite  $r = r_0$ . This problem is solved by a variational method, which for the limiting case of the free atom ( $r_0 \rightarrow \infty$ ) coincides with one of H y l l e r a a s' approaches to the helium problem. The energy and kinetic energy of the electrons in the ground state are calculated as functions of  $r_0$  and the corresponding pressure (§ 5).

§ 1. *Introduction.* The physical situation of molecules in gases at high densities has been described by a useful model, *viz.*, the molecule (or atom, or ion) enclosed in a box. In this model the interaction of the neighbouring particles is replaced by an infinitely high potential wall. The idea of using this model was first introduced by M i c h e l s, D e B o e r and B i j l<sup>1)</sup>, who considered the problem of atomic hydrogen, using the boundary condition of vanishing wave function  $\psi$  at a finite value of the radial coordinate ( $r = r_0$ ), instead of the usual boundary condition,  $\psi = 0$  at  $r = \infty$ , for the free atom. They gave approximate solutions of the problem, valid for large  $r_0$ . S o m m e r f e l d and W e l k e r<sup>2)</sup> treated the same problem by a rigorous method, and the present authors<sup>3)</sup> extended these calculations to a larger range of values of  $r_0$  and gave also results for two excited states. The problem was taken up also by C o t t r e l l<sup>4)</sup>, who treated the case of the hydrogen molecule ion  $H_2^+$ , enclosed in an ellipsoidal box. All the papers mentioned are concerned with one-electron problems, and with atoms or molecules none of which exist as such in bulk.

It seemed therefore worth while to try to solve the problem of a compressed atom for the simplest case of an actual gas, *viz.* helium. To solve this two-electron problem a variational method has been developed (§ 3), which in the limit of free atoms ( $r_0 \rightarrow \infty$ ) coincides with one of H y l l e r a a s' approaches to the helium problem <sup>5)</sup>. It was found that the energy could be obtained as an analytical function of the variation parameters. A number of integration results are tabulated in an appendix (§ 6). The way to find numerical values is expounded in § 4. The results namely the increase of the energy  $E$  of the ground state, the increase of the kinetic energy  $K$  of the electrons, and the increase of the pressure  $P$ , all with decreasing  $r_0$ , are given in § 5. These results may be compared with the relationships between these quantities drawn from experimental data on the compressibility of gases <sup>6) 7)</sup>.

Results for the polarisability as a function of pressure, calculated for the model of compressed helium, will be given in a subsequent article.

§ 2. *On units.* We use H a r t r e e atomic units, which were also used in references <sup>2) 3) 4)</sup>. In this system the fundamental units are  $e$ ,  $m$  and  $\hbar$ ; correspondingly the unit of length is the radius of the first B o h r orbit of hydrogen  $a_0 = \hbar^2/me^2 = .52921 \text{ \AA}$ ; the unit of energy is  $e^2/a_0 = 4.3589 \cdot 10^{-11} \text{ erg}$  ( $6.2747 \cdot 10^2 \text{ kcal/mole}$ ); and the unit of pressure is  $e^2/a_0^4 = 2.9025 \cdot 10^8 \text{ atm}$ .

H y l l e r a a s <sup>5)</sup> used for helium the unit of length  $\frac{1}{2}a_0$  and the unit of energy  $2e^2/a_0$ . M i c h e l s, D e B o e r and B i j l <sup>1)</sup> took  $e^2/2a_0$  as the unit of energy.

§ 3. *Analytical results of the variational method.* The S c h r ö d i n g e r equation for the helium problem is (in atomic units):

$$(H - E) \psi = -\frac{1}{2}(\Delta_1\psi + \Delta_2\psi) + (V - E) \psi = 0, \quad (1)$$

where

$$V = -2/r_1 - 2/r_2 + 1/r_{12}, \quad (2)$$

with  $r_1$  and  $r_2$ , the distances from the nucleus to the electrons, and  $r_{12}$ , the distance between the electrons;  $\Delta_1$  and  $\Delta_2$  are L a p l a c e operators with respect to the coordinates of the first and second electron respectively.

In the variation method we want to minimize

$$E = \int \psi H \psi \, dv / \int \psi^2 \, dv, \quad (3)$$

which, on applying Green's rule to the first two terms in  $\dot{H}$ , obtains the form

$$E = \int \{ \frac{1}{2} (\text{grad}_1 \psi)^2 + \frac{1}{2} (\text{grad}_2 \psi)^2 + V\psi^2 \} dv / \int \psi^2 dv. \quad (4)$$

The wave function of the ground state has spherical symmetry. It depends on  $r_{12}$ , and, in a symmetrical way, on  $r_1$  and  $r_2$ . For our problem of a helium atom enclosed in a spherical box of radius  $r_0$ , the integration region in (3) and (4) is

$$0 \leq r_1 \leq r_0; \quad 0 \leq r_2 \leq r_0; \quad |r_2 - r_1| \leq r_{12} \leq r_2 + r_1.$$

Because of the symmetry in  $r_1$  and  $r_2$ , we can limit ourselves to half of this integration region, namely

$$0 \leq r_1 \leq r_0; \quad r_1 \leq r_2 \leq r_0; \quad r_2 - r_1 \leq r_{12} \leq r_2 + r_1, \quad (5)$$

represented by the tetrahedron of fig. 1.

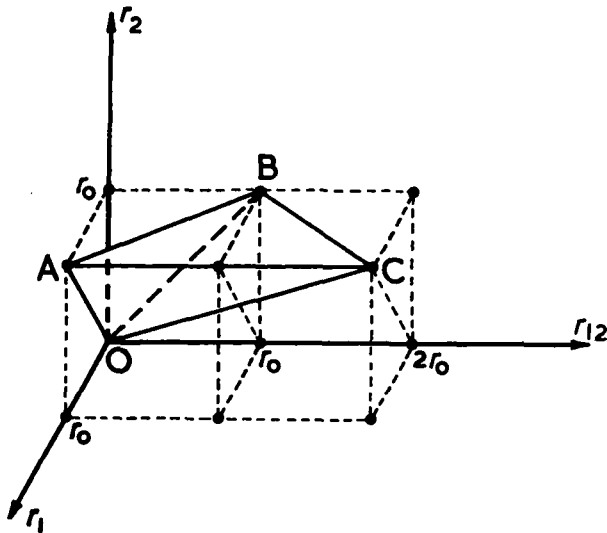


Fig. 1. Integration region for helium atom in a spherical box.

We introduce the new coordinates

$$s = r_1 + r_2; \quad t = -r_1 + r_2; \quad u = r_{12}, \quad (6)$$

which gives:

$$E = \int ds dt du \{ u(s^2 - t^2) (\psi_s^2 + \psi_t^2 + \psi_u^2) + 2s(u^2 - t^2) \psi_s \psi_u + 2t(s^2 - u^2) \psi_t \psi_u - (8su - s^2 + t^2) \psi^2 \} / \int ds dt du u(s^2 - t^2) \psi^2, \quad (7)$$

with a new integration in  $s, t, u$ -space ( $\psi_s$  stands for  $\partial\psi/\partial s$ , etc.). The variation function  $\psi$  must satisfy the boundary condition for the problem of a helium atom in a box, *i.e.*, it must vanish for  $r_1 = r_0$ , or for  $r_2 = r_0$ , or for both. We use the following expression

$$\psi(s, t, u) = \varphi(S, T, U) = e^{-\frac{1}{2}S}(c_0 + c_1 U + c_2 T^2) \{1 - (S - T)/2R\} \{1 - (S + T)/2R\} \quad (8)$$

with  $S = ks, T = kt, U = ku, R = kr_0$ . The parameters  $S, T, U, R, c_0, c_1$  and  $c_2$  are dimensionless, whereas  $s, t, u, r_0$  and  $k^{-1}$  have the dimension of a length.

This variation function contains the parameters  $k, c_0, c_1$  and  $c_2$ . The two final factors make it satisfy the boundary condition. It is an even function of  $T$ , *i.e.*, symmetrical in  $r_1$  and  $r_2$ . Its form is chosen in such a way that all integrations can be carried out, so that an analytical, although lengthy, expression for  $E(k, c_0, c_1, c_2)$  can be found. Furthermore in the limiting case of a free atom ( $r_0$  and  $R \rightarrow \infty$ ) the expression (8) coincides with a variation function introduced by H y l l e r a s <sup>5)</sup>. Using (8) in (7), we obtain

$$E = (k^2M - kL)/N, \quad (9)$$

with

$$M = \int dSdTdU \{U(S^2 - T^2) (\varphi_s^2 + \varphi_t^2 + \varphi_u^2) + 2S(U^2 - T^2) \varphi_s\varphi_u + 2T(S^2 - U^2) \varphi_t\varphi_u\}, \quad (10)$$

$$L = \int dSdTdU (8SU - S^2 + T^2) \varphi^2, \quad (11)$$

$$N = \int dSdTdU U(S^2 - T^2) \varphi^2. \quad (12)$$

( $E$  is in atomic units;  $M, L$  and  $N$  are dimensionless. The latter quantities are respectively equal to, four times and eight times the corresponding quantities in <sup>5)</sup>).

The integration region in  $S, T, U$ -space, corresponding to (5), is shown in fig. 2 as the tetrahedron OABC; it consists of the three parts ODEB, ADEB and AECB, so that we have

$$\int dSdTdU = \int_0^R dS \int_0^S dU \int_0^U dT + \int_0^R dS \int_0^{2R-S} dU \int_0^U dT + \int_0^R dS \int_{2R-S}^S dU \int_0^U dT. \quad (13)$$

After integration we find that  $M, L$  and  $N$  are quadratic functions of  $c_0, c_1$  and  $c_2$ :

$$M = M_{00}c_0^2 + M_{01}c_1c_1 + \dots + M_{22}c_2^2, \text{ etc.} \quad (14)$$

The lengthy calculation of the coefficients  $M_{00}$  etc. may briefly be described as follows. The coefficients  $M_{00}$  etc. turn out to be of the

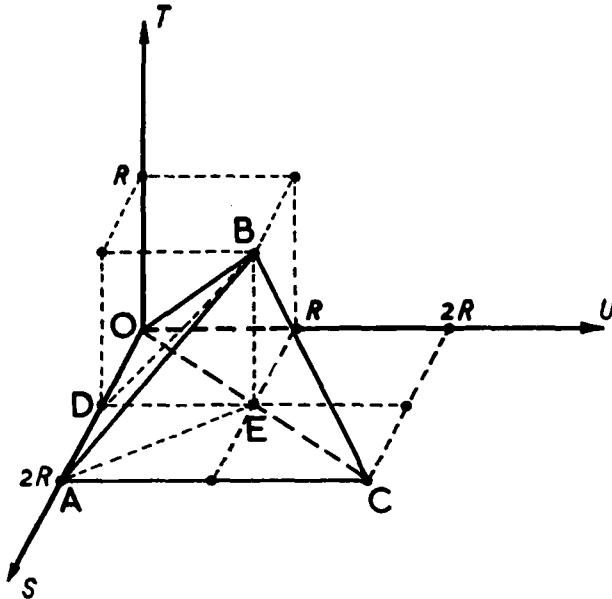


Fig. 2. Integration region in  $S, T, U$ -space.

form  $\Sigma \pm AB$  (see Appendix), where the  $A$ 's are polynomials in  $(2R)^{-1}$ , and where each  $B = B_{\xi\eta\zeta}(R)$  is an integral of the form

$$B_{\xi\eta\zeta}(R) = \int dSdTdU e^{-S} S^\xi T^\eta U^\zeta \tag{15}$$

( $\xi, \eta, \zeta \geq 0$ ). This integral can be reduced to the form

$$\begin{aligned} B_{\xi\eta\zeta}(R) = & (\eta + 1)^{-1} (\zeta + \eta + 2)^{-1} I_{\xi+\eta+\zeta+2}(R) - \\ & - (\zeta + 1)^{-1} (\zeta + \eta + 2)^{-1} J_{\xi,\zeta+\eta+2}(R) + \\ & + (\zeta + 1)^{-1} (\eta + 1)^{-1} J_{\xi+\zeta+1,\eta+1}(R), \end{aligned} \tag{16}$$

where  $I_a(R) = \int_0^R dS e^{-S} S^a$  and  $J_{a,b}(R) = \int_R^{2R} dS e^{-S} S^a (2R - S)^b$ . (17a, b)

The  $I$ 's and  $J$ 's are calculated by means of recursion formulae (see Appendix). For  $R = \infty$  (free atom),  $B_{\xi\eta\zeta}$  reduces to  $(\eta + 1)^{-1} (\zeta + \eta + 2)^{-1} (\xi + \eta + \zeta + 2)!$ ; furthermore a considerable number of the  $A$ 's then vanish. After the coefficients  $M_{00}$  etc. have been found as functions of  $R = kr_0$ , the expression  $E$  (9, 10, 11, 12, 14)

must be minimized with respect to the variation parameters  $k$ ,  $c_0$ ,  $c_1$  and  $c_2$ . To achieve this we choose some value of  $R = kr_0$ . Minimizing with respect to  $c_0$ ,  $c_1$  and  $c_2$  requires

$$\partial E / \partial c_0 = 0 \quad (18)$$

and similarly for  $c_1$  and  $c_2$ . This gives with (9)

$$E \partial N / \partial c_0 - k^2 \partial M / \partial c_0 + k \partial L / \partial c_0 = 0, \quad (19)$$

and similar equations with  $c_1$  and  $c_2$ . These three homogeneous linear equations in  $c_0$ ,  $c_1$  and  $c_2$  have non-vanishing solutions only if the coefficient determinant is zero:

$$\begin{vmatrix} 2N_{00}E - 2M_{00}k^2 + 2L_{00}k & N_{01}E - M_{01}k^2 + L_{01}k & N_{02}E - M_{02}k^2 + L_{02}k \\ N_{01}E - M_{01}k^2 + L_{01}k & 2N_{11}E - 2M_{11}k^2 + 2L_{11}k & N_{12}E - M_{12}k^2 + L_{12}k \\ N_{02}E - M_{02}k^2 + L_{02}k & N_{12}E - M_{12}k^2 + L_{12}k & 2N_{22}E - 2M_{22}k^2 + 2L_{22}k \end{vmatrix} = 0. \quad (20)$$

This is an equation of the third degree in  $E$ , in which the coefficients depend on  $k$ , and of which we need the smallest root. By substituting several values of  $k$ , the value of  $k$  for which  $E$  is a minimum is found. This value of  $E$  is the result for the ground state energy which the variation method gives for the chosen value of  $R = kr_0$ , corresponding to a particular value of the box radius  $r_0$ . The complete procedure just outlined can be repeated for different values of  $r_0$ , so that a set of corresponding values of  $E$  and  $r_0$  are found.

§ 4. *Numerical calculations of the lowest level of compressed helium.* The technique of the preceding section was employed to find numerical results. For a number of chosen values of  $R (= kr_0)$  the values of  $k$  and  $E$  were calculated. This yields also the corresponding  $r_0 = R/k$ . The results are given in Table I, where the units used are indicated.

TABLE I

Quantity Unit	$R = kr_0$	$k$	$r_0$	$E$	$c_1/c_0$	$c_2/c_0$	$P$	$\Delta K$
	—	$a_0^{-1}$	$a_0$	$e^2/a_0$	—	—	$e^2/a_0^4$	$e^2/a_0$
	$\infty$	3.636	$\infty$	-2.902430	.08085	.009886	0	0
	20	3.238	6.176 <sub>5</sub>	-2.901620	.08707	.014299	7.447 10 <sup>-7</sup>	1.3952 10 <sup>-8</sup>
	10	2.796	3.574	-2.88852	.08429	.025117	1.8406 <sub>6</sub> 10 <sup>-4</sup>	9.192 10 <sup>-2</sup>
	7	2.400	2.916 <sub>5</sub>	-2.84812	.06273	.038179	1.2724 10 <sup>-3</sup>	.3424
	6	2.198	2.730	-2.81496	.04619	.046553	2.474 10 <sup>-3</sup>	.5684
	5	1.944	2.572	-2.76204	.02036	.059963	6.198 <sub>5</sub> 10 <sup>-3</sup>	1.1848

From these results a graph of  $\varepsilon = 1 - .001/(E + 2.903430)$  versus  $r_0^{-1}$  has been obtained by graphical interpolation between the  $\varepsilon$ 's

corresponding to the values of  $r_0^{-1}$  of table I.  $\varepsilon$  has been used rather than  $E$  itself, because the slope  $\partial\varepsilon/\partial(r_0^{-1})$  varies much less than  $\partial E/\partial(r_0^{-1})$ , less indeed than one order of magnitude. This is desirable not only for the drawing of the curve, but also for the determination of  $\partial E/\partial r_0$  from this graph by graphical differentiation.

Furthermore we have calculated (by graphical differentiation) the pressure exerted by the electron "gas" on the wall of the box,

$$P = -\partial E/\partial V = -(1/4\pi r_0^2) (\partial E/\partial r_0), \quad (21)$$

which pressure is equal to the external pressure of the surrounding gas outside the box. Finally, according to the virial theorem<sup>1) 4)</sup>, the kinetic energy of the electrons is

$$K = -r_0 \partial E/\partial r_0 - E, \quad (22)$$

which quantity was also calculated. Tabulated in Table I are the increases in kinetic and total energy by compression

$$\Delta K = K(r_0) - K(\infty); \quad \Delta E = E(r_0) - E(\infty). \quad (23)$$

Table II gives all the quantities quoted, found by graphical interpolation at round values of  $r_0^{-1}$ .

TABLE II

Quantity Unit	$r_0^{-1}$	$r_0$	$k$	$R$	$\Delta E$	$P$	$\Delta K$
	$a_0^{-1}$	$a_0$	$a_0^{-1}$	—	$e^2/a_0$	$e^2/a_0^4$	$e^2/a_0$
	0	$\infty$	3.636	$\infty$	0	0	0
	.04	25	3.560	89.0	$1.0011 \cdot 10^{-4}$	$5.701_5 \cdot 10^{-10}$	$1.1838 \cdot 10^{-5}$
	.08	12.5	3.474	43.4	$2.2850 \cdot 10^{-4}$	$1.2666_3 \cdot 10^{-8}$	$8.240 \cdot 10^{-5}$
	.12	8.333 <sub>3</sub>	3.372	28.1	$4.2349 \cdot 10^{-4}$	$1.0256_5 \cdot 10^{-7}$	$3.224 \cdot 10^{-4}$
	.16	6.25	3.242	20.2 <sub>5</sub>	$7.8094 \cdot 10^{-4}$	$6.782 \cdot 10^{-7}$	$1.2998 \cdot 10^{-3}$
	.20	5	3.104	15.52	$1.67380 \cdot 10^{-3}$	$4.599 \cdot 10^{-6}$	$5.550 \cdot 10^{-3}$
	.24	4.166 <sub>6</sub>	2.954	12.31	$4.3763 \cdot 10^{-3}$	$3.048_5 \cdot 10^{-5}$	$2.334 \cdot 10^{-2}$
	.28	3.571 <sub>5</sub>	2.792	9.97	$1.40038 \cdot 10^{-2}$	$1.8498 \cdot 10^{-4}$	$9.189 \cdot 10^{-2}$
	.32	3.125	2.564	8.01	$3.3662 \cdot 10^{-2}$	$5.857_6 \cdot 10^{-4}$	.19096
	.36	2.778	2.256	6.26 <sub>5</sub>	$7.6821 \cdot 10^{-2}$	$2.102_8 \cdot 10^{-3}$	.4895
	.40	2.5	1.806	4.51 <sub>5</sub>	.193175	$1.1867_5 \cdot 10^{-2}$	2.137

Also included in Table I are values of  $c_1/c_0$  and  $c_2/c_0$ , found by solving the equation (19), after  $k$  has been found. The knowledge of  $c_1/c_0$  and  $c_2/c_0$  is not necessary to find  $E$ , but required when the value of the wave function (8) is wanted numerically.

Finally, table III gives the values of  $M_{00}$  etc. for the different values of  $R$ .

TABLE III

	$R = 5$	$R = 6$	$R = 7$	$R = 10$	$R = 20$	$R = \infty$
$2M_{00}$	3.1411642	4.0574086 <sub>5</sub>	4.9058350	6.9872812	10.6287999 <sub>5</sub>	16
$M_{01}$	5.9210406 <sub>5</sub>	8.2929330	10.6607615	17.057387	29.667554 <sub>5</sub>	50
$M_{02}$	4.6665444	7.7030564	11.2098347 <sub>5</sub>	22.524364	49.372769 <sub>5</sub>	96
$2M_{11}$	17.6952008	27.076622	37.193214	67.424252	135.270360 <sub>5</sub>	256
$M_{12}$	14.5899242	26.855343 <sub>5</sub>	42.497345 <sub>5</sub>	110.40134	264.23145 <sub>5</sub>	584
$2M_{22}$	44.614704	94.021906 <sub>5</sub>	164.750688	470.646 $\epsilon$ 2	1519.66600	3840
$2L_{00}$	12.2280856	17.5346164	22.833561 <sub>5</sub>	36.963211	64.214138	108
$L_{01}$	26.706221	42.305375 <sub>5</sub>	59.312531 <sub>5</sub>	109.826680	220.42609 <sub>5</sub>	416
$L_{02}$	19.5363752	35.967516	56.528731	129.283840	321.72473 <sub>5</sub>	696
$2L_{11}$	70.350721	124.037014	188.443808	404.60567	951.52946	2024
$L_{12}$	54.909821 <sub>5</sub>	114.736782	198.767932	547.00657 <sub>5</sub>	1660.21072	4096
$2L_{22}$	88.945828	218.14763 <sub>5</sub>	428.63421 <sub>5</sub>	1509.09096	5982.4833 <sub>5</sub>	17184
$2N_{00}$	4.3912786	6.8664797	9.5277574	17.3003998	34.105600	64
$N_{01}$	10.6215688	18.4394780 <sub>5</sub>	27.656633 <sub>5</sub>	57.870998	132.694369	280
$N_{02}$	6.0113220	12.2458940	20.762850 <sub>5</sub>	54.617794	158.015889 <sub>5</sub>	384
$2N_{11}$	30.903101 <sub>5</sub>	59.949924 <sub>5</sub>	97.746515	238.61436	644.73585 <sub>5</sub>	1536
$N_{12}$	18.0027534	41.757850 <sub>5</sub>	78.267085	249.41408	887.09390	2464
$2N_{22}$	24.369839	66.933559 <sub>5</sub>	143.430771	595.74780	2831.5657	9216

We note that the results for the free atom ( $r_0 = \infty$ ) are those of Hylleraas. The value found for the energy differs only by .03% from the experimental result ( $-637\ 188\ \text{cm}^{-1} = -2.90323$  at. units with respect to  $\text{He}^{++} + 2e^-$  at infinite distances).

§ 5. *Results for the energy and kinetic energy as functions of pressure.* In this section we give a table for some quantities expressed in the units which are usually employed in experiments. We give in Table

TABLE IV

$r_0$	$P$	$\Delta E$	$\Delta K$
$a_0$	atm	kcal/mole	kcal/mole
$\infty$	0	0	0
25	.1655	$6.282 \cdot 10^{-2}$	$7.428 \cdot 10^{-3}$
12.5	3.675 <sub>5</sub>	.14338	$5.170 \cdot 10^{-2}$
8.333 <sub>5</sub>	29.77	.2657	.2023
6.176 <sub>5</sub>	216.1 <sub>5</sub>	.508	.8755
5	1334.9	1.0503	3.482
4.166 <sub>5</sub>	8848.5	2.746	14.644
3.574	$5.342_5 \cdot 10^4$	8.728	57.67
3.125	$1.7001 \cdot 10^5$	21.12	119.82
2.916 <sub>5</sub>	$3.693 \cdot 10^5$	34.08	214.9
2.778	$6.102_5 \cdot 10^5$	48.20	307.1
2.730	$7.181 \cdot 10^5$	54.88 <sub>5</sub>	356.6 <sub>5</sub>
2.572	$1.7991 \cdot 10^6$	88.09	743.4
2.5	$3.444_5 \cdot 10^6$	121.21	1340.8



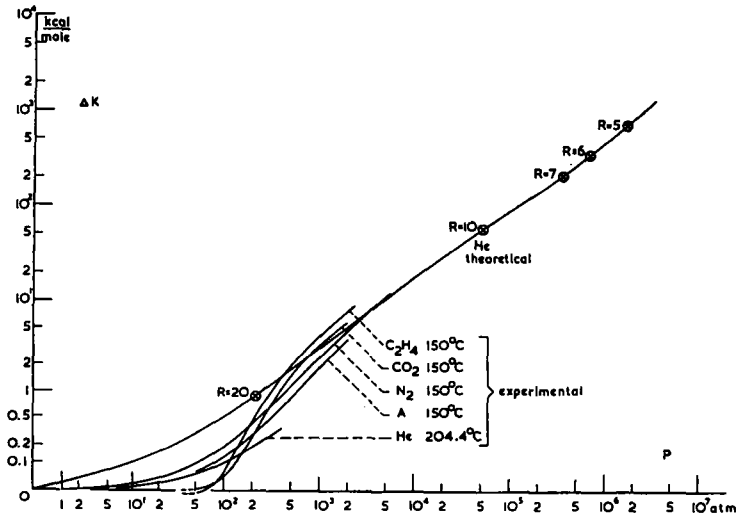


Fig. 3. Kinetic energy  $\Delta K$  (increase of kinetic energy of the electrons by compression) as a function of pressure  $P$ , for engaged helium atoms.

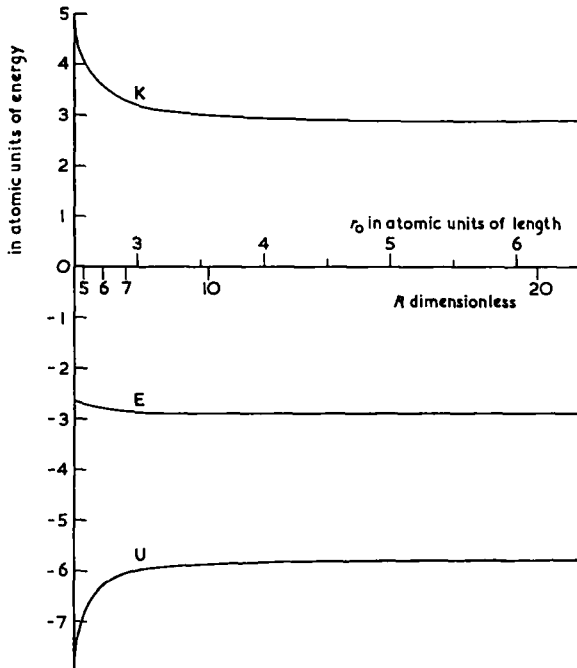


Fig. 4. Total energy  $E$ , kinetic energy  $K$  and potential energy  $U$  of a helium atom in a box with radius  $r_0$ .

IV the pressure  $P$  in atmospheres, the increase in energy  $\Delta E = E(r_0) - E(\infty)$ , and the increase in kinetic energy of the electrons  $\Delta K = K(r_0) - K(\infty)$ , which result from the compression. These energies are expressed in kcal/mole.

Fig. 3 shows  $\Delta K$  as a function of  $P$ , together with some curves, which have been calculated from experimental compressibility results for nitrogen, argon, helium, ethylene and carbon dioxide <sup>7</sup>). (It is hoped that better experimental data for helium, especially in the high pressure region, will be available in the future.) The scales for  $\Delta K$  and  $P$  are "pseudo-logarithmic", *i.e.*, they are linear in  $\log(\Delta K + 1)$  and  $\log(P + 1)$  respectively. For small values of the argument such a scale is linear; for large values it is logarithmic.

Fig. 4 gives  $K$ ,  $E$  and the potential energy  $U = E - K$  as a function of  $r_0$ .

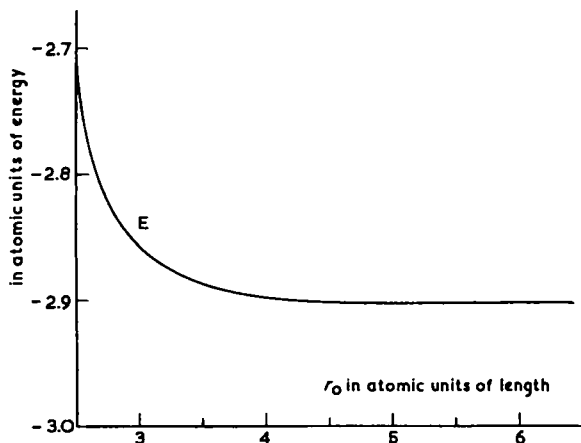


Fig. 5. Total energy as in fig. 4, but on a larger scale.

A similar graph was given before for the hydrogen atom, enclosed in a spherical box <sup>6</sup>).

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§ 6. *Appendix. The formulae for  $M_{00} \dots M_{22}$  and for  $L_{00}$  and  $N_{00}$ .*

Symbols used: Each of these quantities is a sum  $\Sigma \pm AB$ ; the two factors and the sign of each of the terms  $\pm AB$  are given under the headings  $A$ ,  $B$  and *sgn.* respectively.

a) Each  $A$  is a polynomial in  $(2R^{-1})$ . The symbol used is explained by:  $\pm a, b, c, d \dots = \pm \{a + b(2R)^{-1} + c(2R)^{-2} + d(2R)^{-3} + \dots\}$  (24)

Thus:  $+\frac{1}{2}, 8\ 20 = \frac{1}{2} + 8(2R)^{-1} + 20(2R)^{-2};$   
 $-\frac{1}{2}, 4\ 4 = -\frac{1}{2} - 4(2R)^{-1} - 4(2R)^{-2};$   
 $+0, 0\ \frac{1}{2}\ 16 = +\frac{1}{2}(2R)^{-2} + 2(2R)^{-3} - 16(2R)^{-4}, \text{ etc.}$

b) Each  $B = B_{\xi\eta\zeta}(R)$  (see (15)) is represented by its index triple  $\xi\eta\zeta$ .

The formulae for  $L_{01} \dots L_{22}$  and  $N_{01} \dots N_{22}$ . By adding to all index triples of  $B$  belonging to  $L_{00}$  and  $N_{00}$  five triples 001, 020, 002, 021 and 040 (according to the scheme  $\xi\eta\zeta + 001 = \xi, \eta, \zeta + 1$ ;  $\xi\eta\zeta + 020 = \xi, \eta + 2, \zeta$ ; etc.) one obtains the formulae for  $\frac{1}{2}L_{01}, \frac{1}{2}L_{02}, L_{11}, \frac{1}{2}L_{12}$  and  $L_{22}$  respectively; the  $N_{00}$  formula likewise yields the formulae for  $\frac{1}{2}N_{01}, \frac{1}{2}N_{02}, N_{11}, \frac{1}{2}N_{12}$  and  $N_{22}$  respectively. This addition of triples is equivalent to multiplication of the integrand in (15) by  $U, T^2, U^2, T^2U$  and  $T^4$  respectively.

This simple rule does not hold for the  $M$ 's; therefore these have to be given in full.

$M_{00}$ terms		
sgn.	$A$	$B$
+	$\frac{1}{2}, 2\ 4$	2 0 1
-	$\frac{1}{2}, 2\ 4$	0 2 1
-	0, 1 6 8	3 0 1
+	0, 1 6 8	1 2 1
+	0, 0 $\frac{3}{2}$ 6 4	4 0 1
-	0, 0 2 8	2 2 1
+	0, 0 $\frac{1}{2}$ 2 4	0 4 1
-	0, 0 0 1 2	5 0 1
+	0, 0 0 2 4	3 2 1
-	0, 0 0 1 2	1 4 1
+	0, 0 0 0 $\frac{1}{2}$	6 0 1
-	0, 0 0 0 $\frac{3}{2}$	4 2 1
+	0, 0 0 0 $\frac{1}{2}$	2 4 1
-	0, 0 0 0 $\frac{1}{2}$	0 6 1

$M_{01}$ terms (contd.)		
sgn.	$A$	$B$
-	0, 0 0 4 8	4 2 0
+	0, 0 3 16 12	4 0 2
+	0, 0 0 4 8	2 4 0
-	0, 0 4 20	2 2 2
+	0, 0 1 4 12	0 4 2
+	0, 0 0 0 1	5 2 0
-	0, 0 0 2 5	5 0 2
-	0, 0 0 0 2	3 4 0
+	0, 0 0 4 10	3 2 2
+	0, 0 0 0 1	1 6 0
-	0, 0 0 2 5	1 4 2
+	0, 0 0 0 $\frac{1}{2}$	6 0 2
-	0, 0 0 0 $\frac{3}{2}$	4 2 2
+	0, 0 0 0 $\frac{1}{2}$	2 4 2
-	0, 0 0 0 $\frac{3}{2}$	0 6 2

$M_{01}$ terms		
sgn.	$A$	$B$
+	1, 4	1 2 0
-	1, 4	1 0 2
-	0, 4 16	2 2 0
+	$\frac{1}{2}, 8\ 20$	2 0 2
-	$\frac{1}{2}, 4\ 4$	0 2 2
+	0, 0 6 20	3 2 0
-	0, 2 18 28	3 0 2
-	0, 0 2 4	1 4 0
+	0, 2 14 12	1 2 2

$M_{02}$ terms		
sgn.	$A$	$B$
+	$\frac{1}{2}, 4$	2 2 1
-	$\frac{1}{2}, 4$	0 4 1
-	0, 2 12	3 2 1
+	0, 2 12	1 4 1
+	0, 0 3 12	4 2 1
+	0, 0 $\frac{4}{3}$ 16 16	2 4 1
+	0, 0 1 4 16	0 6 1
-	0, 0 0 2 4	5 2 1
+	0, 0 0 4 8	3 4 1
-	0, 0 0 2 4	1 6 1

$M_{02}$ terms (contd.)				
sgn.	A			B
+	0, 0	0 0	$\frac{1}{2}$	6 2 1
-	0, 0	0 0	$\frac{3}{2}$	4 4 1
+	0, 0	0 0	$\frac{3}{2}$	2 6 1
-	0, 0	0 0	$\frac{1}{2}$	0 8 1

$M_{11}$ terms				
sgn.	A			B
+	1,			2 0 1
-	1,			0 2 1
-	0, 4			3 0 1
+	1, 8			1 2 1
-	1, 4			1 0 3
+	0, 0	6		4 0 1
-	0, 4	24		2 2 1
+	$\frac{1}{2}$ , 6	16		2 0 3
+	0, 0	2		0 4 1
-	$\frac{1}{2}$ , 2			0 2 3
-	0, 0	0 4		5 0 1
+	0, 0	6 28		3 2 1
-	0, 1	12 20		3 0 3
-	0, 0	2 8		1 4 1
+	0, 1	8 4		1 2 3
+	0, 0	0 0 1		6 0 1
-	0, 0	0 4 11		4 2 1
+	0, 0	$\frac{3}{2}$ 10 8		4 0 3
+	0, 0	0 4 11		2 4 1
-	0, 0	2 12		2 2 3
-	0, 0	0 0 1		0 6 1
+	0, 0	$\frac{1}{2}$ 2 $\frac{7}{8}$		0 4 3
+	0, 0	0 0 1		5 2 1
-	0, 0	0 1 3		5 0 3
-	0, 0	0 0 2		3 4 1
+	0, 0	0 2 6		3 2 3
+	0, 0	0 0 1		1 6 1
-	0, 0	0 1 3		1 4 3
+	0, 0	0 0 $\frac{1}{4}$		6 0 3
-	0, 0	0 0 $\frac{3}{4}$		4 2 3
+	0, 0	0 0 $\frac{3}{4}$		2 4 3
-	0, 0	0 0 $\frac{1}{4}$		0 6 3

$M_{12}$ terms		
sgn.	A	B
+	4,	2 2 0
-	4,	0 2 2

$M_{12}$ terms (contd.)		
sgn.	A	B
-	0, 16	3 2 0
+	1, 4	1 4 0
+	$\bar{1}$ , 12	1 2 2
+	0, 0 24	4 2 0
-	0, 4 24	2 4 0
+	$\frac{1}{2}$ , 8 $\bar{1}2$	2 2 2
+	$\bar{1}$ , 4 12	0 4 2
-	0, 0 0 16	5 2 0
+	0, 0 6 36	3 4 0
+	0, $\bar{2}$ 18 4	3 2 2
-	0, 0 2 4	1 6 0
+	0, 2 14 $\bar{2}0$	1 4 2
+	0, 0 0 0 4	6 2 0
-	0, 0 0 4 16	4 4 0
+	0, 0 3 16	4 2 2
+	0, 0 0 4 12	2 6 0
+	0, 0 4 $\bar{2}0$ 24	2 4 2
+	0, 0 1 4 24	0 6 2
+	0, 0 0 0 1	5 4 0
-	0, 0 0 2 5	5 2 2
-	0, 0 0 0 2	3 6 0
+	0, 0 0 4 10	3 4 2
+	0, 0 0 0 1	1 8 0
-	0, 0 0 2 5	1 6 2
+	0, 0 0 0 $\frac{1}{2}$	6 2 2
-	0, 0 0 0 $\frac{3}{2}$	4 4 2
+	0, 0 0 0 $\frac{3}{2}$	2 6 2
-	0, 0 0 0 $\frac{1}{2}$	0 8 2

$M_{22}$ terms		
sgn.	A	B
+	4,	2 2 1
-	4,	0 4 1
-	0, 16	3 2 1
+	0, 16	1 4 1
+	0, 0 24	4 2 1
+	$\frac{1}{2}$ , 2 36	2 4 1
+	$\bar{1}$ , 2 12	0 6 1
-	0, 0 0 16	5 2 1
+	0, $\bar{1}$ 6 40	3 4 1
+	0, 1 6 24	1 6 1
+	0, 0 0 0 4	6 2 1
+	0, 0 $\frac{3}{2}$ 6 $\bar{1}6$	4 4 1
+	0, 0 $\bar{2}$ 8 28	2 6 1
+	0, 0 $\frac{1}{2}$ 2 $\bar{1}6$	0 8 1

$M_{22}$ terms (contd.)		
sgn.	A	B
-	0, 0 0 1 2	5 4 1
+	0, 0 0 2 4	3 6 1
-	0, 0 0 1 2	1 8 1
+	0, 0 0 0 $\frac{1}{2}$	6 4 1
-	0, 0 0 0 $\frac{3}{2}$	4 6 1
+	0, 0 0 0 $\frac{3}{2}$	2 8 1
-	0, 0 0 0 $\frac{1}{2}$	0 10 1

$L_{00}$ terms (contd.)		
sgn.	A	B
-	0, 0 0 0 1	6 0 0
+	0, 0 0 0 3	4 2 0
-	0, 0 0 0 3	2 4 0
+	0, 0 0 0 1	0 6 0
+	0, 0 0 0 8	5 0 1
-	0, 0 0 0 16	3 2 1
+	0, 0 0 0 8	1 4 1

$L_{00}$ terms		
sgn.	A	B
-	1,	2 0 0
+	1,	0 2 0
+	8,	1 0 1
+	0, 4	3 0 0
-	0, 4	1 2 0
-	0, 32	2 0 1
-	0, 0 6	4 0 0
+	0, 0 8	2 2 0
-	0, 0 2	0 4 0
+	0, 0 48	3 0 1
-	0, 0 16	1 2 1
+	0, 0 0 4	5 0 0
-	0, 0 0 8	3 2 0
+	0, 0 0 4	1 4 0
-	0, 0 0 32	4 0 1
+	0, 0 0 32	2 2 1

$N_{00}$ terms		
sgn.	A	B
+	1,	2 0 1
-	1,	0 2 1
-	0, 4	3 0 1
+	0, 4	1 2 1
+	0, 0 6	4 0 1
-	0, 0 8	2 2 1
+	0, 0 2	0 4 1
-	0, 0 0 4	5 0 1
+	0, 0 0 8	3 2 1
-	0, 0 0 4	1 4 1
+	0, 0 0 0 1	6 0 1
-	0, 0 0 0 3	4 2 1
+	0, 0 0 0 3	2 4 1
-	0, 0 0 0 1	0 6 1

Calculation of  $I_a$  and  $J_{a,b}$  (eqns. 17a, b).

One can write:

$$I_a(R) = a! - e^{-R} j_{a,0} \tag{25}$$

$$J_{a,b}(R) = e^{-R} j_{a,b} - e^{-2R} k_{a,b} \tag{26}$$

where the  $j$ 's and  $k$ 's are calculated with the help of following formulae:

$$j_{a,b} = R^{a+b} + a j_{a-1,b} - b j_{a,b-1} \quad (a, b > 0); \tag{27}$$

$$k_{a,b} = a k_{a-1,b} - b k_{a,b-1} \quad (a, b > 0); \tag{28}$$

$$j_{a,0} = R^a + a j_{a-1,0} \quad (a > 0); \tag{29}$$

$$k_{a,0} = (2R)^a + a k_{a-1,0} = j_{a,0}(2R) \quad (a > 0); \tag{30}$$

$$j_{0,b} = R^b - b j_{0,b-1} \quad (b > 0); \tag{31}$$

$$k_{0,b} = (-)^b b! \quad (b > 0); \tag{32}$$

$$j_{0,0} = k_{0,0} = 1. \tag{33}$$

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