

TABLE I. Atomic binding energy, $E(T=0, p=0)$, ev/atom.

Z	TF ^a	TFD ^a	DHTF
1	-20.91	-28.07	-26.3
6	-1368	-1492	-1475
26	-41885	-43280	-43590
92	-799150	-810500	-824000

^a Reference 2.

Since n_{++} is everywhere greater than the average value n_{-0} , it follows that the volume inside r_1 must be less than the average volume per atom and hence $r_1 < r_0$. Indeed, at $T=0$, the differential equation (16) and boundary conditions (17) reduce precisely to the Thomas-Fermi equations for an atom of radius r_1 .⁵ In the case of iron with r_0 corresponding to ten times normal density, the TF pressure for an atom of radius r_1 is about five times that for radius r_0 .¹ The fact that the DHTF pressure is only forty percent greater than the TF value (low-temperature portion of Fig. 2) shows that the DHTF theory compensates in large degree for the small value of r_1 . Nonetheless, it is felt that the DHTF results should be viewed with reservations up to temperatures at which the distribution function $n_{++}(r)$ begins to exhibit some semblance of symmetry about the point $r=r_0$.

c. Energy

In Fig. 10, the energy difference $E(T, \rho) - E(T=0, \rho_0)$ (where ρ_0 is the normal density of the material) is plotted against T for normal density iron, for both the DHTF and TF theories. The curves are similar to those of Fig. 3 for the pressure—at high temperatures the DHTF curve lies close to the TF one, but at low temperatures, the DHTF curve may lie as much as a factor two above the other.

Rough values of the binding energy of some atoms are given in Table I. It may be seen that (except at low Z) the DHTF theory gives even greater values for $|E(T=0, p_{p=0})|$ than does the TFD theory. This may be partly due to the correlation energy, which at low densities is greater (in magnitude) than the exchange energy of the TFD theory⁴; probably it is also partly the result of the contraction of the electrons around a nucleus (the fact that $r_1 < r_0$, discussed above).

It may be noted that whereas the TFD theory gives greater binding and lower specific heat than the TF theory,² the DHTF theory gives about the same or even greater binding than the TFD theory but apparently a higher specific heat than the TF theory.

5. DISCUSSION

It should perhaps be pointed out that the DHTF theory as presented in Sec. 2 is inconsistent in that the electron correlation energy is not included in the exponent of the energy-distribution functions used in calculating the electron densities, Eqs. (6), (24), and (26).

The theory is also thermodynamically inconsistent in the manner of all nonlinearized Debye-Hückel theories.¹⁵ This inconsistency is the result of approximating the interaction energy $W_{\alpha\beta}$ between two charged particles α and β by the expression,

$$W_{\alpha\beta} \cong q_\beta \psi_\alpha(r), \quad (53)$$

for use in (5), (6), and (26). As defined earlier, the potential ψ_α is the potential a distance r from the particle α averaged over all configurations of all particles other than α , including the particle β . The correct value of $W_{\alpha\beta}$ is, however, the work required to bring β from infinity to r , the force involved at each stage in this process being that obtained by averaging over all configurations of particles other than α and β .¹⁵ The approximation (53) is therefore best when q_β is small, the density of other charged particles is high, and the temperature is high; for then q_β makes a negligible contribution to ψ_α , and in bringing β up from infinity to evaluate $W_{\alpha\beta}$ the position of β will have only a negligible effect on the configuration of the other charges.¹⁶ This, too, throws doubt on the physical significance of the plateaus in Figs. 3 and 4, which appear at large Z , low density, and low temperature.

¹⁵ R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, London, 1956), Chap. IX (especially §923).

¹⁶ In the limit of very low densities of charged particles, then for not too large r the potential $\psi_\alpha(r)$ becomes just the Coulomb potential of the charge α . Equation (53) again becomes a good approximation, resulting in the well-known validity of the Debye-Hückel theory in the limit of very low electrolyte concentrations.