On the Virial Theorem in the Theory of Metals

R. LANDSHOFF
College of St. Thomas, St. Paul, Minnesota
May 15, 1941

IN the discussion of the many electron problem the virial theorem may frequently be used to great advantage. It has been shown by Fock[1] that not only the kinetic and potential energy of the correct but also of any approximate quantum-mechanical electron configuration will satisfy the virial theorem, provided only that the wave function of the approximate configuration has been determined by a variational method. The proof consists of a discussion of the effect of an infinitesimal uniform dilation of the entire system on the wave function of the electrons. In contrast to the very general method of this proof it is of interest to establish the theorem in a typical example by a direct calculation of the kinetic energy. The variational method has been used with great success in the theory of metals to consider the correlation between electrons with opposite spin[2,3] and we shall carry the demonstration through for this particular case.

The calculation of Wigner applies to the case where the positive ions are replaced by a uniformly distributed space charge. In the Hartree-Fock approximation this leads to products of free electron wave functions, that is plane waves, and both the total energy and the kinetic energy are easily calculated. They come out to be:[4]

$$E=(2.21Ry/r_s^2)-(0.916Ry/r_s) \tag{1}$$

and

$$K=2.21Ry/r_s^2. \tag{2}$$

The virial theorem in the form

$$K=-(d/dr_s)(r_sE) \tag{3}$$

can be easily demonstrated from these formulas. In addition to the energy calculated in the above approximation Wigner obtained the "correlation" correction.

$$E_1=\frac{1}{n!}\int dy\,|y|^2\Sigma_\nu\epsilon_\nu \tag{4}$$

with

$$\epsilon_\nu(y_1\cdots y_n)=\int\psi_\nu(y;x)^* \times\{V-(h^2/m)(\Delta_x-(2\pi i\nu/L)\mathrm{grad}_x)\}\psi_\nu(y;x)dx \tag{5}$$

[Eqs. (3), (3b) of reference 3]. $\psi_\nu(y;x)$ are the modified wave functions* (reference 3, Eq. (9)). It can be easily seen that

$$\kappa_\nu(y_1\cdots y_n)=-(h^2/m)\int\psi_\nu(y;x)^* \times(\Delta_x-(2\pi i\nu/L)\mathrm{grad}_x)\psi_\nu(y;x)dx \tag{6}$$

is that part of ϵ_ν which represents the additional kinetic energy. From the form of $\psi_\nu(y;x)$ one obtains

$$\kappa_\nu=\Sigma_\mu|\alpha_{\nu\mu}|^2t_{\nu\mu}. \tag{7}$$

By solving the minimum problem Wigner finds the coefficients $\alpha_{\nu\mu}$ (reference 3, Eqs. (17a) (17b)). We substitute them in Eq. (7) and obtain

$$\kappa_\nu=\sum_{\substack{2\nu-\mu\\ 0cc}}\frac{|V_{\nu\mu}|^2t_{\nu\mu}}{(t_{\nu\mu}+t'_{\nu\mu})^2}+\Sigma\frac{|V_{\nu\mu}|^2t_{\nu\mu}t^2_{\nu,2\nu-\mu}}{[(t_{\nu\mu}+t'_{\nu\mu})t_{\nu,2\nu-\mu}+t_{\nu\mu}t'_{\nu\mu}]^2}, \tag{8}$$

the corresponding formula for the total energy (reference 3, Eq. (19)) looks somewhat simpler than this one. Since the t do not depend on the y we compute with the help of (reference 3, Eq. (20))

$$K_\nu=\frac{1}{n!}\int dy\,|y|^2\kappa_\nu=\frac{2Ry}{3\pi^3}\int_{\substack{|\sigma+\rho|\geq 1\\ |\sigma-\rho|<1}}\frac{\eta(\sigma)(\sigma^2+\sigma\cdot\rho)d\sigma}{\sigma^4[\sigma^2+\sigma\cdot\rho+c\epsilon'(\sigma)]^2} +\frac{2Ry}{3\pi^3}\int_{\substack{|\sigma+\rho|\geq 1\\ |\sigma-\rho|<1}}\frac{\eta(\sigma)(\sigma^2+\sigma\cdot\rho)(\sigma^2-\sigma\cdot\rho)d\sigma}{\sigma^2[\sigma^4-(\sigma\cdot\rho)^2+2c\epsilon'(\sigma)]^2}. \tag{9}$$

By comparing this with the equivalent formula for the total energy (reference 3, Eq. (22)) we see that it can be written as

$$K_\nu=-F_\nu-c(d/dc)F_\nu. \tag{10}$$

The parameter c is proportional to r_s (reference 3, Eq. (22a)) and we can therefore write

$$K_\nu=-(d/dr_s)(r_sF_\nu). \tag{11}$$

By summing this over all the states ν we obtain for the total kinetic energy the relation

$$K_1=-(d/dr_s)(r_sE_1), \tag{12}$$

which is demanded by the virial theorem.

[1] V. Fock, Zeits. f. Physik **63**, 855 (1930).
[2] E. Wigner and F. Seitz, Phys. Rev. **46**, 509 (1934).
[3] E. Wigner, Phys. Rev. **46**, 1002 (1934).
[4] E. Wigner, Trans. Faraday Soc. **34**, 678 (1938).
* The notation which is employed hereafter is that of Wigner's paper and as it is fully explained there such explanation is omitted in this paper.

Remarks on Energy Losses Attending Thermionic Emission of Electrons from Metals

W. B. NOTTINGHAM
George Eastman Laboratory of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts
November 30, 1940

THE recent publication of a paper on "The energy losses attending field current and thermionic emission of electrons from metals" by Dr. Gertrude M. Fleming and Professor Joseph E. Henderson[1] presents the results of a very valuable experimental study of this subject but, in the opinion of the writer, an error has been made in the assumed physical processes involved. If one considers that the free electrons in a metal can be described as having a Fermi distribution characterized by the thermodynamic potential μ, then at any temperature T the "random" current flow in the positive x direction across any boundary can be calculated. As far as the flow of heat energy is concerned this may be calculated by determining how many electrons with energy greater than μ cross the boundary in a given time and multiplying this by the *average* energy carried by each electron. In addition to this one may consider that there is a "current" of "holes" in the Fermi band crossing the same boundary and that energy is carried by these and may be computed by multiplying the number of holes crossing in a given time by the *average* energy carried by each hole. Fleming and Henderson compute this average energy associated with the current flow of holes and

find $\bar{\epsilon}_0=\mu-1.2kT$. The determination of the 1.2 is necessarily an approximation but is good to better than four percent. They then proceed to compute the heat carried away by electrons emitted in an accelerating field as though the emission current were supplied at the cool part of the filament at the level $\bar{\epsilon}_0$ instead of μ. This leads to the result $\bar{w}=\phi+3.2kT$ for the average energy carried away per electron when emitted thermionically. Here ϕ is the work function $(C-\mu)$ and C is essentially the potential energy of an electron just outside of the emitter relative to the bottom of the Fermi band as zero.

Consider the receiving plate of a tube for studying thermionic emission to be at 0°K. Then the electrons in the emission current cannot fall into quantum states lower than μ upon being received because all of those states are filled. The electric current flows around the circuit at the level μ (except for batteries) and flows into the emitter at this level. Richardson[2] visualized a situation essentially no different from this and showed that the true heat loss per electron attending thermionic emission is $\bar{w}=\phi+2kT$. A reflection effect, or a transmission coefficient $D(W)$ which is constant and therefore independent of W for all values of $W>C$, does not alter $\bar{w}$ where W is the energy associated with the motion normal to the surface. Thermionic studies[3] indicate that $D(W)=1-\exp(W-C)/R$ represents the experimentally determined energy distributions accurately where R is an empirical constant equal to 0.191 electron volt. A paper is being prepared which shows that with this transmission coefficient, $\bar{w}=\phi+kT[2+1/(1+kT/R)]$. For the temperature range 1500°K to 2200°K this coefficient of kT varies from 2.6 to 2.5 as compared with 2 for non-selective transmission.

The possibility that there are misprints on page 893 of Fleming and Henderson makes a detailed checking of their results difficult since three of the integrations have limits μ to ∞ instead of those expected of 0 to ∞ and the brackets are not completed in front of the exponentials as it seems they should be. Although the writer has not yet been able to duplicate the final equation giving $\bar{w}$ as computed for the case of field emission using the indicated limits of μ to ∞, there can be no doubt concerning the final result that an inappreciable heat loss is to be expected for the electrons emitted even though the temperature of the emitter is fairly high. In fact it seems likely that one would find a detectable heating effect when a strong emission takes place from a very sharp point. If one uses integration limits 0 to ∞ and assumes that the electrons enter the emitter at the μ level, the calculation of such heating, if it exists, is straightforward.

It should be clear that the above criticisms apply to aspects of the theory which are on the borderline of the experimental accuracy that one may hope to attain. The main general conclusions, that in the case of thermionic emission the heat loss is largely dominated by an energy very nearly $\phi+2kT$, and that very little heat loss is to be expected in the case of field emission, are well borne out by the experiments.

[1] G. M. Fleming and J. E. Henderson, Phys. Rev. **58**, 887 (1940).
[2] O. W. Richardson, Phil. Trans. **A201**, 497 (1903).
[3] W. B. Nottingham, Phys. Rev. **49**, 78 (1936).

On the Energy Losses Attending Thermionic and Field Emission

GERTRUDE M. FLEMING
Russell Sage College, Troy, New York
AND J. E. HENDERSON
University of Washington, Seattle, Washington
May 15, 1941

IN the preceding letter Professor Nottingham is concerned about a calculation performed in a paper[1] by us to evaluate the energy loss in thermionic emission. The essential difference in viewpoint, as Professor Nottingham chooses to discuss it, depends upon whether the electrical conduction in a metal can occur at levels lower than μ, the Fermi parameter; Professor Nottingham's contention being that conduction physically occurs only at the level μ.

Other than the experimental results themselves, the most important conclusion to be drawn from the paper[1] under discussion is that conduction can occur at levels below μ. This conclusion rests upon the validity of two experimental results: first, the conclusion of the paper in question that there is no measurable temperature change of a field current emitter, and second, that there exists an energy distribution[2] for the electrons involved in field emission, which exhibits a maximum often two volts below the maximum energy corresponding to μ.

To make this conclusion more evident, consider a piece of metal with electrons being emitted at one end and supplied by conduction at the other end. Let $N(E)$ be the rate at which electrons of energy E are emitted, and let the average energy in the current of electrons entering the metal be E_1. Then the rate at which energy is acquired during emission by the metal is $\int_0^\infty(E_1-E)N(E)dE$. Since the experimentally determined energy distribution for field electrons emitted near room temperature shows that $N(E)$ has a maximum for an energy, E, of the order[2] of a volt or more below μ, if E equals μ the integral is essentially positive and equal to at least one electron volt/electron. The temperature change of any point in the emitter depends on the degree of concentration of energy released in the vicinity of the point. For field emission at room temperature an average energy transfer of 0.002 electron volts per electron would, if concentrated at the emitting surface, have been detectable. Thus the experiments[1] show that not more than 1/500 of the energy release is concentrated at the emitting surface. Therefore, either the electrons in the net current are not supplied at the level μ, or their transition from higher to lower levels occurs on the average at a large distance from the emitting surface.

The usual perturbation methods used in the kinetic theory evaluation of conduction take into account three kinds of perturbations (density, temperature and potential variations). It is further required that these perturbations be small. The condition in the vicinity of a boundary may be regarded as a perturbation of another kind and in this case the perturbation is not necessarily small. In view of the deficiency of the theory for this kind of problem, the calculation in the paper[1] is necessarily a rough estimate of the phenomena occurring in the neighborhood of the boundary.