

Work Function of Metals: Correlation Between Classical Model and Quantum Mechanical Treatment

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Abstract— Classical and quantum mechanical treatments of the work function of metals are reviewed and compared. The complex quantum mechanical treatment of Wigner and Bardeen is shown to reduce to our simple semiclassical result $W = \sim (1/2) V$ where W is the work function and V is the ionization energy of the corresponding atom. Our simple result has many desirable features: (1) The direct proportionality between the ionization energy of atoms and their corresponding metallic crystal is explicitly established. (2) This simple expression is surprisingly accurate. (3) A generic dependence of the ionization energy upon the size of particles has been established, which has been subsequently confirmed by experiments. (4) More subtle effects such as the dependence of the work function on crystallographic orientation can also be described within this simple framework. (5) The results have been extended to insulators. (6) The results have been used to describe various charge exchange phenomena.

I. IONIZATION ENERGIES: CLASSICAL MODEL WITH KEY QUANTUM MECHANICAL FEATURES

Note the analogies between the ionization energy of gaseous atoms and the ionization energy of the corresponding solid composed of the same atoms.

This may seem trivial, but scientific disciplines (solids and gases) are often isolated and disjointed so that analogies are not easily recognized. In gases, this ionization energy is usually called the “ionization potential”, whereas in solids it is usually called the “work function” as if there were no connection between the two essentially identical concepts.

Here the ionization energy of gaseous atoms (ionization potential) and the ionization energy of solid metals (work function) are treated in a coherent integrated generic fashion with the following definition.

DEFINITION of Ionization Energy. “The ionization energy is the energy required to remove from the entity (gaseous atom or corresponding solid) the most loosely bound electron(s) to infinity at rest”.

In gases (ex., Bohr model), the above definition is usually rigorously applied, whereas in solids there are numerous different definitions of the work function which vary widely, imprecisely and incorrectly.

(1.1) Ionization Energy of Gaseous Atoms.

The key feature of the well known Bohr model is stable quantized electron orbits, with the outermost electron at distance R the easiest to remove from the atom. Outside the concept of stable electron orbits, the rest of the calculations are from classical physics.

To an approximation, the ionization energy of the elements in the gas phase can be estimated by realizing the inner electrons approximately shield (“shielding factor”) all but one of the nuclear protons. The energy required to remove the easiest electron from its initial outermost position to infinity (at rest) is obtained by operating against this attractive “shielded” Coulomb force. The kinetic energy of the electron in the outermost stable quantum mechanical orbit is obtained by balancing Coulomb and centrifugal forces which must be subtracted from the attractive Coulomb energy. The result for the ionization energy (V) is (Ref.1)

$$(1) \quad V = \sim (e^2/2R)$$

where R is the outermost stable radial position of the weakest bound electron, and e is the electronic charge.

(1.2) Ionization Energy of Solid Metals.

Treat the ionization energy (work function) of metals in a manner somewhat analogous to the Bohr treatment of the ionization energy of gaseous atoms. We retain the key feature of stable electron orbits related to the size of the atoms, but utilize the classical macroscopic image force at long range. Deviations from the image force at short ranges and the existence of a substantial kinetic Fermi energy are accommodated in the following paragraphs.

Consider the ionization energy (work function) of metals as follows. The class of most easily removed electrons will have the following characteristics.

- (1) They possess the maximum kinetic Fermi energy.
- (2) Their momentum is oriented perpendicular toward the metallic surface.
- (3) They are close enough to the surface that their momentum will not be interrupted and their energy will not be dissipated before the emission (ionization) process.

At long range, the classical image force is operational which yields easy calculations.

However, at close range, there will be deviations from the classical image force which are difficult to calculate. Calculation of the Fermi energy is also a difficult quantum mechanical many-body problem.

However, consider the following scenario which greatly simplifies the calculations. As electrons with the maximum kinetic Fermi energy approach the surface, they will lose energy operating against the complex short-range forces. At maximum excursion, all the kinetic Fermi energy has been expended against the complex short-range forces. Calculations at this momentary point are now greatly simplified because the kinetic Fermi energy has been totally expended. In other words, the two complex terms (Fermi energy and short-range forces) have cancelled. Moreover, the maximum excursion from the “sur-

face” (last ionic lattice plane) will be approximately an atomic radius, and at this distance the classical image force is reasonably operational. So we can calculate the required ionization energy simply as the image-force integral from an atomic radius R to infinity. The result from Ref. 1 is

$$(2) \quad W = \sim (e^2/4R).$$

Note it is NOT implied that only those electrons at distance R from the surface are emitted, but only that they represent the entire class of the most easily emitted electrons. This special case is emphasized only because it yields easy representative calculations. This is the essence of our simple classical model, but which retains the quantum concept of stable atomic orbits that establish the atomic size, both in gases and solids approximately the same. All somewhat in the spirit of the Bohr model for gaseous atoms and their ionization energies.

(1.3) Connection Between Ionization Energy of Gaseous Atoms and Corresponding Solid Metal.

Combining Eqs 1 and 2 the yields the simple result (Ref.1)

$$(3) \quad W = \sim (1/2) V.$$

That is, the ionization energy of a solid metal is less than and equal to $(1/2)$ of the ionization energy of its corresponding gaseous atoms. By contrast in the more common terminology, the “work function” (ionization energy) of a solid metal is equal to $(1/2)$ of the “ionization potential” (ionization energy) of its corresponding gaseous atoms. But this common terminology is disjointed and inhibits insight into the commonality of the ionization energy concept. Our original publication (Ref.1) emphasized the commonality (Eq.3) which is reinforced here.

(1.4) Accuracy of Classical Results Due to Cancellation of Approximations.

Reference 2 is an extensive pursuit of the surprising accuracy of our simple classical results. The surprising accuracy stems from the cancellation of certain approximations.

For instance, for a better accuracy, one might introduce a “shielding factor” into Eqs.1 and 2, which will improve their accuracy. The “shielding factor” would account for the imbalance of the electronic shielding of the nucleus for the element under consideration. In any event, the shielding factor tends to cancel when Eqs.1 and 2 are combined to yield Eq.3, which accounts for its relative accuracy as previously discussed (Ref.1).

II. PREVIOUS CLASSICAL TREATMENTS OF WORK FUNCTION

There were many early attempts to calculate the work function of metals from classical physics alone. Debye (Refs.3 and 4) introduced the image force, but there remained the two substantial problems:

- (1) The complex short-range deviations from the image force.
- (2) The substantial kinetic Fermi energy.

Schottky (Refs.5 and 4) introduced an oversimplified description of the short range deviations from the image force, arbitrarily selected to agree with the experimental results. This artificiality did not elicit support. And there was no effort to evaluate the substantial kinetic Fermi energy, and it was incorrectly assumed zero. Thus, previous classical attempts failed to gain favor.

Note that our simple approach described in section 1, circumvents these two complex problems by arguing that they tend to cancel in first order. The remaining image force term is then easy to calculate. So we have not solved the problems explicitly either, but have circumvented the two major computational snags by modeling their cancellation.

III. WORK FUNCTION OF METALS: CORRELATION BETWEEN CLASSICAL MODEL AND WIGNER/BARDEEN QUANTUM MECHANICAL TREATMENT

Wigner and Bardeen (Ref.6) define the work function of metals as the difference between the energy of a large neutral crystal and the same crystal with one electron removed. This is a complex many-body quantum mechanical treatment in which all the complex terms must be calculated. From Ref 6, the final result is

$$(4) \quad W = V + H - (2/3)F - (0.6) (e^2/R) + (0.458)(e^2/3R) - e^2Rf'(R)/3 + eD.$$

where

W = the work function of a macroscopic metal crystal,

V = the ionization energy of the corresponding metal atom,

H = the heat of sublimation of the crystal material,

F = the electronic Fermi energy of the metallic crystal,

e = the electronic charge,

R = radius of the "Seitz" sphere (which is close to our atomic radius, especially for monovalent metals),

f'(R) = the first derivative of the correlation function,

D = the dipole moment of the surface double layer,

$e^2Rf'(R)/3$ = the correlation energy.

Combining the 3rd and 4th terms in Eq.4 yields

$$(5) \quad W = V + H - (2/3)F - (0.45) (e^2/R) - e^2Rf'(R)/3 + eD.$$

John Bardeen noted to the author (Gallo) that the terms with H and F approximately cancel.

$$(6) \quad H - (2/3)F \approx 0.$$

This can be traced to several publications by Bardeen and others (Refs 7-12). That is, the average value of the "lattice potential" (equivalent to "heat of sublimation" (H)) is equal to $(2/3)F$. This is particularly true for most metals in which the Fermi energy is large compared to the energy gaps.

We have confirmed this numerically and thus,

$$(7) \quad W = V - (0.45) (e^2/R) - e^2 R f''(R)/3 + eD.$$

For monovalent metals, Bardeen (Ref 6) assumed $D = 0$ as we shall also assume.

Bardeen later addressed double layers in Ref. 7 for multivalent metals. The double layer is generally a small term, negligible for monovalent metals, and also small (but not necessarily negligible) for multivalent metals.

$$(8) \quad W = V - (0.45) (e^2/R) - e^2 R f''(R)/3$$

Barden noted to Gallo that the “correlation” term $e^2 R f''(R)/3$, is positive but very small compared with $(0.45) (e^2/R)$.

Thus, approximately, Eq. 8 becomes

$$(9) \quad W = \sim V - (0.45+) (e^2/R).$$

Introducing Bohr’s (Eq.1) ionization energy $V = (e^2/R)$,

$$(10) \quad W = \sim V - (0.45+)V.$$

Thus finally,

$$(11) \quad W = \sim (1/2) V.$$

Thus, this quantum mechanical result from Wigner and Bardeen (Eq.4 and Ref.6) is close to our classical result (Eq.3) for the interrelationship of the work function and the ionization energy of the corresponding gaseous atoms. This is particularly accurate for monovalent metals for which the approximations made by both Wigner/Bardeen and ourselves are most appropriate.

IV. SIMPLIFICATIONS DUE TO CANCELLATION OF TERMS IN BOTH CLASSICAL AND QM TREATMENTS

The complex Wigner/Bardeen quantum mechanical expression (Eq.4) simplifies because two big terms cancel (Eq.6). Specifically, the heat of sublimation of the crystal material (H) is cancelled by the electronic Fermi energy term $(2/3) F$.

Somewhat related, our classical treatment is enormously simplified by the dissipation of the substantial kinetic Fermi energy against the complex short range forces.

There is substantial analogy in these two situations, but not an exact correlation. The differences are contained in the other smaller terms of the Wigner/Bardeen expression (Eq.4).

V. USEFUL FEATURES OF SIMPLE CLASSICAL RESULT

The simple equation $W = \sim (1/2) V$ is particularly useful for many reasons.

(1) This equation displays the direct proportionality between the ionization energy of metals (work function) and the ionization energy of their corresponding gaseous atoms (ionization potential) which are conceptually the same.

(2) This simple expression is surprisingly accurate as extensively explored in Reference 2.

(3) This relationship immediately suggests a generic size dependence of the ionization energy. This was a completely new conception that the ionization energy (work function) would depend upon the size of a particle (Refs.1, 13, 14, 15), which has been subsequently confirmed by experiments (Refs. 16 and 2). Or from another perspective, the ionization energy (ionization potential) depends upon the size of a gaseous agglomerates, droplets, mists, vapors, etc. (Ref. 14).

(4) More subtle effects such as the dependence of the work function on crystallographic orientation can also be described within this simple framework by returning to Eq.2 which is $W = e^2/4R$. For R, now use the atomic spacing radius appropriate to the crystallographic plane of interest, not the gaseous radius. No great accuracy is claimed for this procedure, but it indicates the functional dependence of the work function upon crystallographic orientation where the spacing of the surface atoms vary.

(5) These simple concepts have been extended to insulators (Ref. 13) which is an even more formidable task for quantum mechanics. Again there is a strong size dependence, and also an additional dependence upon the dielectric constant which is appropriate for insulators, but not for metals.

(6) All these results have been used to describe various charge exchange phenomena which depend upon the difference in work functions. The size dependence of the work function is very important in many charge exchange phenomena involving powders, mists, fog, dusts, sprays, fracture, vapors, etc. as pursued in Refs. 14 and 16. The dielectric constant is an additional factor in insulators (Refs. 14 and 16)..

VI. CONCLUSION

For the work function of metals, analysis reveals that the quantum mechanical treatment of Wigner and Bardeen reduces to our simple classical result $W = \sim (1/2) V$ where W is the work function and V is the ionization energy of the corresponding atom. This simple result has many desirable features:

(1) The direct proportionality between the ionization energy of atoms and their corresponding metallic crystal is explicitly established.

(2) This simple expression is surprisingly accurate.

(3) A generic dependence of the ionization energy upon the size of particles has been established, which has been subsequently confirmed by experiments.

(4) More subtle effects such as the dependence of the work function on crystallographic orientation can also be described within this simple framework.

(5) The results have been extended to the work function of insulators which exhibit a dependence upon size and dielectric constant.

(6) The results have been used to describe various charge exchange phenomena particularly involving small particles and droplets..

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