



Calculation of the Fermi energy and bulk modulus of metals

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Abstract. This work proposes new assumptions in place of some basic erroneous assumptions of *free electron theory* to determine n , the number of highest energy electrons, and Fermi energies are recalculated accordingly. The bulk modulus of metals are calculated using both the number of highest energy electrons in atoms proposed in this work and original *free electron theory* assumptions. When compared to measured values there is a much better agreement with values determined by this work than those using the original *free electron theory* assumptions. There is fairly good agreement between Fermi energies calculated by the standard theoretical equation and estimates using an approximation proposed by this work.

Keywords. Fermi energy; bulk modulus; free electrons; metals.

1. Introduction

In a solid, at zero temperature electrons occupy the lowest states or the ground state, filling them up to a boundary surface which is termed the Fermi level [1], and the energy at that highest level is the Fermi energy.

The study of Fermi energy is part of the understanding of solid materials and metals [2]. The Fermi energy has to be calculated in many instances such as in modelling oxide semiconductors [3]. The Fermi energy of metals is calculated by an equation derived from the Sommerfeld/Drude theory and also known as the free electron theory of metals [4,5].

The first publication that led to a comprehensive understanding of the theory of chemical bonding was *The nature of the chemical bond* [6] by Linus Pauling. Pauling described in great detail the fundamentals of resonance, covalent bonding, bond strength and bond lengths as well as an ionic character in covalent bonds. The concept of metallic bonding was also included in his discussion on types of bonding, but important aspects of metallic bonding were left out.

Until the beginning of the twentieth century, there was little understanding of metals and their properties. In the first half of the twentieth century, theories or models of metals have been developed. Bloch's molecular orbital theory [7] explained the difference between metals, semiconductors and insulators. However, not all the models of the metallic structure are useful to the understanding of metals. The popular *ions in a sea of electrons* model are erroneous and there is overwhelming evidence that it is a misleading and a poor representation of metallic bonding

[8]. Another model which is based on the concept that metal atoms are compressible spheres accounts for some important characteristics of metals [8–10]. It also demonstrated that there are four major components involved in the bonding of transition metals [11]. They are (I) ionic bonding, (II) covalent bonding, (III) weaker bonding that can be described as three centre bonding and (IV) exchange interactions. It showed how the different bonding allowed metals to be hard, malleable, ductile, and some are good heterogeneous catalysts.

In 1900 Drude [12] introduced a model of *free electron gas* and later revised by Sommerfeld [13] which increased our understanding of electrical conduction and Ohm's law. There is no existing theory that can account for all the properties of metals and so far the *free electron theory* is the theory that most successfully explains Ohm's law.

In the *free electron theory*, it was assumed that each atom contributes at least one electron in conduction but this is physically impossible [14] and a summary to illustrate this is provided in the Appendix. Since the Fermi energy for metals is calculated using the Sommerfeld/Drude theory and the basic assumptions for deriving the Fermi energy are erroneous, the Fermi energies tabulated in the open literature [4,5,15,16] are faulty and not acceptable. Secondly, dependent on the valency used in the calculation, the values of calculated Fermi energies can be significantly different. However, except for groups 1 and 2 metals, the majority of other metals possess multiple valencies [17,18]. For example, there are simple manganese compounds where manganese has a valency of 2 up to 7. This issue of metals having more than one valency has never been logically addressed. This work examines an alternative hypothesis for

the *free electron theory* to improve the reliability of the calculated Fermi energies and proposes a different way for calculating the Fermi energy.

2. Methodology

2.1 Free electron theory assumptions

A basic assumption of the *free electron theory* is that the valence electrons of a metal atom become conduction electrons when there is a potential difference between the ends of a metal wire. Hence, n , the number of conduction electrons per $\text{cm}^3 = Z_v \times 6.022 \times 10^{23} \times \rho/W_A$, where Z_v is the valency, $6.022 \times 10^{23} \text{ mol}^{-1}$ is the Avogadro constant, ρ the density in g cm^{-3} and W_A is the atomic mass number. A unit volume divided by the number of conduction electrons V/N equals the volume of a conduction electron:

$$V/N = 1/n = (4/3)\pi R_s^3, \quad (1)$$

$$N = V k_F^3 / 3\pi^2. \quad (2)$$

Here V is 1 cm^3 , n is the number of conduction electrons per cm^3 , R_s is the radius of the sphere occupied by a conduction electron and the Fermi wave vector is k_F [4]. A second assumption is that the number of conduction electrons per atom is dictated by the valency of the element. This assumption implies that the valency electrons are all fairly similar in energy with the same attraction to the nucleus in energy terms.

2.2 Band theory

In band theory, in metals, the highest energy band which is the conduction band is only partly occupied so that random movement of electrons that are in the highest band is allowed. The exclusion principle states that no two electrons in an atom can have the same set of quantum numbers. Simplistically, a piece of metal consists of numerous atoms all in an equivalent environment and the energy levels composed of the electrons form a vast number of energy bands. Each band consists of many closely spaced discrete energy levels. The energy bands are separated by gaps in which there are no available energy levels. At zero degree only the lowest energy levels are occupied. In metals, conductors, the highest energy band (the conduction band) is only partly occupied so that random movement of electrons that are in the highest band is allowed. When there is a potential difference between the ends of such a solid, these electrons in the conduction band can freely move down the potential gradient forming an electric current. In insulators, because the highest band is fully occupied in an insulator, electrons cannot move across the solid to create a current. Band theory is described slightly differently in molecular orbital theory [19].

2.3 Defects in the crystalline state

For this work, n is defined as the number of electrons per cm^3 in the highest energy band (but not all electrons in this band are necessarily conduction electrons) and R_s is the radius of the sphere with the probability of being occupied by a (highest energy band) electron rather than a conduction electron. In the *free electron theory*, it is assumed there is 1 or more conduction electron per atom and the dimension of R_s as calculated by equation (1) in many instances when compared with observed values of size of atoms [20] or the published values of their metallic or covalent radii [9,21,22] are bigger than the size of those atoms.

Some transition metals have valencies as high as 7 or 8 such as manganese or osmium. Since most metals have multiple valencies, it is not very logical to assume that a particular valency is a criterion determining the Fermi energy. In this work, the value of Z_v , rather than being equal to the valency of the metal, is equal to 1 for all of Group One and Group Two metals, and equal to 2 for all other metals except manganese which is equal to 1.

In his book *The Physical Principles of the Quantum Theory*, Heisenberg [23] affirmed the principles of identical particles that are completely indistinguishable from each other. The Fermi energy is calculated based on the free electron gas model which assumes that all the conduction electrons are all equivalent in every aspect and are part of the same quantum system.

No crystal is 100% perfect and there are many defects of different types in the solid state [24]. It is known that the cohesion of crystals is not the same in all directions. It may be very strong in some directions and very weak in others. This means that the interactions between each other valence/bonding electrons with the nuclei are not the same and electrons are not indistinguishable from each other. Some metals exist in more than one form and the atoms in the unit cell are not exactly equivalent. For example, in ruthenium, which has a hexagonal close-packed structure, each ruthenium atom has six neighbours at 2.705 Å and six at 2.650 Å [20], and the bonding/valence electrons belonging to the different atoms in the unit cell can have very different energies. There are grain boundaries in crystals and atoms in some parts of the crystal do not act the same. It is simplistic to consider that a metal crystal consists of a number of atoms and electrons, and all atoms/electrons are indistinguishable and the energy levels are composed of the electrons that fit into a certain number of energy bands. It is more realistic to picture a crystal being made up of numerous very tiny crystals and each with a slightly different quantum system. Each tiny crystal has its own partly filled highest energy band and in some cases, they overlap with the highest energy bands of the other tiny crystals. It is likely that only a fraction of these topmost bands overlap and form a common conduction band. Hence, not all of the highest energy electrons of each atom in the crystal can participate in conduction.

2.4 Proportion of electrons that are conduction electrons

When conduction electrons are travelling through a metallic solid they collide with atoms and ions in the crystal lattice. The acceleration $a = F/m$, where F is force and m the mass of the electron. $F = eE/m$, where E is the electric field and e the charge. Let λ be the mean free path of the electron between collisions, the average time between collisions t (the mean free time) $= \lambda/v_{av}$ [25].

The velocity is:

$$v = at = (eE/m)(\lambda/v_{av}). \quad (3)$$

Here the average velocity v_{av} is approximated to be nearly equivalent in value to v . Hence, the current density:

$$J = nev = ne^2\lambda E/mv_{av}, \quad (4)$$

where n is the number of *free electrons*. Here t can be expressed as $m/ne^2\rho$. The current down a metal wire is JA , which is equal to $nevA$, where A is the cross-sectional area of the metal. Resistivity ρ expressed as:

$$E/J = mv_{av}/ne^2\lambda. \quad (5)$$

According to the free electron theory, the number of conduction/free electrons per m^3 of copper is 8.49×10^{28} and using equations (3), (4) and (5) the value of the mean free path is calculated to be about 1.7×10^{-19} m [14], which is smaller than the diameter of a nucleus and very much different from a literature value [5] of about 5×10^{-10} m. As pointed out above, most of the valence electrons in a metal is bound up in chemical bonds and not delocalized or free. Hence, only a small fraction of the valence electrons usually participate in the current flow. Quantum theory shows that the velocity of an electron in an atom is approximately 1×10^6 m s^{-1} [26]. When a correction of 0.0001 is multiplied by the number of conduction/free electrons and using a velocity of 1×10^6 m s^{-1} in equation (5), the calculated mean free path then agrees with the literature values. It has also been demonstrated previously [10] that resistivities of different transition metals can be calculated using a very simple equation, which includes a correction of 0.0001 or 0.01%.

As discussed in the Appendix, if in a cm^3 of copper there are 8.49×10^{22} conduction electrons and with each conduction electron travelling at a velocity of about 1.6×10^6 m s^{-1} , the total amount of kinetic energy generated by the conduction electrons is approximately 1×10^7 J. The electrons are slowed down by collisions and the mean time between collisions is of the order of 10^{-14} s⁴, which means there are 10^{36} collisions in a cm^3 of copper. Using the free electron theory assumptions, the calculated electron drift velocity in a copper wire carrying a current of 10 Amps is less than 10^{-3} m s^{-1} . Most of the 10^7 J of kinetic energy resulting from the collisions has to be dissipated as heat and is enough to cause the wire to melt quickly. However, experience tells us that not much heat is generated by an ordinary copper wire carrying a small current. Say for a

current of 0.2 Amps (sufficient to supply the power for a radio or TV set) even if all the power generated is used to heat up the wire carrying the current rather than supplying power to the radio/TV, the heat produced is still very small compared to the value of 10^7 J. Again, when a correction of 0.0001 is applied to the number of conduction electrons, the heat energy produced will be reduced to an order of magnitude of tens of Joules rather than tens of millions of Joules enough to melt the copper wire.

It may be significant also to note that when the Lamb shift [27] is disregarded, the Dirac equation [28] reproduces the values of the hydrogen terms with great accuracy and can be expressed in the following form:

$$E = -RZ^2/n^2\{1 + \alpha^2Z^2/n^2\{n/n_0 - 3/3\} + \dots\}$$

In the above equation, R is the Rydberg constant, Z is the number of charges, n is the principal quantum number, n_0 is the azimuthal quantum number and α is the Sommerfeld fine structure constant. This equation shows that the different energy levels are a function of α^2 and $2\alpha^2$ is equal to 0.000106 or about 0.01%.

Consider the kinetic energy of an electron in a metal atom, at ordinary speeds the relativistic effects are usually neglected. At high speeds, the kinetic energy of the electron is not $\frac{1}{2}mv^2$ but is equal to [29] $\frac{1}{2}mv^2 + \frac{3}{8}mv^4/c^2 + \dots$. Consider the term $\frac{3}{8}mv^4/c^2$, and higher terms that are very small can be ignored, the term $\frac{3}{8}mv^4/c^2$ can be written as $(\frac{1}{2}mv^2)(\frac{3}{4}v^2/c^2)$. The velocity of light is 3×10^8 m s^{-2} and the speed of a valence electron, which is in the highest energy level, depending on the element is of the order of about 2 to 3×10^6 m s^{-2} . Hence $(\frac{3}{4}v^2/c^2)$ can be approximated to about 0.0001 (or 0.01%). In other words, an electron can only be a conduction electron when the value of $(\frac{3}{4}v^2/c^2)$ approaches or exceed 0.0001. When v is smaller than a certain value, the relativistic kinetic energy is not sufficient to enable the electron to overcome the barrier and conduct.

2.5 Corrected assumptions

The classical radius of an electron is 2.817×10^{-15} m and the radius of a Bohr atom is 5.2912×10^{-11} m [30]. In this work, Z_v is treated approximately equal to 1 or 2 as described and n is equal to $6.022 \times 10^{23} \times \rho/W_A Z_v$.

The volume of an ordinary electron, as compared with the highest energy electron in an atom, is compared to an atom $(2.817 \times 10^{-15})/(5.2912 \times 10^{-11})$ and is approximately 0.5325×10^{-4} .

Assuming approximately 0.01% of electrons per atom contribute to current flow the value of V/N in equation (1) should be equal to $(0.5325 \times 10^{-4})/(1 \times 10^{-4})$ or $0.5325/n$. By applying the correction of 0.5325 to equation (1), the value of R_s is equal to,

$$(0.5325 \times \frac{3}{3}/(\pi n))^{1/3}$$

and comparable to or smaller than the size of an atom of the particular element. N/V is then equal to $1.8779 n$.

$N/V = 1.8779n = k_F^3/(3\pi^2)$ and the Fermi wave vector k_F is equal:

$$(3\pi^2 \times 1.8779n)^{1/3} \quad (6)$$

and the Fermi energy is equal to:

$$(\hbar^2 k_F^2 / (2m)) \quad (7)$$

where \hbar is equal $h/(2\pi)$ and m is the electron mass.

2.6 Calculation of the bulk modulus

The matter is usually considered incompressible and a measure of the incompressibility is given by the bulk modulus. The bulk modulus B is generally defined as the (negative) ratio of a change in pressure dp to the volume strain dV/V (fractional volume change) produced and B is equal to $-(dp/(dV/V))$ and calculated by [31]:

$$\begin{aligned} & 2/3(\hbar^2/2m)(3\pi^2)^{2/3}(N/V)^{5/3} \\ & = 2(\pi)^{4/3}/(3^{1/3})(\hbar^2/2m)n^{5/3} \end{aligned} \quad (8)$$

Values of the bulk modulus for some metals are available in a few publications [4,15]. According to this work, the value of n is independent of valency and different from the n calculated with the original *free electron theory* assumptions. A list of the bulk modulus of samples of metals is calculated using the two different values of n and matched against measured bulk modulus as a test of their reliability.

In a solid at zero temperature electrons occupy the lowest states or the ground state, filling them up to a boundary surface which is termed the Fermi level, and the energy at that highest level is the Fermi energy. In a metal, the electrons occupying the highest energy level are the conduction electrons. The Fermi energy is also defined as the energy of the topmost filled level in the ground state of an N electron system and equal to the difference between the highest and the lowest electron energy states of conduction electrons at absolute zero.

Work done is force multiplied by the distance moved. Consider an atom with radius r and Q is equal to $1/(4\pi\epsilon)$, where ϵ is the permittivity of a vacuum. Then $F = Qq_1q_2/r^2$, q is the electron charge and the work done W_k is:

$$W_k = DQq_1q_2/r^2. \quad (9)$$

In the above equation, r is the size of the atom and in a crystal is half the near neighbour distance [20]. Here D is the distance of an electron, moves from the lowest energy level, which is closest to the nucleus, to the highest energy level or the Fermi level. The principle of quantum mechanics [23] shows that the motion of an electron is associated with a wave with length λ . The wavelength of an electron λ is equal to h/p , where h is Planck's constant and

p is the momentum of the electron [32]. Considering that the kinetic energy of the highest level electron of an atom is equal to the first ionization energy of the atom, the wavelength λ and the distance, which is probably to be a quarter of a wave, can be calculated. Depending on the size of the atom, D can take values of 0.529×10^{-10} m to up to about 1.5×10^{-10} m. q_1 is the charge of the conduction electron and q_2 is the effective charge of the nucleus felt by the conduction electron. Since the nucleus is screened by one or more completed (full) electron shells and the conduction electron is in an orbital in the highest electron shell, the effective charge is only approximately equal to 1 (1.6022×10^{-19} C). Of course, it is possible that the effective charge felt by a conduction electron occupying a p or d orbital can be higher than 1 but for simplicity, it is approximated to be equal to 1.

3. Results and discussion

Table 1 shows some of the calculated results using equation (7) with the assumptions discussed in this work and compared with the values published in the CRC Handbook [5], where 1 eV is equal to 1.6022×10^{-19} J.

Since the Fermi energies published in the literature [4,5,15,16] had been calculated with erroneous assumptions, they are not reliable but at first glance, both sets of values seem fairly similar. The values of Fermi energies in this work are calculated by better assumptions and are more reliable. The CRC Handbook shows the number of conduction electrons for some of the metals many times bigger than others, because the valencies of some of the metals can be up to 4 or 5. In this work, the number of conduction electrons is considered to be 0.01% n rather than in the original theory, where the number of conduction electrons is 10^4 higher. Since it is shown by the quantum theory that electrons are in continuous motion at high velocity, the immense number of conduction of electrons constantly colliding with each other should generate a noticeable amount of heat that in reality does not happen. Secondly, some of the values of R_s shown in the CRC Handbook are bigger than the actual size of the atoms [20,21]. The orbital energies of electrons in multi-electron electrons are more complex than hydrogen [16]. Especially for the transition metals, the electronic configurations and ionization energies are not as straightforward as the main groups [33]. This is further complicated that many of the valence electrons have formed bonds as described above, which means molecular orbitals need to be taken into account when considering the band structure of the metals. It is likely that only one or two of the highest energy electrons per atom can be promoted into the conduction band. Hence, for simplicity, the value of 1 is used for Groups 1 and 2 metals and the value of 2 is used for other metals except for manganese. Because manganese has a highly complex structure, each unit cell has 58 atoms and unlike most other transition metals, the

Table 1. Comparison of Fermi energies calculated by this work and published in the CRC Handbook.

Atom	n (10^{28} m^{-3}), this work	n (10^{28} m^{-3}), handbook	R_s (pm), this work	R_s (pm), handbook	E_F (eV), this work	E_F (eV), handbook
Li	4.63	4.70	140	172	7.17	4.74
Na	2.54	2.65	171	208	4.80	3.24
K	1.37	1.40	210	257	3.18	2.12
Rb	1.08	1.15	228	275	2.71	1.85
-Cs	0.87	0.91	244	298	2.36	1.59
Cu	16.98	8.47	91	141	17.03	7.0
Ag	11.72	5.86	103	160	13.30	5.49
Au	11.80	5.90	103	159	13.36	5.53
Be	12.36	24.7	101	99	13.78	14.3
Mg	4.31	8.61	143	141	6.83	7.08
Nb	11.11	5.56	105	163	12.84	5.32
Fe	16.97	17.0	91	112	17.03	11.1
Zn	12.39	13.2	101	122	13.81	9.47
Cd	9.31	9.27	111	137	11.41	7.47
Al	12.05	18.1	102	110	13.55	11.7
Ga	10.21	15.4	108	116	12.13	10.4
Pb	6.57	13.2	125	122	9.04	9.47
Bi	5.64	14.1	131	119	8.17	9.9
Sb	6.61	16.5	121	113	9.08	10.9
Hg	8.17	8.65	116	140	10.45	7.13
In	7.67	11.5	118	127	10.03	8.63
Tl	6.72	10.5	124	131	9.18	8.15

mean number of nearest neighbours is less than three. The majority of atoms in the unit cell have larger inter-nuclear distances than the nearest neighbours, so it is probable that only one highest energy electron per atom can be promoted to the conduction band.

Many of the CRC Handbook values of the Fermi energies are nearly twice to those calculated in this work, because again in the original calculations some of the variables are functions of valency, which this work shows is unnecessary and improbable.

Table 2 shows a comparison between the measured bulk modulus [15], values calculated with the *free electron theory* assumptions and published in the CRC Handbook and values calculated in this work. In many cases, the bulk modulus calculated using the original *free electron theory* assumptions is much higher than the measured bulk modulus. The reason is that in the *free electron theory*, the number n of highest energy electrons (the *free electrons*) are dependent on valency and when the valency of the metal is higher than 1 the calculated values are much higher than the measured values. Comparison between the values calculated by this work and the *free electron theory* assumptions, shown in the table, indicates that there is much better agreement between values calculated in this work and the measured values. Of course, there is no theoretical proof, but it is good evidence that the initial assumption in the *free electron theory* that n depends on valency is incorrect.

Table 3 shows the values of Fermi energy calculated in two quite different ways. The first one is to calculate it in the usual method using equation (7). The second method

uses a rough approximation to calculate the values of Fermi energy with equation (9). Many metals have more than a crystal structure or distorted structures and may not have a single accurate nearest neighbour distance and the calculated results should be treated as crude estimates. As shown in table 3, they are fairly comparable and show that there is some merit in the crude approximation. Although there is no proof of anything but one can argue that this approximation is a valid estimate of the Fermi energy.

Since the initial theories of metals were proposed in the early twentieth century [34], there are no new theories that are any more successful in explaining any or many of the general characteristics of metals. So far, the Sommerfeld/Drude theory can justify Ohm's law and explain metallic conduction clearly. This work has corrected a few of the fundamental assumptions made in the *free electron theory* and other assumptions, and theoretical calculations have not been altered. With these corrections in the assumptions, the calculated Fermi energies are made more reliable and the calculated bulk modulus of selected metals more accurate.

4. Conclusion

No theory of metals can interpret all the characteristics of metals. The Sommerfeld *free electron theory* might have some erroneous assumptions, but it provides a very useful way of accounting for some important principles of conduction and Ohm's law. The corrections proposed in this work to the assumptions made to the theory enable more

Table 2. Comparison of calculated bulk modulus with measured bulk modulus.

Atom	Bulk modulus, (10^{10} N m ⁻²), experimentally measured	Bulk modulus (10^{10} N m ⁻²), free electron theory	Bulk modulus (10^{10} N m ⁻²), this work
Li	1.16	2.33	2.33
Na	0.68	0.86	0.86
K	0.32	0.31	0.31
Rb	0.31	0.20	0.20
-Cs	0.20	0.14	0.14
Cu	13.7	6.39	20.28
Ag	10.07	3.45	10.94
Au	17.32	3.48	11.06
Be	10.03	37.93	11.95
Mg	3.54	6.56	2.06
Nb	17.02	3.15	10.0
Fe	16.83	20.27	20.27
Zn	5.98	12.0	12.0
Cd	4.67	7.45	7.45
Al	7.22	22.51	11.45
Ga	5.69	12.07	8.09
Pb	4.3	13.22	4.17
Bi	3.15	14.89	3.23
Sb	3.83	19.37	4.21
Hg	3.52	5.99	5.99
In	4.11	10.6	5.39
Tl	3.59	8.5	4.32

Table 3. Comparison of values of Fermi energy calculated by 2 different methods.

Atom	Fermi energy (eV), calculated using equation (7)	Fermi energy (eV), calculated using equation (9)
Li	7.17	8.24
Na	4.8	5.64
K	3.18	3.99
Rb	2.71	3.55
Cs	2.36	3.13
Be	13.78	11.37
Mg	6.83	6.23
Ca	4.51	4.58
Sr	3.84	4.0
Ba	3.51	4.09
Nb	12.84	8.24
Fe	17.03	10.22
Zn	13.81	8.24
Al	13.55	8.76
Ga	12.13	9.89
Pb	9.04	6.0
Bi	8.17	7.67

reliable values of the Fermi energy to be calculated and calculated values of the bulk modulus to be more

comparable to measured ones. It also shows that the Fermi energy can be estimated by a crude approximation. The calculations in this work are more evidence that 0.01% of electrons per atom are *free* to participate in current flow and the drift velocity is much higher. The values of n , R_s and the Fermi energies calculated in this work and the agreement between the Fermi energies calculated by two completely different methods is good evidence that the number of conduction electrons per atom is independent of valency.

Appendix

There are serious problems [13] with the assumption that each atom contributes one electron (or more) for conduction. For example, it is assumed that in a cm³ of copper there are 8.49×10^{22} conduction electrons [5,15,16] and with each conduction, the electron travels at a velocity of about 1.6×10^6 m s⁻¹. Hence, the total amount of kinetic energy generated by the conduction electrons is approximately 1×10^7 J. The electrons are slowed down by collisions and the mean time between collisions is of the order of 10^{-14} s⁴, which means there are 10^{36} collisions in a cm³ of copper. The calculated electron drift velocity [25] in a copper wire carrying a current of 10 Amps is less than 10^{-3} m s⁻¹. Most of the 10^7 J of kinetic energy resulting from the collisions have to be dissipated as heat and is enough to cause the wire to melt quickly.

Secondly, the calculated values of R_s , the radius of the sphere occupied by a conduction electron, for some metals are larger than the size of the metal atoms which cannot be correct. Take the examples of rubidium and caesium, R_s are 275 and 298 pm, respectively, and n for the two metals [4,5,15] are 1.15×10^{28} and 0.91×10^{28} m⁻³, respectively. Therefore, in a cubic metre of space, the total calculated volume of conduction electrons equals $4/3\pi(2.75 \times 10^{-10})^3 \times 1.15 \times 10^{28}$ m³ and $4/3\pi(2.98 \times 10^{-10})^3 \times 0.91 \times 10^{28}$ m³, which are 1.002 and 1.009 m³, respectively, and physically impossible. Even if the total volume of the conduction electrons occupies slightly less than one cubic metre, this still violates the rules of closest packing of spheres. More details are available in the original work [14].

Except for the metals in Groups 1 and 2, most metals have more than one valency. The number of conduction electrons per atom and the Fermi energy have been calculated for a sample of different metals [5,15,16]. Some of the particular metals and their specified valencies, including the following elements with their valencies used for the original calculations, are written in brackets: Nb (1), Mn (2), Fe (2), Zn (2), Al (3), Ga (3), Sn (4), Pb (4), Bi (5) and Sb (5). Without exception, all the above-mentioned metals have more than one valency. There is no theoretical justification to use these respective valencies over other valid valencies.

For example, Advanced Inorganic Chemistry [16] reported that niobium exhibits valencies from 1 to 5; manganese with the greatest range of valencies from 1 to 7;

iron has valencies from 1 to 6. Chemistry of the Elements [18] describes similar compounds and valencies for the above-listed metals.

Bonding was not very well understood until the 1930s when *The Nature of the Chemical Bond* was published. It was one of the first publications which described bonding in detail [6]. When the *free electron theory* was formulated, less was understood of valencies and bonding. The majority of metals have more than one valency and there is no experimental or theoretical proof which valency is the correct valency to use to determine the value of n for calculating the correct Fermi energy and valency should not be a factor for producing the value of the Fermi energy. If valency is a variable in determining n (the number of conduction electrons or the Fermi energy), using valency can produce a different set of values of n and very different values of Fermi energies which can be many times bigger or smaller than the correct value.

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