

# Resistivity

Ralph C. Dougherty\*

Received

DOI

\*Department of Chemistry and Biochemistry, Florida State University, Tallahassee FL 32306-4390. e-mail:[ralphd@chem.fsu.edu](mailto:ralphd@chem.fsu.edu)

This paper introduces the formalism for a molecular orbital treatment of resistivity in metals. The molecular orbital property that controls resistivity is electron orbital angular momentum as a property of conducting electrons. The model is a direct extension of partial wave scattering of electrons in atoms. This produces a model that improves qualitative predictive capacity for resistance related properties, such as, comparative resistivity of conduction bands as a function of temperature, and the pattern of superconductivity at one bar in the periodic table. For the purpose of direct comparison of resistivity for crystalline elements we re-introduce atomic-resistivity, a volumetric property of atoms. This change is needed to develop a clear understanding of the periodic, molecular orbital and chemical physical causes of resistivity. Thinking about atomic resistivity leads directly to a phenomenological picture of resistivity based upon electron-nuclear scattering. This picture is simply a variation on the picture of interactions between

conducting electrons and atomic cores in a metal lattice. The mathematical formalism for partial wave scattering of electrons from atomic quantum mechanics, generates the well-known low temperature  $T^2$  dependence of resistivity, when the conduction band has  $p$  basis functions. The quadratic dependence of resistivity on absolute temperature is known experimentally and is a feature of the Bloch-Grüneisen semi-classical model. Use of electron orbital angular momentum in polyatomic molecular orbitals is well known and straightforward. Electron orbital angular momentum in the conducting band is essential for understanding partial wave scattering, one of the main sources of resistivity in metals. The partial wave scattering model accounts for the zero slope as a function of  $T$  for resistivity of ultra-pure samples of copper at low temperatures. The model presented here is qualitative. A basis is presented that should lead to resistivity calculations in the near future. The new model properly anticipates that the limiting resistivity for copper at low temperatures has zero slope.

## INTRODUCTION

Table 1 illustrates the problem that stimulated the work leading to this paper and the two preceeding. Table 1 is a periodic table of the elements showing the elements that are superconducting at one bar.

**Table 1.** Periodic Table of the Elements showing Elements that are Superconducting at One Bar.<sup>1</sup>

1																		18
1	H																	He
2																		2
3	Li	Be															Ne	
5	B	C	N	O	F							Ar						
11	Na	Mg											Al	Si	P	S	Cl	Ar
19	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55	Cs	Ba	57-71	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87	Fr	Ra	89-103	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub		Uuq				
				La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
				Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

The first thing that a chemist notices in looking at Table 1 is that all of the elements that are superconducting at one bar are metals. They are restricted to two main blocks of metals in the  $d$  transition series and main group elements. Our understanding of the elements that are superconducting at one bar differs from a recent report<sup>1</sup> by one element, lutetium, Lu. There is only one report of Lu being superconducting at one bar,<sup>2</sup> all subsequent reports on the superconductivity of Lu, at pressures above one bar, have not confirmed this single result.

There are only six isolated elements outside these two blocks, five of them are in the  $f$  transition series. The alkali metals, alkaline earths (with the exception of Be), and the Ni

and Cu families are missing from the superconducting group. This broad chemical pattern has not yet been satisfactorily explained. It is the objective of this and the two preceeding papers to provide a rational basis for understanding and dealing with this pattern.

In a simplistic understanding, it is the orbital occupancy and the electron orbital angular momentum that change as one moves from column to column in the periodic table. We believe that these two features are essential to understanding the pattern in Table 1. Unfortunately these features are not treated in the standard solid-state physics treatments of metallic resistivity, magnetoresistance, or superconductivity. For that reason we have started at zero to produce a new model for resistivity, magnetoresistance, and superconductivity that explicitly includes these features. This model is the subject of this and the preceeding two manuscripts.

A second stimulus for the publication of the results in this and the preceeding two papers is the appearance of new experimental results that challenge or are not consistent with the standard model for superconductivity.<sup>3</sup> The demonstration by Kenzelmann, *et al.*,<sup>4</sup> that superconducting states of matter can be host to electron spin angular momentum that couples directly with ordinary ferromagnetism, shows that the magnetic susceptibility on the interior of a superconductor is not necessarily  $-4\pi$ .<sup>5</sup> This important observation calls for a complete re-thinking of the theory of superconductivity. There have also been reports of isotope effect,<sup>6</sup> and phase transition studies,<sup>7</sup> with  $A_3C_{60}$  systems (A represents an alkali metal) that cannot be explained using BCS theory.<sup>3</sup>

This paper introduces electron orbital angular momentum into the discussion of resistivity in metals. Electron orbital angular momentum is a very low energy phenomenon that has been of limited concern in both chemistry and physics. It is the cause of the Renner-Teller effect, a symmetry splitting in orbitally degenerate molecules, often linear

triatomic, that have net electron orbital angular momentum.<sup>8</sup> Renner splittings arise from even terms in vibronic electronic perturbation expansions. The better known Jahn-Teller effects come from the odd terms in the same expansions. Electron orbital angular momentum is also the source of the well known partial wave scattering in atomic quantum mechanics.<sup>9</sup>

The phenomenological bases for the development of resistivity in metals and other materials has been known for many years. The first is promotion energy, often known as energy gap or band gap.<sup>10,11</sup> This phenomenon occurs in metals that have a closed or half-filled sub-shell electronic structure in the ground state. In order to form a fermionic conduction band with only one electron in a given wavefunction it is necessary in these cases to promote one or more electrons to orbital(s) at higher energy than the ground state.

The second well-known basis for the development of resistivity in metals is electron lattice scattering.<sup>10-12</sup> As one proceeds across the periodic table of the elements, total electronic angular momentum changes at every step, so does resistivity. Here we discuss the phenomenology of resistivity with emphasis on the influence of electron orbital angular momentum.

## **I. RESISTIVITY**

The standard model of electron transport in metals is a semi-classical theory that originated with Felix Bloch's doctoral thesis.<sup>13,14</sup> The theory has undergone substantial modification since its introduction.<sup>12</sup> There have been a number of small changes that have resulted in the theory reflecting the interaction of conducting electrons with the metal lattice.<sup>12</sup>

Bloch's theory has not generally been used to compare the resistivity of different metals, or to relate resistivity to atomic properties of the metals. The manner in which resistivity is reported is partly responsible for this. Resistivity units are  $\Omega\cdot\text{m}$ , which is a volume basis. To get the resistance of a wire or bar you multiply the resistivity for the temperature by the length of the object in m and divide by its area in  $\text{m}^2$ . We can compare conductors on a chemical elemental basis if we change the length scale for resistivity to an atomic length scale based on the diameter of the atom for elemental metals. This is done in the following section. The data generated by this change should be useful in the theoretical evaluation of the molecular orbital origins of resistivity.

The theory that is presented in the following sections is a simple extension of the Bloch theory,<sup>13,14</sup> with the inclusion of the electron orbital angular momentum of the conducting electrons. In this extension of the Bloch theory, the electron-lattice scattering that is central to the theory is modified to include the partial wave scattering of electrons in wave functions with different azimuthal quantum numbers. Formal development of a quantitative molecular orbital model is underway. For our purposes here, a qualitative treatment based on a perturbation theoretical approach starting with hydrogenic solutions to the Schrödinger equation will be sufficient to introduce the subject. Because we are keeping track of electron orbital angular momentum in the basis sets for the wavefunctions, it will be necessary to abandon reciprocal space, at least for now.

Matthiessen's rule is a piece of 19<sup>th</sup> century wisdom that will start our investigation of the impact of the azimuthal quantum number on resistivity. Matthiessen was the first Physics Professor at University Rostock. His measurements of the resistivity of copper were quoted into the 20<sup>th</sup> century. These measurements, among many others, were the basis for his rule that resistivity in metals decreases with temperature, and at a certain

point becomes constant. The standard textbook explanation for this rule is based on analysis of multiple resistivity mechanisms, in particular impurity scattering of electrons. In the 19<sup>th</sup> century ultra-pure metal samples were generally not available and virtually all metals showed a zero slope for resistivity against temperature at low temperatures.

Because of the economic importance of copper conductors, Matthiessen's resistivity measurements have often been repeated.<sup>15</sup> The measurements have included samples of the purest electrolytic copper metal available. In electrolytic Cu samples the slope for resistivity  $\nu$ . T becomes zero at roughly 8 K.

The lowest energy conduction band for metallic copper has a 4s basis set. Copper is an exceptional conductor because there is no promotion energy associated with electrical conduction in this metal. The same is true for Ag and Au. Partial wave scattering from an s wavefunction should have zero slope  $\nu$ . temperature or electron velocity. The interesting feature of the plot of resistivity  $\nu$ . T for ultra-pure copper is that it is necessary to get to temperatures below 10 K to exclusively populate the 4s conduction band of copper. (See the discussion of the low temperature resistivity of graphene below.)

The connection between electrical conductivity and thermal conductivity is known as the Wiedemann-Franz Law. It was discovered in 1853. In 1927 Arnold J. W. Sommerfeld placed this law on a direct quantum mechanical foundation.<sup>16</sup> Sommerfeld gave the constant that connected thermal conductivity as a function of temperature with electrical conductivity as a function of temperature as,

$$(1) \quad \frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2$$

Thermal conductivity,  $k$ , electrical conductivity,  $\sigma$ , and absolute temperature, T, are related to each other by the constant on the right, where  $k_B$  is the Boltzmann constant and  $e$  is the

electron charge. The close agreement between Sommerfeld's theoretical constant and the measured constant was one of the important factors in establishing the quantum theory of solids.

In deriving the constant on the right of equation (1) Sommerfeld did not use an explicit model for resistivity in metals. He only assumed that the mechanism for the development of resistivity was the same as the mechanism for transfer of thermal energy. This assumption is reasonable since only electrons and the metallic lattice are intimately involved in both effects.

This paper presents the ideas that electrical resistance in metallic conductors is due to: (1) promotion energy (this energy is not dependent upon temperature); (2) near contact scattering interactions between electrons and nuclei;<sup>10</sup> and (3) Fermi contact scattering interactions between electrons and nuclei.<sup>17-20</sup> The number of near contact interactions between electrons and nuclei is larger than those involving Fermi contact.<sup>10,19</sup> The energy, or momentum, transferred per collision are smaller for near contact processes than for Fermi contact. 'Contact' or 'collision' is used here in the sense understood in the confines of quantum mechanics.<sup>10,11</sup> Molecular orbital atomic basis functions for the conducting bands that contain electrons, control the probability for juxtaposition or close approach between the electrons and lattice nuclei.

Feynman's model for the conduction bands for metals is our starting place.<sup>21</sup> Metallic color, luster, and photoionization threshold are three among many examples of wave mechanically controlled properties of metals. All of these properties depend on the wave functions of the metal as a supermolecule.<sup>10</sup> The fact that we cannot exactly solve the wave equations for metals does not mean that solutions do not exist, nor does it mean that metals are somehow exempt from the basic rules of quantum mechanics.<sup>10</sup>



Fermi contact,<sup>17-20</sup> and near contact<sup>10</sup> are a major source of electron scattering and resistivity in metals. This idea has appeared previously in the literature.<sup>3</sup>

The electron orbital angular momentum associated with the conduction band controls the probability of electron nuclear contact interactions. It was known in 1930 that only *s* wave functions participate in hyperfine interactions in atomic spectroscopy.<sup>17-20</sup> Pauli proposed electron-nuclear spin interactions as the source of hyperfine lines.<sup>22</sup> Fermi confirmed the suggestion using atomic spectroscopy.<sup>17</sup> Near contact scattering between electrons and nuclei is somewhat more complicated.<sup>10</sup> This topic is discussed below.

Fermi contact generalizes directly from atoms to molecules. NMR studies of small molecules make detailed use of basis orbital dependent exchange of spin information between nuclei,<sup>23</sup> mediated by electrons. This spin exchange process is due, among other things, to *s*-orbital Fermi contact.<sup>17-20</sup> When an electron is in an *s*-orbital, the gradient of the electron radial distribution has a nonzero slope at the nucleus. *s*-electrons, with a certain probability, spend enough time at or in the nucleus to exchange spin information. Interaction of these electrons with other nuclei, one or more bonds removed from the first, gives rise to a large component of nuclear spin-spin coupling in molecules.<sup>23</sup> Fermi gave the magnitude of the hyperfine splitting for an *s* wavefunction,  $\Delta(s)$ , as (2).<sup>19b</sup>

$$(2) \quad \Delta(s) = \frac{8\pi}{3} \frac{2\kappa + 1}{\kappa} \mu \mu_o \Psi^2(0)$$

$\kappa$  is the spin quantum number of the nucleus.  $\mu$  is the magnetic moment of the nucleus.  $\mu_o$  is the Bohr magneton.  $\Psi^2(0)$  is a single *s*-atomic orbital evaluated at the nucleus. For the hydrogen atom 1*s* orbital this coupling corresponds to 1420 MHz, a line that is used to identify hydrogen clouds in the observable universe.<sup>24</sup>

Another major mode for energy and momentum transfer between conducting electrons and metal nuclei is electron-nuclear close-approach scattering, often called partial wave scattering.<sup>10</sup> These scattering processes depend strongly on electron orbital angular momentum and velocity. The magnitude of the scattering can be directly calculated at the atomic level and is a part of all introductory graduate courses in quantum mechanics.<sup>10</sup>

Resistance in metallic conductors is a function of a large number of parameters in addition to the atomic composition of the metal. Important factors include lattice structure, geometry of the macroscopic metal, temperature, electron population in the conduction bands by basis function, pressure and magnetic or non-magnetic impurities. To understand resistivity from an atomic perspective it is essential to make comparisons on an atomic basis. Resistivity is reported as a volumetric property of materials. The substantial variance in the size and arrangement of atoms renders comparisons on this basis somewhat obscure. Conversion to an atomic basis is straightforward (3).

$$(3) \quad \rho_a (\Omega \cdot \text{atom}) = \rho (10^{-8} \Omega \cdot \text{m}) * (\text{atom}/\text{m})$$

It is possible to obtain the atom/m conversion factor either from the elemental density and the atomic mass, or from the x-ray structure of the metal. This approach is not new. Atomic conductance for metals was in use in the 1920's,<sup>25</sup> but the concept subsequently dropped from usage.

Values of atomic resistivity derived from density data,  $\rho_a$ , for metallic elements through the lanthanides and period 6 are listed in Table 2. Properly, resistivity of an elemental metal is a tensor.<sup>26</sup> This is particularly important if the unit cell for the crystal has low symmetry. When the data for resistivity tensors becomes both more standardized and available, the values in Table 2 should be replaced by axis dependent values for unit cell resistivity or proper tensor indices. Lattice dissymmetry has a significant effect on the

components of the resistivity tensor, but does not significantly impact the difference between atomic and bulk resistivity, both of which are isotropic.

The values for the atomic resistivities,  $\rho_a$ , in Table 2 are plotted in Figure 1. The corresponding values for the bulk resistivities,  $\rho$ , reported in the literature are plotted in Figure 2. It is interesting that the two sets of values appear to be more or less similar, with the exception of the scaling. The variation in the relative values between the two data sets does not exceed 2.5. The variations between Figures 1 and 2 are due partially to different packing fractions for different lattices which is ignored in bulk resistivity. The striking features of both figures, such as the relatively high resistivity for both Mn and Hg, are largely due to element specific differences in promotion energies.

For a zero current resistance measurement to be possible using a bridge circuit for a fermionic conductor, it is necessary that a conducting path exist between the ends of the

**Table 2.** Atomic Resistivity of Metals, from density (  $\cdot 10^3 \Omega \cdot \text{atom}$ )<sup>27</sup>

C o l	1	2	3	4	5	6	7	8	9	10	11	12	13	14
2	Li .338	Be .199												
3	Na .138	Mg .154											Al .104	
4	K .165	Ca .097	Sc 1.88	Ti 1.54	V .833	Cr .553	Mn 6.95	Fe .426	Co .270	Ni .315	Cu .076	Zn .238	Ga .519	
5	Rb .265	Sr .341	Y 1.75	Zr 1.47	Nb .572	Mo .201	Tc .827	Ru .298	Rh .180	Pd .408	Ag .063	Cd .251	In .270	Sn .367
6	Cs .401	Ba .871	La 1.83	Hf 1.07	Ta .496	W .199	Re .735	Os .336	Ir .195	Pt .428	Au .088	Hg 3.36	Tl .490	Pb .673
5	Ce 2.27	Pr 2.14	Nd 1.95	Pm 2.33	Sm 2.90	Eu 2.47	Gd 4.05	Tb 3.78	Dy 2.88	Ho 2.99	Er 2.81	Tm 2.25	Yb .795	Lu .181

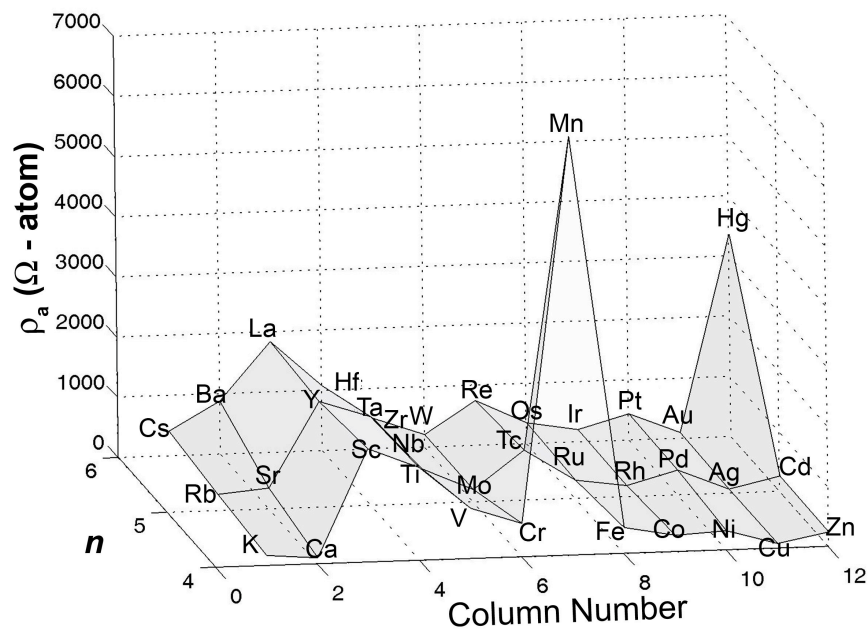


Figure 1: Atomic resistivity of main group and transition metals as a function of  $n$  and column number in the periodic table.<sup>27</sup>

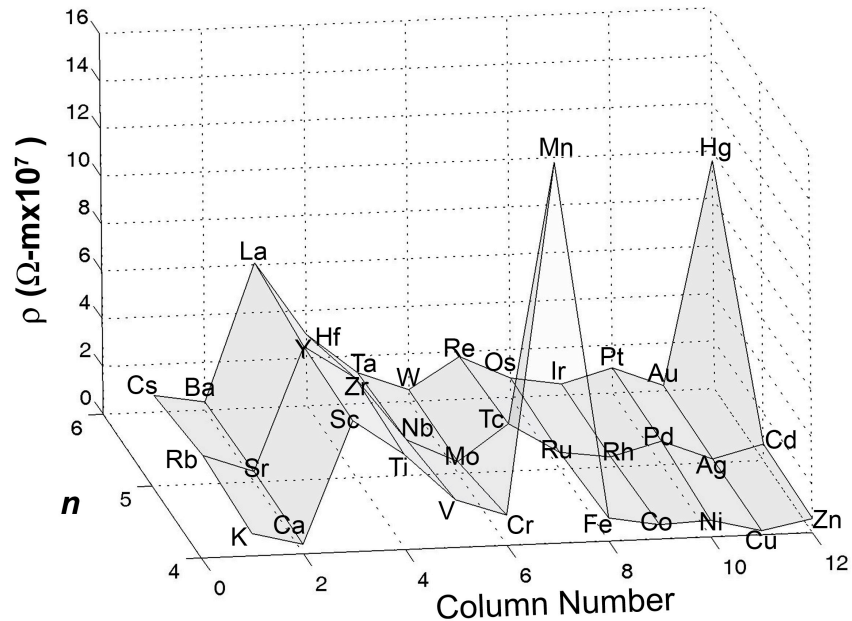


Figure 2: Bulk resistivity of main group and transition metals as a function of  $n$  and column number in the periodic table.<sup>27</sup>

bridge. In the case of a ground state closed sub-shell metal like Zn this means that a conducting band must be created by promotion of an electron from the non-conducting ground state band. This energy cost is a per-electron cost. The energy is not available for useful work after the electron leaves the conducting medium. The promotion energy depends on the current density as orbital occupancy changes with the current density.

Small effects are expected from the density of electrons in the conduction band. Once a conducting band saturates, the promotion energy will change as a new conducting band is utilized. Examples of this phenomenon can be found in the literature on two-dimensional junctions.

Manganese is an example of a high promotion energy in a metallic conductor. The high values of the atomic resistivity for mercury and the lanthanides (see Table 1) are also due largely to promotion energies. The atomic resistivity for manganese is 6,950  $\Omega$ -atom, more than 125 times larger than that of the elements adjacent to it in the periodic table, Cr, 553  $\Omega$ -atom and Fe, 426  $\Omega$ -atom. This difference in atomic resistivity should be temperature independent. It is intriguing that Hall probe measurements of the number of carriers per atom in Mn metal give four electrons.<sup>28</sup> The ground state of atomic Mn has five unpaired spins in its half-filled *d*-subshell. The loss of a single spin per atom suggests the formation of a bond between Mn atoms in the process of electron promotion and generation of a conduction band. The nature of this bond is not known. It could be delocalized in the lattice, or localized to some number of atoms in a restricted environment. The promotion is probably more complex than  $4s^23d^5 \rightarrow 4s^13d^6$ ; however, formation of a  $3d-3d$  bond in that state would give a metal with four electron carriers that would not be expected to be superconducting.<sup>29</sup>

To a first approximation the promotion energy for a given conduction band will be temperature independent, just as the energy differences between electronic states are temperature independent. In cases where the Born-Oppenheimer approximation does not hold rigorously, temperature effects on the promotion energy can be substantial and are easily detected.

Once an electron has attained the energy appropriate to a conduction band, the major impediment to its motion toward the outlet is partial wave scattering from lattice nuclei.<sup>10</sup> For a zero current bridge measurement of resistivity, the resistivity will show a temperature dependence that will depend on the basis functions for the conducting band. Impurities or dopants will also contribute to resistivity. The effect of impurities on temperature dependence is well treated in contemporary texts.<sup>30</sup>

## II. PARTIAL WAVE SCATTERING OF ELECTRONS

Estimation of the importance of Fermi contact electron-nuclear scattering is reasonably straightforward. When a 1000-volt electron in an  $s$  wave function makes Fermi contact with a nucleus, the electron and nucleus approach to a distance such that both exchange of spin information (spin angular momentum) and linear momentum is possible. The transfer of linear momentum from conducting electrons to nuclei (electron scattering)<sup>10</sup> is important for generation of both the heating of the metal and the change in electrical potential energy of the flowing current. The general form for the contact probability between an electron and the nucleus for the case of a single hydrogen like atom is given by (4).<sup>31</sup>

$$(4) \quad P_{n,l}^2(r) = \frac{(n-l-1)Z}{n^2[(n+l)!]} \left( \frac{2Zr}{n} \right)^{2(l+1)} \Psi^2(r)$$

The probability of electron-nuclear contact, Fermi contact, for exchange of linear momentum between an electron in a  $6s$  wave function and a lead, Pb, nucleus using the approximations above is given by (5).<sup>31</sup>

$$(5) \quad P_{6,0}^2(0) = \frac{(5! \cdot 82)}{36 \cdot (6!)^3} \Psi^2(0) = 4.6 \cdot 10^{-3}$$

A 1 kV electron has a velocity of  $\sim 5.93 \cdot 10^6$  m/s. A single direct contact ( $90^\circ$  angle) with a  $^{208}\text{Pb}$  nucleus will transfer  $1.69 \cdot 10^{-22}$  J/atom or 102 J/mol. We know that Fermi contact happens in systems with  $s$  basis functions. In those interactions there is no orbital angular momentum for the electron in the scattering process. The quantized orbital angular momentum of electrons in  $s$  basis functions is exactly zero. Fermi contact does not occur in systems with basis sets that have  $l > 0$ . The reason for this is that there is a node at the nucleus for all wave functions with  $l > 0$ . The first derivative of electron density as a function of  $r$  is also zero at the nucleus for these functions.<sup>31</sup> We use the probability for Fermi contact of a  $6s$  electron, (5), as a guide for estimating the magnitude of the partial wave scattering for a given principal quantum number.

The participation of electron scattering in resistivity is well-known and well documented.<sup>32</sup> There is positive evidence of the occurrence of Fermi contact, and hence electron-nuclear scattering, for electrons in  $s$  basis wavefunctions.<sup>33</sup> In the formulae and equations (6)-(9)  $k$  is the reciprocal spatial coordinated (generally referred to as the momentum coordinate) and  $r_o$  is the scattering range, a negative value that must be explicitly calculated, determined by experiment or estimated.

The partial wave equations for coulomb scattering are well known.<sup>10</sup> The wave mechanical solutions for coulomb scattering are tedious because of the infinite range of the coulomb potential. For scattering inside metals a full coulomb potential is not realistic, as Gauss' Law requires that the electric field be zero external to a closed neutral electron carrier. The use of a screened coulomb potential in this case is much more realistic for obtaining scattering amplitude in a metal.<sup>34,35</sup> The partial wave scattering results for a screened coulomb potential in the Born approximation are available.<sup>36</sup> For a screened Coulomb potential given by (6) the scattering amplitude will scale as (8),<sup>37</sup> where (7) gives the phase shifts.<sup>36</sup>

$$(6) \quad V(r) = \frac{Ze^2}{r} e^{-\left(\frac{r}{r_o}\right)}$$

$$(7) \quad f_k(\theta) = \frac{1}{k} \sum_{l=0}^{\infty} (2l+1) e^{i\delta_l(k)} \sin \delta_l(k) P_l(\cos \theta)$$

Term (8) is controlling for the magnitude of the scattering amplitude.<sup>37</sup>

$$(8) \quad const \cdot \frac{1}{k} (kr_o)^{(2l+1)}$$

$$(9) \quad k = \frac{p_e}{\hbar}$$

If we approximate the energy of a thermal electron as,

$$(10) \quad \frac{3}{2} k_B T = \frac{1}{2} m_e v_e^2$$



we can find the temperature dependence of resistivity to a reasonable approximation. For electrons in a conducting band formed with *s* basis functions there is no temperature dependence, slope of zero. *p* basis functions give the well known  $T^2$  temperature dependence. A  $T^4$  dependence results from *d* basis functions and *f* basis functions should give a  $T^6$  dependence for resistivity.

At low temperatures there will be another complication in the temperature dependence of resistivity because of the temperature dependence of thermal population of the relatively low lying conducting bands. Without the thermal population of low lying conducting bands constructed from basis sets with  $l > 0$  the temperature dependence of the resistivity of copper, for example, would be expected to be zero at all temperatures. The best available data suggests that a ground state thermal population occurs only at very low temperatures.<sup>15</sup>

The value of the scattering range,  $r_o$ , is critical for estimating the impact of different conduction band basis sets on resistivity. We know that  $r_o$  must be less than zero.<sup>36</sup> In this treatment the scattering range is analogous to the phase shift in x-ray scattering.<sup>36</sup> It is negative when the potential is attractive. We have taken the Bohr radius,  $5.3E-11$  m as the magnitude for  $r_o$  just for the sake of this discussion. The actual value is not significant. The table that it allows us to generate illustrates the impact of both temperature and electron orbital angular momentum on scattering amplitude. Table 3 presents the ratio for electron-atom scattering for  $l > 0$  and  $l = 0$  for the values of  $l = 1, 2$ , and  $3$ . I am not aware of any systems that presently utilize *f* orbital conduction bands. Nonetheless these systems should be quite interesting. By taking a ratio in Table 3 we have eliminated the unevaluated constant in formula (8).

**Table 3** Order of Magnitude Resistivity Ratios  $\nu$ . T

Temperature	300 K	200 K	100 K	10 K	1 K
$\rho/s$	$7 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$2 \cdot 10^{-6}$	$2 \cdot 10^{-7}$
$d/s$	$5 \cdot 10^{-9}$	$2 \cdot 10^{-9}$	$6 \cdot 10^{-10}$	$6 \cdot 10^{-12}$	$6 \cdot 10^{-14}$
$f/s$	$4 \cdot 10^{-13}$	$1 \cdot 10^{-13}$	$1 \cdot 10^{-14}$	$1 \cdot 10^{-17}$	$1 \cdot 10^{-20}$

The temperature dependence of the resistivity of potassium and its alloys has been the subject of extensive and careful study.<sup>38</sup> Marder's re-plot of the data from several investigators in that review shows slopes corresponding to  $T^2$ ,  $T^5$ , and  $T$  as the temperature rises for resistivity in potassium.<sup>39</sup> Each break in the slope of the resistivity must represent some order of phase transition or shift in population of the conduction bands in the material. The nature of these transitions is not presently known.

### III. WHERE ARE THE PHONONS?

The Block-Grüneisen model is semi-classical and uses phonons, lattice vibrational quanta for the purpose of approximately calculating the scattering of electrons by the lattice. Phonons have frequencies that are of the order of  $10^{12}$  Hz. Their corresponding energies are too low for them to effectively scatter electrons with energies near the Fermi level,  $\sim 6$  eV. If a phonon beam and an electron beam intersected each other, we would expect to see phonon scattering, but no electron scattering because of the energetics.<sup>40</sup> This fact is not important to the Block-Grüneisen model which was stated to be approximate at the start.

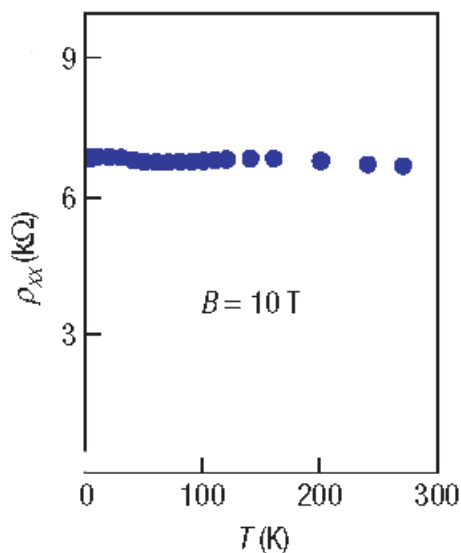
In a fully quantum mechanical model, partial wave scattering describes the scattering interaction between electrons and lattice nuclei.<sup>10</sup> This is what we have used here. The vibrational signature of the lattice will be associated with the electron scattering because

the Born-Oppenheimer approximation holds, as long as the time constant for the observation or calculation exceeds the vibrational frequency.

#### IV. RESISTIVITY OF BILAYER GRAPHENE AT LOW TEMPERATURE

Graphene (graphite monolayers prepared by carefully spalling and selecting graphite flakes) is a simple macromolecular model for a metal. The resistivity of bilayer graphene at low temperatures has been reported in the presence of a 10 T magnetic field,<sup>41</sup> Figure 3. Zero slope for  $\rho$  v.  $T$  in Fig. 3 is compatible only with the conduction band in this sample being a  $3s$  band. Zero slope indicates that this sample will have an approximately 7 k $\Omega$  resistivity at the lowest temperatures attainable.

Approximate molecular orbitals for graphene like systems are well known.<sup>42</sup> The slope of the resistivity v.  $T$  indicates that bilayer graphene as prepared has a  $3s$  conducting band. This band is above the energy of the lowest vacant molecular orbital for the molecule that is constructed from  $2p$  wavefunctions.



**Figure 3.** Resistivity of bilayer graphene v.  $T$ .<sup>42</sup>

We attribute the fact that the  $2p$  manifold of vacant orbitals are not used for conduction, to their having been blocked by excitonic Bose-Einstein-Correlates,<sup>43,44</sup> temperatures ranged from mK to approximately the ice point.<sup>41</sup>

#### IV. EVALUATION OF ELECTRON TRANSPORT IN METALS

Slater's approach to the calculation of metallic conductivity is the most reasonable starting point,<sup>11</sup> as long as we work in conventional coordinates, so we can keep track of orbital angular momentum. The explicit inclusion of scattering in a time-independent model will not be simple if the approximations are well done. The requirement for time independence is that the  $\Delta t$  for the entire system must be of the same order as the relaxation time for electron scattering in the metal.

With the explicit inclusion of electron orbital angular momentum in the wavefunctions, the definitions of conduction bands will change from one based on the Brillouin zone in reciprocal space to one based on atomic orbital basis sets in ordinary space. This change is substantial. The explicit use of orbital angular momentum more or less precludes the use of reciprocal space because the two coordinate systems are not compatible. Reciprocal space adds mathematical complications to calculations and does not provide a computational benefit, such as is found in x-ray scattering, to offset the increased cost. In x-ray scattering it is essential to know the scattering trajectory for the x-rays. In resistivity it is not essential to know the direction of electron scattering.

The material presented here forms a structural basis for solving the question about the pattern of superconducting elements at one bar. Development of the answer still requires an understanding in this context of the subjects of magnetoresistance and superconductivity, the subjects of the two preceeding manuscripts.

## SUMMARY

Atomic resistivity values are presented for a substantial group of elemental metals. Atomic resistivity uses individual atomic diameters as the scale foundation. This scale has the advantage that it allows quantitative comparisons of resistivity on an atomic basis. Previous reports of resistivity are restricted to a macroscopic volume basis ( $\text{m}^3$ ), which is variable across substances and crystal types from an atomic point of view. The presentation of atomic resistivity with units of  $\Omega\text{-atom}$ , where atom refers to the diameter of the atom, shows how resistivity depends on the charge on the nucleus among other periodically varying factors.

The material presented here shows how resistivity in metals arises from 1) promotion energy, 2) Fermi contact, and 3) non-contact scattering between electrons and atomic cores. Partial wave scattering of electrons as a source of resistivity in metals follows directly from the ideas of Fermi contact, quantum mechanics.

**ACKNOWLEDGMENT:** J. Daniel Kimel and Louis N. Howard have been patient and careful listeners and critics during the development of these ideas. It is a pleasure to express my deep gratitude to them for their help. Stephan von Molnar clearly critiqued an early version of this manuscript for which I am most grateful.

## References

1. C. Buzea, K. Robbie, *Supercond. Sci. Technol.*, **2005**, 18 R1–R8.
2. E. I. Nikulin, *Fizika Tverdogo Tela* (Sankt-Peterburg) **1975**, 17, 2795-2796.

3. J. Bardeen, L. N. Cooper and J. R. Schrieffer, *Phys. Rev.*, **1957**, *108*, 1175-1204.
4. M. Kenzelmann, Th. Strässle, C. Niedermayer, M. Sigrist, B. Padmanabhan, M. Zolliker, *Science*. **2008**, *321*, 1652-1654.
5. W. Meissner and R. Ochsenfeld, *Naturwissenschaften*, **1933**, *23*, 787-788.
6. M. Riccò, F. Gianferrari<sup>1</sup>, D. Pontiroli<sup>1</sup>, M. Belli<sup>1</sup>, C. Bucci<sup>1</sup>, and T. Shiroka, *EPL*, **2008**, *81*, 57002 (6pp).
7. Y. Takabayashi, A. Y. Ganin, P. Jeglič,<sup>3</sup> D. Arčon, T. Takano, Y. Iwasa, Y. Ohishi, M. Takata, N. Takeshita, K. Prassides, M. J. Rosseinsky, *Science*, **2009**, *323*, 1585-1590.
8. T. C. Smith, H. Li, D. A. Hostutler, D. J. Clouthier, and A. J. Merer, *J. Chem. Phys.*, **2001**, *114*, 725-734.
9. G. Herzberg. *Molecular spectra and molecular structure III. Electronic spectra and electronic structure of polyatomic molecules*, **1966**, van Nostrand Co., New York, p. 26, **1991**, Reprint Edition, Krieger, Malabar.
10. J.J. Sakurai, *Modern quantum mechanics, revised ed.*, S.F. Tuan, Ed., **1994**, Addison, Wesley, Longman, New York, pp. 399-410.
11. J.C. Slater, *Quantum theory of matter, second edition*, **1968**, McGraw-Hill, New York; p. 591.
12. U. Mizutani, *Introduction to the electron theory of metals*, **2001**, Cambridge University Press, Cambridge.
13. F. Bloch, *Z. Physik*, 1929, **52**, 555-601.
14. F. Bloch, *Z. Physik*, 1930, **59**, 208-214.

15. M. Khoshenevisan, W.P. Pratt, Jr., P.A. Schroeder and S.D. Steenwyk, *Phys. Rev. B*, **1979**, *19*, 3873-3878.
16. A. Sommerfeld, *Die Naturwissenschaften*, **1927**, *15*, 825-832.
17. E. Fermi, *Nuclear Physics, Rev. Ed.*, 1949, University of Chicago Press, Chicago IL, p. 148.
18. E. Fermi, *Nature*, **1930**, *125*, 16-17.
19. a) E. Fermi, Mem. Acad. D'Italia, , **1930**, *1*, (Fis.), 139-148; b) E. Fermi and E. Segré, Mem. Acad. D'Italia,, **1933**, *4* (Fis.), 131-158.
20. E. Fermi, *Collected Papers, Vol. I*, 1962, University of Chicago Press, Chicago IL.
21. L. Solymar and D. Walsh, *Electrical properties of materials, seventh edition*, **2004**, Oxford University Press, Oxford, p. 105.
22. W. Pauli, cited in ref. (20) e), p. 328.
23. A. Wu, J. Gräfenstein and D. Cremer, *J. Phys. Chem. A*, **2003**, *107*, 7043-7056.
24. <http://www.ras.ucalgary.ca/CGPS/pilot/>
25. C.A. Kraus, and W.W. Lucasse, *J. Amer. Chem. Soc.*, 1922, *44*, 1941-1949.
26. M.P. Marder, *Condensed Matter Physics*, 2000, J. Wiley & Sons, New York, p. 461.
27. <http://www.webelements.com/webelements/scholar/>
28. Ref. 26, p. 147.
29. R.C. Dougherty, **2009**, *submitted*.
30. Ref. 26, p. 486.

31. Ref. 11, p. 121.
32. N.W. Ashcroft and N.D. Mermin, *Solid State Physics*, 1976, Thompson Learning, p. 315.
33. See, e.g., J.E. Peralta, V. Barone, G.E. Scuseria and R.H. Contreras, *J. Amer. Chem. Soc.*, **2004**, *126*, 7428-7429.
34. E. Merzbacher, *Quantum Mechanics, Third Ed.*, **1998**, J. Wiley, New York; exercise 13.20, p. 309.
35. L.D. Landau and E.M. Lifshitz, *Quantum Mechanics, Course of Theoretical Physics, Vol. 3, 3rd Ed.*, **1977**, Butterworth-Heinemann, Oxford; p. 525.
36. R. Shankar, *Principles of Quantum Mechanics, Second Ed.*, **1994**, Springer, New York; p. 523.
37. I am indebted to J. Daniel Kimel for providing me with this result.
38. J. Bass, W.P. Pratt, Jr. and P.A. Schroeder, *Rev. Mod. Phys.*, **1990**, *62*, 645-744.
39. Ref. 26, p. 487.
40. M. L. Goldberger and K. M. Watson, *Collision Theory*, **2004**, Dover, Mineola NY.
41. K. S. Novoselov, E. Mccan, S. V. Morozov, V. I. Fal'ko, M. I. Katsnelson, U. Zeitler, D. Jiang, F. Schedin and A. K. Geim, *Nature Phys.*, **2006**, *2*, 177-180.
42. C.A. Coulson and A. Streitwieser, Jr., *Dictionary of  $\pi$ -electron calculations*, **1965**, W.H. Freeman, San Francisco.
43. R. M. Weiner, *Introduction to Bose-Einstein Correlations and Subatomic Interferometry*, **2000**, J. Wiley, New York.



44. S. A. Moskalenko, D. W. Snoke, *Bose-Einstein Condensation of Excitons and Biexcitons*, 2000, Cambridge U. Press, New York.