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Electrical Conductivity Equations Derived with the Rate Process Theory and Free Volume Concept

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Abstract

Under the stimulation of Marcus theory of electron transfer, electrical conductivity equations without binding to any specific materials are derived on the basis of Eyring's rate process theory and free volume concept. The basic assumptions are that electrons are assumed to have a spherical physical shape with an imaginative effective radius inferred from the latest experimental evidences; Electrons traveling from one equilibrium position to another may obey Eyring's rate process theory; The traveling distance is governed by the free volume available for electrons to transport. The derived equations fit very well with experimental data, and seem to trend consistently with the currently observed experimental phenomena, too. The obtained equations predict that the superconductivity happens only when electrons form certain structures of a small coordinate number like electron pairs with the coordinate number equal to 1 at low temperatures, which is in line with the popular Cooper pairs concept in the BCS theory for superconductivity. The current work may provide new insights on rich conductive behaviors at low temperatures.

I. INTRODUCTION

Electrical conductivities of various materials have been extensively addressed for many decades. The rich and distinctive conductive phenomena have led to many different theories and/or models for unveiling the underlying physical mechanisms. From pure crystalline materials like metals, semi-conductive metal oxides, amorphous solids, to superconductors, each class of materials gives remarkable different conductive behaviors, and thus researchers have to modify the theories continuously with more complications added in. What we don't know seems to grow proportionally with what we have already known so far, especially after the discoveries of Kondo effect, Mott transition, Anderson transition, high temperature superconductors, ferropnictides superconductors, topological insulators, and so on. As scientific history has demonstrated repeatedly, we always start with simple and idealized models, enjoy the success of those achievements for some periods of time, be surprised and puzzled with new experimental discoveries that cannot be explained with the current mechanisms/models, be excited with new theories that seem to work perfectly for everything we have observed, and then start a new cycle again. A good example is Einstein's photoelectric theory published in 1905. At that time, almost all physicists believed Maxwell's wave theory of light and strongly opposed Einstein's particle theory. Nevertheless, Einstein was confirmed to be correct many years later and we have no choice but to adopt an important wave-particle duality principle for elementary entities like photons and electrons.

Electrons have the particle and wave duality properties. An external electric field may "induce" electrons to show "particle" properties more often, especially when the temperatures are low in the same time. The electron was discovered by Thomson in 1897 due to its "particle" properties under an electric field.[1] However, the "wave" rather than the "particle" properties of electrons have been paid a huge attention and explored exhaustively during last century; The "particle" properties of electrons seem not being weighed and investigated equally in a similar profound manner. The negligence of the "particle"properties of electrons may be due to the fact that the electron was identified as a particle before the quantum mechanics was well established and the abundant wave properties were really overwhelming.

Electrons play a paramount role in conductive behaviors of many materials. Although there are many conductivity problems that we don't understand, the following facts seem widely accepted: 1) The conductivity is resulted from the movements of charge carriers like electrons and ions; 2) The inter-electron interactions cannot be overlooked even in metallic materials; the resistivity comes from not only electron-lattice interactions, but also electron-electron interactions; 3) At low temperatures close to zero Kelvin, electrons may tend to condensate, forming pairs as suggested in BCS theory[2] and even crystal lattice structures predicted by Wigner.[3] Recent experimental evidences may confirm the existence of cooper pairs,[4] the body-centered cubic (bcc) structure in 3D,[5] and triangular lattice structure in 2D,[6] those unique electron packing structures. An improved precise measurement on the shape of electrons indicates that an electron is a perfect sphere[7] and the electrical dipole moment of an electron determined very recently is indeed very small due to its perfect spherical shape.[8] All those facts listed above may infer that electrons could be reasonable assumed to be negatively charged spherical particles with a "physical" radius. They may analogously behave like colloidal particles, as colloidal particles usually carry charges, interact repulsively each other, and can form various crystal lattice structures, too.[9–11]

Similar to electron systems containing a huge amount of fast-moving electrons, colloidal suspensions contain thousands of thousands particles that are non-stop moving due to the Brownian motion. Both systems have complicated many-body problems, and the exact solution to the total interaction energy between particles/electrons is hard to be estimated. In colloidal suspensions, we know that the inter-particle forces are important to physical properties of whole systems. For example, the viscosities and the micro-structures of colloidal suspensions are strongly dependent on how strong the inter-particle forces are[12]; If an external electric or a magnetic field is applied to a colloidal suspension, the particles would be polarized; The polarization will generate additional amount of charges on particle surfaces and dramatically enhance the inter-particle forces, leading to several orders of magnitudes of viscosity increase. Those suspensions are called electrorheological fluids[13] or magnetorheological fluids,[14] and have been explored extensively within last several decades. The dramatic increases of rheological properties are attributed to the crystallized bcc lattice structure formed by polarized particles and induced by the applied external field. The conductive mechanism of electrorheological fluids obey the variable ranges hopping model.[15] The particle volume fractions, which scale how crowded the particles are in a suspension, can induce a very similar viscosity increase, due to a percolation type phase transition.[16] Analogous to charged colloidal particles, the electrons, if have a physical shape, can be easily polarized under either an electric or magnetic field and might easily form a crystallized structure, which may strongly control the conductivity, even superconductivity properties of materials.

The Eyring's rate process theory is based on quantum mechanics,[17] and has been widely used in many fields since it was first incepted in 1935.[18–20] In the article titled "Quantum statistical theory of rate process" published in 1972 by Eyring,[17] many rate processes like diffusion, dielectric relaxation, electron transfer reactions, nonradioactive decay, resonance energy transfer, and many other thermally activated motions, were generically treated with quantum mechanical approach, and the obtained rate constant equations have a very similar form as the original rate constant equations obtained from the absolute reaction rate theory.[18] Although Eyring's simple and elegant treatment approaches have been fiercely criticized from day one, the success in resolving many fundamental problems like chemical reaction rate, viscosity and diffusion, electrochemical process, and biophysics, etc.., has demonstrated again that the truth is alway simple and his approaches are powerful and accurate, indeed. Especially, Eyring's rate process theory has been confirm to work not only for classical systems like molecular diffusions but also quantum mechanical electrons like electron transfer reactions.[21] When dealing with electron transfer or transport from one species to another, which plays significant role in all of respiration, photosynthesis, and biochemical reactions, Marcus theory of electron transfer clearly shows that electron transport rate obeys essentially the same equation as described with Eyring's rate process theory.[22–24] The quantum mechanical treatments of electron transfer reaches a same exponential term in rate equation as predicted by the classical Marcus model,[25] indicating that the rate process theory can be effectively employed to describe electron transport, though quantum tunneling effect is recognized to make functional contributions in certain biological processes.[26–29] Marcus' electron transfer theory further supports that the rate process theory holds for quantum mechanical electrons.

The free volume concept has been widely employed in chemistry and physics fields with great success in determining various equilibrium properties of both liquids[30] and solids.[31] The free volume is the space unoccupied by atoms in materials or particles in colloidal suspensions, providing freedoms for atoms or particles to relax or re-orientate under stimulations. Successful examples include explaining the location of melting transition,[32] the glass transition temperatures of polymers,[33] and the yield stress of electrorheological fluids under an external electric field,[34] etc.. Together with Eyring's rate process theory, the free volume theory is successfully utilized to describe the viscosity of colloidal suspensions with and without an electric field.[35] The idea is very simple: The free volume unoccupied by the particles in suspensions determine the free "walking" distance of particles, and the process of particles traveling from one equilibrium position to another is considered to obey Eyring's rate process theory[36]; The viscosity of whole systems is inversely proportional to the available free volume and the rate of particle motions. Instead of trying to figure out the exact multiple-particle interaction forces, the impact of surrounding particles is grouped into the average "free volume " available to each particle. If many random, disordered, and multi-body systems can be well treated with Eyring's rate process theory, especially for quantum mechanical electron transfers between different species under Marcus' framework, the electrical conductivity that frequently involves electron transport could be treated with Eyring's rate process theory, too. Such an attempt is made in this article with the aid of the free volume concept. The obtained conductivity equations seem able to describe many distinctive conductive behaviors, especially the superconductivity, at low temperatures.

Electrical conductive behaviors of various materials, especially at low temperatures, are extremely rich and fascinating. There are many models or theories proposed so far to understand the puzzling conductive phenomena, and one of the most successful microscopic theories is BCS theory for superconductivity proposed in 1957.[2,37] However, as indicated in literature,[38,39] the BCS theory only can apply for the very special case of electron-phonon coupling, limiting to the lowest temperature superconductors called conventional superconductors. The conductive behaviors of high temperature superconductors, the iron-based superconductors, and topological insulators/conductors, etc., classified as unconventional superconductors, need many new theoretical frameworks to explain, as each requires a different physical picture to describe. There is no a single theory that can provide a reasonable explanation to all those fascinating conductive behaviors, which prompts us to utilize unconventional approach for deriving conductive equations from a more generic and fundamental basis.

II. THEORY

The conductivity, σ, can be expressed as[40]:

$$\sigma = eN_c\frac{v_d}{E} \tag{1}$$

where e is the charge of an electron, N_c is the number of conduction electrons, v_d is the drift velocity of electrons, and E is the applied electric field. For calculating conductivity, one may need to determine the drift velocity, v_d. Assume that an electron moving from one equilibrium position to another obeys Eyring's rate process theory, then according to Eyring,[36] a reactant molecule(an electron in this article) should cross a potential barrier (the activation energy) in order to react with another molecules and produce the final product. As illustrated in Fig.1, when an external electric field is applied, this activation energy is reduced by an amount of αw, making the reaction much easier in the forward direction. However, the potential barrier will be raised by an amount of $(1-\alpha)w$ in the backward (reverse) direction, where w is the amount of work done in moving an electron from one equilibrium position to the next, and α is a fraction operative between the initial and activated states. In his late article published in 1958,[41] Eyring pointed out that in condensed systems, α is directly related to the coordinate number (c_n) of a molecule in the system with the relationship, $\alpha = 1/c_n$. The number of electrons crossing the energy barrier in unit time in the electric field direction should be given:

$$\text{Rate in the forward direction} = K^{+}\lambda[\exp\frac{\alpha w}{k_B T}] \tag{2}$$

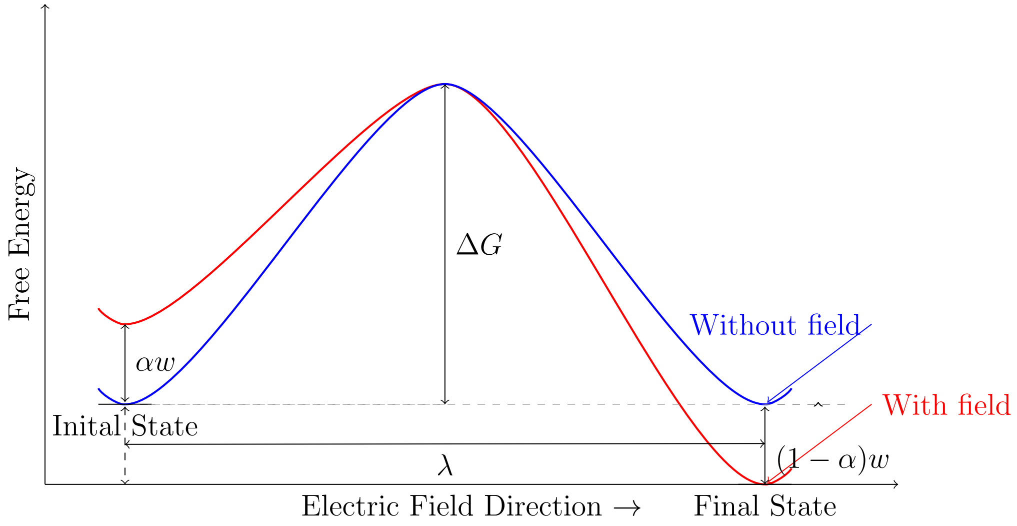

FIG. 1: Illustrative diagram for activation potential energy with and without an electric field

Where $K^{+} = \frac{k_B T}{h} \exp(-\Delta G/RT)$, is the specific velocity rate in any direction for the undisturbed system, k_B is the Boltzmann constant, ΔG is the standard Gibbs free energy of the activation process, R is the gas constant, h is the Planck constant, and λ is the distance between the initial equilibrium position to the final position. In analogy, the number of electrons crossing the energy barrier in unit time in the reverse direction should be given:

$$\text{Rate in the backward direction} = K^{+}\lambda[\exp \frac{-(1-\alpha)w}{k_B T}] \tag{3}$$

The net rate, the velocity of an electron in the direction of an applied electric field, is thus written as:

$$\text{Net Rate } = K^{+}\lambda[\exp \frac{\alpha w}{k_B T} - \exp \frac{-(1-\alpha)w}{k_B T}] = v_d \tag{4}$$

By the definition, the work needs to move an electron in a distance λ under an electric field, E, may be expressed as:

$$w = e\lambda E \tag{5}$$

Combining Eqs.4 and 5, one may obtain the velocity of an electron:

$$v_d = K^{+}\lambda[\exp \frac{\alpha e\lambda E}{k_B T} - \exp \frac{-(1-\alpha)e\lambda E}{k_B T}] \tag{6}$$

Now, one may need to determine λ, the distance that an electron can travel from one equilibrium position to the next. It should be related to how much the free volume is available for a conduction electron in systems. According to standard solid state physics, the Fermi wavevector (radius) k_F can be expressed as[40]:

$$k_F = (\frac{3\pi^2 N_v}{V_u})^{1/3} \tag{7}$$

Where N_v is the number of valence electrons in one unit cell and V_u is the volume of unit cell. Assume that the conduction electrons can only take the space outside the Fermi spheres and all electrons initially stay inside Fermi surface. In one unit cell, the free volume V_c available may be expressed as:

$$V_c = V_u - V_F \tag{8}$$

Where V_F is the volume of Fermi sphere that can be expressed as:

$$V_F = \frac{4\pi}{3} {k_F}^{-3} = \frac{4V_u}{9\pi N_v} \tag{9}$$

Thus Eq. 8 can be expressed as:

$$V_c = (1 - \frac{4}{9\pi N_v})V_u \tag{10}$$

If the number of unit cells in a material is N_u, and the total volume of the material under consideration is V_m, the total free volume V_f:

$$V_f = N_u V_c = (1 - \frac{4}{9\pi N_v})N_u V_u = (1 - \frac{4}{9\pi N_v})V_m \tag{11}$$

as $N_u V_u = V_m$ by definition. The V_f is the free volume that all conduction electrons can have in the whole material body, V_m. As mentioned in Section I, the electrons may be considered as spherical shape particles dispersed in a continuous ”solid atomic lattice”, similar to colloidal particles dispersed in a continuous liquid medium. In this scenario, we may be able to estimate the effective radius of an electron based on the free volume shown in Eq. 11 by utilizing a same analogous method for calculating the free volume in colloidal suspensions. Hao has developed a method for calculating the free volume of particulate systems using the inter-particle spacing (IPS) concept.[13,35,42] The inter-particle spacing (IPS) that scales the distance between two particle surfaces was used for estimating the free volume of whole systems to derive the viscosity of colloidal suspension systems.[13,35] For estimating IPS, Hao[42] used Kuwabaras cell model[43] that was extended by many other researchers[44–46] for calculating the electrophoretic and electroacoustic mobility of particles. The obtained IPS may be expressed as:

$$IPS = 2(\sqrt[3]{\phi_m/\phi} - 1)r \tag{12}$$

where r is the effective radius of an electron, ϕ_m is the maximum packing volume fraction achieved by the conduction electrons, and ϕ is the volume fraction of conduction electrons. Suppose that an electron can move three dimensionally on both left and right sides, the free volume of such an electron may occupy can be expressed as:

$$V_{fe} = (2IPS)^3 = 64(\sqrt[3]{\phi_m/\phi} - 1)^3 r^3 \tag{13}$$

Eq. 13 gives the free volume of each individual conduction electron. If the number of conduction electrons in the whole system is N_c , then the total free volume is:

$$V_f = V_{fe} N_c = 64 N_c(\sqrt[3]{\phi_m/\phi} - 1)^3 r^3 \tag{14}$$

Note that Eq.11 should be identical to Eq.14, one thus can obtain the effective radius of an electron:

$$r = \frac{1}{12(\sqrt[3]{\phi_m/\phi} - 1)}[\frac{(27\pi N_v - 12)V_m}{\pi N_c N_v}]^{1/3} \tag{15}$$

Since an electron may move both left and right sides with the distance of IPS, the equilibrium distance of an electron can travel, λ, may be expressed as:

$$\lambda = 2IPS = \frac{1}{3}[\frac{(27\pi N_v - 12)V_m}{\pi N_c N_v}]^{1/3} = [\frac{(9\pi N_v - 4)V_m}{9\pi N_c N_v}]^{1/3} \tag{16}$$

Now, we have the velocity of conduction electrons as shown in Eq. 6, the distance that a conduction electron can travel as shown in Eq.16, one may easily obtain the conductivity equation based on Eq.1:

$$\begin{aligned}\sigma &= \frac{eN_cK^+\lambda}{E}[\exp\frac{\alpha e\lambda E}{k_BT} - \exp\frac{-(1-\alpha)e\lambda E}{k_BT}] \\ &= \frac{ek_BTN_c^{2/3}}{hE}\exp(\frac{-\Delta G}{RT})[\frac{(9\pi N_v - 4)V_m}{9\pi N_v}]^{1/3}[\exp\frac{\alpha e\lambda E}{k_BT} - \exp\frac{-(1-\alpha)e\lambda E}{k_BT}] \\ &= \frac{ek_BTN_c^{2/3}}{hE}\exp(\frac{-\Delta G}{RT})[\frac{(9\pi N_v - 4)V_m}{9\pi N_v}]^{1/3} \\ &\quad [\exp\frac{\alpha eE}{k_BT}[\frac{(9\pi N_v - 4)V_m}{9\pi N_v N_c}]^{1/3} - \exp\frac{-(1-\alpha)eE}{k_BT}[\frac{(9\pi N_v - 4)V_m}{9\pi N_v N_c}]^{1/3}]\end{aligned} \tag{17}$$

As one may see, the conductivity has complicated relationships with the number of valence electrons in unit cell, N_v; the number of conduction electrons in whole system, N_c; the volume of a material under study, V_m; A parameter related to the structures that electrons may form, α; the standard Gibbs free energy, ΔG; and the most importantly, the temperature, T. In thermodynamics, the Gibbs free energy, ΔG, has a relationship with the equilibrium constant, K_{eq}:

$$-\Delta G = RT\ln K_{eq} \tag{18}$$

$$K_{eq} = \exp\frac{-\Delta G}{RT} \tag{19}$$

We may be able to use the equilibrium constant K_{eq} to replace the Gibbs free energy term in Eq.17. As we mentioned earlier, in condensed systems, α is related to the coordinate number of an electron in the system, c_n, with a simple relationship;

$$\alpha = \frac{1}{c_n} \tag{20}$$

When $c_n = 1$, then $\alpha = 1$. At this condition, electrons form pairs, and the conductivity equation Eq.17 may be written as:

$$\sigma = \frac{ek_BTN_c^{2/3}}{hE}\exp(\frac{-\Delta G}{RT})[\frac{(9\pi N_v-4)V_m}{9\pi N_v}]^{1/3}[\exp\frac{eE}{k_BT}[\frac{(9\pi N_v-4)V_m}{9\pi N_vN_c}]^{1/3}-1] \tag{21}$$

When $c_n = 4$, then $\alpha = 1/4$. At this condition, electrons form tetrahedron lattice structure, and the conductivity equation Eq.17 may be written as:

$$\begin{aligned}\sigma = \frac{ek_BTN_c^{2/3}}{hE}\exp(\frac{-\Delta G}{RT})[\frac{(9\pi N_v-4)V_m}{9\pi N_v}]^{1/3}&\\ [\exp\frac{0.25eE}{k_BT}[\frac{(9\pi N_v-4)V_m}{9\pi N_vN_c}]^{1/3}-\exp\frac{-0.75eE}{k_BT}[\frac{(9\pi N_v-4)V_m}{9\pi N_vN_c}]^{1/3}]&\end{aligned} \tag{22}$$

When $c_n = 8$, then $\alpha = 1/8$. At this condition, electrons form body-centered cubic (bcc) lattice structure, Wigner crystal at 3D,[3] and the conductivity equation Eq.17 may be written as:

$$\begin{aligned}\sigma = \frac{ek_BTN_c^{2/3}}{hE}\exp(\frac{-\Delta G}{RT})[\frac{(9\pi N_v-4)V_m}{9\pi N_v}]^{1/3}&\\ [\exp\frac{0.125eE}{k_BT}[\frac{(9\pi N_v-4)V_m}{9\pi N_vN_c}]^{1/3}-\exp\frac{-0.815eE}{k_BT}[\frac{(9\pi N_v-4)V_m}{9\pi N_vN_c}]^{1/3}]&\end{aligned} \tag{23}$$

We will evaluate all these situations in a more generic manner in next section, for the purpose of extracting what are the generic trends/correlations between the conductivity and all those parameters in the equations.

III. RESULTS

It would be insightful to compare the obtained equations with the experimental data for demonstrating the applicability of the derived equations in a quantitative manner. An Iron-based superconductor is selected for the reason that this type of superconductors is still surprising even nine years after the initial discovery.[47–50] The resistivity of $\alpha - FeSe$ against the temperature shown in the Figure 3 of the literature[51] is selected for comparison, only because this article is widely cited and readily available. The experimental data points and the regression computed with Eq. 21 is shown in Fig. 2. Since the superconductivity is centered in this comparison, Eq. 21 with $\alpha = 1$ is used for regression. The best fit comes with the assumptions that $\alpha = 1$, $\frac{ek_BN_c^{2/3}}{hE}\exp(\frac{-\Delta G}{RT})[\frac{(9\pi N_v-4)V_m}{9\pi N_v}]^{1/3} = 10^4$, and $\frac{eE}{k_B}[\frac{(9\pi N_v-4)V_m}{9\pi N_vN_c}]^{1/3}] = 18$. Note that only the experimental data at transition area is focused on for concisely

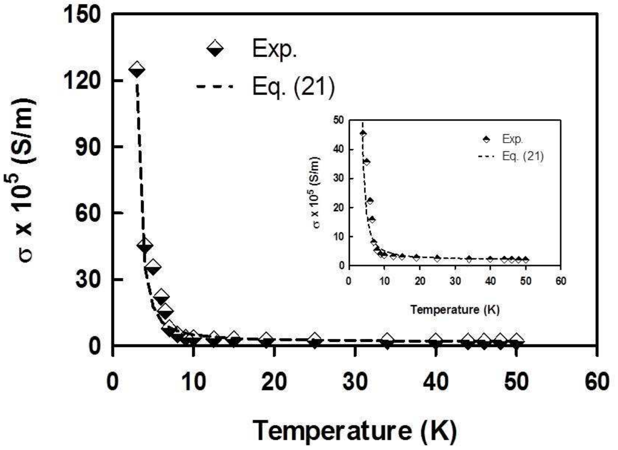

FIG. 2: Conductivity of $\alpha-FeSe$ vs. temperature obtained experimentally and predicted with Eq. 21. $\alpha=1$, $\frac{ek_BN_c^{2/3}}{hE}\exp(\frac{-\Delta G}{RT})[\frac{(9\pi N_v-4)V_m}{9\pi N_v}]^{1/3}$ is assumed to be 10^4. The term $\frac{eE}{k_B}[\frac{(9\pi N_v-4)V_m}{9\pi N_vN_c}]^{1/3}]$ is assumed to be 18. The experimental data points are taken from Fig.3 in the literature.[51]

demonstrating how Eq. 21 would fit the experimental data; the inset in Fig. 2 shows the same data points at further small scales. The purpose is to provide as clear comparison as possible, and y-axis range thus has be kept small. We have to say that Eq. 21 fits the experimental data very well.

For illustrative comparison purpose, one may need to further simplify the conductivity equations listed in the section II based on some approximations. The low temperature regions will be focused on due to the rich and fascinating conductive behaviors. First, let's concentrate on temperature dependence. The electron traveling distance, λ, should vary with temperature, on the basis of Fermi-Dirac distribution function with the relations $N_v \propto T^{3/2}$, $N_cN_v \propto T^3$, and $\lambda \propto T^{-1/2}$ approximately.[52] Since the temperature range in the evaluation below is very narrow, it would be reasonable to assumed that the electron traveling distance is independent of temperature for simplicity and easy evaluation purpose, assigned as about 100 nanometers as a starting point. The sole purpose is to present some ideas on how these equations work. So $eE\lambda/k_B$ is about 10 for a small electric field, 10 V/mm. The term ek_B/Eh is in the orders 10^{-13}. The number of conduction electrons per unit volume is $\sim 10^{23}$, about one conduction electron per atom. The equilibrium constant $\exp(\frac{-\Delta G}{RT})$ is usually a fairly large number, typically $\sim 10^4$. So the term $\frac{ek_BN_c^{2/3}}{hE}\exp(\frac{-\Delta G}{RT})[\frac{(9\pi N_v-4)V_m}{9\pi N_v}]^{1/3}$

is $\sim 10^5$. The term $\frac{eE}{k_B}[\frac{(9\pi N_v-4)V_m}{9\pi N_v N_c}]^{1/3}]$ is ~ 10. Under those approximations, the conductivity equation may be written as:

$$\sigma = AT[\exp\frac{10\alpha}{T} - \exp\frac{-10(1-\alpha)}{T}] \tag{24}$$

where A is a constant, $\sim 10^5$. The constant 10 comes under assumption that the electron traveling distance is assumed to be 100 nm; It will be 1 if the electron traveling distance is assumed to be 10 nm. Note that the predicted conductivity from Eq. 24 will be divergent if the temperature is equal to zero, which will be contradictory to Eq.1. However, according to the 3rd laws of thermodynamics,[53] it is impossible to reduce any systems to absolute zero temperature in a finite series of operations. In other words, the temperature can never be zero and the predicted conductivity from Eq. 24 can never be divergent, thus there is no conflict between Eq.24 and Eq. 1. On the other hand, Eq. 24 further assures that the zero temperature cannot be achieved; otherwise it will be unnecessary divergent and contradict to the fundamental conductivity equation, Eq.1. For simplicity and easy comparison reason, A will be considered as 1 when we plot figures. Using Eq. 24, one may easily see how conductivity is going to change with temperature, which is shown in Fig. 3. Three electron condensation structures are evaluated: the electron pairs, the tetrahedron lattice, and the bcc lattice. First, under all those three conditions, there seem to be a sharp conductivity increase when the temperature approaches to zero: When electrons form pair structures, the conductivity slowly increases with temperature decrease and suddenly starts to jump up when the temperatures reach a critical point, about 5 K, which may be the transition point for superconductivity. When electrons form tetrahedron lattice structure, an abnormal phenomenon appears: the conductivity decreases with the decrease of temperature, opposite to the situation when electrons form pair structures. However, there is still a sharp conductivity increase but occurring at a much lower transition temperature, less than 1 K. When electrons form Wigner crystals of bcc lattice structures, again the conductivity decreases with the decrease of temperatures and sharply increases when the temperature is very close to zero. Very similar conductive behaviors are demonstrated when electrons form Tetrahedron or Wigner crystal structures, which is remarkably different from that when electrons form pair structures. Those findings at

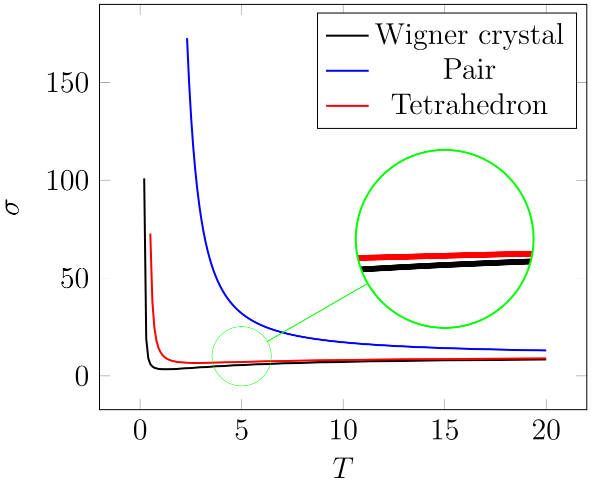

FIG. 3: Conductivity vs temperature at different lattice structures predicted with Eq. 24 under an assumption that the electron traveling distance is 100 nm. The parameter A is $\sim 10^5$ but $A = 1$ is assumed in the plot for simplification reason. The coordinate number is 1 for pair structures, 4 for tetrahedron structures, and 8 for Wigner crystal (bcc) lattice structures.

least demonstrate three things: 1) Electron pair structures seem to favor superconductivity behaviors, which is in consistence with the Cooper pair concept in BCS theory for superconductivity[2]; 2) The conductive behaviors are strongly dependent on the coordinate numbers of an electron may attain; a small increase of the coordinate number seems to have a dramatic impact and may change the conductivity from increase to decrease when temperatures are lowered; 3) With electron coordinate numbers increasing from 1 to 8, the transition temperatures move toward to lower regions, implying that electron trapping or localization from the formed crystalline structures may become a great hindrance for electron movements.

For further elucidating the trends, 3D plots are used to illustrate the conductivity vs. both the temperature and α, first under the presumption that the electrons can still travel 100 nm from one equilibrium position to another, computed with Eq. 24 and shown in Fig.4; second under the presumption that the electrons may travel a smaller distance, 10 nm, shown in Fig.5 and computed with a same equation: Eq. 24. As clearly demonstrated in Fig. 4, a sharp conductivity increase that may represent the superconductivity transition, occurs at low temperature regions and at α about 1; when temperatures are relatively high, the conductivity is flat and low, independent of the values of α. If the electron traveling distance is as low as 10 nm, as shown in Fig.5, the conductivity only increase a little bit when the temperatures are low

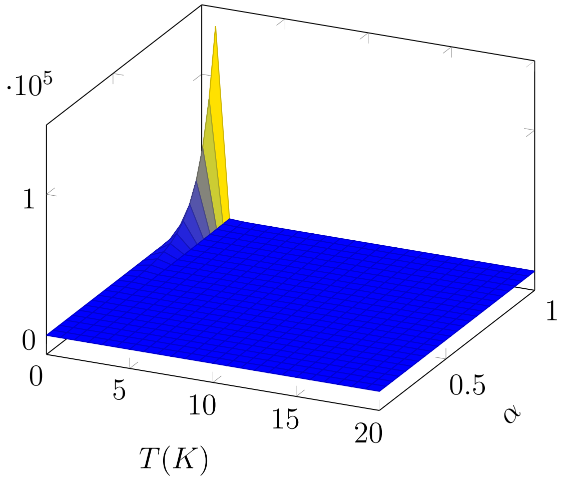

FIG. 4: Conductivity vs both temperatures and the structure related parameter α at electron traveling distance about 100 nm. The prediction is based on Eq. 24. The parameter A is $\sim 10^5$ but $A = 1$ is assumed in the plot for simplification reason

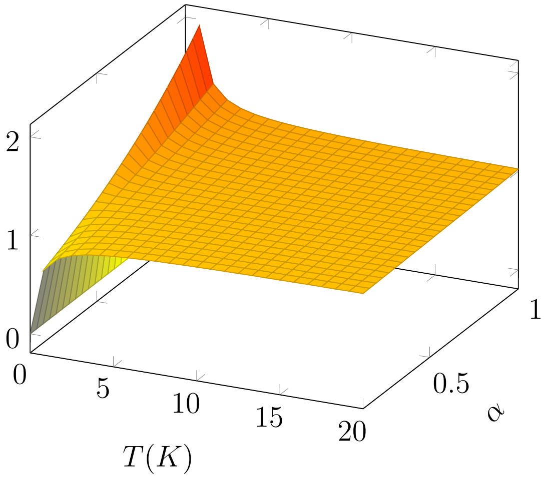

FIG. 5: Conductivity vs both temperatures and the structure related parameter α at electron traveling distance about 10 nm. The prediction is based on Eq. 24. The parameter A is $\sim 10^5$ but $A = 1$ is assumed in the plot for simplification reason

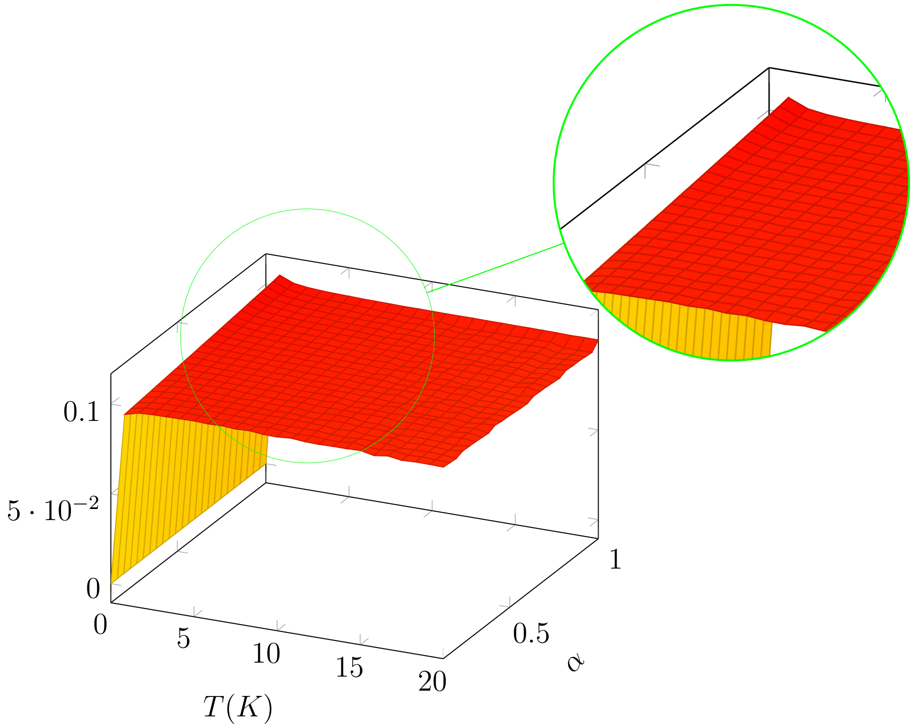

FIG. 6: Conductivity vs both temperatures and the structure related parameter α at electron traveling distance about 1 nm. The prediction is based on Eq. 24. The parameter A is $\sim 10^5$ but $A = 1$ is assumed in the plot for simplification reason

and in addition α is about 1; The conductivity increment at such conditions is very low in comparison with that when the electron traveling distance is 100 nm. An intriguing thing happens when both temperature and α are low, the conductivity actually decreases sharply instead increases, which is opposite to superconductivity transition. As one may know, the Mott transition is resulted from the Coulombic repulsion among electrons and the degree of electron localization (band width).[54,55] Low α means that each electron may have high coordinate number and associates with many other electrons under certain crystalline bonding structures. Electrons could be localized if the "crystalinity energy" created by other associated electrons is strong enough. The conductivity thus should decrease dramatically, as electrons are trapped and unable to move freely. The phenomenon shown in Fig. 5 seems to correspond to the Mott transitions observed in many transition metal oxides at low temperatures.[54]

In the light of the physical size and quantum mechanical nature of electrons, 10 nm is still a huge distance for electrons to travel. However, the resulted conductivity already starts to sharply decrease as demonstrated in Fig. 5 at such a long traveling distance for electrons. What happens if the electron traveling distance further goes down to 1 nm? The illustrative graph computed with Eq. 24 is shown in Fig. 6. In this case, the conductivity goes down substantially even when $\alpha = 1$. As one may already realize, at such conditions electrons only form pair structures and the obstruction to electron movement from the "crystalinity energy" created by another associated electron should be pretty weak, but apparently strong enough to localize electrons. This seems to contradict with what one may conclude from Fig. 5: the electron-electron interaction or called the electron confounding/confinement effect only becomes strong enough, when each electron has a relative large coordinate number and then the formed "crystalline structures" may be able to trap or localize electrons, preventing electrons from transporting freely. In contrast, what is demonstrated in Fig. 6 is that everything seems to completely stop, probably not due to the strong localization resulted from the other coordinated electrons, but something else like strong interferences between paired electrons due to the quantum mechanical nature of electrons. Such a kind of localization seems to be very similar to the Anderson localization that has been explored extensively in disordered materials since it was first proposed in 1958.[56–58] If what we postulated above is correct, one may come to the conclusion that the Mott localization may be resulted from crystalline structures formed by electrons in low temperatures, corresponding to the low α region in both Fig. 5 and Fig. 6; while the Anderson localization may be resulted from the strong interference between electrons at high α regions as shown in Fig. 6.

Another intriguing phenomenon shown in Fig. 6 is that when electrons form pair structures at $\alpha = 1$, the conductivity seems to slowly increase as temperature approaches to zero, go through a maximum, and then suddenly drop off; the conductivity peak could become much more pronounced if the electrons only can travel even smaller distance, less than 1nm. In low α regions, there is no such a kind of conductivity bump. This phenomenon seems to correspond to the Kondo effect observed in metallic alloy doped with magnetic impurities[59] and resulted from a strong spin-spin coupling between two electrons,[60,61] once again, the interaction or interference resulted from the electron pair structures. Theoretically, Anderson localization model at low temperatures is found to be equivalent to what has been discussed for Kondo model,[62,63] and the similarity seems to be demonstrated in Fig. 6 at low temperatures, low traveling distances, and high α for electrons.

As demonstrated earlier, the electron pair structures usually favor superconductivity when electrons are assumed to travel a relatively long distance as shown in Fig. 4; while it could induce Kondo transition when electrons can only travel a very short distance as shown in Fig. 6. The Cooper pair that is the essence of BCS theory for superconductivity and the spin-spin coupling that is the main culprit for Kondo effect seem to contradict each other, but are harmonically correlated in our current conductivity equations: same electron pair structures but different traveling distance could produce remarkable even opposite conductive behaviors. If this coincidence is true, it may imply that Kondo insulators could potentially be very good superconductors as well, as the electron pair structures are already formed and only thing needed is to let electrons travel a relatively long distance; On material surfaces, electrons could potentially travel a much longer distance than the electrons in the interior. The reason may be pretty simple: there are only half amount of atomic sites and thus half amount of electrons available on material surfaces than interiors; electrons thus have less chances of being hindered or localized and transport more freely on surfaces. Therefore, the Kondo insulators and superconductors could potentially co-exist together on a material, with surfaces of superconductivity and interior of Kondo insulation. Theoretically predicted and experimentally confirmed existence of topological insulators,[64–66] where the surfaces show high conductivity properties and the interior is Kondo insulator, may support what we just postulate. The very recent evidences indicate that the superconductivity do exist on the surfaces of topological insulators both theoretically[67,68] and experimentally,[69] further supporting this surprising postulation. In the interior of topological insulators all paired electrons are strongly localized probably due to the strong electron-phonon interactions; However, on the surfaces the electron-phonon interactions may become weak due to only half amount of atomic sites available to hinder the electron movements. If this physical picture is true, a material containing an element of a high electro-negativity or high ionization energy like oxygen and fluorine and an element of a low electro-negativity or low ionization energy like Caesium, Barium, and Francium, etc., may form a good topological insulator. An element of a high electro-negativity will ensure that electrons can be strongly pulled together to form pairs, while an element of a low electro-negativity will not hinder the electron movements too much, so electrons can travel a relatively long distance and the surfaces will show superconductivity. The ratio between those two elements could be critical, too, as we don't want too many atoms of a high electro-negativity in the systems to hold off the electron movements. In the meanwhile, since Kondo insulators are potentially good superconductors, any magnetic element like Iron, Nickel, and Cobalt, that has unpaired electrons and can induce Kondo insulator as a dopant, could be a very good superconductor candidate once it is bonded with other proper elements of low electro-negativity. The discovery of Iron-based superconductors called ferropnictides[47,70–72] usually contain iron and other elements of a high electro-negativity or high ionization energy like oxygen and fluorine, supporting the statements above derived from the conductivity equations.

The electron traveling distance seems to play a critical role in conductivity. It would be interesting to see how conductivity is going to change with the electron traveling distance, λ, especially when electrons form pair structures, as this is the most favorable condition for superconductivity.

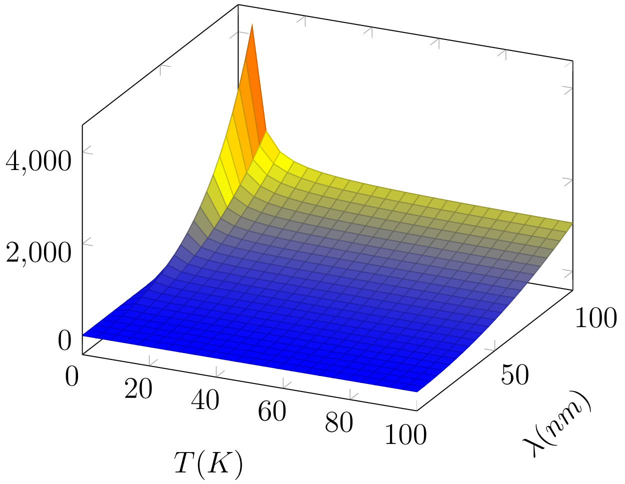

FIG. 7: Conductivity vs both temperatures and electron traveling distance, λ, when electrons pair each other. The prediction is based on Eq. 24. The parameter A is $\sim 10^5$ but $A = 1$ is assumed in the plot for simplification reason

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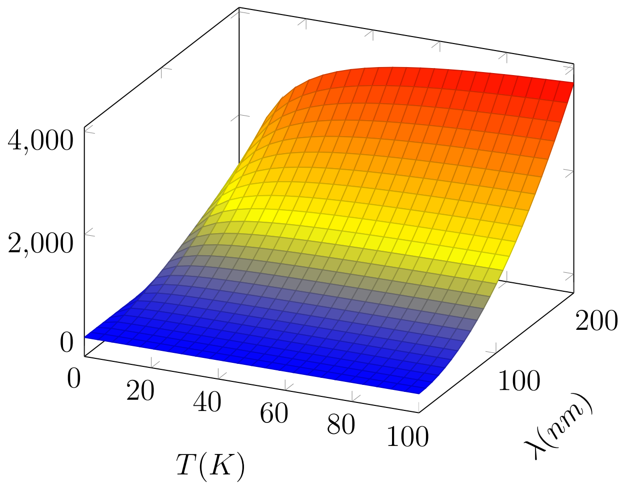


FIG. 8: Conductivity vs both temperatures and electron traveling distance, λ, when Wigner crystal forms. The prediction is based on Eq. 24. The parameter A is $\sim 10^5$ but $A = 1$ is assumed in the plot for simplification reason

The predicted conductivity with Eq. 24 is plotted against both temperature and electron traveling distance and shown in Fig. 7, under an assumption that electrons form pair structures. As expected, the conductivity increases with the increase of λ, and superconductivity appears when the temperature is low and electrons can travel a long distance like $100nm$. Note that the superconductivity transition temperatures seem to shift to higher temperature regions when electrons are able to travel a long distance, which may give some clues on what drives high temperature superconductivity. In other words, if electrons can form pair structures and are able to travel a relatively long distance, the superconductivity may appear at higher temperatures. This is an important prediction, clearly revealing why some superconductors have a high transition temperature and which physical parameter contributes to. It may suggest that for searching high temperature superconductors attention should be put on materials of high electron velocity.

For curiosity, what happens if Wigner crystal forms and the electron traveling distance λ is large? The graph computed with Eq. 24 is shown in Fig. 8. Again, the parameter A is assumed to be 1. Without a surprise, the conductivity becomes larger when λ increases, but becomes smaller when temperature goes down. A remarkable decrease occurs at higher λ and low temperatures, probably implying that electron interaction or interference may become more pronounced at low temperature and higher traveling distances.

The conductivity obviously has something to do with the volume of a material, as demonstrated in Eq. 17. We will use the conductivity equation, Eq. 21, to evaluate the relationship between the conductivity and the volume of the material, still under the assumption that electrons form pair structures, as this condition will give more relevant information on superconductivity. The conductivity dependence on both temperature and the volume of a material is shown in Fig. 9. The conductivity increases very slightly when the volume of the material becomes large at high temperature regions, and increases quite substantially at low temperature regions. The external high pressure that typically shrink materials may lower the conductivity, foreseeably lowering the superconductivity transition temperature too. However, under extremely high pressures, the electron density must increase for maintaining the stability of chemical bonds; Such an increase in electron density comes laterally from the region normal to the bond,[73,74] providing more valence electrons and potentially bringing the superconductivity transition temperature higher. Those physical scenarios are qualitatively consistent with the experimental observation on how an external pressure would change the superconductivity transition temperatures[75,76]: most times high pressures initially lower superconductivity transition temperatures and then raise them up once the pressures further increase. The consistency shown here further demonstrates again that our equations may truly grasp the underlying physical mechanisms of conductivities.

The conductivity may have a complicated relationship with the numbers of conduction electrons and valence electrons. The impact of the numbers of both the valence electrons in unit cell and the conduction electrons in whole system is shown in Fig. 10, computed with Eq. 21. The number of conduction electrons has a deep impact on conductivity as shown in Fig. 10 (a): the conductivity dramatically increases when the number of conduction electrons reach a certain level, a phenomenon similar to the percolation transition observed in amorphous systems. In contrast, the valence electrons only show a huge impact on conductivity at low temperature regions very close to zero temperature with a gradual manner, but almost no impact at higher temperature regions, see Fig. 10 (b)). This may imply that at very low temperatures the valence electrons may participate the conduction as well.

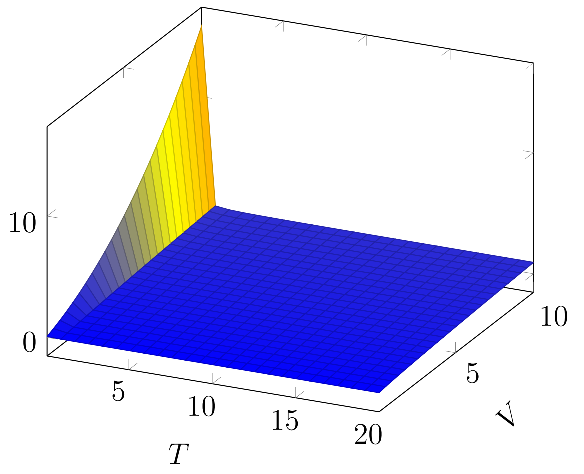
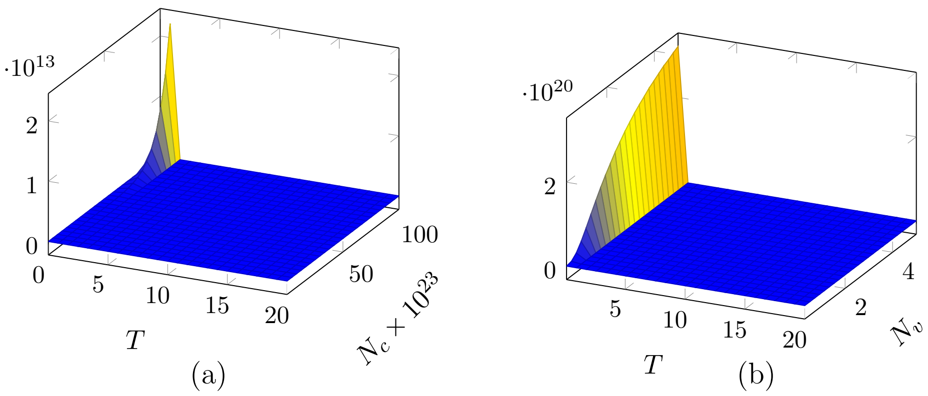


FIG. 9: Conductivity vs both temperature and the volume of a material. The prediction is based on Eq. 21. The term $\frac{ek_B N_c^{2/3}}{hE}\exp(\frac{-\Delta G}{RT})[\frac{(9\pi N_v-4)}{9\pi N_v}]^{1/3}$ is assumed to be 1, and therm $[\exp\frac{eE}{k_B}[\frac{(9\pi N_v-4)}{9\pi N_v N_c}]^{1/3}]$ is assumed to be 0.2 in the plot for simplification reason.



(a) (b)

FIG. 10: (a) Conductivity vs both temperature and number of conduction electrons, N_c; The term $\frac{ek_B}{hE}\exp(\frac{-\Delta G}{RT})[\frac{(9\pi N_v-4)V_m}{9\pi N_v}]^{1/3}$ is assumed to be 1, and the term $[\exp\frac{eE}{k_B}[\frac{(9\pi N_v-4)V_m}{9\pi N_v}]^{1/3}]$ is assumed to be 5; (b) Conductivity vs both temperature and number of valence electrons, N_v . The term $\frac{ek_B N_c^{2/3}}{hE}\exp(\frac{-\Delta G}{RT})$ is assumed to be 1, the term $[\frac{4V_m}{9\pi N_c}]$ is estimated to be 0.142. All predictions are based on Eq. 21

.

The important question is of course how we can have a superconductor with higher transition temperatures and what implications we may obtain from the newly derived conductivity equations. From all figures shown in Fig. 3 to Fig. 10, one may easily come up that the longer traveling distance for electrons, the larger number of conduction electrons, the larger number of valence electrons, and most importantly the electron pair structures, probably will favor superconductors of higher transition temperatures. From Fig. 9, one may conclude that the volume decrease of a material such as from the bulk to a thin film, the transition temperature could be lowered, which has been confirmed experimentally.[77–79] We may not be able to control the electron condensation structure at this moment, but we may be able to do it in the future with new technologies that can help us better manipulate and monitor. If we can increase the numbers of both conduction and valence electrons using extremely thin epitaxy film deposited on a substrate, we may be able to increase the superconductivity transition temperatures, as confirmed experimentally.[80,81] The negative impact from the material volume decrease possibly is well compensated from the dramatical conductivity increase from more conduction and valence electrons.

IV. DISCUSSION

The main conductivity equation derived in this article is shown in Eq. 17, and other equations shown in Eq. 21, 22, and 23, are just special cases of Eq. 17. Eq. 24 is an approximated form of Eq. 17, and is used for illustrative purpose for readers to gain some ideas how the obtained equations looks like. All conductivity equations indicate that the temperature cannot be zero; Otherwise the predicted conductivity will be divergent, which contradicts to Eq. 1. On the basis of the 3rd law of thermodynamics, we never can reach the absolute zero temperature, and the predicted conductivity from all equations can never be infinite. All conductivity equations in this article thus automatically carry a condition of $T \neq 0$. So in reality, there is no divergence, and the predicted conductivity may just be very high at low temperatures due to the low values of T. There is no contradiction to the basic thermodynamic law and to the experimental results.

It is worth emphasizing again that electrons have the particle and wave duality properties. Most researchers are paying a huge attention on the ”wave” properties rather than ”particle” properties, likely due to the rich and overwhelming wave properties of electrons just discovered after the electrons were identified as particles initially. The extremely low electrical dipole moment determined recently[58] and the perfect spherical shape of an electron precisely measured a few years ago[7] may indicate that an electron may be reasonably assumed as a spherical particle of a physical shape. The implication that the extremely small electrical dipole moment would infer an ”spherical” symmetrical shape of electrons is directly from the literature.[7,8] Any question on the duality principle or the shape of electron is out of scope of this article. I simply borrow these results and concepts from other physicists’ work and cautiously use them as assumptions in this article. Even if these experimental results are later found untrue, the assumption that an electron has a physical shape with an effective radius is just an alternative convenient way for calculating the free volume. That is all.

Eyring’s rate process theory has been examined for over 80 years. It holds not only for classical molecular thermal systems but also quantum mechanical electrons as evidenced in literature.[17,37] Marcus’ electron transfer theory has a very similar mathematical form as Eyring’s, further supporting that the Eyring’s rate process theory holds for quantum mechanical electrons and thus can be used for describe rich conductive behaviors mostly involving electron transports.

Free volume theory always employs some odd assumptions like hole in the liquids to explain multi-body phenomena, for example to explain the glass transitions in polymers and many other phenomena in amorphous solids. It is borrowed in this article to treat conductivity issues for estimating the free traveling distance of conduction electrons, due to its impressive power in dealing with the multi-body phenomena. The final equations don’t contain anything related to electron radius.

Our conductive equations present some kind of hints to all novel conductive phenomena like topological insulators, Cooper pairs, Kondo effect, Mott transition, Anderson localization, and so on, as demonstrated from the illustrative graphs from Fig. 3 to 10. For example, from Fig. 3 to 6 the superconductivity transition is observed to only and preferably happen when electrons form pair structures. There is no choice but to attribute this observation to the Cooper pair concept in BCS theory proposed more than a half century ago. Same things happen for Anderson transition, Mott transition, Kondo effect, topological insulators, etc.. I need to find some terms that can be easily understood by condensed matter physics community and in the same time can match what are observed from the derived equations. Discussing those novel phenomena in this article is not merely because they are important in understanding conductivity behaviors. Instead, they are addressed is solely because the illustrative plots from my equations hint me to do so; The connections between what have been already explored and discovered in conductivity areas and what can be deduced from our equations are clearly there, indeed.

In my personal discretion, two criteria may be employed to judge a theory right or wrong: 1) Is the theory consistent with the currently observed experimental phenomena? 2) Does the theory predict something new and provide new insights to the puzzles we have now? As demonstrated in the section III, our equations basically provide hints to all novel phenomena observed so far and can fit the experimental data very well, too. Regarding the predictions, I will present one example inferred from the plots shown in Fig. 3 to 6): a Kondo insulator and a superconductor may co-exist together, as both Kondo insulators and superconductors share a same physical origin—the electron pair structures. The only difference between those two is that in superconductors the electrons can travel a long distance like 100 nm, in comparison with a very short distance like 1 nm in Kondo insulators. If certain conditions allow, like the criteria hypothesized in the section III, the superconductivity presented on the surfaces and Kondo insulation preserved in the interior could be realized experimentally. This is a prediction directly coming from our equations. It is something even unexpected to the author, however, it appears to be true with new evidences revealed very recently, both theoretically[67,68] and experimentally.[69] The study shown in the reference[69] claims that ”by doping the topological insulator, bismuth selenide, with copper, it’s possible to make the topologically ordered electrons superconducting, dropping electrical resistance in the surface states all the way to zero”.

Conductivity, especially superconductivity, is a very complicated issue. There should be no coincidence to obtain an equation very powerful but physically baseless. Our initial motivation is to derive a generic conductivity equation that holds for more materials. However, after the equations were obtained and plotted out at various conditions, I really was surprised but excited to see that the obtained equations are in line with many conductive phenomena at low temperatures. With many supportive experimental results and phenomena dug out from literature, I become more confident on the assumptions used in the article.

Somebody may argue that it is electronic structures of materials and quantum transport nature of electrons that dominate the conductive properties of materials. Yes, I agree. Many researchers have followed this direction and developed many different theories to explain rich and distinctive conductive behaviors. However, my great concern is that each class of materials needs a different theory to cover its conductive behaviors. A theory truly reflecting the underlying physical mechanisms would work not only for Kondo insulators but also for Mott insulators or topological insulators. A theory that only works for certain types of low temperature superconductors but doesn't work for pnictides or high temperature superconductors may miss something important, as the nature doesn't typically operate in this manner. A theory that works for conductive behaviors of all materials is anticipated. It is time to retreat back and think differently from more fundamental basis, which is what I have attempted in this article.

The obtained equations directly suggest that a material containing an element of a high electro-negativity or high ionization energy and an element of a low electro-negativity or low ionization energy may form a good topological insulator: an element of a high electro-negativity could ensure that electrons can be strongly pulled together to form pairs, while an element of a low electro-negativity may not hinder the electron movements too much, so electrons can travel a relatively long distance and the surfaces will show conductivity even superconductivity. Any magnetic element, like Iron, Nickel, and Cobalt, that has unpaired electrons and can induce Kondo effect as a dopant, could be a very good superconductor candidate once it is bonded with other proper elements of low electro-negativity. A typical example is pnictide superconductors. A material of high electron velocity containing chemical elements of high electro-negativity and unpaired electrons may show superconductivity at higher temperature regions. Again, the ratio between the chemical elements of high and low electro-negativities seem to be very important, as high electro-negativity usually means low electron velocity. Both Kondo effect and superconductivity seem to share a same physical origin–the electrons form pair structures but travel different distances at those two cases. The electron pair structures are already formed in Kondo insulators and only thing needed is to let electrons travel a relatively long distance. The topological insulators are naturally expected to exist, with surfaces of conductive even superconductive properties and interiors of insulating properties. The reason may be pretty simple: there are only half amount of atomic sites and thus half amount of electrons available on material surfaces than interiors; electrons thus have less chances of being hindered or localized and may transport more freely on surfaces. Therefore, the Kondo insulators and superconductors could potentially co-exist together on a material. Many of those predictions/suggestions need to be confirmed experimentally.

Although this article is little bit leaning to the low temperature conductive behaviors in the section III, the obtained equations don't have such a limitation, as demonstrated in the section II. There is no any assumption in the derivation procedures that may limit the applicabilities. The equations, Eq. 17, Eq. 21, 22, and 23, should work for both low and high temperature regions.

The particle properties of electrons are paid more attention in this article. However, this by no means indicates that the wave properties of electrons are unimportant. Many phenomena can still be explained with the wave properties of electrons, and both the particle and wave properties of electrons should be equally weighed.

V. CONCLUSION

Under the stimulation of Marcus theory of electron transfer, Eyring's rate process theory and the free volume concept are used to come up conductivity equations under three major assumptions: 1) Electrons are assumed to have a spherical physical shape with an imaginary effective radius; 2) The electron traveling rate is assumed to obey Eyring's rate process theory; 3) The available free volume for each electron is assumed to determine how far electrons may travel from one equilibrium position to the other.

The obtained conductivity equations show that there is a complicated relationship between the conductivity and the electron condensation structure, the electron traveling distance, the numbers of both the conduction and the valence electrons, the volume of the material under investigation, and the most importantly, the temperature. When electrons form pair structures, the predicted conductivity increases with the decrease of temperatures, and the superconductivity occurs when temperature is below a critical point; while when electrons form tetrahedron or Wigner crystal lattice structures, the predicted conductivity decreases when the temperature decreases. Even electrons form pair structures, the predicted conductivity could sharply decrease rather than increase, if the electrons can only travel a short distance, like $1nm$. In the mean while at low temperatures and high α regions, the predicted conductivity may go through a peak, which may correspond to the Kondo effect. The Anderson localization seems to have a lot of similarities as Kondo effect, such as electron pair structures and low traveling distances at low temperatures.

As expected, the conductivity increases with the electron traveling distance, no matter which structures electrons may form, pair, tetrahydron, or Wigner crystal. It increases with the volume of the material, the numbers of both the conduction and the valence electrons. Anything that can change the volume of the material like the pressure and the thin film that may change the numbers of the conduction and the valence electrons, could potentially change the conductivity as well. For obtaining a superconductor with higher transition temperatures, electrons may better form pair structures and are capable of traveling a relatively long distance.

In a word, the derived conductivity equations can well fit the experimental data, provide hints to many novel low temperature conductive phenomena, and offer new insights on the mechanisms of conductivity at low temperatures.

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