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Challenges Confronting High Temperature Superconducting Materials: From Nanoscale Theories to Exascale Energy Applications

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ABSTRACT

We review the present state of the understanding and application of high temperature superconductor materials ranging from attempts to clarify pairing mechanisms on the energy scale of a few milli-electron-volts to their use to embody terra-kwh continental wide deployment within the electricity enterprise. Examples include the use of density functional theory to study the relative roles of spin-fluctuation and/or lattice vibration induced Cooper pairing to modelling the incorporation of long distance HTSC transmission cables within the same natural gas pipeline rights-of-way infrastructure now emerging worldwide.

INTRODUCTION

We begin by noting it is some 28 years since the discovery of high temperature superconductivity (HTSC) in the copper oxide perovskites in late January, 1986 [1]. Much progress has ensued in the interval. We now have materials exhibiting transition temperatures as high as 135 °K [2], and wire/tape manufacturing technologies capable of producing kilometer lengths displaying useful critical field and current values at liquid nitrogen temperatures. In addition, many successful demonstrations of power applications ranging from rotating machinery to long-length transmission/distribution cables have taken place [3]. Nevertheless, unlike conventional low temperature superconducting materials, such as the niobium intermetallics whose microscopic BCS pairing physics are well understood, and which have experienced extensive deployment in medical MRI and deflection/confinement magnets in large hadron colliders, the pairing mechanism yielding superconductivity in the HTSC materials above 30 °K remains poorly understood and their significant commercialization in the electric power sector is yet to be arrive.

METHODOLOGY

The methodologies employed to examine the issues raised in this paper are 1) computational density functional theory [4] along with the EMAD formalism to explore microscopic pairing mechanisms via electron-phonon coupling, and 2) straightforward "engineering economy" models to assess dual use of natural gas pipeline rights-of-way to co-transport electricity via HTSC cables using data freely available from the US Department of Energy [5].

DISCUSSION

The title of this paper employs two "scaling prefixes, nano (10^{-9}) and exa (10^{19})," both of which are intended to qualitatively apply to extremes in energy and distance, as observed at the pairing level compared to those anticipated in power delivery applications . E.g., the superconducting gap of a typical HTSC material is around 10^{-12} erg, whilst the energy delivered in one year by a 1 GW nuclear power plant is approximately $3{\cdot}10^{23}$ ergs. On the other hand, a typical HTSC coherence length is ~ 10^{-9} meter (or 1 nm), and a 6000 km transcontinental cable would stretch about $6{\cdot}10^{6}$ meters (or $6{\cdot}10^{16}$ nm!). We now examine both extremes with respect to the current knowledge regarding HTSC materials.

Nanoscale

The overall nanoscale scenario for HTSC copper oxide and iron pnictide materials is summarized by their phase diagram shown in figure 1 [6].

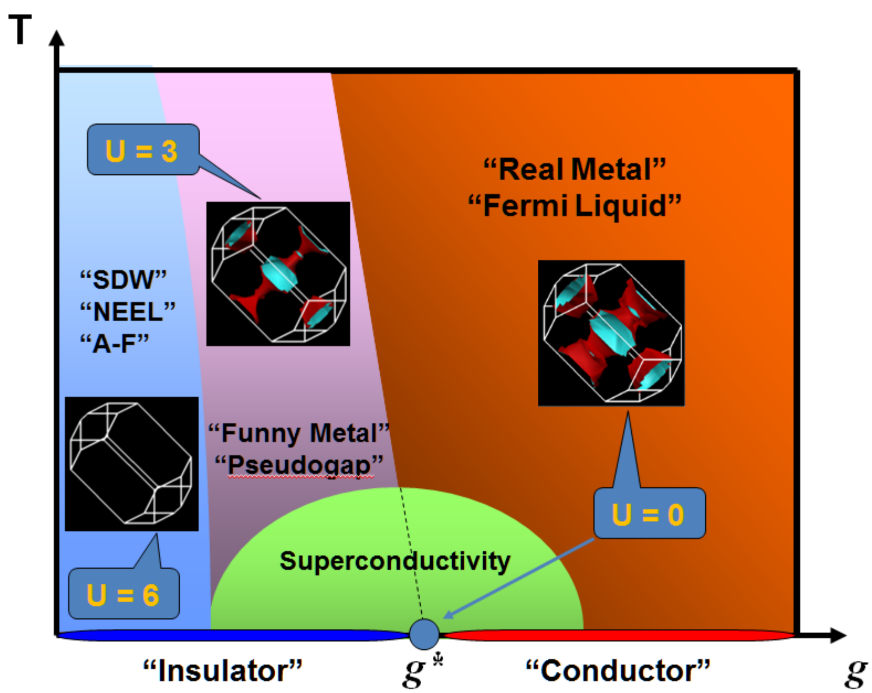


Figure 1. Generalized phase diagram of the HTSC copper oxide perovskites as a function of order parameter, g, which is generally determined either by doping level, pressure or applied magnetic field. U is the on-site coulomb repulsion implicit in the Mott-Hubbard model of antiferromagnetic insulators, and here is assumed to undergo screening as a function of g, viz., $U \approx U_0 \exp(-\alpha g), g < g^*; 0; g > g^*$, g^* defining an appropriate "quantum critical point" separating respective insulating from conducting phases for $T > T_C$ as shown, and α an empirical screening parameter reducing coulomb repulsion. The three Fermi surfaces shown represent the onset of a metallic state as U decreases for an ideal, proxy rocksalt CuO unit cell. See text for further details.

Debate continues on the exact fermion-boson-fermion pairing physics that determines the state underneath the "superconducting dome" of figure 1. Because the salient host crystal system, prior to doping, is an antiferromagnetic insulator, it has been often been speculated that a novel pairing interaction whereby the mediating boson may arise from spin density wave interactions. Yet, at present, at least to the knowledge of the author, no algorithmic formalism exists, analogous to the very successful Eliashberg-McMillan-Allen-Dynes (EMAD) expression (equation 1) for obtaining the superconducting transition temperature via electron-phonon coupling [7].

On the other hand, from the very beginnings of the HTSC era, experimental evidence existed that electron-phonon coupling may substantially contribute to the observed elevated values of T_C. For the copper oxide perovskites, isotopic substitution of copper and/or oxidation results in a shift of the critical temperature [8]. Moreover, T_C has also been found to scale with the lattice Debye temperature, albeit opposite to the trend observed in most low-T_C materials [9]. From the very beginning, in early March, 1987, Raman scattering in single phase $YBa_2Cu_3O_{7-y}$ displayed a distinct "softening" beginning near 90 °K [10].

Hence, we undertook a computational DFT+U study of electron-phonon-mediated pairing in several "proxy" structures postulated for rock salt cubic and tetragonal CuO and applied the EMAD equation to the results,

$$T_C = \frac{\Theta_D}{1.45} \exp\left\{ -\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right\}, \tag{1}$$

where Θ_D is the lattice Debye temperature, λ the dimensionless electron-phonon coupling constant and μ^* an empirical estimate of electron-electron coulomb interaction.

Initial results were reported in 2008 where it was noted values of λ implied by the respective Eliashberg kernel, $\alpha^2F(\omega)$, for pure cubic rocksalt Cu monoxide were of the order to support critical temperatures in the 30-40 °K range [11]. This is not a really surprising finding given that such high symmetry structures for copper monoxide are not found in nature, as opposed for their Fe, Mn, Co and Ni analogues. CuO exists as the mineral tenorite, with a very low symmetry monoclinic crystal structure. Such suggests, and as we have found, the Cu-O bond in high symmetry is extremely Jahn-Teller degenerate, lending credence to Mueller's original speculation that high-T_C in the copper oxide perovskites arises from a J-T induced bipolaron coupling [12]. Notwithstanding this instability, it has been possible to experimentally force-epitaxially grow 5-6 monolayers of tetragonal rocksalt CuO on strontium titanate substrates [13].

In figure 2, we show the results of DFT calculations, with Hubbard U = 0, for the experimental lattice parameters found in reference [13] using "doping" levels of ±0.15 holes/electrons per CuO unit. Subsequent calculation of the respective electron-phonon dimensionless coupling constant, λ, yielded values of roughly 1.2 for holes and 0.7 for electrons, respectively. Assuming a Debye temperature of 440 °K consistent with the lower T_C copper oxide perovskites [9], and $\mu^* \approx 0.01$ on the assumption, as implied by the right-hand panel of figure 1, that Hubbard U at the doping levels above is almost completely screened, we obtain the T_C values given below. Note these are in rough agreement with experimental values for the "LSCO" family of HTSC compounds.

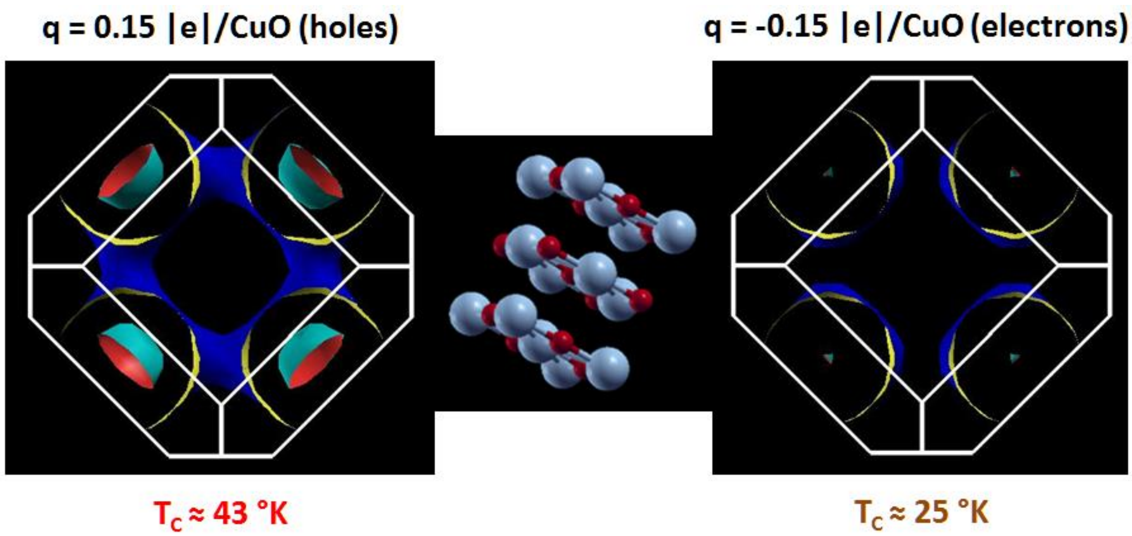


Figure 2. Rocksalt Cubic/Tetragonal Copper Monoxide, a proxy for the family of superconducting copper oxide perovskites (unit cell shown in the middle, a = 3.06 Å, c/a = 1.3, large spheres are Cu). Shown on the left and right are the Fermi surfaces obtained from U = 0 DFT calculations for the given hole and electron doping concentrations.

We conclude from these "first principles" calculations that electron-phonon interactions may play a significant role determining the transition temperature in copper oxide perovskites. We suggest experiments be undertaken to fabricate thicker tet-CuO films and "doping" such by depositing alkali metal overlayers, perhaps inducing a "topological" metallic and superconducting state.

Exascale

Now let's expand our scope by 19 orders of magnitude. Ever since its discovery in 1911, many large scale applications of superconductivity to electric power have been "imagineered" throughout the decades that followed. However, by the early 1980s, the principal application of low temperature superconductors were to magnetic resonance imaging (MRI) and deflection magnets deployed in large hadron colliders. Although a number of power applications had been successfully demonstrated, none were ever commercialized [14]. With the advent of high temperature superconductivity, power application development and demonstrations were revisited, and several continue to the present day, in the United States, Japan, Korea, China, the EU and Russia, in the hope the simplicity and favorable economics of liquid nitrogen refrigeration would eventually spur power application deployment.

In addition, the discovery of superconductivity in magnesium diboride at 40 °K and its favorable critical state properties at the boiling point of liquid hydrogen (21 °K) [15] triggered consideration of a visionary energy society based on a symbiosis of nuclear, hydrogen, photovoltaics and superconductivity, completely "green" and "non-ecoinvasive" [16]. Various embodiments of such a vision, a "SuperVision" if you will, are summarized in figure 3.

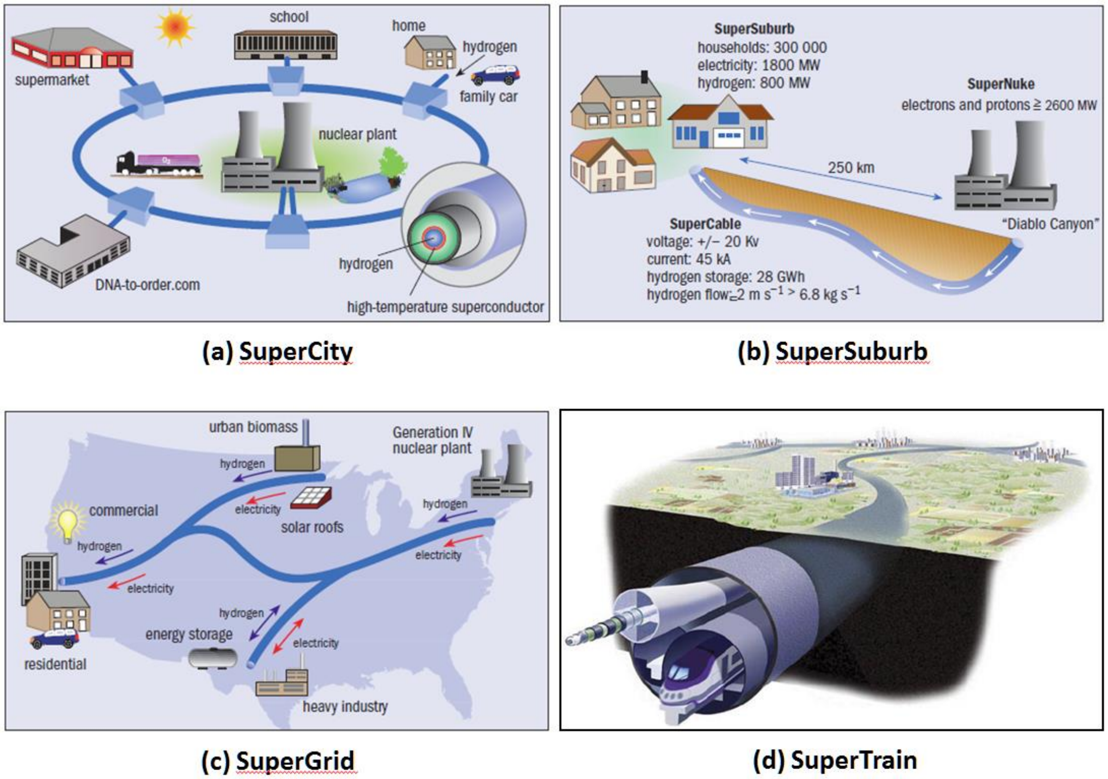
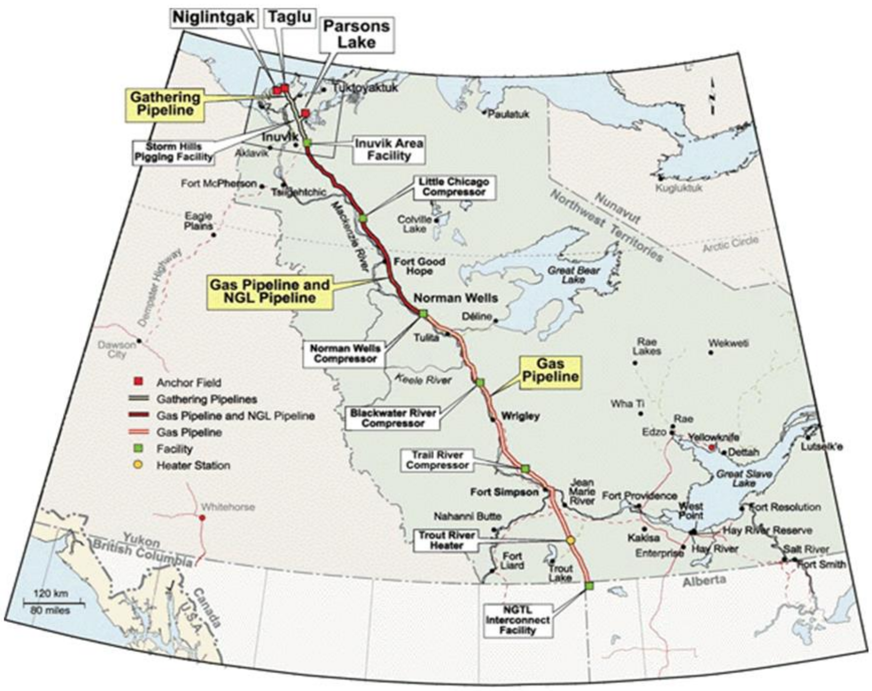


Figure 3. The SuperVision [17]. The ROW dual use concept depicted in terms of the co-transport of electrical and chemical power (electrons via HTSC cables and protons as liquid hydrogen…"hydricity") in four exascale-scenarios [18,19]. Recently, a short 10-m "SuperCable" segment has been successfully demonstrated by a Russian collaboration [20]. Note that the SuperCable concept would apply equally well to electricity and natural gas, the latter in either liquid or gaseous form [21, 22].

Power applications of superconductivity using either low or high temperature materials have long lacked a "compelling need" related to either present or future energy societies, given current technologies perform quite satisfactorily. HTSC technology and supporting materials now "sit on the shelf" awaiting use should it prove economically feasible to do so [23]. An illustration of the economic and societal complexities underlying deployment of high capacity HSTC dc cables is outlined in a recent review by the Institute for Advanced Sustainability Studies (IASS, Potsdam) [24]. However, wherein lays the "compelling need" remains an open question. For example, consider the 1300 km, 1000 kV, 3 kA per pole, 3 GW HVDC overhead transmission line, the Pacific Intertie, running from the Columbia River basin in the state of Washington to just south of Los Angeles. It is estimated the total ohmic losses are well below 10%. Would recovering such losses economically justify tearing down this existing infrastructure replace such by a far more costly underground HTSC cable system?

Suppose, instead, we were to ask is there a looming "compelling opportunity?" Given that the advance of 3-D imaging combined with pressurized recovery technologies ("fracking") over the past several decades has revealed vast planetary reserves of natural gas, it appears there exist at least 3-4 more decades of inexpensive recovery of natural gas and "tight crude" from such resources. Exploiting this inventory will likely lead to a vast expansion of pipeline networks in North America, Eastern Europe and China. An example that has been under study for the last two decades is the proposed Mackenzie Valley natural gas pipeline shown in figure 4.



The Mackenzie Valley Pipeline

Figure 4. The Mackenzie Valley Pipeline [26]. Route shown runs 1220 km southward from the Mackenzie River delta on the Arctic Ocean to the Alberta/Montana border between the US and Canada. It is expected to be capable of transporting 1.6 US billion cubic feet (45 million cubic meters) per day, the equivalent of 18 GW thermal, roughly the electric power generated by the Three Gorges hydroelectric facility in China. It is important to note that due to expanded shale production in the US and Canada, thus lowering the price of natural gas, this project has been put on indefinite hold. Nonetheless, it still provides an interesting engineering economy study.

Approximately 1/3 of natural gas in North America is combusted at delivery point to produce electricity, mostly employing 50% Carnot efficient combined cycle gas turbine (CCGT) generation [26]. Suppose these units were stationed at the gas wellhead fields, this electricity generated thereon, and transported over HTSC cables alongside an LNG pipeline in a common right-of-way? Using MVP numbers, reasonable cable parameters would be 3.0 GW @ ±15 kV, 100 kA, all possible with today's "on the shelf" HTSC technology. Moreover, were the remaining 12 GW (HHV) natural gas to be liquefied, the pipeline diameter could be reduced by almost a third [21]. Finally, when the fields run dry in 4-5 decades, the CCGT units could be modified to use steam from modern, safe nuclear power to make hydrogen and electricity. An interesting "homework problem" indeed!

However, a nearer term "play" scenario may be available for "production [27, 28]." Figure 5 lays out the broad stage presently under public discussion for to increase "light crude" imports to the United States for refinement…the so-called "Keystone Pipeline" [29].

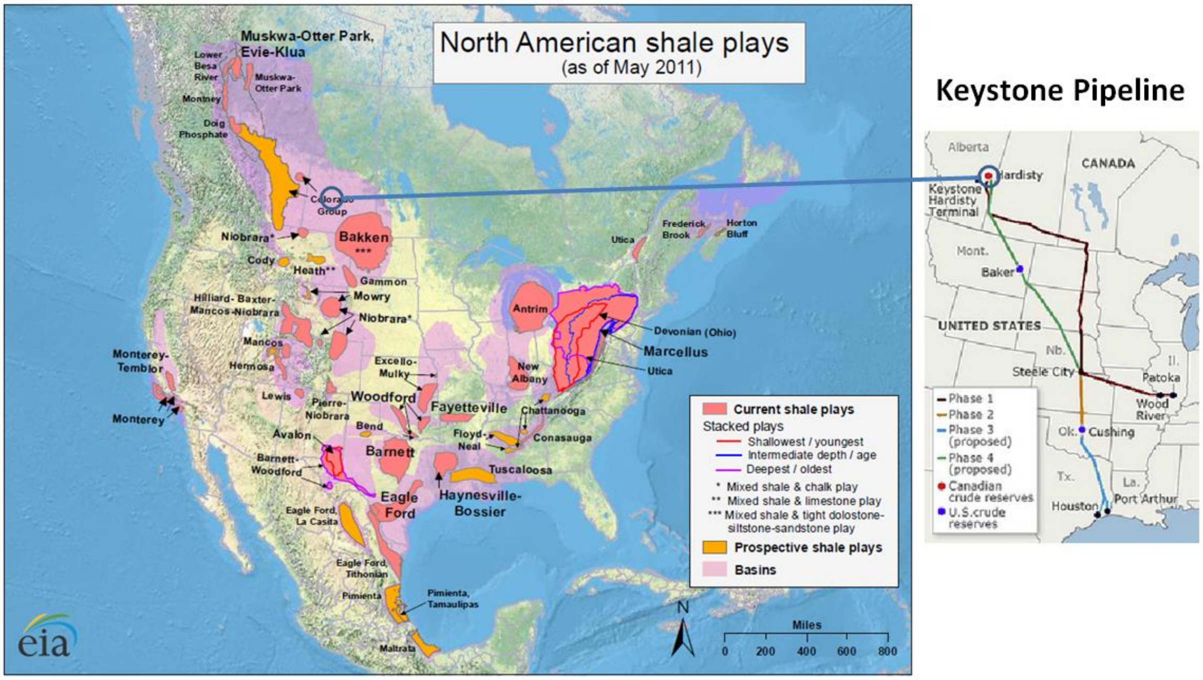


Figure 5. Keystone Pipeline Scenarios. The map on the left designates several routing scenarios for what has been called the "Keystone Pipeline." Note that, although the pipeline is intended to transport primarily crude oil, all routes pass near natural gas fields as well.

The Keystone Pipeline project provides the optimum near term "compelling opportunity" to deploy present technology HTSC cables. Construction of the pipeline infrastructure will almost certainly take place, so why not consider "dual use" of those rights-of-way? But each opportunity will likely be unique and will require its individual detailed "engineering economy" analysis. We suggest DOE convene and sponsor a "study team" comprising staff from the Electric Power Research Institute, the American Gas Association and the Interstate Natural Gas Pipeline Companies (INGAA), and relevant individual state energy agencies to consider possible scenarios.

Back to the Future (Nanoscale - Again)

Hope persists someday a "room temperature" superconductor will be synthesized. Actually, assuming such a material will incorporate BCS "fermion-boson-fermion" mediated pairing and be type II in character, a transition temperature in excess of 100 °C would be required in order for it to be useful at 25 °C. The most obvious path, at least to the author, would be to exploit a boson with a characteristic energy in excess of 1 eV ($\approx 10^4$ °K), an exciton perhaps, as suggested in 1963 and thereafter by Bill Little (30, 31, 32, 33). Plug-in that energy for Θ_D above in equation 1, assume a coupling $\lambda \approx 0.65$, and $\mu^* \approx 0.05$ and you get $T_C \approx 500$ °K.

Little's basic model involved a one-dimensional metallic chain surrounded by "aromatic, polarizable" molecules (e.g., phenan-throline-dye). As is well known, a periodic 1D "metal" is unstable to charge-density-wave fluctuations gapping its planar Fermi surface. A possible solution would be to "decorate" a quasi-periodic Fibonacci chain, such as might be produced over a dislocation line along the (100) direction on the surface of silicon (Si has excitonic excited states of order 1 eV), with odd-electron elements, i.e., sodium, and see what happens [34, 35]. In fact, one should be able to extend the variety of response functions (e.g., a form of the generalized Lindhardt dielectric function, such as proposed in ref. [33]) employing appropriate DFT eigenstates.

Stay tuned.

CONCLUSIONS

Within this admittedly cursory review, the author has attempted a journey over 19 orders of magnitude in energy and distance on Planet Superconductivity, exploring both progress made and issues that remain. The exascale depends on the nanoscale to engender cost/performance, and vice versa to supply economic support for ongoing and future R&D. But…to paraphrase the wisdom expressed a quarter century ago by Foner and Orlando [36] in the aftermath of the Woodstock of Physics…that still holds today: *"All indications suggest that superconductivity has entered a dynamic new phase. But a great deal remains to be done!"*

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