

The momentum of models

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ABSTRACT

There are opportunities for the application of chemical physics style thinking to models central to solid state physics. Solid state physics has largely been left to its own devices by the chemical physics theory community, which is a shame. I will show here that cross fertilization of ideas is real and beneficial to science. This essay is written with the hope of encouraging young theorists with a chemical physics background to enter this rich and promising area. There are many low hanging fruit available essentially because condensed matter physics traditions, models, and standards for progress are so much different than in chemical physics. By way of a warning label, right now neither community is supporting this endeavor. I am hoping this article will help, a little. I make the apology for using mainly (but not exclusively) my own narrow experience and contributions to illustrate this essay. I understand it is only a small piece of the pie, but I do believe the message here is larger: a chemical physics mindset is complementary to the condensed matter physics mindset, and they would work best together.

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CONDENSED MATTER AND CHEMICAL PHYSICS THEORY

Chemical physics theory and condensed matter theory are not strangers. Density functional theory, for example, is a mainstay of chemical physics, but it got its start in solid state physics. It is interesting and somewhat indicative of the divide that although Walter Kohn was very happy to have received a Nobel Prize, I knew him and know he was disappointed that the prize was in Chemistry and not in Physics. His community, his most admired colleagues, were physicists. Indeed, there is nothing inherently “chemical” about density functional theory. Yet, chemical physics theory and condensed matter theory are very much two different worlds. I have worked in both worlds since 1993. Kohn was a remarkable, free intellectual spirit, and attending just a few of his group meetings over the years left a deep impression on me.

The condensed matter theory community, like every intellectual discipline, is pretty happy with its paradigms and progress. Since the systems it deals with are infinitely complex, the standard of “explanation” cannot be very close to the details of the truth. As with human affairs, also infinitely complex, models are needed, even superior, to the unattainable absolute truth. The models are understandable and inspire new ideas and even predictions. The nature

of models, however, differs between condensed matter theory and chemical physics theory. Condensed matter theory considers the more detailed models of chemical physics as seeing the trees but not the forest, diagonalizing matrices rather than first order perturbation theory, as an oversimplified example. I strongly disagree with this.

There is a danger with models like the broad brush ones that condensed matter theory is often content with. The models seem to have explained things. Whole academies of scholars once believed the Earth was flat. If you had come along and said you had a better idea, the reply would have been: “Why are you wasting your time? You can see for yourself that the earth is flat.” There is actually an intellectual justification for this, and you hear it today: “We only want the model to make predictions.” Indeed, flat Earth makes great predictions of many things and does not have the problems of falling off the planet that round Earth theory presents.

Models have tremendous momentum. Like any spoken language, they are taught to new generations by those who grew up with them, almost unchanged. If you want to speak to your colleagues, you must also speak and write that language. This is perfectly understandable. Models do not have to be the best possible; they just have to be serviceable. This is a way to make rapid progress. To question them rather than to write original works in the language on the

models is left to specialists and crackpots. Real players solve hot problems with the models. However, models persist in some fields that are like (and as old as) a Model T Ford, when one could, in fact, drive a Tesla.

The models are like a deck of cards. The analogy with poker is very apt I believe. At any time, there are several high stakes games going on. The players vie for the pot using a fixed deck of cards. Personality and cunning matters to the outcome, as certainly they should. Apart from luck, the best poker player wins. An outsider will be dismissed if they say “did you know, the Jack is actually higher value than the Queen?” This would indeed be grounds for dismissal, except unlike poker, humans did not make the ultimate rules of this game. The players, however, have pretty much agreed to a certain set of rules anyway.

You are supposed to learn the models and move on to the important questions of the day, or get left behind. The rewards go to those who use existing models and methods in the most clever way. However, one of the “important questions of the day” is the origins of high temperature superconductivity, a mystery for well over 30 years. Maybe that is like the problem of tall ships appearing mast first over the horizon, which flat Earth believers struggled to explain. What if the top players are using a bad deck of cards?

As I pursue a rather unconventional path through solid state physics these past nearly three decades, there are two phrases I keep hearing from my condensed matter colleagues: “we have explained that” and “we could have done that.” Below, I will describe a qualitatively different and better understanding of normal metallic resistivity than the ancient perturbation theory implementations of the Drude model. Normal metallic resistivity has after all already been explained and is not a hot topic, but there are tall masts appearing on the horizon. Actual measurements are qualitatively like the theory predicts, but not quantitatively. It seems people are content with this, real matter will always be too difficult to understand in detail.

QUANTUM CORRALS

As I was taking up residence in Massachusetts again in 1993, a plain brown document envelope arrived in the mail. Opening it, I found a glossy 8×10 print of Fig. 1. There was a return address, but nothing else. This is vintage Don Eigler. Even though we did not know each other then, it was certain that I would contact him to find out how the picture had been made. His, Lutz’s, and Crommie’s image shows a stunning achievement that should never be taken for granted: a 76 Fe atom “quantum corral” sitting on the surface of a copper crystal, made atom by atom. This was a variant on the circular corral they had published.² The waves are those of perturbed surface electrons, imaged by using the same scanning tunneling microscope (STM) tip that arranged the atoms in the first place. That the surface electrons could be seen this way was an accidental discovery when they lifted the tip pretty high off the surface. The corral was in the shape of a stadium because the theoretical quantum chaos community was obsessed with that shape, it being one of the few known to be classically ergodic. We had discovered that the quantum eigenfunctions were not completely ergodic-like after all, with many of them “scarred” by unstable classical periodic orbits that do not bias the classical averages.³ Crommie and Eigler

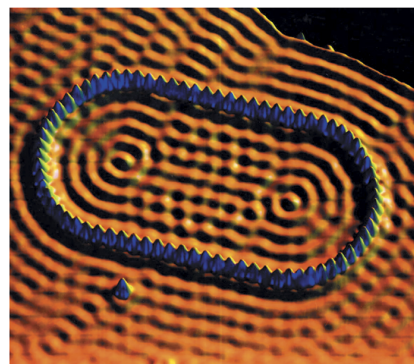


FIG. 1. 76 atom quantum corral, courtesy D. Eigler. This was quantitatively explained by s-wave multiple scattering theory and was the beginning of a fairly steady stream of projects in solid state physics.

were hoping to image scars and other aspects of quantum chaos. This was my start in solid state physics.

My Ph.D. background with Bill Reinhardt at Harvard had been in quantum scattering theory. This set me up to try to understand the quantum corral electron imaging. The Fe atom surface “impurities” placed on the surface are very small in comparison to the deBroglie wavelength of the surface electrons, which live in their own world on Cu(111), only venturing into the bulk by evanescent tunneling. The faux 3D perspective image is 2D data: tunnel current through the scanning tunneling tip vs its position near the surface plane. There are subtleties about keeping current constant and measuring height instead, but these are minor.

The tip is essentially a Green function electron source. If electrons are going to venture or “tunnel” off the tip onto the surface, they can do so at a certain rate onto a perfect, infinite two dimensional surface. However, what if an electron hits some impurity on its journey from the tip along the surface? Some scattered amplitude will be sent back to the tip. It is the same electron amplitude just leaving the tip and also coming back after a collision with an impurity. (If you can get your students to understand this, you have taught them quantum mechanics.) So ... what is the phase of the returning amplitude? If in phase with the tip, the amplitude constructively adds *and the current is enhanced*. If out of phase, the amplitude adds destructively *and the current is suppressed*. The current is proportional to the square of the amplitude just under the tip.

As the tip is moved, the impurity stays put—the distances change and the interference oscillates from constructive to destructive and back again. The current waxes and wanes according to whether the collective reflections off the corral fence and other defects are in phase or out of phase with the amplitude emerging from the tip. This is spectacularly instructive stuff, a single electron wavefunction coherently and simultaneously in the tip, leaving the tip, traveling on the surface to an object, bouncing off that object, traveling back to the tip, and interfering with itself there.

The atoms are tiny compared to the electron wavelength, and multiple s-wave scattering of surface electrons off the iron atoms was

in order, and it worked. The electron-iron atom scattering phase shifts were a best fit to experiment at $\delta = i\infty$, implying that the iron atoms are acting like ideal point absorbers. Unitarity requires that the points can soak up exactly half of the s-wave amplitude coming in to them, at a maximum. The 50% loss represents spin flip and electrons being scattered by the defects into the bulk bands.

Don Eigler became a good friend, but he never liked to hear that his electron “horses” were escaping under the corral fence. The STM images are not individual eigenstates of a stadium billiard because the corral is not very high Q . When I told them this, the Eigler group then made corrals with two fences, one just inside the other. That might work for horses, but for electrons, it is like trying to reflect sound from rows of pillows—you get some sound reflected, but you will not increase reflection much by adding a second row of pillows just beyond the first.

I was very happy with this little success. A few days later, entertaining a prominent visiting condensed matter theorist at dinner, I recounted the work to him. When he understood it, he said of my theory, “any of us could have done that.” The culture divide was laid bare.

Could have, yes. Would have, no, because there was and still is an aversion to microscopic real space pictures and quantum scattering theory in condensed matter theory. Condensed matter theory leans much more toward momentum space, statistical methods, and second quantized perturbation theory formalism.

The paper explaining images was co-authored with Professor Mike Crommie and Don Eigler and had an interesting review process. It languished at Physical Review Letters (PRL) for over 3 months, before it finally got rejected by a silly referee who complained that we had not also made an oxygen corral on the surface. I ripped the paper out of there and sent it off to Nature. It was accepted in four days.⁴ Any good journal is, however, a crap shoot, but the H-index matters (see Fig. 1).

THE H INDEX

This is not the h-index invented for scientific publishing; the present one uses a capital H to distinguish it. H stands for hyperbolic. We will use the H index in the discourse to follow.

The principle behind the H index is something everybody understands intuitively, but by giving it a name, we might save 2–3 sentences with two words and make it easier nip trendy subjects with little hope of success in the bud.

The concept is simple: to get funded, publish a book, whatever, you need the product of the perceived importance of the claim B times the probability it is actually true S to be greater than 1: $B \cdot S = H > 1$. The H index should lie in a hyperbolic region to get funded, published, or become the president of the United States.

Suppose the claim is that Barak Obama was not born in the USA. This is a very important, hyperbolic claim because he would not be qualified to be the president if it were true. Let us give its importance B a value of 1000. What is the probability it is true? With photocopies of birth certificates from a time when no plan to become the president of the USA was possibly in the works, we give the probability of it being true $S = 0.002$. The product $B \times S = H = 2 > 1$. The concept has legs, at least with some people, or in

other cases, with some publishers or some funding agencies. Obviously, both numbers are just invented, but you get the point. If the outlandish claim you make is important enough, it might fly. It reminds me of a sign that transiently stood on the bridge into Washington DC from the Washington National airport: “Don’t bother coming in if you are asking for less than a billion dollars.” This is all in the stream of human discourse, and probably all of us are susceptible as creators or consumers of outlandish but important claims. Conspiracy theories obviously fall in this category. However, let’s identify them for what they are: hyperbolic.

Imagine how outlandish it seemed when Wegener proposed that the continents were drifting around. The S factor must have been 10^{-6} . His proposal came out in 1912 (I would like to know about publications battles), and it was finally and suddenly accepted in the 1950s when the paleomagnetic evidence of sea floor spreading made it obvious. Wegener had died in 1930 at age 50 on a polar expedition. $H \ll 1$ and it took 40 years for continental drift to catch on. Landauer’s theory of resistivity (see below) also took almost 40 years, but fortunately he lived to see it accepted. I estimate $H \sim 0.4$. B and S were both small—the problem of resistivity after all was already understood by first order perturbation theory.

Harlan Bretz’s theory of catastrophic floods in the northwest had an $H \ll 1$ and also took 40 years to be accepted (see below). Both he and Wegener were victims of organized stealth attack sessions at meetings of respected, national level geological societies. If there is an attack session organized against you, you are onto something.

I find it interesting that these low H , long delay in acceptance examples share a common trait: they were not solutions to hot or even lukewarm problems, a factor contributing to low B factors. They came out the blue, did not conform to conventional wisdom or intuition, had big implications if true, but nobody was even asking the questions they answered. If you think the motion of the Heavens has an adequate, (flat) Earth centric explanation, the importance of something quite different is low. I propose that there is a ~ 40 year time constant for the acceptance of such unanticipated revolutions because it takes that long for the established senior people to completely retire.

An example of a high H proposal involves the light harvesting complexes (LHCs), a key to life on Earth. The question arose, do the LHCs use quantum coherence to make sugar? This conjecture resulted in a trove of papers and lots of public money spent. I have said to dozens of colleagues privately and now will say in print: (1) a set of proximate, nearly identical rigid antennas will exhibit coherence effects in radiation reception for wavelengths greater than their spacing. The LHC molecules are close together on the scale of visible light. (2) The LCH molecules need to be as rigid as possible (small reorganization energy) *so as not to waste the sun’s energy in heating the receptor molecules*. Thus, (3) coherence can be seen as a side effect of (1) and (2), not a design to get constructive interference in the final, hopelessly incoherent steps. When this work came along, it had an extremely high H index—photosynthesis always in the forefront, so discovering that Nature used quantum coherence garnered a huge B factor. If you asked, people would probably have said the probability S that it is true and might be 0.25. The idea is a bust now, but the activity it created was extremely useful and instructive, a huge net plus overall.

H only tells you if the idea will fly. The author normally does not have the perspective to predict the H index of his/her own work with any confidence. The main point of the H index as I said is clear to us all. The slightly new point is, when judging the merits of a claim, try to consider the judgment in a hypothetical context: What if the subject of the claim were a hot topic?

LANDAUER-BÜTTIKER THEORY

The condensed matter theory community's reticence to think in terms of real space and of scattering theory is a matter of long record. If you are a regular member of the solid state field, you need to get on to the "hot problems" *du jour* or else you miss the bus. Hence, the field evolves in certain ways, without questioning some old models and ideas and without some alternative powerful ways of thinking. Rarely does anyone introduce a new card in the deck, and certainly no outsider can do it.

The bias in condensed matter theory favoring perturbation theory and statistical, momentum space ideas was made crystal clear by Rolf Landauer's experience with the now famous Landauer-Büttiker (3000 + citations)^{5,6} formula for conductivity of electronic devices. Landauer used microscopic single particle quantum scattering theory in coordinate space with potentials given by electronic device characteristics, which could vary from one sample to the next: no perturbations, no second quantization, no statistical averaging required, or even helpful. The first issue of the IBM Journal of Research contained Landauer's now famous paper in 1957.⁷ It landed with a thud. Landauer tried unsuccessfully (part time—he was busy with many foundational things) for about 30 years to get the now famous Landauer formula accepted. The Landauer story points to the opportunity those of us in chemical physics still have. H index $\ll 1$. Both B (remember, B is *perceived*, not eventual, importance of the question) and S were small.

In 1989, Landauer wrote a paper⁸ showing that Johnson-Nyquist fluctuations arose from his theory. In it, he said:

"There still are, however, some who are uncomfortable with a viewpoint which separates the elastic scattering responsible for the size of the resistance from the irreversible events which are necessary for the occurrence of a dissipative process. These reservations continue despite the successful extensions refinements of the viewpoint, in recent years. It can be hoped that this additional demonstration may help the remaining skeptics."

Landauer was still having difficulty convincing his colleagues of what now is considered almost obvious gospel, i.e., that resistance is calculable from multichannel scattering theory, more than 30 years after his theory was published. Landauer's colleague down the hall at IBM, Büttiker, had just published a multi-lead version⁵ that generalized Landauer's theory and finally convinced many people that the ship was sailing, with them or without them.

Landauer was no wallflower, and even though he was already known as a pioneer and originator of quantum information theory, that did not matter much. It makes me think that a strategy for a young scientist might be to carefully study the poorly cited papers of Nobel-quality people. For example, Einstein had defined the field of quantum chaos decades before it became popular. His paper (A Einstein, Verh. Deutsch. Phys. Ges., 1917) was rediscovered by

Joseph Keller (an English translation of Einstein's article by C. Jaffé is available as JILA Technical Report No. 116). There are four citations of Einstein's paper from 1917 to 1970 and 774 from 1970 to 2020).

RAMAN THEORY FOR CRYSTALS

We turn to solid state spectroscopy, specifically Raman spectroscopy for polyacetylene and graphene. I had cut my teeth playing with wavepackets and casting Raman spectroscopy into the time domain, with the help of very good students, as an assistant professor UCLA. The time domain is equivalent to the frequency domain formulation but so much easier to compute and much more physically compelling, especially for polyatomic systems. Semiclassical implementations suggest themselves, wherein vibrational wavepackets run around. My first post-doc Soo-Y. Lee was incredible in getting this program going, and following shortly after, another talented UCLA Ph.D. student, David Tannor, took it much further, successfully implementing Raman spectroscopy for 15° of vibrational freedom back in the 1980s.

After a halcyon moment with buckyball and then carbon nanotubes, the chemistry theory community ceded pure carbon and especially graphene theory and spectroscopy to the physics community. Indeed, the characterization and classification of graphene in the world of science is telling. Is it a molecule or a crystal? To the extent that it is a periodic structure of large extent, it is a crystal. Since it is only one atom thick, it ought to be considered a molecule too. It has been an uphill battle trying to convince NSF Theoretical Chemistry that graphene is a molecule. The successful evolution of fields requires enlarging the perimeters of the discipline.

POLYACETYLENE

Polyacetylene is a segue into the solid state, a periodic one dimensional crystal. Graphene is 2D and is literally "the new polyacetylene." We will get to graphene in a moment. The 1970s synthesis and electrical discoveries with polyacetylene⁹ were the basis of the 2000 Nobel Prize in chemistry. Polyacetylene became a theoretical physics playground for some interesting speculation on solitons based on the question of which way the single bond symmetry will break to make the familiar inequivalent alternating single-double bonds of polyacetylene, the Su-Schrieffer-Heeger model or SSH model (a Jahn-Teller distortion for chemists, and a Pierls instability for physicists). This is also a model for topological insulators.

Polyacetylene was our testbed in preparation for graphene. It proved far more interesting than we expected. Most of the small-medium sized molecular Raman theory we did at UCLA and Los Alamos did not apply.¹⁰ The geometry change in excited electronic states relative to the ground state is the normal cause of much of the picturesque time dependent physics of molecular spectroscopy. However, in a homogeneous crystal, even a 1D crystal, promoting a single delocalized π electron is not going to change geometries much in, say, a 400 carbon atom chain. That leaves the other mechanism for inducing Raman amplitude, namely, coordinate dependence of the electronic transition moment. This mechanism is not nearly so picturesque, but for crystals, a new kind of beauty emerges.

Polyacetylene Raman spectroscopy had been the focus of hot debate in the 1980s. It centered around bands that shifted with incident laser frequency. Raman bands are not supposed to do this; molecular Raman Stokes or anti-Stokes shifts reflect ground electronic state vibration-rotation transition energies that do not depend on the incident laser frequency. The story grew up that since polyacetylene in the lab was polydisperse, of many different lengths, including defects, bluer lasers would excite the shorter members of the ensemble, which presumably carry higher frequency vibrational modes, explaining the shift of the Raman bands to the blue with laser frequency (see, e.g., Ref. 11). It was sobering when clean, monodisperse batches of polyacetylene became available, yet the blue shifts were the same. After intense but transient interest, the attempt to understand the spectroscopy of polyacetylene was abandoned, left unsettled by the chemical spectroscopy community in the late 1990s. By 2015, the race to explain polyacetylene spectroscopy was long forgotten. Nobody was interested, least of all the National Science Foundation. In fact, I had struck out with NSF for 10 years running already by then. They were much more interested in the idea of quantum constructive interference in LHC molecules. Finally, understanding the coherent spectroscopy of an iconic molecule¹² that only recently had generated a Nobel Prize? Not so much.

Without any funding, we worked in peace and poverty, but there was a pleasant turmoil nonetheless almost daily in my office as my excellent students Yuan Yang and Lucas Kocia and I hashed it out. They were wonderful collaborators in every sense of the word. The problem of the moving Raman sidebands was solved definitively using Kramers-Heisenberg-Dirac (KHD) together with the electronic and vibrational band structure. The mystery of polyacetylene Raman spectroscopy had been solved: Different wavevectors k were excited as laser frequency changed, for momentum and energy matching reasons, so the Raman bands shifted because mode frequency ω is really $\omega(k)$. The Raman band shifts matched the k dependence of $\omega(k)$.

The polyacetylene paper was rejected from Nature on the grounds that the controversy happened many years ago, and even though it was never resolved, interest has waned. Translation: even if you are 100% correct, people will not get excited enough to generate many citations. Fair enough.

GRAPHENE

Until about 2015, few people outside the graphene physics community noted that in 2000, a theory for Raman scattering in graphene called double resonance had sprung up in the carbon spectroscopy community. Raman scattering is the number one way to characterize graphene and to probe its quantum mechanics. About 6000 papers mentioning Raman scattering, graphene, and the home grown “double resonance” Raman theory had been published by 2015. That is fine, but what is strange is that not one of them ever mentioned or compared to the seminal Kramers-Heisenberg-Dirac Raman scattering theory. This you can discover with search engines. Nor did I ever see any reference to how Raman scattering had been done in a million papers before the year 2000.

It is still a source of amazement to me just how this could happen, given the way academic fundamental research is supposed to work: the scholars, the editors of journals, the referees of papers, the students who presumably would like to best their professors, and

especially the funding agencies: no one apparently asked, with any force, “how was Raman scattering done before this, and why doesn’t it apply to graphene?” There are even hundreds of papers over many decades on the spectroscopy (including some Raman studies using KHD theory) on large graphene-like flakes, in the astrophysics literature, because of the suspicion that such molecules are the cause of the “diffuse interstellar bands.”

The double resonance approach¹³ may have been concocted in secret desperation since in solid state spectroscopy, the electronic transition moment is always, without exception, taken to be constant, independent of nuclear position. This is a bedrock, foundational approximation. Any such dependence was at best let in through the back door through electron-phonon perturbation theory. With no excited state geometry change and assuming a fixed transition moment, KHD comes up empty. The fault lies not with KHD but with the fixed transition moment premise.

Looking for something to yield Raman photons, electron-phonon inelastic scattering following photoabsorption came to mind. In the chemical physics community, this would be called vibronic coupling. The double resonance model involves nominal resonant absorption of a photon. The truly resonant process is fine but would not yield a Raman photon since no phonon would be produced. That requires a simultaneous off resonance electron-phonon inelastic scattering. If this happens after a photon is resonantly absorbed, all is lost because the electron, changed in both energy and momentum by the inelastic collision, cannot match energy and momentum anymore and cannot emit back to the hole it left behind, providing a Raman photon. So, in spite of the “double resonance” name, the electron-phonon interaction would have to be nonresonant and quick.

Our polyacetylene paper was a stealth move to put a precedent in the literature. Bringing KHD theory to graphene spectroscopy was not going to be a popular endeavor since double resonance had much effort invested in it. Double resonance is a model that is unfortunately not easy to implement and not up to the standards of understanding and explanation that we are used to in molecular spectroscopy. It has pigeon holes for different processes but little in the way of physical insight.

Our KHD-based paper compactly explained years of important observations in graphene, including laser frequency dependent Raman shifts and the astounding brightness of the D band overtone 2D, the brightest of all the Raman bands. The double resonance approach cannot address why the 2D Raman band is so bright, and why 2D fades out completely as the laser heads into the UV. Double resonance is also a model exclusively applied to graphene.

This brightness is remarkable because overtone bands normally tend to suffer oblivion in polyatomic molecules. A coherence effect stemming from the linear dispersion near the Dirac point is at the root of the 2D band brightness. Essentially, many different resonant transitions up and back down give exactly the same two phonon final state, and these amplitudes add before being squared to give a greatly coherence enhanced Raman intensity. At higher energy, the Dirac cones are no longer linear; the phonons differ from each other, meaning distinguishable final states; the amplitude get squared before they are summed; no resonant enhancement. KHD fits graphene like a glove. After four months trying to get reviews to come back at Nature, the last reviewer said of the polyacetylene precursor, “we could have done that.”

The key difference between KHD and double resonance is the transition moment. If you assume that it does not depend on where the nuclei are as in double resonance, you have to work hard to explain how phonons are produced. If you relent and just say at least that transition moment is a constant plus a linear term in nuclear positions, you get phonons for free, resonantly. It is as simple as

$$\mu(x)|0\rangle = (\mu_0 + \mu_1 x)|0\rangle \sim a|0\rangle + b|1\rangle,$$

and if “ x ” is a normal mode coordinate, then you have a phonon amplitude. This is no *ad hoc* assumption. Of course, the tendency to absorb radiation depends on the electronic structure, and that structure changes, even in the tight binding model, with internuclear separation.

Since 2016 when our Raman paper was published, there have been 60 citations, mostly technological papers that probably just latched on to the title “Theory of Graphene Raman Scattering.”¹⁴ There have been 3000 more papers containing “double resonance, Raman, and graphene” since 2016. It is naive to think that one paper pointing to a much closer to the bone model, properly connecting to a much larger literature, should have any impact on a community of a couple 100 workers who all speak the “double resonance” language, learned with considerable effort. It works for them.

This points to my biggest failing, which I freely admit: It is not enough to “get it right, and move on” even if you do get it right. Science is in large part a political and social endeavor and always has been; the impact of your work in your lifetime, or maybe ever, depends on a full court press. I have zero regrets about that because I find I cannot do science any other way.

PSEUDOMOMENTUM

One of the “traditions” in solid state physics that most chemical physicists would question is declining to consider a real crystal with real boundaries when setting up the formalism. Crystals are not considered to be huge molecules but instead taken to be infinite (total momentum ill-defined and just lost) or with periodic boundary conditions, including the atoms at a surface. The edge atoms are taken to have a neighbor on another face of the crystal. Unfortunately, this is unphysical in the extreme. There will be a price paid down the road.

Physicists are well aware that edges, faces, etc., exist and that crystals are finite. Yet, the foundations for the conceptual and formal fabric, the common currency and language, are as if everything were infinite or periodic. This has been problematic.

An example: It is standard and correct to say that an electron has pseudomomentum, derived by symmetry in a periodic potential. The electron experiences potentials when traveling from one equivalent unit cell to the other, so ordinary free space momentum cannot be constant. Instead, there is a pseudomomentum $\hbar\vec{k}$, existing by virtue of the symmetry of translation by discrete lattice vectors. This is embodied in Bloch waves $\psi(\vec{k}, \vec{r}) = \exp[i\vec{k} \cdot \vec{r}]G(\vec{r})$, where G is periodic with the periods of the crystal. So far, so good. Pseudomomentum of the electron is a constant of the motion in a perfect infinite crystal at 0 K.

What if the electron bounces elastically off a crystal face? Electron pseudomomentum changes drastically. The usual explanation

is that the wall breaks the symmetry, so pseudomomentum does not have to be conserved. This is true, but only half the story. When a traditional mechanical momentum changes because of a collision, there is always the conservation of total momentum to console us. Is there no total pseudomomentum of some sort that is conserved? The electron has pseudomomentum, but the crystal has, you would think, a mechanical momentum. The usual answer is that “the whole crystal recoiled to conserve momentum.” However, the two cannot have intercourse: one is a mechanical momentum, and the other is a pseudomomentum.

The way momentum is mistreated may have started with the seemingly innocent particle in a box model. The trouble with that ubiquitous model is that there is no translational symmetry, and momentum is not a constant of the motion. This is rarely mentioned, and we get used to living without a conserved total momentum. This is almost as dangerous as ignoring conservation of total energy.

None of the box eigenfunctions has a definite momentum. Yet, the eigenfunctions are a complete set, so we can make a wavepacket in the center of the box with plenty of momentum that is conserved—for a while. Then, it hits a wall. One important lesson here is finding useful local symmetries even where no global symmetry exists. Translational symmetry applies in the box but only for some distance. This is actually the basis of scattering theory.

Let us consider a “real” (or closer to real) particle in the box, a heavy box with a particle inside afloat in the space shuttle. The wavefunctions of *local* symmetry for “a particle in a real box” are

$$\psi = e^{iKY} e^{ik(x-X)}, \quad e^{iKY} e^{-ik(x-X)},$$

where x is the particle of mass m lab coordinate, X is the center of mass lab coordinate of the box of mass M alone, and $Y = (mx + MX)/(m + M)$ is the box + particle center of mass laboratory coordinate. The eigenfunctions are linear combinations of the two solutions chosen to match boundary conditions. Hitting a wall at $\pm L/2$, where L is the length of the box with center of mass at $L/2$, changes $k \rightarrow -k$, and automatically, the momentum changes of the particle and the box are equal and opposite, owing to the form of the exponential.

Suppose that the potential inside the box undulates periodically. The local momentum is no longer a constant of the motion, but according to Bloch, we can write

$$\psi = e^{iKY} e^{ik(x-X)} G_k(x-X), \quad e^{iKY} e^{-ik(x-X)} G_k(x-X),$$

where $G_k(x-X)$ is a periodic function of $x-X$ with the period of the undulations. The “pseudomomentum” k is now a local constant of the motion. This little trick actually clears up decades of sloppy thinking about momentum in crystals. The pseudomomentum is not carried by the particle, but by the relative coordinate. Now the box and the particle exchange pseudomomentum.

Now, when the electron hits a crystal face, there is a total foreground + background pseudomomentum (that is actually the total mechanical momentum also) and it is conserved. This is not nit-picking: If you agree, you never have to worry again about concocting a phonon to balance the momentum change of the electron in some process. Whatever the electron does, phonon or not,

total pseudomomentum, foreground electron + background crystal (which after all includes the phonons), is conserved. This means, very importantly, that even in a pure, infinite crystal, an electron can change direction (at finite temperature) without creating or annihilating a phonon. This is heresy, I could be excommunicated, except that I am not a member of the order to begin with. It follows from a nonperturbative theory.

ADIABATIC BORN-OPPENHEIMER APPROXIMATION: AWOL

It is a relatively simple step to assume that the “box” is actually a finite chain of identical atoms with overlapping p-orbitals connected by “springs” (a result of other unspecified bonds). The particle is an electron treated by tight binding. The electron cannot travel beyond the ends and is reflected by them. The wavefunction becomes, approximately,

$$\psi(x, \vec{R}) = e^{iKY} e^{\pm ik(x-X)} \sum_j g_k(x - R_j), \quad (1)$$

where all coordinates are in the lab. This is close to a textbook Bloch wave, with one crucial difference. Instead of e^{ikx} , we have $e^{ik(x-X)}$. Any change in the electron pseudomomentum $\hbar k$ is automatically compensated by an equal and opposite change in the background pseudomomentum by $-\hbar k$. This form is based on a local symmetry.

The adiabatic Born–Oppenheimer (ABO) often comes into solid state physics through a back door: the tight binding approximation. One or a few orbitals centered on atoms constitute a basis set, and the Hamiltonian is defined in terms of on-site energies and overlap parameters with neighboring atoms. It is hopeless to start from first principles with such a minimal basis set. At high symmetry geometries, the resulting Hamiltonian can be reduced by symmetry to the dimension of the number of atoms per unit cell times the number of orbitals per atom. In the case of hexagonal graphene, at the frozen high symmetry position, there results a k (momentum dependent) 2×2 matrix giving the band structure that contains the now famous pair of Dirac cones touching at a point. This was done already by Wallace in 1947.¹⁵ A slice of a lower cone at constant energy is a circle of degenerate states that differ in (pseudo) momentum. If the atoms change positions in a way that breaks the hexagonal symmetry, the Hamiltonian needs to be diagonalized “by hand”; the Wallace solution will not work. This is very rarely mentioned. Within the ABO, putting an atom or group of atoms out of place couples every state on the circle to groups or all of the other degenerate states. Pseudomomentum is no longer a good quantum number, and the ABO eigenfunctions are a mess, infinitely sensitive to detailed atomic positions, and no longer look like the beautiful 1947 Wallace graphene solutions.

In a paper titled “Lazy Electrons in Graphene,”¹⁶ Vaibhav Mohanty, then an undergraduate at Harvard, sets up the *time dependent* tight binding equations for π electrons in the presence of a *classically vibrating* hexagonal graphene lattice. The evolving electronic state as the nuclei move was found numerically within the tight binding basis—no reliance on ABO whatever. One solves the time dependent tight binding problem, with the nearest neighbor

transfer matrix element depending on the classical nuclear positions. The electrons proved to be very lazy: the exact time dependent solution showed that the electrons could not even begin to follow the Born–Oppenheimer adiabatic evolution and instead followed a diabatic evolution very close to (now the center of mass Y is safe to omit)

$$\psi(\vec{x}, \vec{R}, t) \sim e^{\pm i\vec{k} \cdot (\vec{x} - \vec{X})} \sum_j a_j g_k(\vec{x} - \vec{R}_j(t)), \quad (2)$$

i.e., the wavefunction evolved diabatically with a_j remaining nearly constant for many lattice vibrations as the atomic orbitals, followed the nuclei around [this is atomically adiabatic, molecularly diabatic (AAMD)]. This led us to tack on a nuclear harmonic oscillator “phonon” wavefunction, proposing a viable many body diabatic basis set, which remains largely unexplored due to lack of resources,

$$\psi_{k,\vec{n}}(\vec{x}, \vec{R}) \sim e^{\pm i\vec{k} \cdot (\vec{x} - \vec{X})} \sum_j g_k(\vec{x} - \vec{R}_j) \chi_{\vec{n}}(\vec{R}), \quad (3)$$

where $\chi_{\vec{n}}(\vec{R})$ is a many body harmonic lattice wavefunction. Equation (3) makes explicit something that is clearly implicit in textbook discussions of Bloch waves (whether the book’s author worried about this or not): the assumption that if the nuclei move a little, it does not matter; otherwise, the Bloch wave analysis would be irrelevant. The nuclei spend no time at their high symmetry positions. The adiabatic Born–Oppenheimer (ABO) approximation therefore cannot strictly apply: If you pick a nuclear configuration and find all the electronic eigenfunctions, each eigenvalue is essentially infinitely degenerate in a large crystal. Arbitrary small nuclear displacements will radically mix the degenerate eigenfunctions, making the ABO ill defined. The nemesis of the ABO, i.e., conical intersections, is arbitrarily dense in a metal or semiconductor. One must ignore this maelstrom, thereby making an implicit *diabatic* assumption. A diabatic ansatz such as Eq. (3) must replace the ABO. It is still properly called a Born–Oppenheimer approximation though, a DBO. For example, the electronic state returns to itself if the nuclei do. Inelastic scattering (vibronic coupling) is not included. It is indicative of the slippery slope that famous books like Ashcroft and Mermin,¹⁷ Kittel,¹⁸ or Harrison¹⁹ never even mention ABO or Born–Oppenheimer at all.

Equation (3) is deceptively familiar. It carries a proper accounting of momentum, but that is fairly mild compared to the second aspect, which is quite alarming: the nuclear positions are no longer fixed to high symmetry locations as in the Bloch form, but can take any values, governed by the probability amplitudes of the phonon wavefunction. The electronic wavefunction changes modestly as the nuclei move and drag their orbitals around.

It is easiest to see the potential power of this form in the case of graphene and analogous systems. The vibrational part arises from a strongly bound lattice of nuclei, making a playground for π electrons they carry with them combining to make a “diabatic Bloch wave.” The functions are atomically adiabatic since the atomic orbitals can easily follow their vibrating parent nuclei. This is unlike another diabatic form, the crude Born Oppenheimer (CBO) approximation. The basis is an atomically adiabatic, molecularly diabatic Born Oppenheimer approximation, (AAMD-BO). The functions are a complete set, easy to use for matrix elements, and can actually be

defined, unlike the nonexistent, “absent without leave” AWOL-ABO wavefunctions for crystals. The diabatic functions should open up some π conjugated systems to new levels of understanding. They have coordinate dependence of the transition moment and correct symmetries built in. There is no alternative ABO wavefunction for a crystal since it is infinitely complicated and the electronic ABO states are infinitely dense with conical intersections.

The term “electron–phonon coupling” seems a bit fuzzy and fungible. The adiabatic or diabatic adjustment of the electronic wavefunction and energy as nuclei move toward or away from each other is a type of electron–phonon coupling, but this is reversible, i.e., if the nuclei return the electric wavefunction and energy does also. Another type of electron–phonon coupling is often not clearly distinguished from the first: electron–phonon coupling leading to inelastic scattering, where electrons and phonons *irreversibly* exchange energy and momentum. This is what chemists call vibronic coupling, leading to radiationless transitions and irreversible changes of electron and vibrational states. I believe that more chemical intuition and methods could be very fruitful in this field.

MÖSSBAUER EMISSION

Recently, Donghwan Kim and I published a paper on the classical and quantum mechanics harmonic crystals.²⁰ We used “Schrödinger correspondence,” a term we came up with, to illustrate the power of treating harmonic lattices exactly using Gaussian wavepackets or coherent states. In 1926, Schrödinger had solved the problem of a displaced ground state Gaussian wavepacket in a harmonic potential. The parameters defining the average position and momentum move exactly classically, as he first noted. This is manifestly the first post-Schrödinger equation correspondence principle. It holds for any number of harmonic oscillators and thus is true for harmonic crystals. Get *anything* to happen classically: you are looking at quantum mechanics too. This is pretty boring for one oscillator, but with 10^{23} atoms around, even harmonic systems can pack some surprises. You can discover emergent phenomena instantly that are hidden and extremely tortured to describe in the second quantized, occupation number picture. Disturbances can travel to the right with their momentum heading to the left, Umklapp processes become visual and intuitive, and new insights into Mössbauer emission emerge (see Fig. 2). Many things are obscured by the time independent creation and annihilation operators, occupation number eigenstates, and incessant perturbation theory. Second quantized occupation number eigenstate formalism treats phonons as particles in direct analogy to photons. The coherent state representation is the other half of the duality, the wave half of wave-particle duality, analogous to the classical field limit.

Our paper “Schrödinger Correspondence Applied to Crystals,”²⁰ clearly irritated the referees. It barely got published, kind of a charity case because our intentions were good. The thesis of it was forget second quantization, phonon occupation number representations, and perturbation theory and use instead the 1926 Schrödinger correspondence principle. Its H index (see below) was way less than 1, with perceived importance B about 0.1 and probability that it is correct S at least close to 1. The notion that second quantized formalism was the particle half of the wave-particle duality, and that

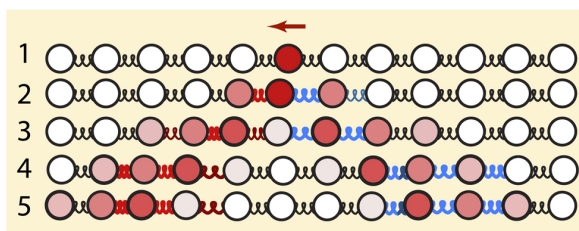


FIG. 2. Accounting for momentum in Mössbauer emission. The classical (and therefore quantum) manifestation of this is that a kick toward the left of the Fe atom by a γ ray leaving to the right causes a compression pulse to be sent to the left as expected, but another expansion pulse of equal energy goes to the right. Both pulses have the same *real* momentum, pointing to the left.

many problems still in the quantum regime could be better understood with waves, was new and evidently boring. More than a year later, there is just one citation—our own, as happens with papers having H factors that are low. Now, there will be two. It became the basis of our new theory of resistivity, described below, which may be the most important advance of my career.

In Mössbauer emission,²¹ an excited nucleus, such as Fe^{57} , emits a γ ray, going to a ground state Fe^{57} . The lifetime of the excited state is close to 10^{-7} s.

However, what phonons can be produced, with what probability? The Nobel Prize winning aspect of Mössbauer emission is the marvelous and ultimately chemically informative totally elastic fraction leading to the elastic Mössbauer peak. The γ ray is emitted packing a momentum punch, and yet, there is a high probability that no phonon is created in the material from which the γ ray came. Momentum is conserved by recoil of the whole block of material from which the γ ray came. We can tell experimentally if a completely elastic or “0 phonon” event happened by whether the γ ray is stopped by another block of material containing ground state Fe^{57} . A ground state Fe^{57} is ready to reverse the emission process and resonantly absorb the γ ray, with a very large cross section, *if it was elastically emitted*. The resonance line is so narrow that moving the absorber by less than 1 mm/sec Doppler shifts it out of resonance and γ rays will pass through the absorber. This is what got Mössbauer the Nobel Prize. If the emission leaves behind a phonon in the solid, its energy will be slightly reduced. At low temperature, there are no phonons around to supply the extra energy for a ground state nucleus to absorb the energy-deficient γ ray, and it passes through the absorber into the radiation counter.

The physics of the elastic fraction can already be seen in a one-dimensional oscillator. If the ground state of the oscillator is boosted in momentum, there is a good chance it will still be found in its ground state unless the kick is very strong. The projection onto states differing by one or more quanta will also be non-zero. However, the elastic fraction is unique in that no energy is spilled except the tiny amount required kicking the whole crystal. The projection onto states with no change to the quantum numbers will be pretty large for γ ray emission; this is the elastic, Nobel Prize winning (deservedly) Mössbauer fraction.

PHONONS AS WAVES: THE MISSING THEORY
OF RESISTIVITY

We have just completed a paper on this topic.²² It turns out that the instruction manual for phonons was unfinished. Is a phonon a wave or a particle? My limited experience with myself, my students, and colleagues is that we tend to loosely think of phonons as waves or corpuscles with wave-like properties. However, phonons have been theoretically treated universally as a particle, encouraged by second quantized formalism. If occupation number states are used, phonons are being treated as countable, like eggs in a basket, like photons are. You create *one phonon*, you annihilate *one phonon*, changing the balance sheet by one.

There *is* a wave description dual to the particle based, occupation number state representation, a way to *really* treat phonons as waves, not just loosely think of them that way: the coherent state representation. Coherent states for the phonons had never played a role in dealing with the interactions of electrons and phonons, or phonons with phonons for that matter. It was a big oversight. A lattice in an occupation number eigenstate is unwieldy and impossible to depict, but a lattice in a coherent state is compelling and immediately recognized as a wave, Fig. 3.

Using coherent states for the lattice brings it alive, giving every atom a nonequilibrium position and momentum, suggesting an active phonon sea. There are lattice compressions and dilations running around, many lattice constants across (long wavelength). It is reasonable to suppose that the band structure changes locally, subjecting electrons to smooth, time and space dependent forces. We find this idea to be immediately and remarkably rich and rewarding, allowing, on the one hand, nonperturbative, semiclassical treatment of the electrons and, on the other hand, exact agreement with low and high temperature 2D and 3D Bloch–Grüneisen formulas in the weak coupling limit. The Bloch–Grüneisen laws state that resistivity should rise as T^5 (Bloch’s T^5 law) in a pure metal at low T , rolling over to T above the Debye temperature (the rollover can start at lower temperature in some electron poor metals, for reasons we will not go into here) in a pure 3D crystal, and as T^4 rolling over to T in 2D materials. Specific prefactors are known. These results were long ago derived by one phonon (particle picture) perturbation theory. It

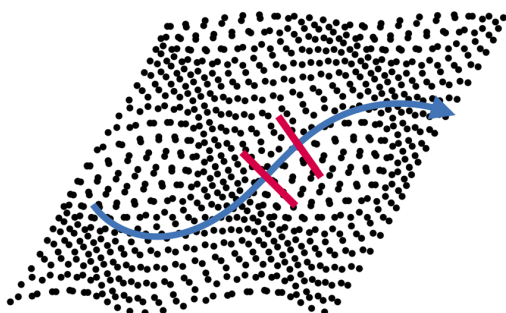


FIG. 3. The nuclear positions specified by a multivariate coherent state of a lattice, specifying displaced normal modes, is seen to correspond a wave. The nuclear positions for a carbon lattice coherent state are at least as well defined as the dots in this illustration, even given the uncertainty principle. It is very tempting and semiclassically justified to surf this wave with conduction electron trajectories.

is a dirty little secret that real metals experimentally rise closer to T^4 at low T and look like $T^{1.2}$ or larger exponents at high T . Our results, derived nonperturbatively using classical trajectories for the electrons (the Fermi level electrons are in a semiclassical regime, with short wavelengths compared to the force field—see below), agree *exactly* with the Bloch–Grüneisen laws if we use first order *classical* perturbation theory. Otherwise, we get non-integer power law rises numerically. There is no *a priori* reason why nonlinear, many body systems should have integer power laws for resistivity and, indeed, experimentally they do not.

The common currency of electron–phonon interactions is the “deformation potential,” a local change in the band structure due to aggregation and rarefaction of atomic density coming from the summation of all phonons present. For 70+ years, the deformation potential has been sandwiched between phonon occupation eigenstates and treated as a perturbation, with phonons being counted like eggs in a basket. We took the deformation potential seriously and saw that it interacts semiclassically with the electrons, exerting forces on them.

We were freed to ask: what would an electron do in such a field? This is just the sort of problem we had been working with since 2000, inspired by the Westervelt group’s imaging of electrons flowing in a two degree of freedom electron gas: “branched flow,” which made the cover of *Nature* in 2001.²³ There will be a review of the nature and very wide applications (not to mention its beauty), of branched flow soon in *Physics Today*. The smooth thermal deformation potential bumps also cause branched flow (see Fig. 4) and momentum will diffuse, leading to finite resistivity. This is a classical picture, *justified by the fact that the Fermi surface electrons doing the conducting have short wavelength compared to the deformations*. Moreover, the deformations are moving at the speed of sound (about 1/10 the speed of the Fermi level electrons), meaning that *colliding with these moving objects allows energy accommodation between electrons and the phonon bath*.

The question “how can the phonons act like a wave when we always count them like particles?” is central, as we bring wave-like methods to bear on a problem heretofore treated only by particle-like methods. Exactly this issue was central to the swirling controversy surrounding the Brown and Twiss²⁴ effect. They claimed to have measured the apparent diameter of the star Sirius with widely separated telescopes using weak visible light. The detection signals were correlated in a way that did violence to the notion of separate quanta arriving at each detector. Everyone “knew” and Einstein had taught us that visible light was supposed to behave like particles from such an incoherent, weak (at Earth) source. A range of objections were raised to the Hanbury Brown and Twiss work, including claims of violation of thermodynamics and the uncertainty principle. To quote Baym,²⁵ “In the end Hanbury Brown and Twiss prevailed, . . . – and the field of quantum optics was born.” It took only a few years, and the H index (see below) was above 1, owing to the importance B of the problem.

The no-longer-missing theory of resistivity²² was found hiding behind a thin curtain of wave-particle duality for phonons.

BLOCHBUSTERS

Bloch’s theorem and Bloch waves are correct for a nailed down high symmetry lattice, but there needs to be much more wandering

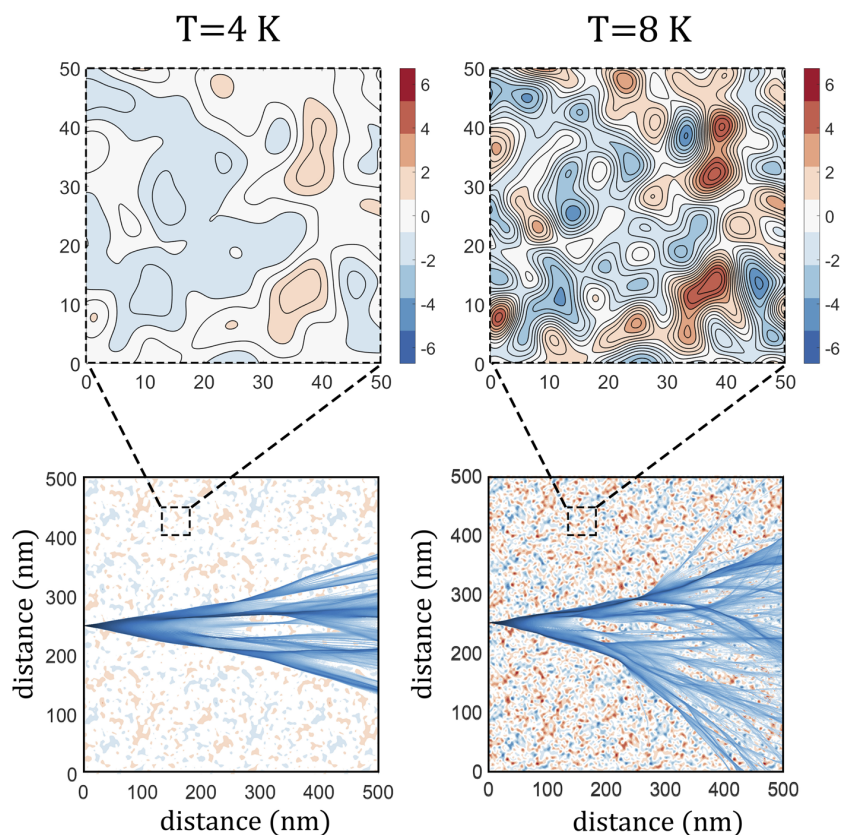


FIG. 4. A snapshot of the moving deformation potential is shown at the top for two different temperatures. Below, bundles of electron trajectories are shown in blue lying on the potential used to propagate them. This is the ubiquitous pattern of branched flow.

from that comfortable place. We have tremendous respect and admiration for Felix Bloch, but we are trying to break out of the mold(s) he set that have taken on an Aristotelean dogma. We have just discussed a type of “Blochbusting,” i.e., breaking the usual rules (like not fixing the nuclei) of Bloch wave theory. Now, we are going to break the rules in other ways. Getting out of a Bloch mindset is necessary because real lattices are not nailed down.

The trial basis function 3 is very nearly the Bloch ansatz found in every text book, except we *let the nuclei move* while keeping the same form and tack on a many body nuclear wavefunction. This is justified by the lazy, diabatic response of conduction electrons to nuclear motion. The vibrational wavefunction modulates how the nuclei can move, making a complete many body electron-nuclear wavefunction, one that is extremely convenient to manipulate and it has something to offer for direct estimation of a large number of processes. We do not yet know what corrections and improvements are needed.

Bloch waves are eigenstates of the high symmetry, fixed lattice potential. They are infinitely delicate. They have definite pseudomomentum. Adding even two such waves of different pseudomomentum but the same energy together gives another eigenstate, but no longer a Bloch wave. What can you construct out of an infinite number of degenerate Bloch waves now that you have escaped prison? The answers are very interesting.

Oddly, it is very difficult to find even one picture of a Bloch wave in a textbook or on the web. Try looking it up on the Internet. What you will find is one dimensional examples, and tennis shoes. Linear combinations of Bloch waves may be nonexistent since there is only pairwise degeneracy in 1D.

One insight is provided by the “Sinai billiard,” an infinite rectangular array of hard disk scatterers in the plane. A particle bouncing among these disks was the first classical dynamical problem to be proven to be ergodic: a particle goes everywhere and with every velocity consistent with fixed energy over time. No long range order to the chaotic classical motion. Yet, this system is a periodic lattice, so there are perfectly regular Bloch wave solutions. What is going on? There could not be more opposite paradigms.

The correspondence principle somehow has to work for this system. The key is to think well beyond the first Brillouin zone, which means there can be many deBroglie wavelengths per lattice constant (the distance between disks). In condensed matter texts, this possibility is sometimes ignored or even discouraged. The problem comes first of all from the ubiquitous tight binding method, which is normally applied with one or a very few orbitals per unit cell. That being the case, the wavefunctions obtained cannot oscillate faster than a couple times per unit cell. However, there clearly are solutions that do more than that. What about a fast electron traveling through the crystal? Such experiments are done all the time.

Channeling

The problem is most acute in superlattices. Twisted bilayer graphene, a “superconductor” (in quotes because all that has been shown is zero resistance, a watered down version of superconductivity), is a superlattice of a triangular “window screen” Moire pattern formed when two monolayer sheets of graphene are overlain at some angle. Other superlattices could be made artificially with nano-fabrication techniques.

We constructed an eigenstate of a triangular superlattice consisting of small potential mounds: How did my colleague Alvar Daza find such a state, a linear combination of all the Bloch waves at that energy? He did not need to find any Bloch waves. Instead, he launched a narrow wavepacket $\psi(\vec{x}, 0)$, and we Fourier transformed the evolving wavefunction, determined numerically,

$$\psi(\vec{x}, E) = \int dt e^{iEt} \psi(\vec{x}, t), \quad (4)$$

with $\psi(\vec{x}, t)$ determined by split operator Fourier transform techniques. We only had to integrate the Fourier integral until the wave left the scene. Integrating further is futile since nothing is in the frame. So we have precisely found an eigenstate in finite time.

The channeling of the eigenstate along rows is apparent. This is a dynamical confinement; there is no impenetrable potential barrier keeping the wave in the channel. Other waves are living on *top* of the bumps. This is related to scarring of periodic orbits.³

The channeling is intriguing. It seems to be difficult for the electron to talk to phonons when traveling in a channel state; matching both energy and momentum is difficult to impossible. Zero resistance?

This is an example of something a chemical physics theorist would think to do, but it is almost inconceivable that a condensed

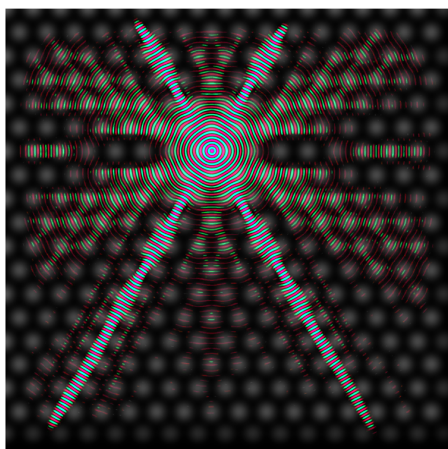


FIG. 5. We Fourier transformed $\psi(\vec{x}, t)$, where $\psi(\vec{x}, 0)$ was a narrow wavepacket traveling over a triangular lattice of bumps (faint blurry dots) launched at the center of the beams. We only had to integrate the Fourier integral until the wave left the scene. Integrating further is futile since nothing is in the frame. So we have already precisely found an eigenstate in finite time. This wave is clearly Blochbusted.

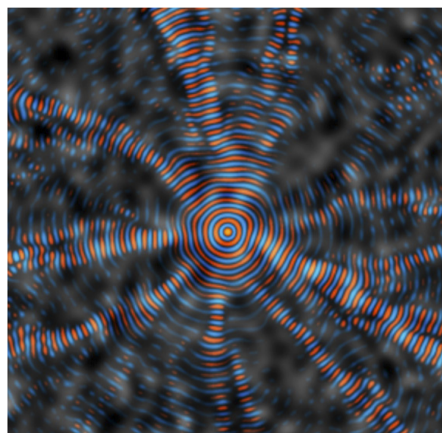


FIG. 6. Alvar Daza Fourier transformed $\psi(\vec{x}, t)$ until it left the scene, where $\psi(\vec{x}, 0)$ was a narrow wavepacket at the center of the random potential. This yielded a particular eigenstate of the potential, shown, that would have been difficult to get any other way.

matter theorist would have done it, given their mindset and training. It flies in the face of a Bloch wave, momentum space mindset. The field is also still somewhat bound to the old 20th century ethos of holding pictures like Fig. 5 in contempt, a lowly occupation compared to writing formalism. We do simulations and make pictures *because* we want to do mathematics. We want to do something that is physically relevant, not merely correct. Perhaps, we are numerical experimentalists. It does not matter what it is called, we came up with a radically new theory of resistivity this way. The dynamical channeling that Alvar Daza discovered could be very useful, including for producing artificial superconductivity. The relevant mathematics involves nonlinear stability and instability of classical trajectories in force oscillator potentials. It is related to scar theory; in fact, some of the channeling is scarring.

The deformation potential turns Bloch waves into rubble

A deformation potential is a pseudo-random field experienced by electrons in a metal, caused by phonons. If we freeze such a potential at one moment and ask what an eigenstate would look like, we get Fig. 6. This is a lot closer to what the electrons are doing in the deformation field than in a Bloch wave.

SOLID FOUNDATIONS

Solid Foundations is the title of my third full length book, now under construction, and it will contain expansions of some of the points raised here, and others. (My first two books were, “Why You Hear What You Hear,”²⁶ a 640 page book on acoustics that I consider to be, in part, a tardy answer to Hermann Helmholtz’ s “Sensation of Tone,” a book full of deep insights and bad mistakes, and “The Semiclassical Way,”¹ a book about quantum mechanics of physical systems, as opposed to the quantum mechanics of 0’s and 1’s.)

The motivation for Solid Foundations is the following: As I worked through the existing foundations, the deck of cards so to speak, for my own understanding, I found misconceptions, quick and sloppy “let’s move on” compromises, and outright errors. As I learned more, it became impossible for me to write a paper without quoting my own unpublished work. If I tried to serially publish the new foundational things like the pseudomomentum of the background crystal one at a time, there would be a long uphill battle for each. One group of referees would say it is wrong, while another would say “we knew this, we could have done this.” There would be no in between. The editor would say “they don’t like your paper” without noticing that the reviews cancel each other. It has become imperative to set what I have learned down coherently in one place, in one accessible book, that hopefully some young students will read.

One of my favorite stories like this is when we figured out why the interference fringes were persistent in the Westervelt group’s 2DEG images farther from the source (S) than the thermal length, after which they were “supposed” to disappear. The explanation for the fringe survival was beautiful and simple,²³ involving interference between backscattering from defects (D) and backscattering from the STM tip (T). There would be interference as long as the S–T distance and the S–D distances differed by less than the thermal length. It was not hard to model this, very realistically, with a couple of Bessel functions. It came back from PRL, rejected. One referee said it was wrong, that is normal enough, but the other said it was “too simple,” I am not kidding. If you ever noticed that PRL theory papers have to be too formal to understand, there is the proof. The editor did not notice that the reviews were contradictory, only that neither referee wanted it published. This paper had an H index of around 0.5, with perceived importance B factor about 1 and probability of being right S about 0.5.

Sir Michael Berry tells of a case that fits in beautifully in a couple of respects. He submitted a paper with John Nye, reporting the discovery of phase singularities in sinusoidal wave trains that were overlapping but had come from a single source. The paper was rejected by the Royal Society, on the grounds that the calculations were too simple. On re-submission, the next referee said the paper “might have been written by Lord Rayleigh or Lord Kelvin, but seems to have escaped them,” and it was published after all. The work was ignored for several decades, but eventually it stimulated the worldwide and still-growing field of “singular optics.” Now, it is Sir Michael’s second-most cited paper. Another case of too simple and also of decades of delay after discovering and solving a problem nobody knew was there. H index about 0.1, with perceived importance B factor 0.1 and probability S factor 1 (see below).

The primary job of editors of scientific publications is to enhance the standing of the journal, now quantified by the citation index, and especially to sell more magazines. Careers rise and fall according to citations too. It is a sad development. It makes unexpected discoveries difficult to publish if there is no large standing constituency to refer to it in the first two years. Papers that put deserving wet blankets on a thriving field, like our graphene Raman paper throwing doubt^{12,14} on the strange double resonance Raman model, have no chance in the very places they should be published, i.e., the popular journals for that topic. They will in effect average in a negative number to the journal’s citation index. On the other

hand, papers of mild interest with big constituencies have a much easier time getting published. With a laptop and copy-paste, anyone can throw whole lists of the “usual suspect” references into a paper that they did not even know existed five minutes before.

BRETZ FLOODS

I close with an inspiring episode that influences my life today. It involves Harlen Bretz, a high school teacher in Seattle in the 1920s. This story is a good one for scientists of all stripes to know. Bretz studied geology at a small college before taking a high school science teaching position. He spent summers prowling the strange geology of the Eastern Washington state. He was led to a radical idea by many pieces of evidence, including ripple marks in a rocky plain a half mile from crest to crest, and giant erratic boulders hundreds of miles from their source and from the farthest advance of glaciers. These must have been caused by biblical scale, fast moving floods, not that long ago. Geology had gotten over biblical events, and it was not ready for this. Geology was known to happen slowly. Bretz did not carry a professional geological union card. He wrote 14 papers about local geology of Seattle but was roundly dismissed about the floods and publicly derided. He proposed a radical solution to problems people were not even aware existed and had the wrong professional pedigree—a bad mix. $H \ll 1$, 40 years to acceptance. However, the evidence was not subtle and plain for anyone to see.

The floods were real. The reason turned out to be the ice age Glacial Lake Missoula to the east, formed by an ice dam. Ice dams can catastrophically fail, draining in this case about 500 cubic miles of water in a day or so.

Bretz became a Professor of Geology at the University of Chicago, based mostly on other work, although he continued to probe eastern Washington. Finally, in the 1950s, high altitude aerial photographs made his points obvious. The Eastern Washington state looks like a bucket of water was poured into a sandbox, carving the formations he called the scablands of eastern Washington. Bretz received the US geological society’s highest honor, at age 96. He told his son: “All my enemies are dead, so I have no one to gloat over!” I had the privilege of talking to him in the late 1970s, a few years before he passed, with regard to the idea of creating a Bretz Floods National Monument at flooded sites over half the state of Washington. Some, like Dry Falls, were already commemorated and preserved, without knowing (at first) why they were there. The vision came true, the effort of many people, in 2014, as the Ice Age Floods National Geologic Trail, managed by the National Park Service.

CONCLUSION

Fortunately for me, my colleagues in chemical physics have been marvelous even when they have not agreed with me, apart from a few anonymous referees perhaps. I see us as being especially collegial to each other and as conducting an intellectually open discourse. Chemical physics has a remarkably good professional demeanor. We are perhaps used to it but like democracy; it should not be taken for granted. I am lucky to have landed in this community.

Finally, I find myself compelled to pay tribute to the many fine colleagues that are no longer with us. Colleagues that guided and developed the field and many careers, and me personally. Some with bigger than life personalities. Each loss is a blow to me, and I always

have the same sense of disbelief: Wait, the world is supposed to have him, or her, in it.

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DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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