Anderson and Line Shape Analysis

Sushanta Dattagupta

We present here an overview of Late P. W. Anderson’s doctoral thesis on Spectral Line shapes in the backdrop of his very intimate relation with the physics community of Japan—in particular, R. Kubo.

1. Introduction

In P. W. Anderson’s passing, we have lost a colossus of modern solid-state physics. Some colleagues who had known him personally and have worked with him, have written extensively on Anderson’s long-lasting and insightful contributions to many-electron quantum solids [1]. I did not either collaborate with or know him from close quarters but curiously enough my own doctoral work was an extension of Anderson’s PhD thesis at Harvard University in the late 1940s, done under the tutelage of J. H. Van Vleck, with whom he shared the Nobel Prize in 1977. As it turns out, this thesis topic of Anderson’s is perhaps not as widely known as his other deep forays into magnetism, in particular anti-ferromagnetism, broken symmetry and superconductivity, resonance valence bonds, localization, etc.

What I am referring to is the theory of spectral line shapes about which Anderson had written [2]: “My interest in detailed relaxation and spectral problems....... led eventually to localization and in magnetism, to super-exchange". He went on to say: “In hindsight it was a beautifully chosen topic, at least for a good student. Wartime electronics had made available all kinds of microwave electronics gear and immediately pre-war and during the war a number of people, Van among them, had pointed out a very rich variety of fundamental molecular spectroscopy which could be done with this gear”. It is this topic that I want to write briefly

Keywords
Solid state physics, magnetism, spectral line shapes, the Kubo-connection.

*Vol.25, No.8, DOI: https://doi.org/10.1007/s12045-020-1027-6
Figure 1. L. R. Walter, S. Geshwind, P. W. Anderson, A. Clogston, and R. Kubo (from left to right). (Photo credit: Professor H. Fukuyama, Tokyo University of Science)

about.

But before I do that, it is of significance to mention another giant of line shape theory and magnetism: Ryogo Kubo who, apart from Van Vleck, had greatly influenced Anderson in his formative years. Kubo persuaded him to come to Tokyo University during 1953–54 on a Fulbright lectureship and formed a close bond which led PWA to write: “Whatever lucky stars I may have had the fortune to walk under, surely one of the most important was the one which led Ryogo Kubo and me to meet.... It was a wonderful thing to have known this man” [2]. The exhibited photographs are a testimony to the very close relationship with Japan that PWA enjoyed (Figure 1).

So, what in essence is the line shape theory? In Anderson’s own words: “Atoms and molecules, in isolation, are characterized by sequences of ‘energy levels’ in quantum mechanics, pairs of these being connected by ‘spectral lines’: more or less sharp frequencies where the atoms absorb energy according to Planck’s relation: $hν = E_1 - E_2$. These sharp lines are familiar in ordinary light, for instance from the sun, but to see them with coherent, man-made radiation from electron tubes, was exciting, especially given that the pre-laser precision of optical spectroscopy...
was laughable compared to microwaves. This made precision measurement of width and shape easy, ... but the theory... was a different matter.” Earlier, “... only a couple of papers really addressed the problem from first principles by relating it to the real, calculable forces between molecules.” “In the spring semester ’48, I solved my problem, .... developing a new method which in that field was eventually to be apotheosized by at least two other authors in review papers, and is still used. The implications of what I did still reverberate in the methodology of modern physics, ..... and it was only much later that I understood how revolutionary it was. I had effectively combined some of Schwinger’s new mathematical tools of Green’s functions for dealing with abstract quantum-mechanical problems with Van’s sense of the real physics of experimental systems of many particles, which had not in fact been done before in anything like that way. In my awe of my elders, I credited such gurus as Van, Weisskopf, and Schwinger himself with having really understood the basic thrust of what I did.....” (Incidentally, Julian Schwinger was PWA’s teacher at Harvard while Victor Weisskopf in nearby M. I. T. was another big influence.)

2. Genesis of Line Shape

Let me now, in simple mathematical terms, attempt to explain the genesis of line shape, line-broadening and line-narrowing. For the sake of simplicity, we consider an ‘emitter’—which could be an atom or a molecule in a gas. The emitted spectral line is characterized by a phase

\[ \Phi(t) = \exp[\hat{k} \cdot \vec{x}(t)], \]  

where, \( \hat{k} \) (\( k = \omega_0/c, \) \( \omega_0 \) frequency and \( c \) the speed of light in vacuum) is the wave vector and \( \vec{x}(t) \) is the instantaneous time-dependent position of the emitter. Now

\[ \vec{x}(t) = \int_0^t dt' \vec{v}(t'), \]
with \( \vec{x}(0) = 0 \) and \( \vec{v}(t') \) being the instantaneous velocity. If the latter is a constant,
\[
\vec{k} \cdot \vec{x}(t) = \pm \frac{\omega_0 v}{c},
\]
where the plus or minus sign in front of the right hand side depends on the direction of the velocity \( \vec{v} \) vis a vis \( \vec{k} \), though the two vectors have been assumed to be collinear. The line shape is defined by the Fourier transform of (1):
\[
\Phi(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp\left[-i(\omega - \nu_0/c)t - \Gamma|t|\right].
\]
(4)
\(\Gamma\) being the natural line-width. From the exponent of (4), it is clear that the ‘observer’ frequency \( \omega \) is Doppler-shifted by an amount \( \frac{\omega_0 v}{c} \). Splitting the integral into negative and positive time domains and upon switching the integration variable, we arrive at
\[
\Phi(\omega) = \frac{\Gamma}{\pi[\Gamma^2 + (\omega - \Delta\omega)^2]},
\]
(5)
with \( \Delta\omega = \frac{\omega_0 v}{c} \), and it exhibits a Lorentzian line peaked at \( \omega = \Delta\omega \), but broadened by \( \Gamma \). However, if the gas is in equilibrium at a temperature \( T \), \( \nu \) will have to be drawn from an underlying Maxwell–Boltzmann distribution, and upon averaging,
\[
\Phi(t) = \exp\left[-(\omega_0 t/c)^2 < v^2 > / 3\right],
\]
(6)
with \( < v^2 > = < \vec{v}^2 > = \frac{3k_BT}{m} \), \( k_B \) being the Boltzmann constant and \( m \) the mass of the particle. Here, we have assumed equipartition theorem and isotropy so that the mean-squares of all velocity components are identical.

Now the exponent is real and it contributes to the width, upon taking Fourier transform. This leads to thermally induced ‘Doppler line-broadening’.

On the other hand, in the gas phase, we expect the emitter to undergo random, incessant collisions with all other particles. (In a general context, ‘collision’ is a euphemism for many-body interactions.) This will render \( \nu(t) \) a random process, much like the velocity of a Brownian particle.
A physical picture, in which the frequency can also randomly jump—due to Anderson’s guru Van Vleck—is the following [3]. Imagine the emitter to be a transmitter tuned to two frequencies $(\omega_0 + \Delta \omega)$ and $(\omega_0 - \Delta \omega)$. At each impact, the transmitter jumps to a new position with a sudden change in phase (cf., Eq. (1)). At the same time, the collision is envisaged to switch the frequency from one value to the other. Two cases were considered by Van Vleck: (1) complete persistence of the position and velocity of the transmitter at each collision; (2) no persistence, i.e., ‘hangover’, at all.

Anderson, in his 1954 paper [4], made a detailed study of case (1) in which the frequency of the transmitter was viewed to randomly jump amongst a large set of values. We will simplify the discussion here by restricting to just two values $(\omega_0 + \Delta \omega)$ and $(\omega_0 - \Delta \omega)$, as in the Van Vleck example [3]. If the transim
ter is in the ‘frequency-state’ \((\omega_0 + \Delta \omega)\), it emits a signal whose phase is given by \( p_+(t) = \exp[i(\omega_0 + \Delta \omega)t] \) and similarly for \( p_-(t) \).

However, because of random switching, \( p_+(t) \) obeys a differential equation:

\[
\frac{dp_+}{dt} = i(\omega_0 + \Delta \omega)p_+(t) - \gamma(p_+(t) - p_-(t)). \tag{7}
\]

\[
\frac{dp_-}{dt} = i(\omega_0 - \Delta \omega)p_-(t) - \gamma(p_-(t) - p_+(t)). \tag{8}
\]

The discerning student reader would note that if the frequency terms were not there, the above are just two-state rate equations, in which \( \gamma \) has the interpretation of the rate of switching.

It is clear that (7) and (8) can be written in a compact form as a matrix equation:

\[
\frac{d}{dt} P = UP, \tag{9}
\]

with \( P = \begin{pmatrix} p_+ \\ p_- \end{pmatrix} \), and \( 2 \times 2 \) matrix \( U \) is given by:

\[
U = \begin{pmatrix} i(\omega_0 + \Delta \omega) - \gamma & \gamma \\ \gamma & i(\omega_0 - \Delta \omega) - \gamma \end{pmatrix}. \tag{10}
\]

The matrix \( U \) is characterized by the eigenvalues

\[
\lambda_+ = -i\omega - \gamma + \sqrt{\gamma^2 - (\Delta \omega)^2},
\]

\[
\lambda_- = -i\omega - \gamma - \sqrt{\gamma^2 - (\Delta \omega)^2}. \tag{11}
\]

The net signal will be a superposition of \( \exp(\lambda_+ t) \) and \( \exp(\lambda_- t) \). However, when the rate is rapid, i.e., \( \gamma \gg (\Delta \omega) \), the radical can be expanded, and to leading order,

\[
\lambda_+ = -i\omega - \frac{(\Delta \omega)^2}{\gamma},
\]

\[
\lambda_- = -i\omega - 2\gamma. \tag{12}
\]

Therefore, in the long time limit, the signal associated with \( \lambda_- \) would wither away while the one associated with \( \lambda_+ \) will get sharper as \( \gamma \) increases, leading to what is called the ‘motional narrowing’ of spectral lines.
Though $\gamma$ appears here as a phenomenological rate, it is within $\gamma$ is hidden, like in the Drude relaxation rate in electrical conductivity, the quantum mechanical transitions (per unit time) amongst energy levels, and hence all the intricacies of many-body interactions. To amplify this remark, consider an NMR experiment in which the probe nucleus is in strong coupling with the atomic electrons via the magnetic hyperfine interaction. The electrons themselves are a part of the surrounding many-body system of phonons, other electrons, defects, etc. The rate $\gamma$ which modulates the hyperfine frequencies arises from details of such interactions, the treatment of which can be quite challenging.

It is this topic that propelled Anderson to Van Vleck in early 1947 to: “... the new field of radio-frequency coherent spectroscopy, e.g., NMR.” Here we have sharp spectral lines due mostly to the magnetic hyperfine interaction between the nucleus and its surrounding electrons. But the electronic spin component of this interaction undergoes fluctuations/relaxations because of many-body interactions involving phonons, and other electrons. At this juncture, Anderson connected with Kubo when together, in the 1952 Maryland meeting on magnetism, they discussed line broadening and exchange narrowing. The point is, in electron paramagnetic resonance (EPR), wherein the electrons (and not the nuclei, as in NMR) are directly probed, the transition operator is the total electronic spin perpendicular to the direction of the static Zeeman field. However, the total spin is the generator of rotation in the spin-space around the direction of the spin and commutes with the Heisenberg exchange interaction, the latter being spherically symmetric. This isotropy implies that the exchange interaction would have no influence on the transitions but for the presence of dipolar coupling, which is anisotropic. This yields what Anderson and Kubo called ‘exchange narrowing’ because of modulations of the dipolar interaction by the much stronger exchange forces, and resulted in three comprehensive papers [4]. The underlying theory is referred to as the Kubo-Anderson model of line shape. A quantum generalization of this model to include the so-called non-secular effects in the line shape was done by my colleagues and I. The total spin is the generator of rotation in the spin-space around the direction of the spin and commutes with the Heisenberg exchange interaction, the latter being spherically symmetric.
PhD supervisor Martin Blume, who interestingly, followed into the footsteps of Anderson, first at Harvard and then as a Fulbright Fellow in the late 1950s in the group of Ryogo Kubo [5]. I applied the Blume model in my thesis, to study non-secular phenomena in nuclear hyperfine and EPR line shapes [6].

The Tokyo stint allowed Anderson and Kubo to further explore the connection between the line shape problem and irreversibility. In PWA’s own writings [2], “We were both intrigued by the possibilities we saw in the correlation function methods we had pioneered, that the calculation of the response functions from the fluctuations in the equilibrium state avoided all the complications of Boltzmann’s equation and the formal difficulties of irreversibility.” “... after I left (Tokyo) Kubo came up with the ‘Kubo formula’ for conductivity as a paradigmatic example of fluctuation-dissipation methods, and showed its relationship to the standard Boltzmann approach.”

There is a lesson here for all our young scientists in this great example of two stalwarts of physics who broke all the cultural barriers to take solid-state physics to new and glorious heights.

3. Conclusion

In conclusion, we recall what Anderson felt about his Fulbright tenure: “It is interesting to look back and realize after all these years, what the experience of working with Kubo in Japan made to my career. Above all, his confidence in me gave me confidence in myself. I was expected to perform as a leader and teacher, at the age of 29 and 30, of a large and able group, and I more or less did. .... More subtly, he helped me to pass an important stage in maturity”.

Acknowledgements

I am grateful to the referee for providing a couple of photographs which underscore P. W. Anderson’s strong Japanese bonding. I am also thankful to the Indian National Science Academy for its
support through the Senior Scientist Scheme.

Suggested Reading


