My personal and professional relationship with Van Vleck started in 1957 with a letter from him, and as I hope to show in my talk, this relation made a dominant impact on my professional life and I am extremely indebted to him for his generosity and kindness to me and to my wife. Our relationship lasted to the end of his life and then the friendship continued with our communication and visits to his wife Abigail. My talk will therefore be concerned with our scientific and personal relationship, with memories, correspondence and some amusing stories. So let me start with the necessary scientific background.
(Slide 2) In one of his early papers published in 1928 in the Physical Review, “On Dielectric Constants and Magnetic Susceptibilities in the new Quantum Mechanics Part III, Application to dia- and paramagnetism”, Van Vleck calculated the magnetic susceptibility on the basis of the Hund theory of molecular quantization, and in particular he dealt with the susceptibilities of gaseous “free” molecules of oxygen $O_2$ and nitric oxide NO.
At that time no spectroscopic evidence existed on the proper term assignment for oxygen, and therefore Van Vleck decided that the simplest was to assume that in the normal state of O\textsubscript{2} were three closely spaced $^3S$ levels and he used his formula for Curie’s law and found good agreement with recent susceptibility measurements at room temperature and at lower temperatures above the boiling point. They confirmed his assignment of the spectroscopic terms. He remarked in his paper that “in fact oxygen is the only known paramagnetic molecule with an even number of electrons, whereas paramagnetism is the usual rule for molecules with an odd number of electrons”.

In the liquid and solid state, the measured susceptibility of O\textsubscript{2} diluted in N\textsubscript{2} – to diminish the O\textsubscript{2} – O\textsubscript{2} interactions, was found to obey Curie’s law. But what happens well below 60K, when k\textsubscript{B}T becomes comparable with the $^3S$ structure splitting? Some twenty years later, A.H. Cooke and W.P. Wolf made a quantitative prediction for the O\textsuperscript{16}O\textsuperscript{16} gas, namely: As T $\to$ 0, $\chi$ $\to$ Const. But more about this later.
Nitric Oxide NO: $^2\Pi$ doublet

\[
\begin{align*}
\Sigma &= \frac{1}{2} \\
\Delta / k_B &= 173K \\
\Sigma &= -\frac{1}{2}
\end{align*}
\]

$\Lambda = 1$ orbital angular momentum

\[
\chi = (N\beta^2/3k_B T) \times \Phi(173/T) \quad \text{Free gas.}
\]

Experimental results from several labs above 120 K

But what happens at lower temperatures?

(Slide 4) A more interesting and challenging situation for Van Vleck was that for NO, which, (as he wrote): “provided the most striking confirmation of his entire theory, both because the NO band spectrum furnishes unambiguous term assignments and also because the doublet width is of such magnitude as to test quantitatively the finer points of the theory”. Spectroscopic measurements had determined the splitting between the two lowest doublet P levels to be $120.1 \text{ cm}^{-1} = 173 \text{ K}$, and Van Vleck developed the complete mathematical formula for the magnetic susceptibility of NO as a function of temperature, which was to be tested down to temperatures where NO liquefies, 122 K.

In this paper he gave full details of his calculation. By the time he had written his famous book “The theory of electric and magnetic susceptibilities”, further measurements on the susceptibility of NO below room temperature had been made, which he compared with his theory and found good agreement. He must have been very pleased indeed.
In his book he did not repeat the detailed derivations made in his ’28 paper. This was no doubt prompted by an encounter with Wolfgang Pauli he relates in a 1968 paper on travels to Switzerland. “When I informed Pauli that I was writing a volume on “Electric and Magnetic Susceptibilities” he remarked “I don’t republish my papers as a book”. Perhaps this remark made me extra careful that my volume had more in it than my earlier papers in the Physical Review”.

Condensation of both O₂ and NO at temperatures of the order of 100 K set a limit to the comparison between theory and experiments on “free gases”.

\textbf{Slide 5}

Molecules trapped in β-quinol clathrates

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{slide5.png}
\caption{Structure of a β-quinol clathrate cage containing a trapped clathroionic molecule (shaded). The heavy black lines represent indirect bonds formed by hydrogen atoms between neighboring oxygens (conshaded spheres), not direct bonds. The hexagons represent benzene rings.}
\end{figure}


\textbf{Symbols : Data .} \quad \textbf{Dashed line :} Predictions for the free O₂ gas

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{slide5_data.png}
\caption{Graph showing susceptibility vs temperature for O₂ in clathrates.}
\end{figure}

\textbf{(Slide 5)} However a new promising approach to study the magnetic properties of quasi-free molecules was made by their inclusion in β quinone clathrates, organic compounds which have almost spherical cavities in which at most one molecule can be trapped. The word “clathrate” derives from the greek meaning “enclosure”. These clathrates are grown from a saturated quinone solution in n-propyl alcohol under pressure of the gas to be enclosed in the cavities. Depending on the pressure, which spans the range between ~ 40 and 150 atm., roughly 30 to 80 % of the resulting
cavities can be filled. If the gas pressure is too low, the $\beta$ form is unstable and no gas molecules can be trapped.

Here is a sketch of the clathrate crystal that shows the cavities, slightly ellipsoidal with the long axis parallel to the crystalline axis. Hence one can expect that at low enough temperatures the trapped diatomic molecules will be oscillating around the direction of the crystalline axis and also rattling in the cage. The X-ray data by Palin and Powell (who coined the word "clathrates") show that all the holes are equivalent. But owing to slight distortions of the cages by the trapped molecules, the electric environments are not quite equivalent at all holes.

Clathrate compounds are produced in various forms, such as gas hydrates, and are used for room temperature storage of gas molecules at high densities.

When Mary O’Brien, a fellow at Radcliffe College at Oxford was on a year’s sabbatical at Harvard to work with Van Vleck, she told him about the magnetic susceptibility measurements between 1 and 20 K carried out at the Clarendon Labs at Oxford by Cooke, Wolf and myself, which greatly interested him, as this tied in well with his interest in the $O_2$ molecule. To interpret the results, they first noted that the calculated susceptibility for the rigidly frozen $O_2$ molecule, subjected to an infinite hinderance potential $V(\text{infinity})$, did not agree with the experiments that extended to 1 K. However they expected that a smaller potential, which permits hindered rotation, might work. They had developed a theory which took into account the hindered rotation of the $O_2$ molecules in the cages. They argued that the molecules could not rotate freely in their cages at low temperatures when the hindering potential was larger than $k_B T$. However from an analysis of the Oxford susceptibility experiments above 1 K, the curve derived from their theory could not be distinguished from that for the freely rotating molecules, calculated by Werner Wolf.

Mary O’Brien informed Van Vleck that I was going to extend the measurements below 1 K, which would clearly decide between the two theories: free rotation or hindered rotation. Then, out of the blue, I received a letter from Van Vleck in fall 1956 which I reproduce on the screen (Slide 6). From the fit of the theory to experiments, Van Vleck and O’Brien derived the hinderance potential, from which the oscillating frequency could be determined.
I responded him that I was trying my best and was fortunate in that the experiment worked well, the results were sent on schedule to Van Vleck and he was able to present a short 10’ paper at the APS meeting, as he had hoped.

The results are shown on the screen (Slide 7), establishing the validity of his and O'Brien’s theory. From the fit of the theory to experiments, Van Vleck and O'Brien derived the hinderance potential, from which the oscillating frequency could be determined. From the fit of the theory to experiments, Van Vleck and O'Brien derived the hinderance potential, from which the oscillating frequency could be determined.
Stimulated by Van Vleck, who was very interested in the susceptibility of NO, I then set out to make measurements over the temperature range between 1K and 300K, and completed these before summer 1957, to the delight of Van Vleck. However I was unable to get the use of the cryostat for temperatures below 1K, as Van Vleck had wished.

Although I had appointment offers from two institutions in the US which I was considering, a sudden unexpected offer from Van Vleck for a junior faculty position at Harvard led me to accept it. Our correspondence shows that he was instrumental, with the help of friends in high places to have my immigration papers issued in a short time. (Slide 8).

\[ V_0 / k_B = 32 \text{ K} \quad \rightarrow \quad \text{ hindered rotation frequency } v = 0.49 \times 10^{12} \text{ sec}^{-1} \]
When my mother and I finally arrived in New York by boat and we took the train to Boston, Van Vleck was at the train station to welcome us and to bring us to a hotel. He was most hospitable to us, and helped my family and me getting settled near Cambridge, after my mother had returned to Europe. He also took me to a football game to explain the rules of American football. During the two years of our stay in the Cambridge area, he and his wife Abigail were most hospitable to us, taking us out for drives, inviting us for meals to their large and elegant home.

Van Vleck's marriage was a very happy one. His students and myself were in awe of him, he was the great theorist, he was infallible but always courteous and indulgent to them and also to me. However to Abigail he was not the towering eminence he was for us and she appeared to be running the show at home. One
excursion in particular with the Van Vlecks remains in our memory. He was driving, Abigail was sitting on the passenger seat, my wife and I sitting on the back seats. After some driving, Van Vleck took a wrong turn at a bifurcation. Abigail turned to him and said sharply: “Van, you are SO stupid”, which came as a great shock to us, and was an unforgettable experience for us, which we later found very amusing.

Knowing that I would move to North Carolina, Van Vleck delighted in introducing me to the South by reciting “Nothing can be finer, than to be in Carolina in the mo-o-o-orning” which he repeated on several occasions. And he also recited the words of the Chattanooga Choochoo:

    Pardon me, boy
    Is that the Chattanooga choo choo?
    Track twenty-nine
    Boy, you can gimme a shine, etc....

Developing a theory to explain the susceptibility results of NO proved to be much more difficult. It took Van Vleck several years of work off and on until he was ready to publish a long and complicated paper for the comparison between predictions and the experiments. We published our respective papers in same issue of the J. Chem Physics of Solids in 1961, after I had already left for Duke. (Here again I was aware of Van Vleck’s positive input to the Duke Physics Chairman, who was a friend of his. Another impact he had made on my future career)
Here (Slide 9) I show a comparison of the experimental data with the theory. To his original 1928 theory of the susceptibility of the free NO gas, Van Vleck had added the contribution from the hindered rotation assuming a trigonal field. He took the potential energy value of 45 K for the hindered rotation of NO, intermediate between that of O₂ (32 K) deduced from his susceptibility theory, and 75 K, determined for N₂ in clathrates from nuclear quadrupole resonance experiments by Tom Scott and myself. This fit agreed quite well with the experiments down to about 2 K, but Van Vleck was very bothered by the fact that an additional term in 1/T he had predicted was not observed in the experiments at low temperatures. He was quite unhappy that the experiments had not been extended below 1 K to settle this question, and he devoted a long discussion in his paper why this had not been observed.

He suggested to me spin resonance experiments at low temperatures, and gave me the order of magnitudes for the conditions of observations. My research associate
Earle Hunt got our radio frequency spectrometer tuned up. I prepared a sample of aligned single crystals of NO clathrates into a radio frequency coil, and we cooled the sample to 1 K, and ramped slowly the magnetic field to search for the resonance but were unable to find it in spite of numerous attempts. This was a great disappointment to Van Vleck.

However he was greatly cheered up by two other clathrate experiments which confirmed quantitatively his theory of molecular hindered rotation. (Slide 10)

**Slide 10**

\[ \text{O}_2 \]

Confirmation of the O’Brien and Van Vleck theory by paramagnetic resonance experiments of \( \text{O}_2 \) in clathrates:

Hindered potential \( \Rightarrow V_o/k_B = 34 \text{ K} \) \( \text{(O’B,VV : } V_o/k_B = 32 \text{ K) } \)

Fine structure of resonance observed: Interaction with molecules in neighboring cages

\[ \text{NO} \]

Infrared spectra measurements

\( \Rightarrow \) Hindering potential energy \( V/k_B = 47 \text{ K} \). Van Vleck’s estimate : \( V/k_B = 45 \text{ K} \)

The first one was electron spin resonance of \( \text{O}_2 \) clathrates, where I collaborated with Simon Foner and Walt Kleiner in 1959. Resonance was observed in aligned single clathrate crystals, and the data analysis yielded a hindering potential \( V/k_B = 34 \text{ K} \) which compared with 32 K from the analysis of susceptibility measurements. The second series of experiments consisted in far-Infra-red spectra of gas molecules trapped in these clathrates, where I collaborated with Paul Richards and Joe Burgiel at Bell labs in 1964. These experiments gave absorptions at frequencies interpreted to correspond to molecules rattling in the cages and carrying out hindered rotation.

For NO, the absorption for hindered rotation was at a frequency of \( 33 \text{ cm}^{-1} = 47 \text{ K} \), agreeing well with the value of the potential \( V/k_B = 45 \text{ K} \) Van Vleck had used in his theory of susceptibility.
After this experiment, correspondence with Van Vleck shifted to rare earth iron garnets, (Slide 11) where calorimetry experiments had been carried out at Harvard and subsequently in my group at Duke, and also NMR experiments at Duke. The garnets were a hot topic of investigation in several laboratories in the US and abroad. These garnets, and in particular the europium iron garnet, where the Eu ion is trivalent, were a long time interest of Van Vleck and remained so until late in his seventies. The reason is as follows:

The ground state of the trivalent europium ion is J=0 and the first excited triplet J=1 states lie at an energy of 458 K, 500 and 561 K above. There is a second order Zeeman effect which is important because of the proximity of the first excited J=1
state and the J=0 ground state. This leads to a magnetic moment for the ground state, and a susceptibility tending to a constant value as T -> 0, instead of following Curie’s law.

These ferrimagnetic garnets are compounds that are magnetically ordered into two sublattices with Fe spins, the so-called tetrahedral and octahedral sites, denoted by (d) and (a), with antiparallel alignment. There are 3/2 as many (d) as (a) sites, and the spins, each 5/2, are antiparallel. It was discovered that the rare earths on the (c) sublattice, are much more strongly coupled to the (d) than to the (a) sites. These sites can be filled with ions without and with magnetic spins, such as yttrium (no spin) and europium or gadolinium (with spin). It turns out that the coupling between the (d) and the (c) sublattice is antiferromagnetic, and so the resulting magnetization of Europium IG is smaller that of YIG.

Limited time does not permit a description of the personal interaction I had with Van Vleck on this topic, and of the Duke results that were of interest to him. However I mention that these compounds are very important in industrial use because of their magneto-optic properties, for instance the so-called Faraday rotation, namely the ability to rotate the polarization of light passing through the garnet. The garnets are key elements in several technical applications, such as Faraday rotators, optical isolators, holographic storage, magnetic field sensors.

Already in 1960, two years after these rare-earth ferrites had their magnetization measured by Pauthenet in France, Van Vleck published a paper with W.P. Wolf on the magnetization of europium iron garnet. But besides the static response of the europium ion to the exchange fields, Van Vleck was even more interested in the dynamical problem on how the europium ion achieves thermodynamic equilibrium in rapidly varying fields. He was always extremely well informed on the experimental and theoretical advances in this topic, as correspondence with him showed. The experiments and theory were discussed during my visits to Harvard.
But Van Vleck was not happy with the progress in the understanding of the dynamics. In the summary of his 1968 review article, Van Vleck wrote:

“In conclusion we can simply say that it is frustrating that we do not yet adequately understand the relaxation processes involved in the magnetic resonance experiments, and that there are more unsolved theoretical problems connected with the magnetic behavior of the trivalent europium ion than there were thirty five years ago.”

But progress was made all the same. In the seventies, he published his last papers on the dynamics of magnetic interactions in EuIG with Mario Foglio and Robert Sekerka. These publications appeared in the Proceedings of the Royal Society, because in 1973 Van Vleck had been elected as a foreign member of the Royal Society, - a great honor, preceding his award of the Nobel Prize in 1977 - and he was then invited to publish papers in this Journal.

After his last 4 page handwritten letter to me in 1969, showing keen interest in our experiments on EuIG, there are no further records of letters from him, but he delighted in sending me vintage postcards from various places, several from Switzerland. Here is one from the Duke Medical School in the early thirties. (Slides 12,13) He apparently must have had a collection of such antique postcards, some of them from turn of the century.
Schieber tells me the values of $M_d$ we used were from Geller. I think that the work of Pearson et al. is a big improvement over our cubic field. They claim they fit the susceptibility O.K. Your paper on EuG just received. Many thanks. Will write about it later.

Van

Here is the latest letter re the AVC which may interest you. Don’t return.

I do not think this is a picture of you and Rosemary on the card, despite the location
(Slide 14) A visit to Harvard in 1975 led me to take a photograph of him before the ivy-covered walls of a Harvard building. His expression hints the kind and generous person he was.

My colleague and Chair of this session, Chun C. Lin, kindly provided me with the following information: “Van Vleck gave his last lecture “Fine Structure of Molecular Spectra in Madison and Interstellar Space” at his Alma Mater, the University of Wisconsin, in the spring of 1979, lively and witty as ever. A reception was held in his honor in the Van Vleck Hall, the mathematics building named after his father (Slide 15). On 27 October 1980, he took a peaceful nap and never woke up. He made his final journey home when Abigail brought him back to Madison for burial alongside the graves of his beloved parents”. (Slide 16)
Slide 15

Van Vleck’s last lecture at the University of Wisconsin, (May 1st, 1979)

Slide 16

Graves of Abigail and John H. Van Vleck, Madison, Wisconsin  (Photo credit: C.C. Lin)
Vive Van Vleck !!

During my visits in the late seventies, Van Vleck liked to reminisce about his travels, and about the international time tables he had memorized. He sent me a reprint of his article published in Helvetica Physica Acta that contained remembrances of this travels there. (Slide 17) He autographed the reprint with “Vive la Suisse”. And so, as the fond memory of him continues to live in many of us, I would like to conclude my talk with a heartfelt:

"Vive Van Vleck !