Lucy Mensing's Three Most Important Papers

Michel Janssen (University of Minnesota), 2024

Mensing arrived in Göttingen while matrix mechanics was taking shape and she took full advantage of having a front row seat for these developments. She wrote two important papers on the new quantum mechanics during the year following her PhD and co-authored another one. She wrote the first one in Göttingen but the second and the third at least partly after she had gone back home to Hamburg (where her co-author Pauli was still based in 1926 although he also visited Göttingen and Copenhagen). She was the first to apply the new quantum mechanics to diatomic molecules, which she had already written a paper about in the context of the old quantum theory in 1923/24 in Hamburg (which was only published, however, right before the one on the new quantum quantum mechanics)

- "Die Rotations-Schwingungsbanden nach der Quantenmechanik." *Zeitschrift für Physik* 36 (1926): 814–823 DOI
- With Wolfgang Pauli, "Über die Dielektrizitätskonstante von Dipolgasen nach der Quantenmechanik." *Physikalische Zeitschrift* 27 (1926), 509–512.
- "Die Intensitäten der Zeemankomponenten beim partiellen Paschen-Back-Effekt." *Zeitschrift für Physik* 39 (1926): 24–28. DOI

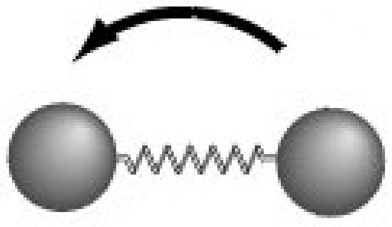
In the first paper, entitled "The rotation-vibration bands according quantum mechanics," Mensing applied the new rules for the quantization of angular momentum—first published in early 1926 in the famous *Dreimännerarbeit* (Three-Man-Paper) of Born, Heisenberg and Jordan (DOI)—to diatomic molecules and solved a puzzle that the spectrum of such molecules had posed for the old quantum theory. In the process she sharpened the quantization rule: Born, Heisenberg and Jordan had shown that the quantum number for angular momentum could take on integer *or half-integer* values. Mensing showed that *orbital* angular momentum (as opposed to intrinsic angular momentum or spin) could only take on integer values.

Impressed by these results, Pauli invited her to collaborate with him on a related puzzle concerning the electric susceptibility in diatomic gases. Their solution of this puzzle, in a paper entitled "On the dielectric constant of dipole gases according quantum mechanics," was one of the first successes of the new quantum mechanics outside of the field of spectroscopy for which the theory was originally developed. This was emphasized by John Van Vleck who found the same result as Mensing and Pauli, using some results on angular momentum from Mensing's earlier paper on rotation-vibration bands. In an interview for the Archive for the History of Quantum Mechanics, Van Vleck said: "One always thinks of [quantum mechanics'] effect and successes in connection with spectroscopy, but I remember Niels Bohr saying that one of the great arguments for quantum mechanics was its success in these non-spectroscopic things such as magnetic and electric susceptibilities." Van Vleck was so taken with this result that it figures prominently in his 1977 Nobel lecture.

In the third paper, entitled “The intensities of the Zeeman components in the partial Paschen-Back effect,” Mensing returned to spectroscopy. The Zeeman effect is the splitting of spectral lines when the atoms emitting light are placed in an external magnetic field. Pieter Zeeman originally found a splitting in three components. Hendrik Antoon Lorentz could explain this on the basis of classical theory and the two of them shared the 1902 Nobel Prize for this work. Soon thereafter, however, splittings in more than three components were found. As this could not be explained classically, this became known as the *anomalous* Zeeman effect, even though it was more common than the “normal” Zeeman effect. An important hint to its eventual explanation in quantum mechanics came from the discovery by Friedrich Paschen and Ernst Back in Tübingen in 1912 that in sufficiently strong magnetic fields the splitting in just three components returned. This Paschen-Back effect thus suggested that the Zeeman effect was due partly to magnetic fields within the atom. Using the new concept of spin and the associated magnetic moment of the electron as well as the new framework of quantum mechanics, Heisenberg and Pauli were finally able to explain the Zeeman effect in terms of spin-orbit coupling. Building on their paper, Mensing successfully dealt with the *partial* Paschen-Back effect, i.e., the absence in some cases of lines in normal Zeeman triplets.

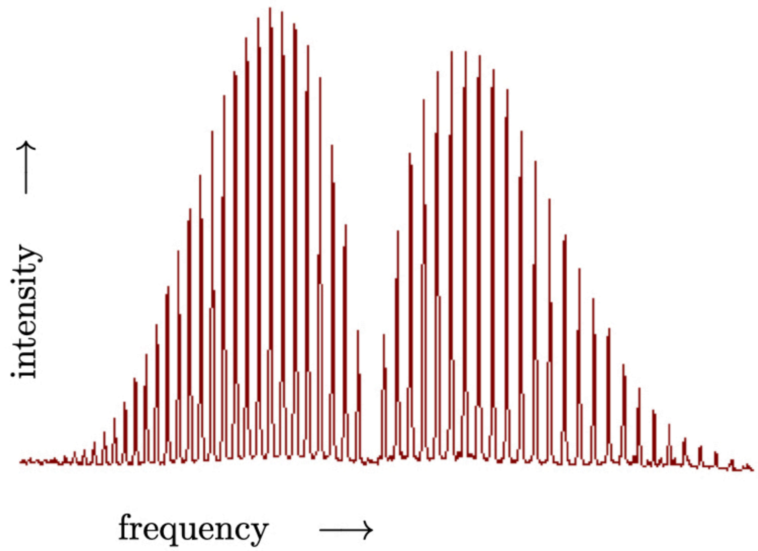
The vibration-rotation spectra of diatomic molecules

In both the old and the new quantum theory, diatomic molecules, like carbon monoxide (CO) or hydrogen chloride (HCl), can be modeled as systems of two bodies connected by a spring. The system can execute both vibrations and rotations as indicated in the figure below.



Model of diatomic molecule

The spectrum of the light emitted by these molecules consists of a number of equally spaced lines in the infrared on both sides of a missing central line.



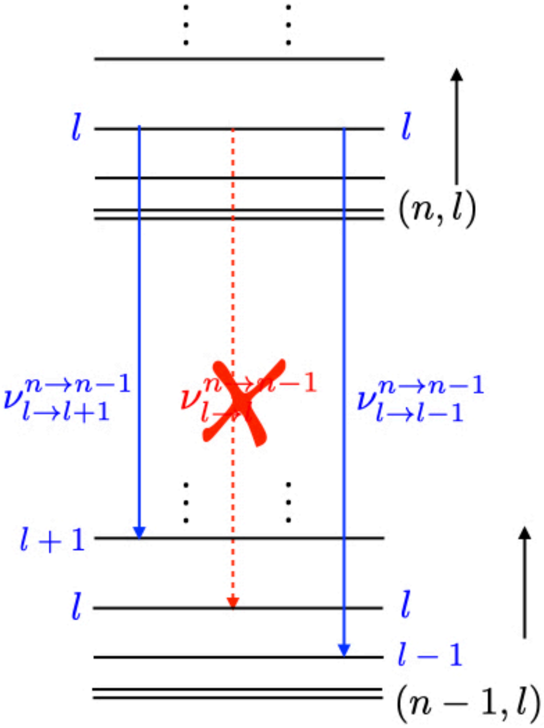
Typical spectrum of a diatomic molecule

These spectral lines originate from transitions in which the molecule simultaneously changes its vibrational and rotational state. The energy gap between different vibrational states is much larger than the energy gap between different rotational states. These transitions thus give rise to what are called rotational bands.

In both the old and the new quantum theory, the energy of diatomic molecules can only take on discrete values, labeled by two quantum numbers, n for vibrational, l for rotational energy:

$$E(n, l) = E_{vib}(n) + E_{rot}(l) \ ,$$

where $E_{vib}(n) \gg E_{rot}(l)$. The figure below shows two sets of vibrational energy levels, labeled by *n* and *n*+1, split into many rotational energy levels, labeled 0,1,2,3,…



Energy levels of a diatomic molecule plus two allowed (blue) and one forbidden (red) transition between them.

The rotational energy is proportional to L^2, the angular momentum squared. The quantization rule for angular momentum in the old quantum is

$$L = l\,\frac{h}{2\pi} \quad \text{with } l = 1, 2, 3, \ldots$$

where h is Planck's constant. So, according to the old quantum theory, the possible values of the rotational energy are

$$E_{rot}(l) = Cl^2 \quad \text{with } l = 1, 2, 3, \ldots$$

where C is some combination of h, π, the masses of the two molecules and the distance between them. For our purposes, we can treat it as a constant.

Only transitions in which n decreases by 1 and l increases or decreases by 1 are allowed. Schematically:

$$(n + 1,\ l) \to (n,\ l \pm 1)$$

The Bohr frequency condition says that the energy difference between initial and final state is equal to Planck's constant times the frequency $\nu_{l\to l\pm1}$ of the light emitted in the transition:

$$\begin{aligned} h\nu_{l\to l\pm 1} &= E(n+1,l) - E(n,l\pm 1) \\ &= E_{vib}(n+1) - E_{vib}(n) + E_{rot}(l) - E_{rot}(l\pm 1)\,. \end{aligned}$$

The difference in vibrational energy gives the frequency of the missing central line, which corresponds to the forbidden transition $l \to l$. The difference in rotational energy gives the shift in frequency of the lines on both sides of this missing line:

$$Cl^2 - C(l+1)^2 = -2Cl - C\,,$$

$$Cl^2 - C(l-1)^2 = 2Cl + C\,.$$

The old quantum theory thus predicts that the spectrum is symmetric around the missing line. In fact, it is shifted a little to the left. As physicists realized at the time, a better fit with the data is obtained if half-integer quantum numbers are used for angular momentum, i.e., if the expressions for L and E_{rot} are replaced by:

$$L = \left(l + \tfrac{1}{2}\right)\tfrac{h}{2\pi}, \quad E_{rot}(l) = C\left(l + \tfrac{1}{2}\right)^2.$$

In that case the frequency shifts are given by:

$$C\left(l + \tfrac{1}{2}\right)^2 - C\left(l + \tfrac{3}{2}\right)^2 = -2Cl - 2C\,,$$

$$C\left(l + \tfrac{1}{2}\right)^2 - C\left(l - \tfrac{1}{2}\right)^2 = 2Cl\,.$$

So the entire spectrum is shifted C/h to the left, which is in better agreement with the data. Unfortunately, it was completely unclear where these half-integer quantum numbers were coming from.

Mensing provided a simple solution to this puzzle in the course of treating the problem with the new quantum mechanics. The new rule for the quantization of angular momentum is

$$L^2 = l(l+1)\frac{h^2}{4\pi^2} \quad l = 0, 1, 2, \ldots$$

So the rotation energy becomes

$$E_{rot}(l) = Cl(l+1).$$

We now have

$$E_{rot}(l) - E_{rot}(l\pm 1) = Cl(l+1) - C(l\pm 1)(l\pm 1+1)\,,$$

which works out to:

$$Cl(l+1) - C(l+1)(l+2) = -2Cl - 2C\,,$$

$$Cl(l+1) - C(l-1)l = 2lC.$$

This is the same result found with half-integer quantum numbers in the old quantum. This is not surprising given that

$$l(l + 1) = \left(l + \frac{1}{2}\right)^2 - \frac{1}{4}$$

(the term $\frac{1}{4}$ does not matter since only energy differences matter in the end). Mensing thus explained why half-integer quantum numbers had worked better in the old quantum theory.

The electric susceptibility of diatomic gases

The electric susceptibility of a gas is a measure of how the gas responds to an external electric field (similarly for magnetic susceptibility). Consider a gas of diatomic molecules such as HCl. Such molecules will have a permanent electric dipole moment, with the hydrogen atom the positive and the chlorine atom the negative pole. When such molecules are placed in an electric field, their dipole moments will try to align with the field. In addition, the field will move the positive and negative poles a little further apart. The electric susceptibility χ of a gas of diatomic molecules is a combination of these two effects. It is described by a formula proposed by Peter Debye in 1912, modeled on a similar formula proposed by Paul Langevin for magnetic susceptibility (where only the alignment effect plays a role). The formula for χ thus became known as the Debye-Langevin formula:

$$\chi = N\left(\alpha + \frac{\mu^2}{3kT}\right),$$

where N is the number of molecules, α is a constant, μ is the permanent electric moment of individual molecules, k is Boltzmann's constant, and T is the temperature.

For our purposes, only the alignment effect, captured by the second term in the Debye-Langevin formula, is important. The alignment is frustrated by the thermal motion of the molecules. This is why this second term has the temperature in its denominator: the higher the temperature, the smaller the alignment effect. Put differently: the greater the energy of the molecules, the smaller the alignment effect. In fact, in classical theory only the lowest energy states contribute to χ.

The second term of the Langevin-Debye formula can be written as

$$\chi = C\frac{N\mu^2}{kT}.$$

Classical theory correctly predicted that $C = \frac{1}{3}$. The old quantum theory predicted a much larger value. Using integer quantum numbers, Mensing's mentor Wolfgang Pauli found $C = 1.54$ when he did the calculation in 1921, almost five times the classical value. Unlike the situation with the spectrum of these diatomic molecules, half-integer quantum numbers only made matters worse. When Linus Pauling redid Pauli's calculation a few years later with half-integer quantum numbers, he found $C = 4.57$, almost 14 times the classical value! This is the problem Pauli hoped Mensing could help him solve in the new quantum mechanics.

The root of this problem for the old quantum theory, as with the problem of the spectrum of diatomic molecules, was the rule for the quantization of angular momentum. The calculation of the contribution of the alignment effect to the electric susceptibility proceeds in two steps, taking two different averages. First, one has to take the *time average* of the component of a molecule's dipole moment in the direction of the electric field. Then one has to take an *ensemble average*, i.e., one has to average the time average of individual molecules over all molecules in the gas, assuming a normal (Boltzmann) distribution of these molecules over all states they could be in.

If one does this calculation in classical mechanics *for all but the lowest energy states*, the time average gives an expression of the form

$$A(L)\left(3\overline{\left(L_z^2/L^2\right)} - 1\right),$$

where L is the length of the molecule's angular momentum vector, L_z is the z-component of that vector, $A(L)$ is some combination of quantities which depend on L, and the overbar indicates the time averaging mentioned above. If we average this time average over all molecules, using a double bar for this ensemble averaging, we get

$$\overline{\overline{\left(L_z^2/L^2\right)}} = \frac{1}{3},$$

since $L^2 = L_x^2 + L_y^2 + L_z^2$ and the x- y- and z-directions will be represented equally among the molecules in the gas. It follows that the contribution to the alignment effect coming from the bulk of the molecules' energy states vanishes. The only contribution comes from the lowest energy states, as one would expect, and it could be shown that this contribution is of just the right amount, with $C = \frac{1}{3}$.

Both in the old and in the new quantum theory, one arrives at expressions for the time average of the component of a molecule's dipole moment in the direction of the electric field by using the quantization rules for angular momentum. In the old quantum theory, these rules are $L = l\frac{h}{2\pi}$ (with $l = 1, 2, 3, \ldots$) and $L_z = m\frac{h}{2\pi}$ (with $m = -l, \ldots, 0, 1, \ldots, l$) and the time average becomes:

$$A(L)\left(3\frac{m^2}{l^2} - 1\right).$$

In the new quantum theory, the first of these quantization rules gets replaced by $L^2 = l(l + 1)\frac{h^2}{4\pi^2}$ (with $l = 0, 1, 2, 3, \ldots$) and the time average becomes

$$A(L)\left(3\frac{m^2}{l(l+1)} - 1\right).$$

To find the contribution to the alignment effect, we need to average these expressions over all possible states, i.e., over all possible values of the quantum numbers l and m labeling these states. To get the empirically correct answer, it had better be the case that only the lowest energy state contributes and that the contributions of all other states sum to zero.

In the old quantum theory, this is not the case. Since the value $l = 0$ is ruled out, the lowest energy state is forbidden and thus does not contribute to the alignment effect at all. In that sense, as Pauli pointed out when he did the calculation in 1921, it was fortunate that the higher energy states contributed. Unfortunately, their contribution was almost five times too large. And with half-integer quantum numbers it was almost fourteen times too large! As Van Vleck said in his AHQP interview, the old quantum theory produced some “wonderful nonsense” on this score.

Mensing and Pauli took care of this “nonsense” in their 1926 paper. First of all, the value $l = 0$ is no longer ruled out and they showed that this state accounts for the full alignment effect, restoring the constant C to its classical value of $\frac{1}{3}$. Furthermore, they showed that the contributions coming from all other states are zero! This follows immediately from the well-known sum of squares formula. Customized to the situation at hand, this formula says that

$$\sum_{m=-l}^{l} m^2 = 2 \sum_{m=1}^{l} m^2 = \frac{1}{3} l(l + 1)(2l + 1).$$

We can use this formula to compute the average of the time average over all possible values of m for a given value of l, the two quantum numbers labeling the allowed states of the system. This average, it turns out, vanishes for all values of $l \neq 0$:

$$\frac{1}{2l+1} \sum_{m=-l}^{l} \left(\frac{3m^2}{l(l+1)} - 1 \right) = \frac{1}{2l+1} \left(\frac{3 \sum_{m=-l}^{l} m^2}{l(l+1)} - (2l + 1) \right) = 0 .$$

As Mensing and Pauli, with obvious relief, note in an italicized the clause in their paper: “*Only the molecules in the lowest state will therefore give a contribution to the temperature-dependent part of the dielectric constant*.”