James Franck, the Ionization Potentials of Helium, and the Experimental discovery of Metastable states

James Franck
(1882–1964)

Fritz Haber's KWI for Physical and Electrochemistry

Clayton Gearhart
St. John's University (Minnesota)

HQ- 4
Donostia/San Sebastian, Spain
July 2015

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Henry Gilbert Small, *The Helium Atom in the Old Quantum Theory,* Ph.D. dissertation, University of Wisconsin, 1971

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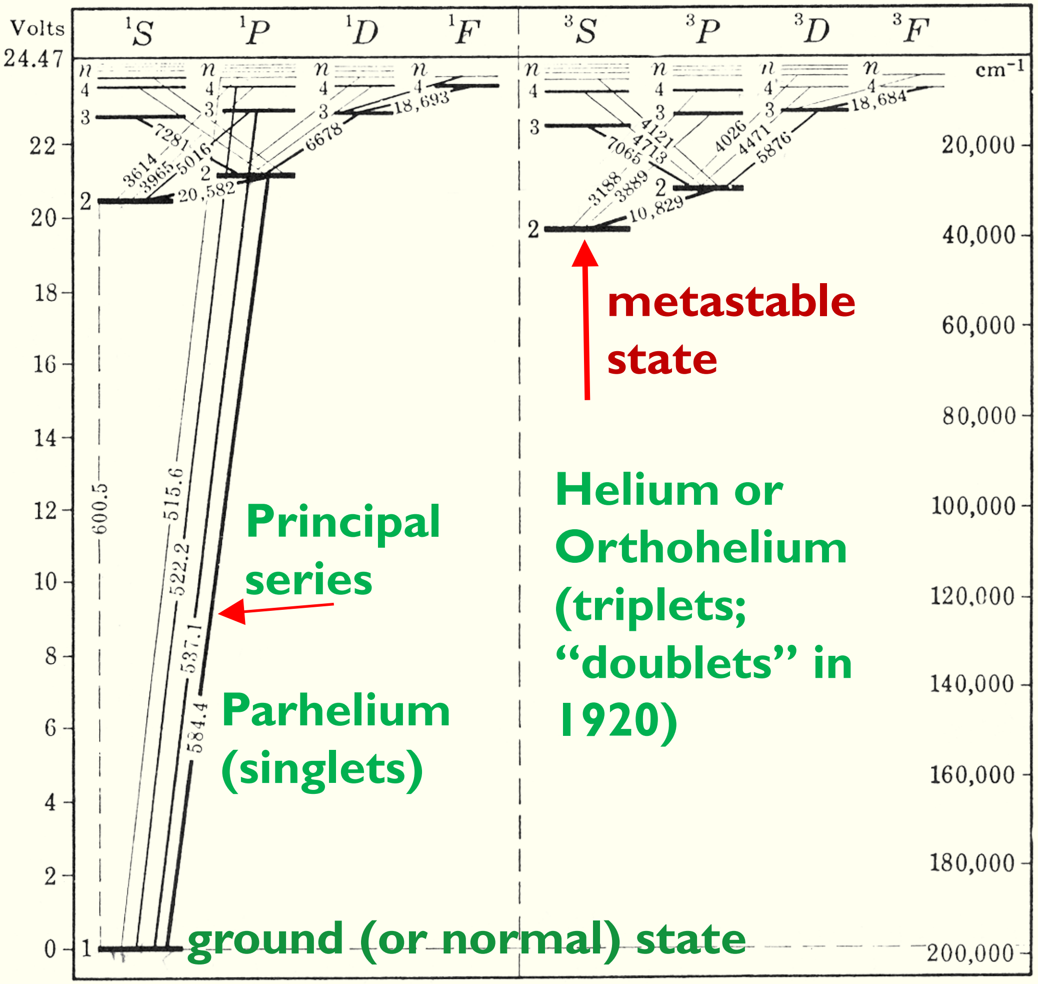
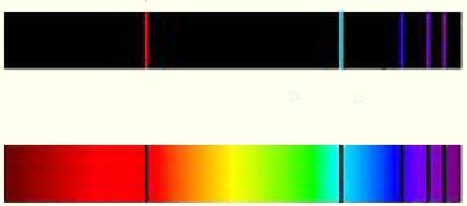
METASTABLE STATES--HELIUM



Helium term diagram (after Bohr, energy level diagram)



- No optical transitions from "doublet" (triplet) terms (orthohelium) to singlet terms (parahelium)
- In particular, no optical transition from **metastable** state 2^3S of helium to ground state

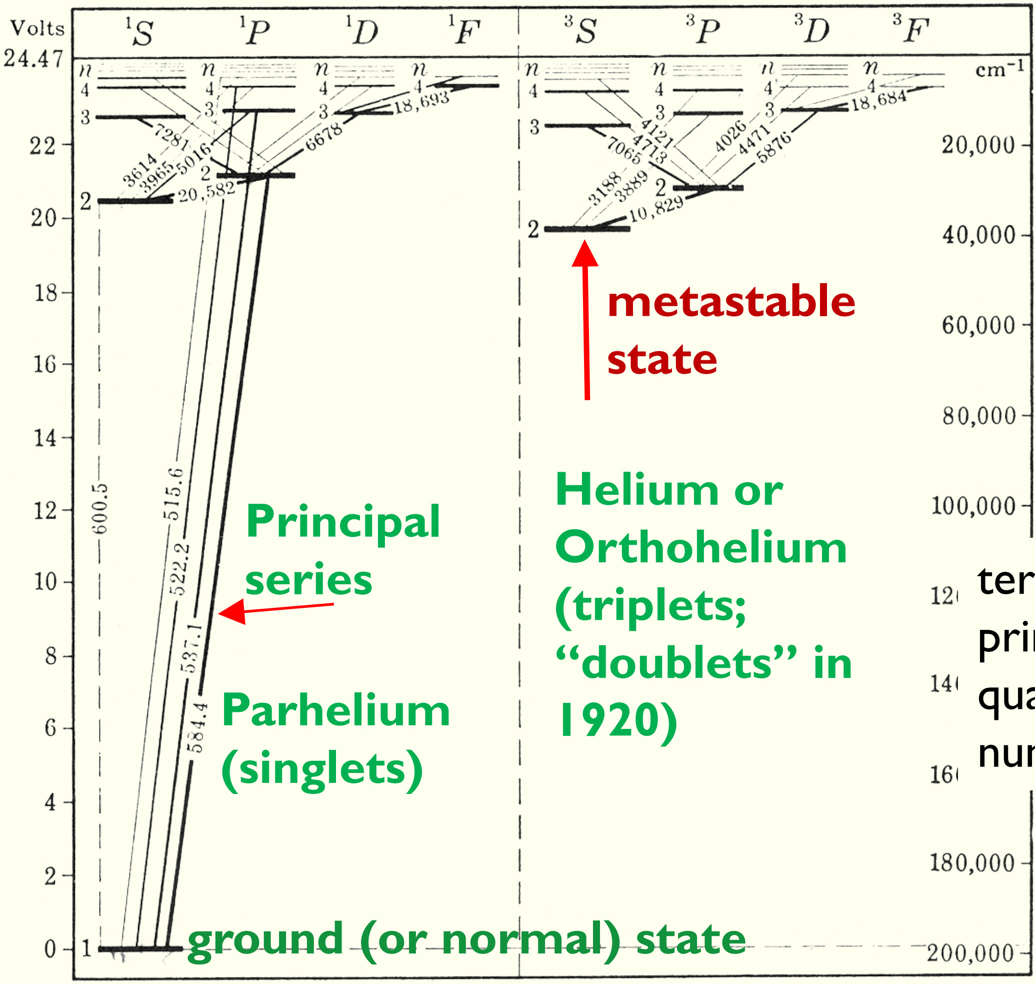
Some texts, but not all, talk about "metastable states" in context of

- Selection rules
- Transition probabilities/rates

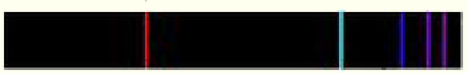
But in 1919–1920, such theories were in their infancy.

Franck, together with Paul Knipping and Fritz Reiche, discovered metastable states in the course of experiments on the ionization potential of helium.

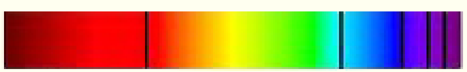
Metastable States--Helium



Helium term diagram (after Bohr, energy level diagram)



emission



absorption

will use modern spectroscopic notation:

multiplicity: singlet, doublet, triplet …

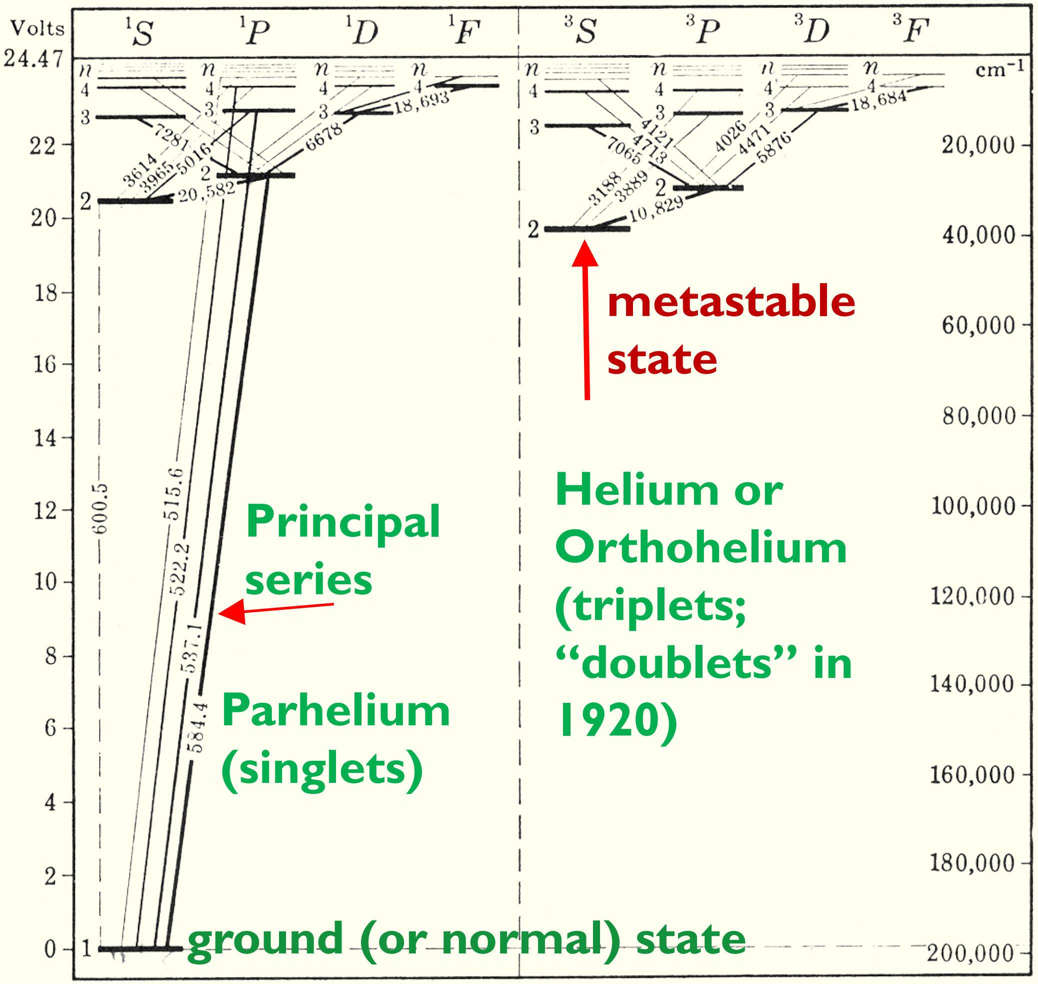
$$2\,^3S$$

term number/ principal quantum number

term type (Sharp, Principal, Diffuse, …); and also

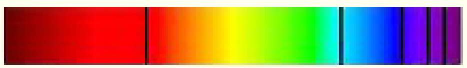
azimuthal/angular momentum quantum number

Metastable States--Helium



Helium term diagram (after Bohr, energy level diagram)

emission



absorption

Principal Series

- ends on S state (usually ground state)
- since it ends on the ground state, it is the only series seen in absorption
  - ⇒ allows calculation of series limit (and in Bohr picture, ionization energy)

The Franck-Hertz Collaboration, 1911–1914

James Franck
(1882–1964)

The Physical Institute, University of Berlin

Gustav Hertz
(1887–1975)

Goal: To investigate John Sealy Townsend's theory of ionization by collision

The original goal of our experiments had nothing to do with atomic or quantum physics.

Gustav Hertz, 1975

THE FRANCK-HERTZ COLLABORATION, 1911–1914

James Franck

The Physical Institute, University of Berlin

Gustav Hertz

The Franck-Hertz Experiments, 1911–1914
Experimentalists in Search of a Theory

With an appendix, "On the History of our Experiments on the Energy Exchange between Slow Electrons and Atoms" by Gustav Hertz

Clayton A. Gearhart*

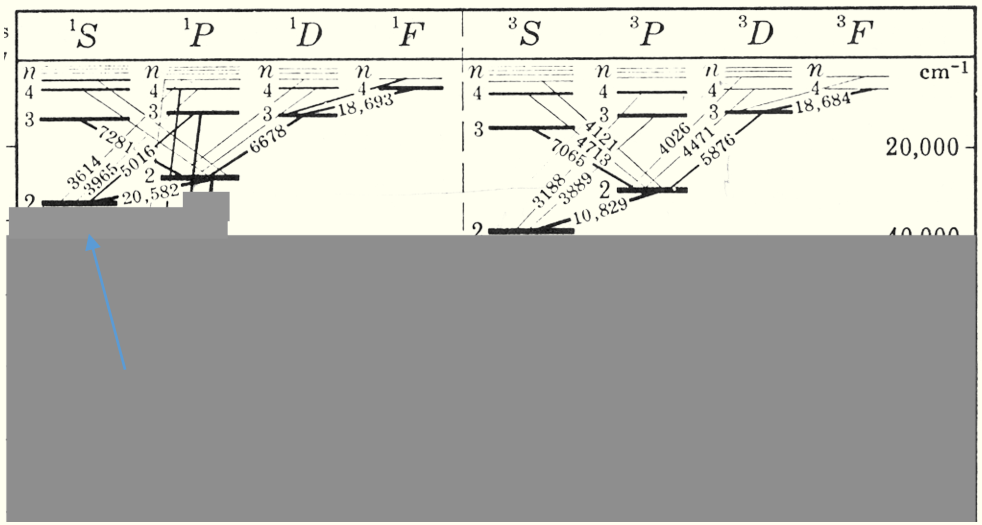
Physics in Perspective **16** (2014) 293–343

Helium Term Diagram in 1911

Sommerfeld, *Atombau* (1919), ch. 2, "The Neutral Helium Atom:

„Hier stock' ich schon, wer hilft mir weiter fort?" (*Faust*, I, 1225)

("Here I falter, who will help me onward?" [Enter Mephistopheles!]



Where and in which series (if either) is the ground (or "normal") state?

- No lines had seen in absorption (i.e., principal series, from ground state)
- Ground state transitions presumed to be in far ultraviolet—Theodore Lyman eventually found them spectroscopically, but not until 1921–1922.
- Before Bohr (1913): Spectroscopic terms were NOT energy levels

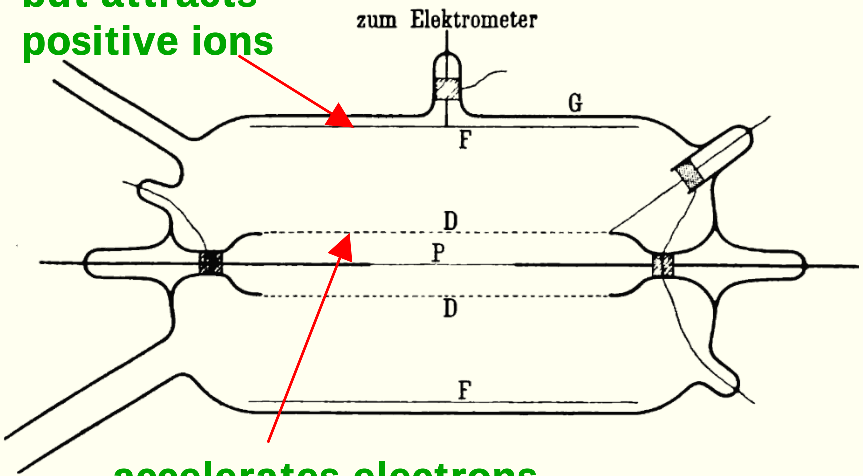
In 1913, James Franck and Gustav Hertz used collisions of slow electrons with gas atoms to measure (unsuccessfully) the ionization energy of helium.

In 1919–1920, Franck and his collaborators at Fritz Haber's KWI for Physical Chemistry in Berlin returned to this theme, along with others in England and the U.S.

Franck and Hertz, January 1913

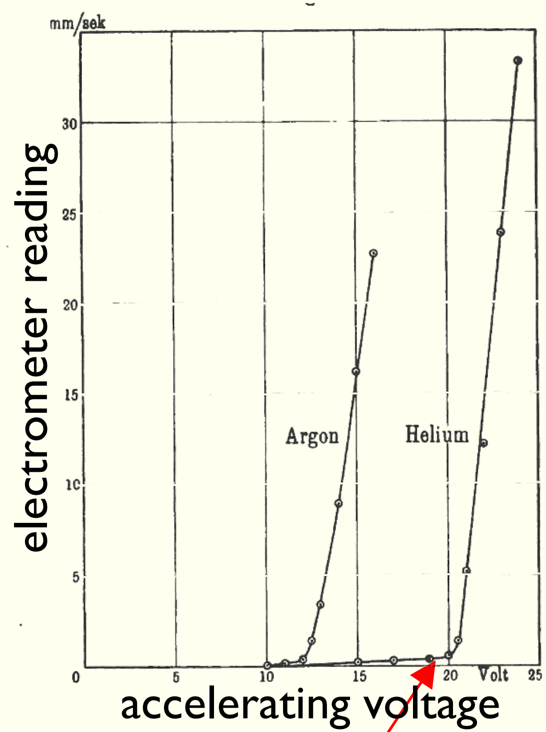
"Measurement of the Ionization Potential in different Gases"

repels electrons but attracts positive ions



accelerates electrons

design adapted from Phillip Lenard, who had tried to measure ionization potentials by **directly detecting positive ions**



Helium: 20.5 V "ionization" potential

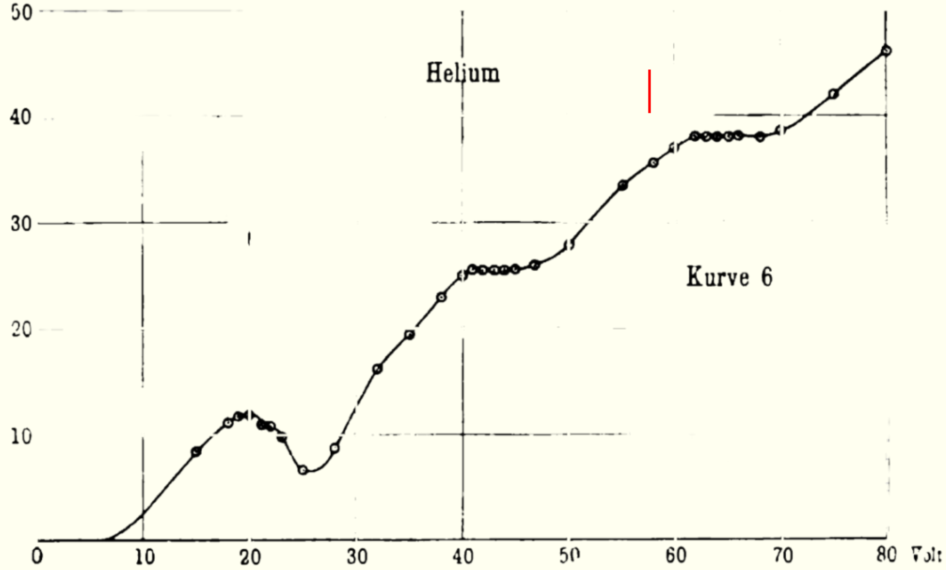
The experiment was designed to measure the ionization potentials of helium, argon, and several other gases by detecting (**what they thought were**) positively charged ions. In fact, were seeing **photoelectrons** ejected from the collecting electrode.

Franck and Hertz, April 1914

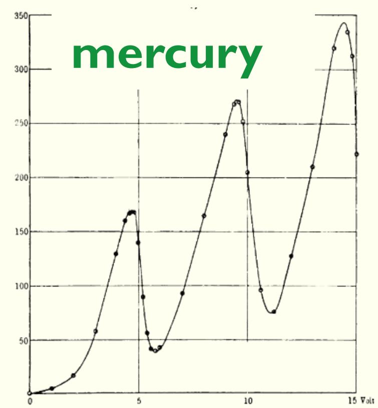
"On Collisions between Electrons and Molecules of Mercury Vapor and the Ionization Potential of the Same"

- could not use their1913 method (detect positive ions) for mercury
- adopted instead a variation of their method for measuring energy loss in collisions

  peaks ⇒ inelastic collisions
- They also measured the "ionization" potential of helium using this new method, and found the same value (20.5 volts) they had found in 1913.



In fact, as in 1913, they were NOT seeing ionization, for either helium or mercury.



Enter the (mostly) North Americans

In August 1914, Franck and Hertz found themselves in the German army. They did not resume experimental work until after the Great War.

Nevertheless, the Franck-Hertz experiments inspired widespread interest and emulation during the war, mostly in North America.

I will mention only

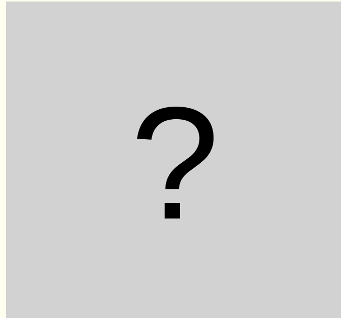
Bergen Davis and Frederick S. Goucher, 1917; Columbia University

Bergen Davis and Frederick Goucher, 1917

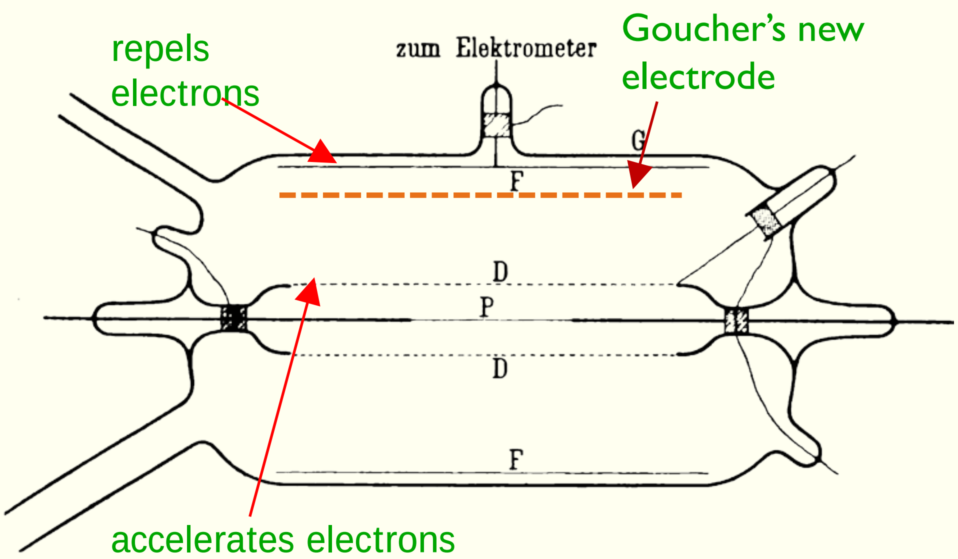
"Ionization and Excitation of Radiation by Electron Impact in Mercury Vapor and Hydrogen"

Bergen Davis
(1869–1958)

Goucher contrived a clever technique—a new mesh electrode close to the collector—for distinguishing between positive ions arriving at the collecting electrode, and photoelectrons leaving.



Frederick S. Goucher
(1888–1973)



Goucher's new electrode could be biased either positively or negatively with respect to the collecting electrode *F*

- In this way, they could control behavior of both photoelectrons and positive ions and distinguish between them

Their results were unambiguous: Franck and Hertz had been seeing photoelectrons, not positive ions.

Franck and Hertz, 1919

"The Confirmation of Bohr's Atomic Theory through Investigations of Inelastic Collisions of Electrons with Gas Molecules"

Franck and Hertz, January 1919

In January 1919, barely two months after the armistice, Franck and Hertz published a long review article.

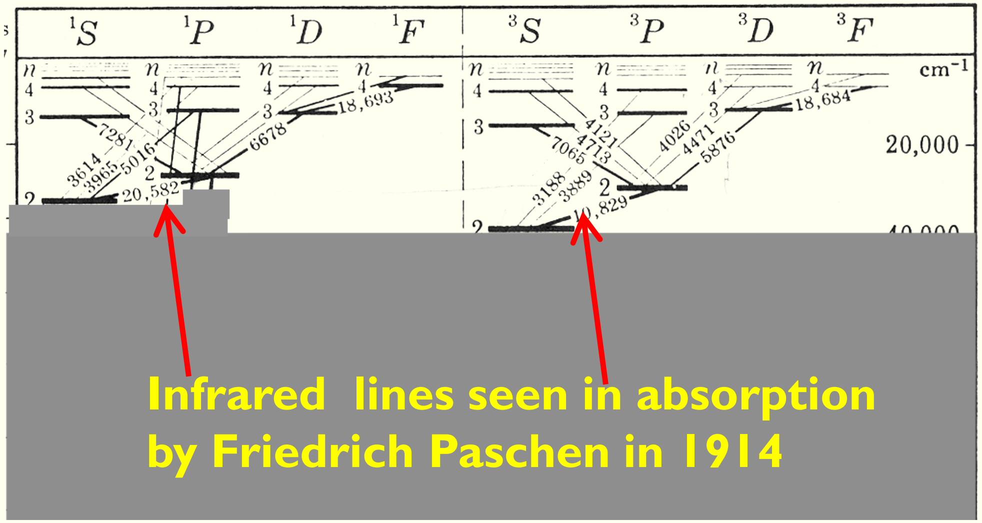
They had learned of the North American work, and realized that in both mercury and helium, they had been seeing excited states, and not ionization potentials.

In addition, they had become enthusiastic proponents of Bohr's theory—not mentioned in 1914.

Aside: ionization by multiple collision ⇔ metastable states

So what is the ionization potential of helium?

Franck and his coworkers returned to this question in 1919; in the process, they encountered metastable states.



Where and in which series (if either) is the ground (or "normal") state?

Theoretical context:

Alfred Landé's 1919 model of the helium atom

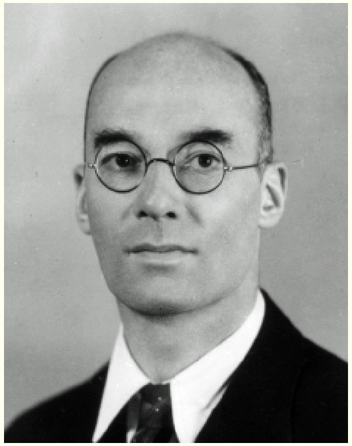
Experimental context:

Friedrich Paschen's 1914 discovery of resonance absorption in helium

Three Papers

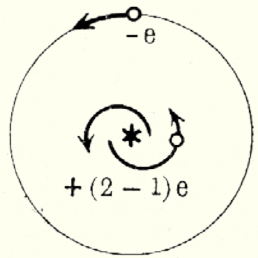
1. Franck and Paul Knipping: Measured helium ionization potential**s**, June 1919
   - also measured by Frank Horton and Ann Catherine Davies in Britain (1919) and Karl Compton in U.S. (1920)
2. Franck and Fritz Reiche, (argument for **metastable states**): January 1920.
3. Franck and Knipping: Second experimental paper, on helium excitation potentials and **metastable states**, March 1920

Theoretical Context: Landé's Helium model (1919)



Alfred Landé
(1888–1976)

Fig. 19.



Sommerfeld's "double star"
Atombau, 1919

Arnold Sommerfeld
(1868–1951)

Landé's 1919 model of a helium atom built on Sommerfeld's "double-star" model. It envisions one electron close to the nucleus, the other farther out. The orbits are inclined at roughly 90° for singlet states ("**crossed** orbits"), but are **coplanar** for "doublet" states.

note resemblance to hydrogen, alkalis

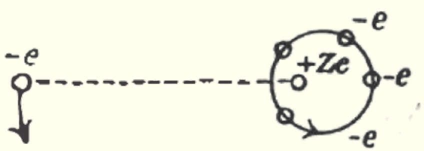


Fig. 1.

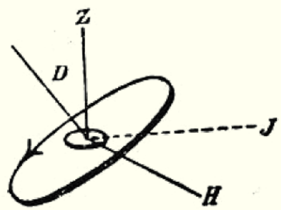
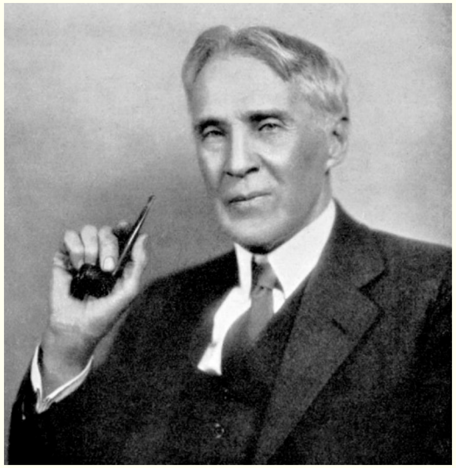


Fig. 2.

Sommerfeld was initially (1919) impressed with Landé's results, but dropped all mention of it in the second (1921) edition of the *Atombau*.

Experimental Context: Resonance Fluorescence



Robert W. Wood
(1868–1955)

Resonance fluorescence was discovered by the American spectroscopist Robert W. Wood in 1904.

Illuminate sodium vapor at low pressure with a beam of light from bright yellow sodium D lines. The vapor absorbs the light, and fluoresces (radiates in all directions) with light of the same wavelength.

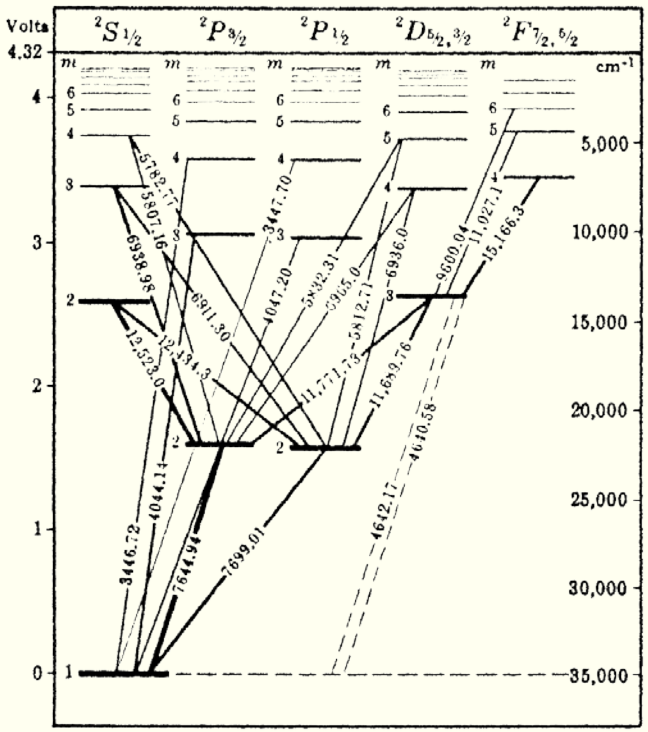
Ditto in 2536 Å line in mercury (measured by FH in 1914).

In other words, we take hold of, and shake, so to speak, but one of the many electrons which make up the molecule.

Robert W. Wood, 1911

In modern terms: atoms excited to lowest energy state have only one decay path.

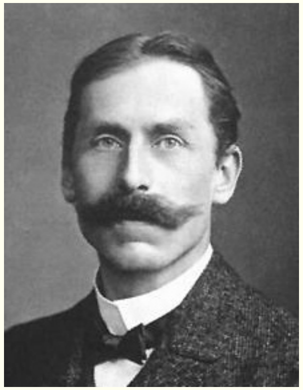
In 1914, both Paschen, and Franck and Hertz, interpreted resonance lines as atomic electrons behaving like quantized Planck oscillators; no mention of Bohr.



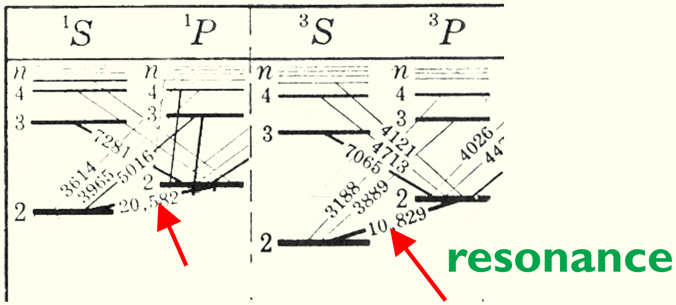
term diagram for potassium

Friedrich Paschen and Resonance in Helium, 1914

“Absorption and Resonance of Monochromatic Radiation”



Friedrich Paschen
(1865–1947)



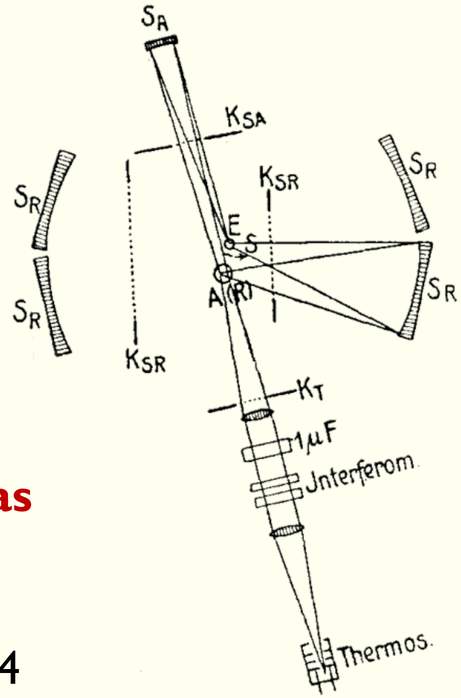


Fig. 4.

Paschen’s experiments showed that practically all of the energy… from the primary beam was reëmitted as resonance radiation. … these experiments stand out as perhaps the most remarkable ever performed in the field of radiation…

Robert W. Wood, 1934

In 1914, **no absorption lines had been seen in helium**, though these two infrared lines (10,830 Å and 20,582 Å) had been seen in emission.

By running a weak current through a discharge tube containing VERY pure helium, Paschen was able to see these lines **in absorption**.

Paschen showed that the 10,830 Å line $(2^3S \rightarrow 2^3P)$ showed resonance, but that the 20,582 Å line $(2^1S \rightarrow 2^1P)$ did not.

Franck and Paul Knipping, 1919

“The Ionization Potentials of Helium”

James Franck

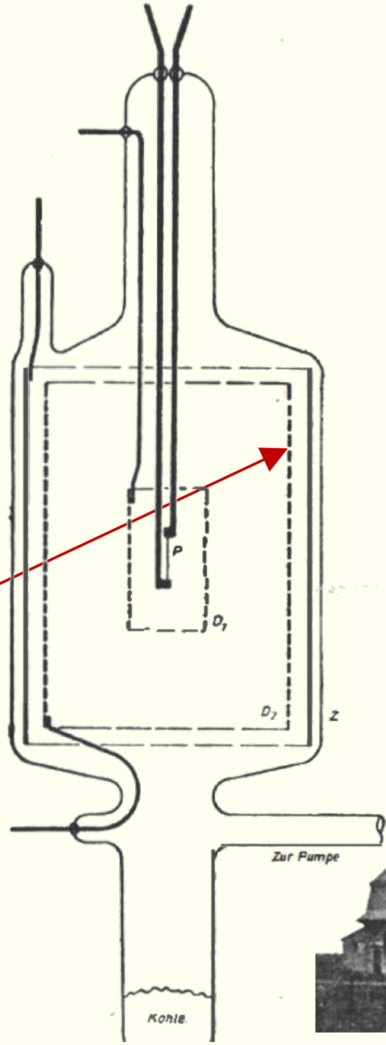
In 1919, at Haber’s Institute for Physical Chemistry in Berlin, Franck and Knipping used **three methods** to measure the ionization potentials of helium.

Paul Knipping (1883–1935)

Knipping had studied with Röentgen in Munich. In 1912, he and Walter Friedrich had confirmed Laue’s prediction of interference in X-rays.

Apparatus: Returned to FH 1913 (Lenard’s method for direct detection of positive ions).

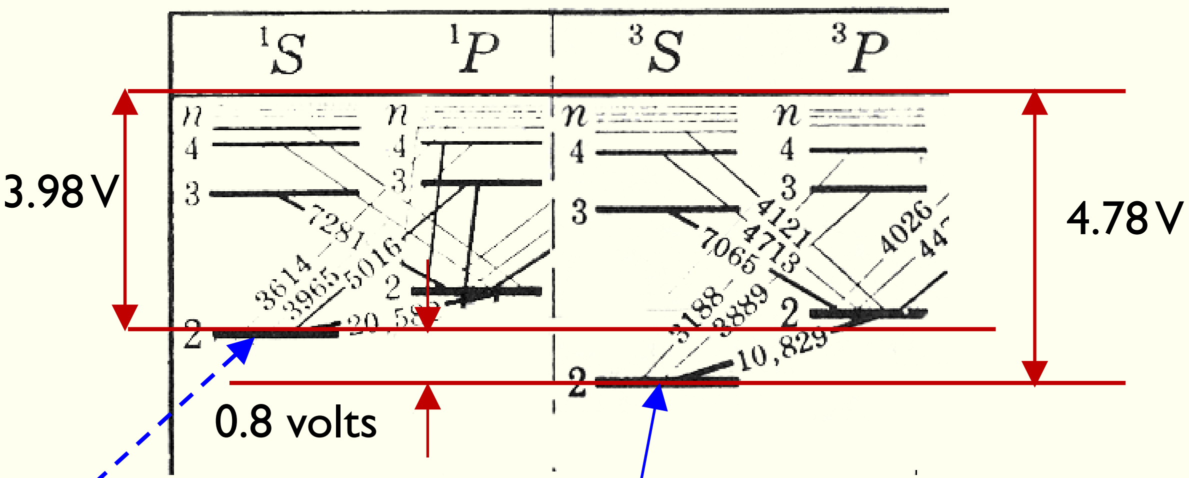
extra mesh electrode to distinguish ions from photoelectrons (Davis and Goucher)



Franck and Paul Knipping, 1919

"The Ionization Potentials of Helium"

First Method



Note that helium has two "principal series" 0.8 volts apart, starting from 2 ^{1}S and 2 ^{3}S terms.

Series limits were known.

1. Measured first excited state (20.5 volts), identified with lowest helium state 2 ^{3}S and **confirmed that they were seeing photoelectrons**
2. To find ionization potential, add to series limit:

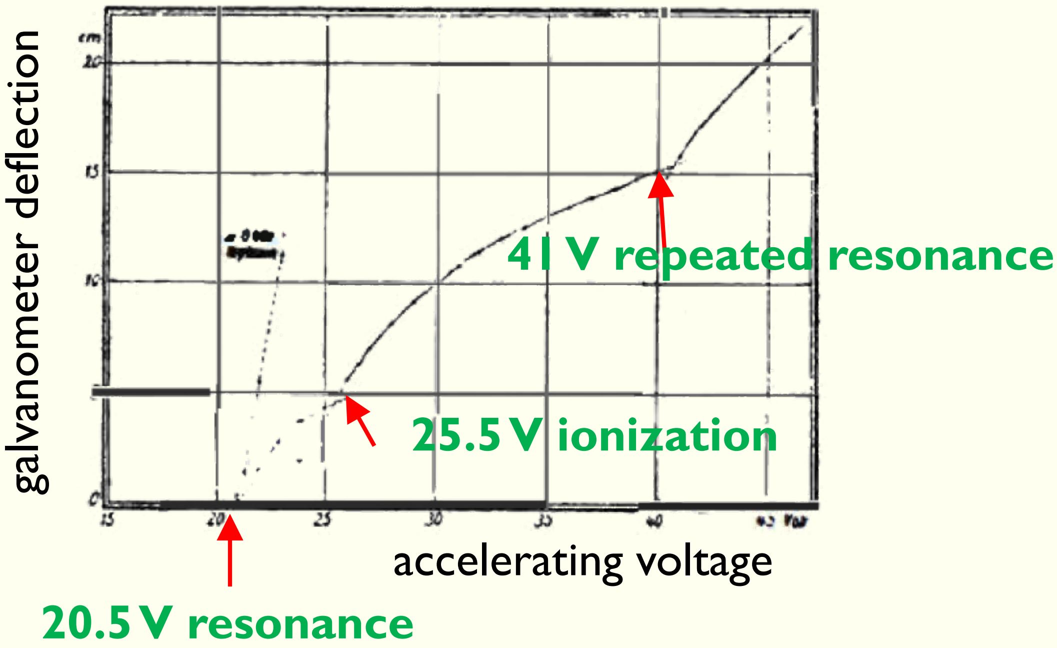
   20.5 V + 4.78 V = 25.3 V

3. Theoretical predictions about 30 V (Bohr, Sommerfeld, and Landé)
4. Suggestion of 2 ^{1}S state 0.8 V higher

Franck and Paul Knipping, 1919

"The Ionization Potentials of Helium"

Second Method



This time, Franck and Knipping took a current-voltage curve over the entire region, and found "knicks" as shown.

- no sign of photoelectrons at ionization knick at 25.5 volts.

But what if the 25.5 V knick was another excited state and not the ionization potential? Unlikely, but to check, they used …

Franck and Paul Knipping, 1919

"The Ionization Potentials of Helium"

Third Method

Measure the ionization potential for the removal of **both** electrons:

- Result: 79.5 V

The ionization potential of **singly ionized** helium was accurately known both experimentally (spectroscopic series limit) and theoretically (Bohr model) to be 54.08 V; hence

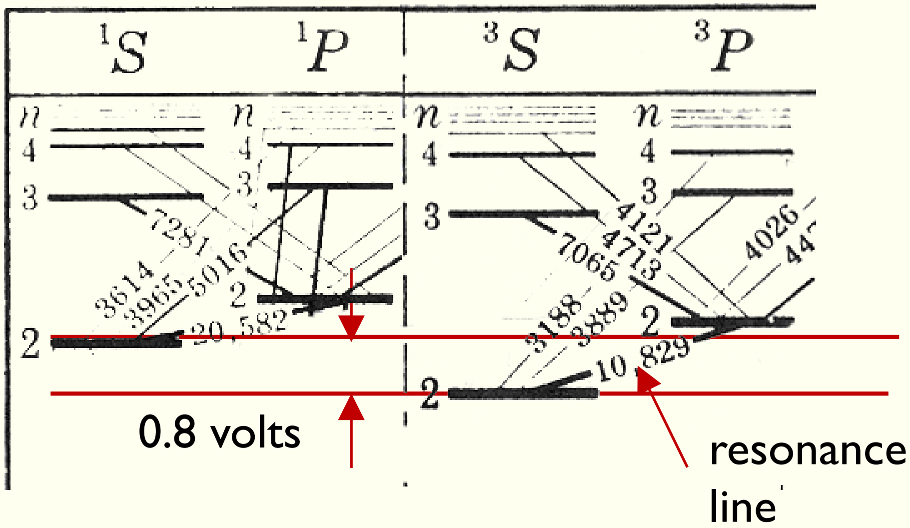
ionization potential = 79.5 V – 54.08 V = 25.4 Volts

… where the exact agreement is of course a coincidence. …

Franck and Paul Knipping, 1919

"The Ionization Potentials of Helium"

Metastable States



The first term of the series going out from the two-quantum orbit is following Paschen a resonance line 1.08 μ corresponding to 1.2 volts, so that a third inelastic electron collision to a higher potential by this amount is to be expected. We hope … make sure of the observation of this resonance potential, and want here only to suggest this point with all reserve.

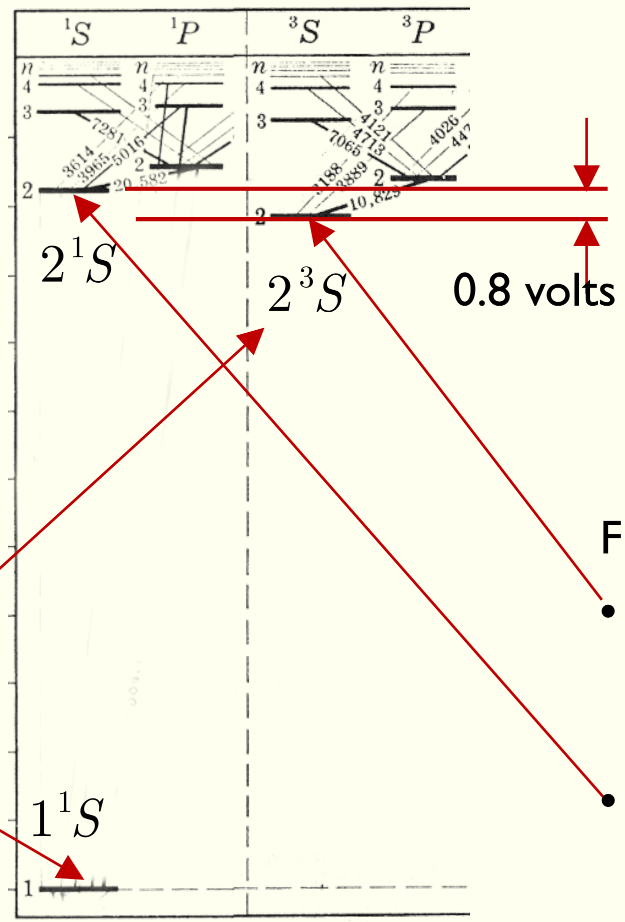
in a footnote: This point … appears to us to suggest that the alkali-similar state of helium is so to speak metastable.

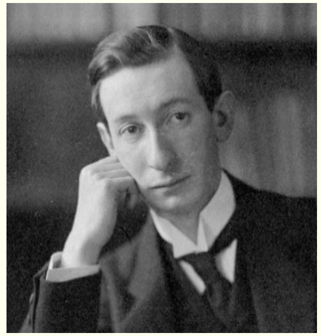
In 1920, Franck, Knipping, and Fritz Reiche developed a two-pronged attack to argue for metastable states.

Franck, Fritz Reiche, and Paul Knipping, 1920

The Discovery of Metastable States

James Franck





Fritz Reiche (1883–1969)

Paul Knipping

Franck and Reiche used Paschen's experiment to argue that

- the 2 ^{3}S state is metastable
- the ground state belonged with the singlet series

Franck and Knipping

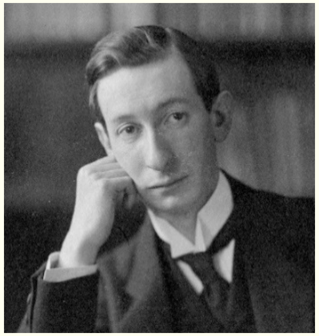
- the 2 ^{3}S state (20.5 volts) only appeared in **impure** helium ⇒ 2 ^{3}S state is metastable.
- Found the 2 ^{1}S state (21.2 volts), 0.8 volts higher.

Both papers used purely experimental arguments. Yet both emphasized (unnecessarily?) Alfred Landé's helium model for a physical picture.

State of quantum theory circa 1920?

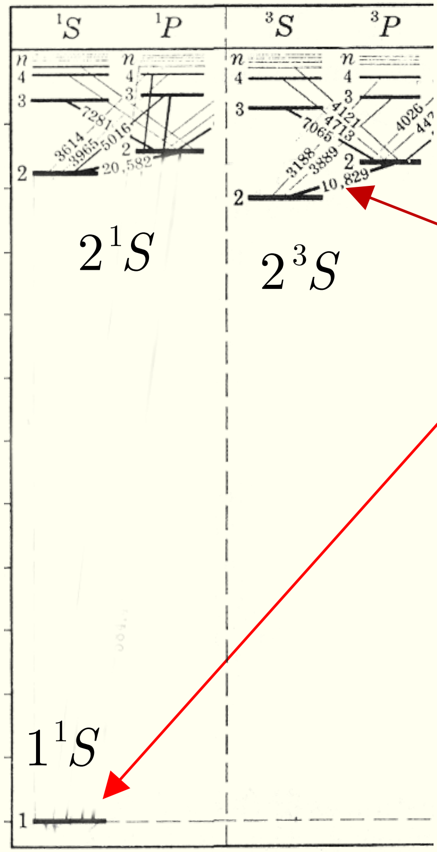
Franck and Fritz Reiche, 1920

"On Helium and Parhelium"



Fritz Reiche (1883–1969)

Fritz Reiche was a student and later an assistant of Planck, and part of the Berlin circle of physicists in which Franck moved. In 1919–1920 he was a theoretical advisor at Haber's Institute for Physical Chemistry. He made numerous contributions to early quantum theory. In 1921 he was appointed professor of physics at Breslau.

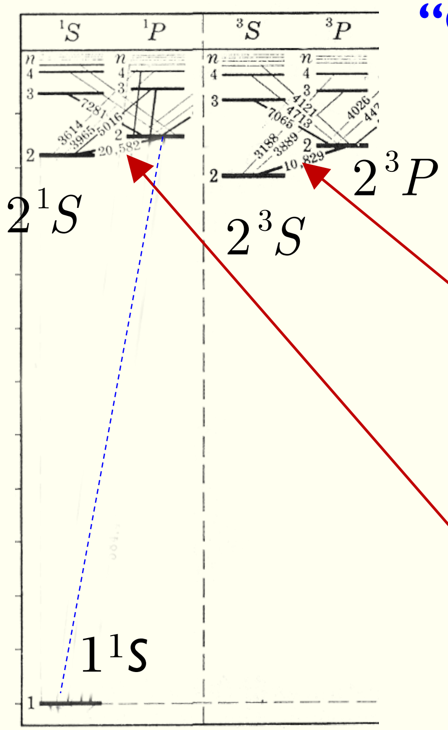


From the evidence that the 1.083 μ line belonging to the system of coplanar helium is a resonance line, one can conclude with certainty that in normal [ground state] **helium only the crossed … state is present.**

Franck and Reiche, 1920

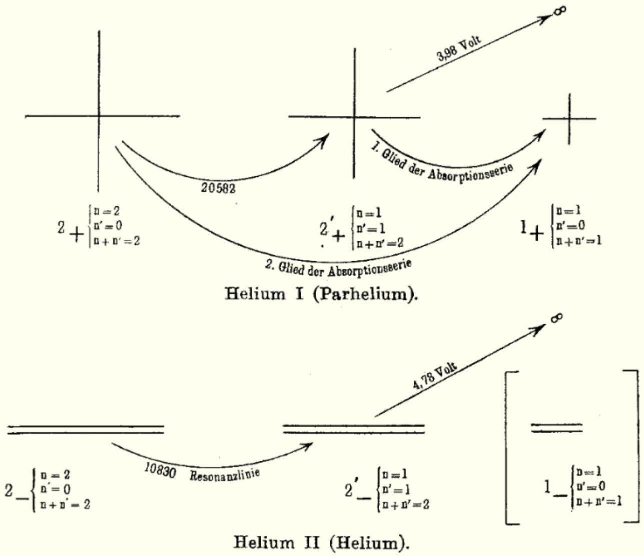
Franck and Fritz Reiche, 1920

"On Helium and Parhelium"



- No transitions between singlet and "doublet" series
- Paschen's experiment saw absorption of the10,830 Å and the 20,582 Å lines in weakly excited helium.
- The 10,830 Å line showed resonance ⇒ $2\,^3P$ state could go only to the $2\,^3S$ state and NOT to a ground state

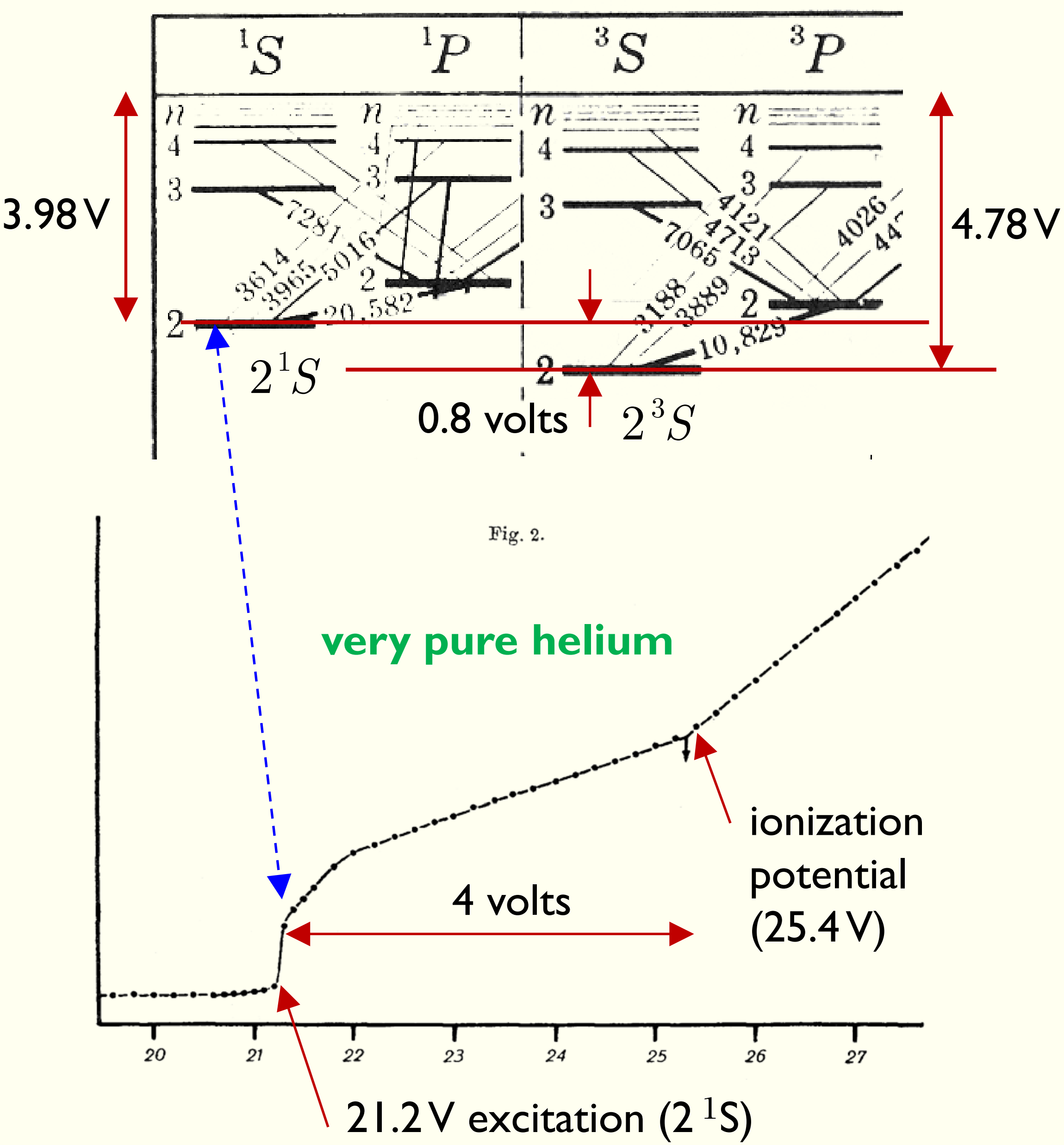
  ⇒ $2\,^3S$ state must be "metastable."
- The 20,582 Å line did **not** show resonance ⇒ $2\,^1P$ state could undergo transitions to **both** $2\,^1S$ and to a ground state that **must** be in the singlet series, i.e., $1\,^1S$ state



Franck-Reiche diagram

Franck and Knipping, 1920

"On the Excitation Potentials of Helium"



improved apparatus, purer helium:

- confirm hint of 2 ^{1}S state
- is 2 ^{3}S state metastable?.

In very pure helium, 20.5 Volt state (2 ^{3}S) disappears!

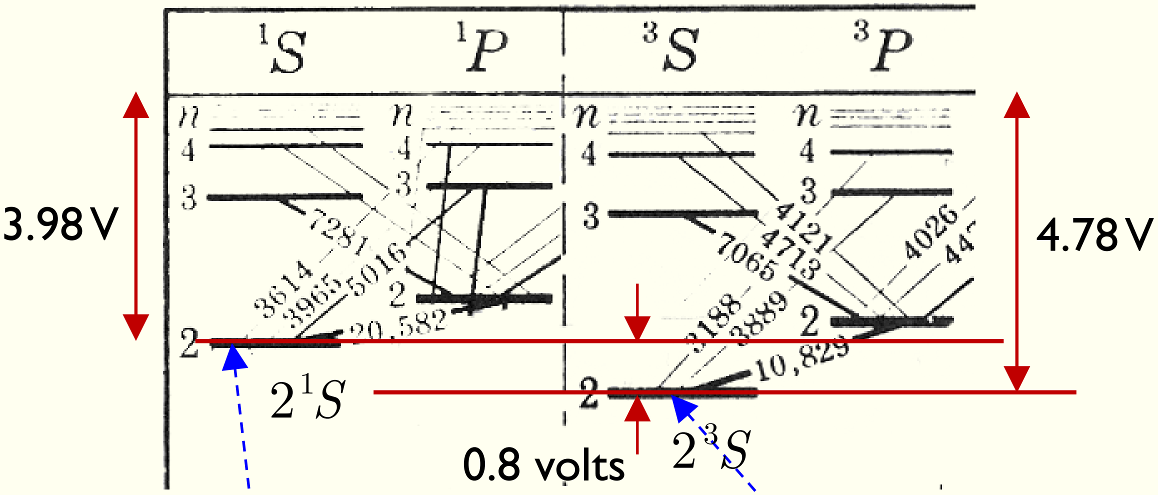
Because of uncertainties in initial electron velocities, excitation potentials are most accurately found from voltage **differences**, measured from ip.

For **very pure** helium, saw only the 2 ^{1}S state at 21.2 V (20.5 + 0.8) level, 4 V below the ionization potential.

They did **not** see the 20.5 V state, 2 ^{3}S though it must have been excited. It apparently did not decay to ground state ⇒ metastable.

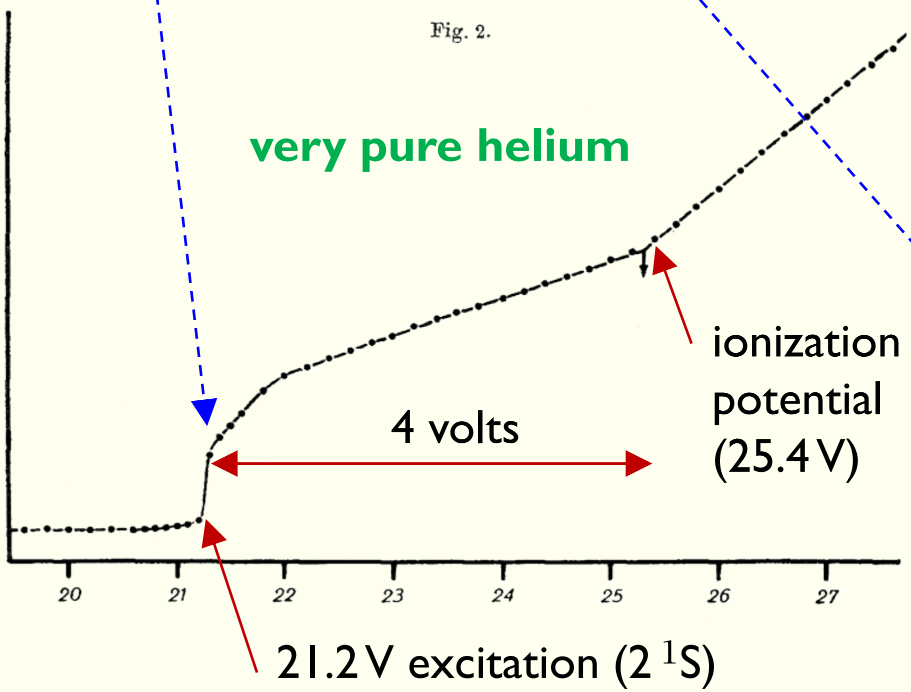
Franck and Knipping, 1920

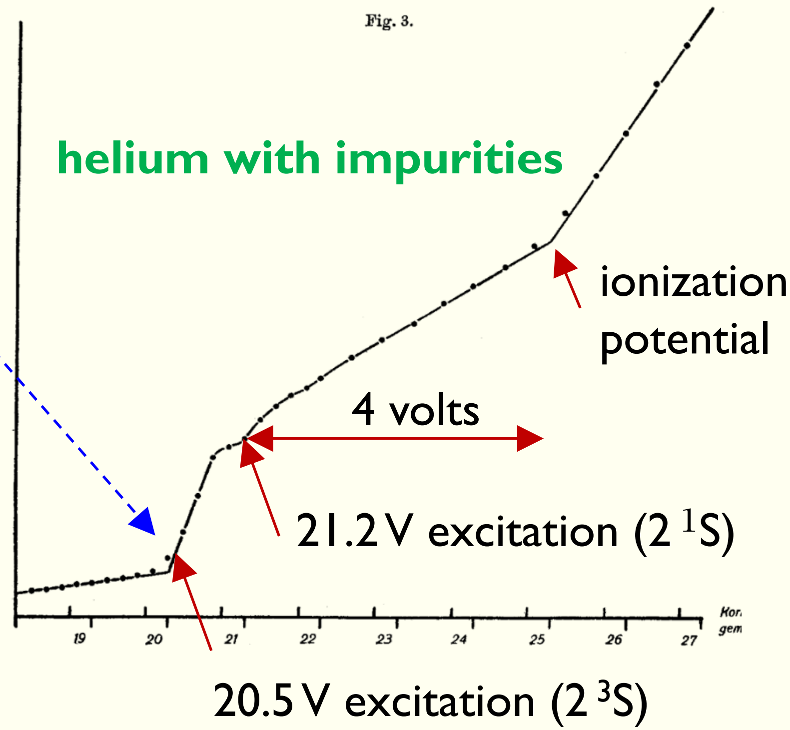
"On the Excitation Potentials of Helium"



In very pure helium, 20.5 Volt state (2 ^{3}S) disappears!

Then, **repeat for less pure helium: the 20.5 V state is back!**





Franck, Reiche, and Knipping, 1920

The Role of theory: Landé's model

In pure helium, an electron will just sit in a $2\,^3S$ metastable state. It does not undergo an optical transition to the ground state.

For less pure helium: Helium in excited coplanar states (Landé model!) is chemically "**very similar to a lithium or a hydrogen atom**" and in collisions with impurity atoms,

- helium and impurities can form short-lived compounds which decay with the emission of uv light,
- In the process, helium returns to the ground state **without** itself radiating.

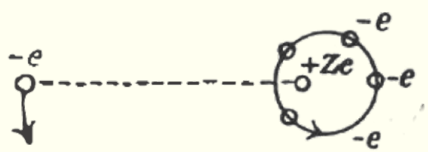


Fig. 1.

In 1926 book with Pascual Jordan, Franck had more or less abandoned this idea, and noted only the likelihood of "collisions of the second kind" with impurity molecules.

Franck, Reiche, and Knipping, 1920

The Role of theory: Landé's model

Note that in both papers, the arguments for metastable states are **entirely experimental**: Paschen's resonance experiment and FK's electron collision experiments.

Nevertheless, Franck, Reiche, and Knipping were impressed with and relied on Landé's (and Sommerfeld's) picture, and speak consistently of "crossed orbits" and "coplanar orbits" instead of singlet and "doublet" states. They wanted a physical picture.

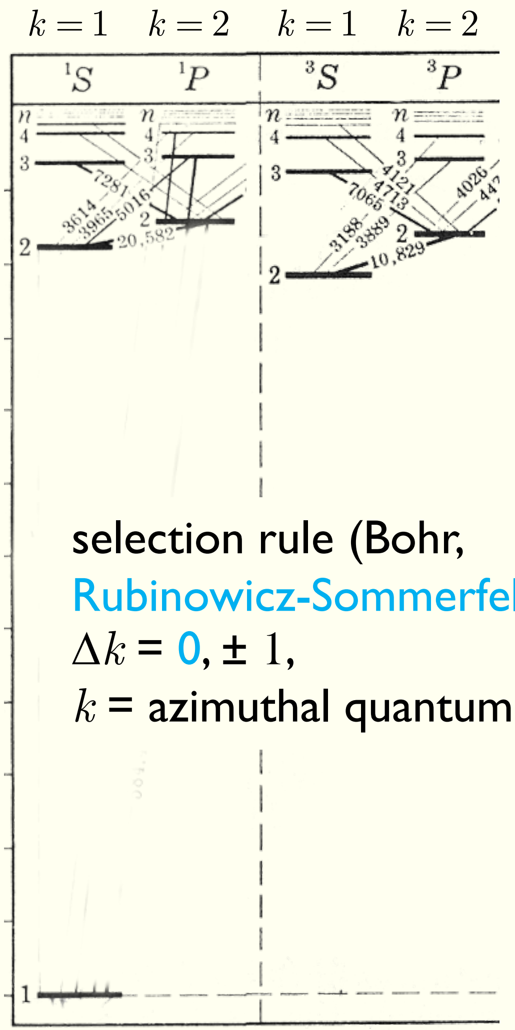
Landé has carried out the spatial quantization only provisionally, and a new exact calculation … is expected. … however, absolutely no ground exists to doubt the correctness of the chief conclusions.

Franck and Reiche, 1920

Moreover, their use of selection rules is puzzling:

Franck, Reiche, and Knipping, 1920

The Role of theory: selection rules



selection rule (Bohr, Rubinowicz-Sommerfeld):
$\Delta k = 0, \pm 1$,
k = azimuthal quantum no.

From the absence of combinations of the two systems with each other, we further conclude that a transition from a higher quantum orbit of one system into a lower of the other never takes place by monochromatic radiation. These facts describe a very impressive confirmation of the selection rules [*Auswahlprinzipen*] of Bohr, Rubinowicz, and Sommerfeld, which leads to the conclusion that for radiation the invariable plane of the atom remains fixed.

Franck and Reiche, 1920

There appears to have been no such selection rule.

Franck and Reiche may have thought that Landé's use of the"invariable plane" (direction of angular momentum) in his 1919 theory imposed such a rule.

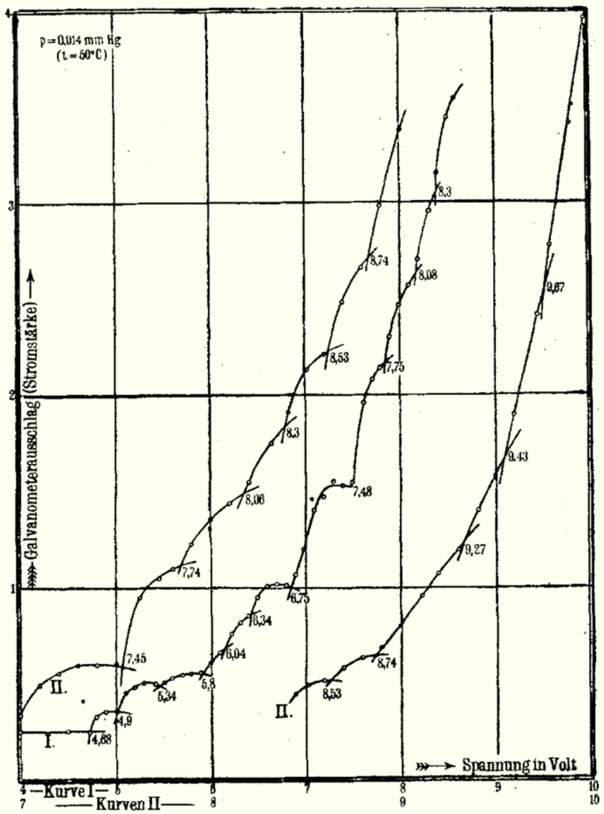
Franck and Erich Einsporn, 1920

Metastable states in mercury

"On the excitation potentials of mercury vapor"

James Franck

Fig. 1.

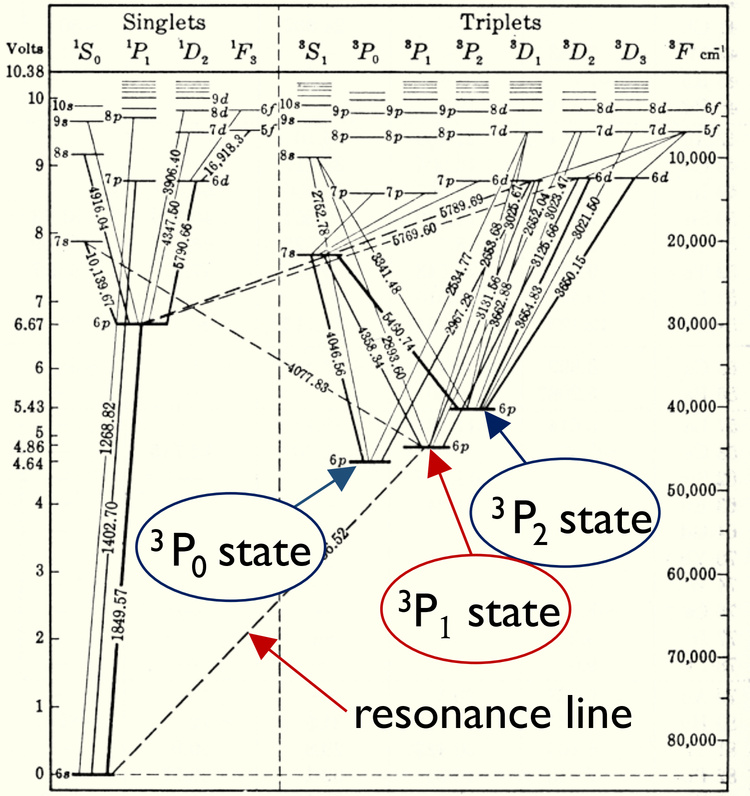


Erich Einsporn
(1890–1964)

As an overall result, we would like to point out that the conclusions of Bohr's theory can be confirmed with great rigor [*Schärfe*], and that this experiment appears to us to describe a useful supplement to spectroscopic methods in many cases.

Franck and Einsporn, 1920

Metastable states in mercury



Term (energy level) diagram for mercury.

- Note combination lines

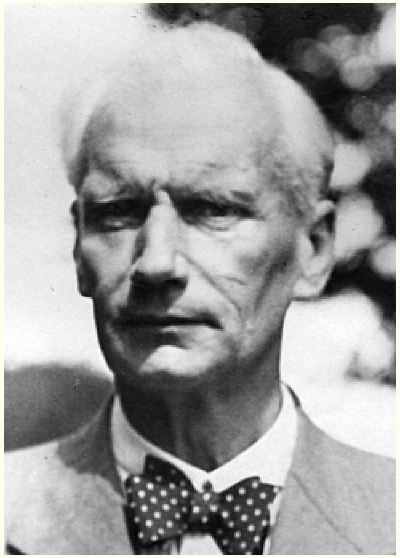
FE excited the $^3P_0$ and $^3P_2$ states with electron collisions; such transitions not seen optically.

Mercury has separate singlet and triplet series, but with occasional intercombination lines

- the three lowest-lying ^3P states are well separated in energy
- one of them, circled in red ⇒ the prominent resonance line found by Wood and FH
- the other two, circled in blue, show **no** optical transitions to the ground state, but FE excited them by electron collisions.

The selection rule [*Auswahlprinzip*] could give us a possible answer. … if one considers radial, azimuthal, and spatial quantization, then from the selection rule, an electron, which can be raised to a higher quantum orbit by an electron collision, cannot in all cases fall back into the rest state by monochromatic emission. On the contrary, the occurrence of metastable states in analogy to the behavior of helium is exceedingly probable.

Confusion Reigns!



Walther Gerlach
(1889–1979)

Walther Gerlach, *The Experimental Foundations of Quantum Theory* (1921)

That both [helium and parhelium] **have entirely separated series is the realization of the requirement that electron jumps from a crossed into a coplanar state or inversely may not take place, from the *Auswahlprinzip* (Sommerfeld, Rubinowisc, Bohr**, **which we cannot go into here.)**

…

The two-quantum coplanar helium thus shows a metastable form, to which a type of alkali is to be attributed. But then coplanar helium must also have electron affinity, and with it chemical activity.

Gerlach 1921

Confusion Reigns!

Paul D. Foote
(18881971)

The Origin of Spectra (1922)

Bohr concludes that in the normal state both electrons move in 1 quantum paths which make an angle of 120 degrees with each other…

Lande has shown that the single-line system belongs to a crossed-orbit configuration, … while the doublet system arises in … a coplanar configuration. …

Fred Loomis Mohler
(1893–1974)

The return to 1S [1^1S] from 2 s [2^3S] is prevented by the general law that intercombination lines between the crossed and coplanar orbital systems do not take place.

… Franck and Reiche concluded that only the 2 s state should be considered as a metastable modification of helium.

In the 2 s state … helium should resemble lithium and might therefore be expected to be capable of forming compounds. Franck and Reiche have suggested several means, some involving processes of this type by which the electron … can return to the normal without emitting the monochromatic wave number 1 S – 2 s. At the present time, however, most of these hypotheses are highly speculative, and … the transitions from either 2 s or 2 S to normal are not satisfactorily explained.

Concluding Unscientific Postscript

Sommerfeld, *Atombau* (1919), ch. 2, "The Neutral Helium Atom:

„Hier stock' ich schon, wer hilft mir weiter fort?" (*Faust*, I, 1225)
("Here I falter, who will help me onward?"

[Enter Mephistopheles]

„ Wozu der Lärm? Was steht dem Herrn zu Diensten?"
("What's the fuss? What can I do for you?" (Faust, 1, 1322)

Franck and Knipping had found the ionization potentials of helium, along with Frank Horton and Ann Catherine Davies, and Karl Compton.

Franck, Reiche, and Knipping had also argued persuasively for the existence of metastable states. Their argument was entirely experimental, and would have been unchanged if they had spoken only of singlet and "doublet" spectral series.

Nevertheless, they badly wanted a physical picture, and so consistently used Landé's crossed and coplanar orbits to describe parhelium and orthohelium, and even appealed to (non-existent?) selection rules.