Canonical Applications?

1926–1933

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QUANTUM HISTORY PROJECT

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Introduction:

Canonical Applications ?

...or Loci for Maturation?

- Techniques for handling the many-body problem began developing in the old quantum theory and were not immediately or fully replaced by quantum mechanics.
- In the process of solving sundry many-body problems, researchers came to understand the physical meaning of new aspects of the mathematical formalism of quantum theory, such as the exclusion principle and the superposition of eigenstates.
- Solutions to these problems introduced concepts we now commonly employ to understand quantum mechanical phenomena, such as exchange and tunneling.

“Seven in one Blow”

Born, “Über Quantenmechanik,” June 1924

“As long as one does not know the laws of the influence of light on the atom, and thus the connection between dispersion, the structure of the atom, and the quantum jumps, one will certainly remain in the dark concerning the interactions between multiple electrons in an atom.”

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Complex Spectra: Exclusion Principle and Statistics

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Complex Spectra: Exclusion Principle and Statistics

Wolfgang Pauli

- Pauli (Jan 1925), novel rule to explain complex spectra
- **exclusion principle** ("housing office for equivalent electrons")
- **no derivation or physical interpretation**:

  "The problem of a further justification of the occurence of equivalent electrons in the atom [...] likely can only be tackled after a **future deepening** of the fundamental principles of quantum theory."

- However, even deepening of fundamental principles brought along by quantum mechanics at first **failed** to provide any lead on how to tackle the physical interpetation of the exclusion principle.

Complex Spectra: Exclusion Principle and Statistics

- Fermi (Mar 1926): "The quantization of ideal gases necessitates an **additional rule** [Pauli's exclusion principle] to complement Sommerfeld's quantization condition."
- no mention or use of **quantum mechanics**
- Along the way, shows that gas of particles obeying Pauli's exclusion principle satisfies **new statistics**.

Enrico Fermi (1927)

- Dirac (Aug 1926) independently derives similar results in more general way from formalism of quantum mechanics.
- "Thus the **symmetrical** eigenfunctions alone or the **antisymmetrical** eigenfunctions alone give a complete solution of the problem. The theory at present is **incapable** of deciding which solution is the correct one."
  - **symmetrical eigenfunctions**: Bose-Einstein, correct for light quanta
  - **antisymmetrical eigenfunctions**: Pauli principle trivial consequence, lead to "**different statistical mechanics**," "probably the correct one for gas molecules"

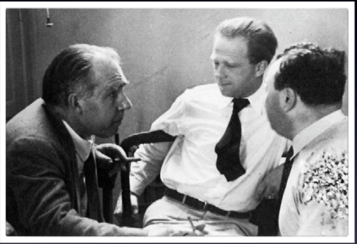
Paul Dirac

Complex Spectra: Exclusion Principle and Statistics

- Heisenberg (June 1926), **Mehrkörperproblem und Resonanz**
- Analogy with classical picture of coupled oscillators: Helium spectrum splits up in two **noncombining** subsystems.
- Heisenberg chooses subsystem that does not contain equivalent orbits (i.e., satisfies Pauli's rule), without physical justification: "when trying to remove this deficiency, one will uncover **deeper-lying connections.**"
- **Unaware** of Fermi: "Pauli's exclusion prescription and Bose's rule are the **same**, [...] they **do not contradict quantum mechanics**" (Heisenberg to Born, May 26, 1926)
- Conclusion: "the quantum mechanics allows for a qualitative description of the spectrum **also of atoms with two electrons** up to the finest details."

Werner Heisenberg
(1927, photo by F. Hund)

Complex Spectra: Exclusion Principle and Statistics



Bohr, Heisenberg, Pauli

- Already on 5 May 1926, Heisenberg wrote to Pauli:

  "I have found a rather decisive argument that your exclusion of equivalent orbits is connected to the distance between singlet and triplet [terms in neutral Helium]. [...] thus, **para- and orthohelium** do indeed have different energies, **independent of the interaction between the magnets** [i.e., the magnetic moments associated with potential **spinning** electrons]."

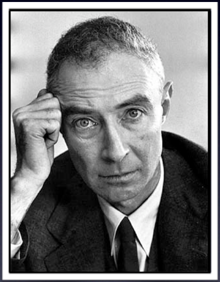
- Para- and orthohelium connected to (still dubious) spin?

- Problem features on **list of problems** compiled by Bohr and Pauli in Berlin in late 1925.

Complex Spectra: Exclusion Principle and Statistics

Oppenheimer on Heisenberg's paper:

"I regarded it as a kind of discovery of the **meaning of quantum theory**. [...] I think that if Heisenberg had found that there wasn't anything new but just that the integrals of wave functions happened to give the helium spectrum right, it would have been problem solving. It was the fact that there was an **element of novelty** and something which had never been described before which turned it from solving a problem into **exploring the content and meaning [of quantum mechanics].**"



J. Robert Oppenheimer

[Oppenheimer interview by Kuhn, Nov 20, 1963, AHQP]

Complex Spectra: Exclusion Principle and Statistics

Heisenberg and Wigner

John C. Slater

- Confusion about exclusion principle and statistics lifted only **gradually** in the second half of 1926.
- Complex spectra played important role in developing **symmetry arguments** and formalism of **many-body quantum mechanics** :
  - Eugene Wigner: relied heavily on multi-electron atoms in articles on application of **group theory** to quantum mechanics.
  - John Slater: formulated "**Slater determinants**" as part of his treatment of complex spectra.

Molecules: Separation and Superposition

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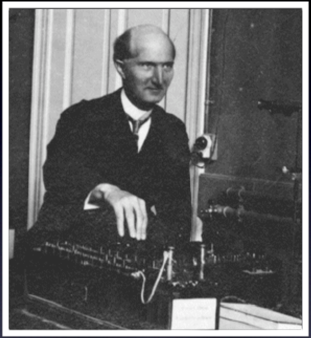
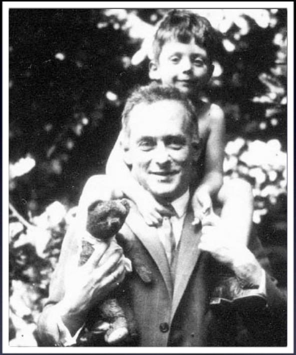
Molecules: Separation



Niels Bjerrum

- Bjerrum (1912-1914) uses a quantized vibrating rotator model to separate far infra-red (pure rotation) from near infra-red (rotation-vibration spectra).
- Both models **ignored** ultra-violet spectra and the motion of electrons.
- Robert Mulliken and Raymond Birge formalize the division of the energy of a molecule into electronic, vibrational, and rotational components.
- Wolfgang Paui (1923), Henrik Kramers (1923), and Arnold Kratzer (1923) show that the angular momentum of the electrons is of the same order of magnitude as that of the nuclei.

Molecules: Separation



Max Born with Son Gustav (1925)

- Born-Heisenberg 1924, "finalized" account of molecular spectra by modeling with only nuclei and electrons.
- Expanded the total energy of the molecule in terms of

$$\sqrt{\frac{m}{M}}$$

- Found the first order vanished, 0th order Electronic, 2nd order vibration-rotation of nuclei.
- Assumed the problem of the distribution of electrons already solved, treated only the nuclei.
- Explicitly reworked using QM and 4th root as **Born-Oppenheimer** (1927). Perturbation expansion markedly simpler.

Molecules: And

- Pauli (1922) demonstrated that there were stable electron configurations for the H_2^+ ion.
- Adiabatic transition to bound state **never found** using old quantum theory.
- Hund (1927) demonstrates generally the possibility of adiabatic transition in quantum, compares electronic structure of molecules to Stark effect of heavy atoms (linear and quadratic).
- Robert Mulliken (1928) and John Lennard-Jones (1929) develop further the idea of correlations between atomic and molecular states.

Friedrich Hund

Molecules: Superposition

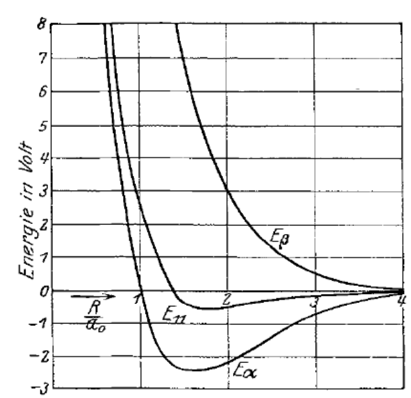
- Heitler and London (1927)
- "We were aware of the fact that the spin was the problem, which we couldn't solve, that it was just attached to Schrödinger's wave equation or superimposed on it, but there was no natural amalgamation between wave mechanics and the spin...It would never have occurred to us that you could combine the wave equation of Schrödinger with some matrix mechanical ideas..."

[Heitler interview by Heilbron, March 1963, AHQP]

Linus and Ava Helen Pauling in Munich, with Walter Heitler (left) and Fritz London (right), 1927.

Molecules: Superposition

- The 'solution' was to construct two anti-symmetric wave functions by hand, and perform a perturbation approximation.
- The resulting integral, Heitler and London analyzed into "Overlap," "Coulomb," and "Exchange" components.
- They associated the "exchange" component with the formation of the chemical bond.



E_{11} without exchange
E_α "symmetric" bonding
E_β "anti-symmetric" repelling

Molecules: Superposition

- “The whole [exchange] phenomenon is closely related to the resonance phenomenon handled by Heisenberg. Whereas, however, in resonance electrons in different orbits of one and the same set of eigenfunctions exchange energy [with one another], here electrons of the same orbit (same energy) but in different systems of eigenfuctions exchange locations.”
- “**For a long time** I really thought it was a major and ununderstood problem of quantum mechanics to explain what the exchange really means...One can define a frequency of exchange in a certain manner... But this does not really occur in the finished molecule...I think the only honest answer **today** is that the exchange is something typical of quantum mechanics, and should not be interpreted—or one should not try to interpret it—in terms of classical physics.”
- Max Born (1926) interprets linear combinations of eigenfuctions, this was not widely viewed as a **general** meaning of such linear combinations (Carson, 1996).

Conclusion

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Conclusion

- Besides complex and molecular spectra, quantum mechanics evolved in several **other areas**:
  - magnetism (Heisenberg, van Vleck, Stoner,...)
  - electron theory of metals and band theory of solids (Sommerfeld, Bethe, Bloch, Peierls, Brillouin, Wilson, Wigner,...)
  - quantum theory of chemical valence (Born, van Vleck, Mulliken,...)
  - study of the nucleus and nuclear disintegration (Gurney& Condon, Gamow, Born, Heisenberg, Bethe,...)
  - ...
- Many of the protagonists of the history of “mainstream” quantum mechanics played important roles in **several** of these areas.
- By ca. 1933, the above areas had gained **coherence** and a certain independent identity.
- **Review papers** and first monographs on newly-emerging **subdisciplines** of physics appeared in years 1933-1935.

Conclusion: Debye's Leipzig Weeks


LEIPZIGER VORTRÄGE 1928

QUANTENTHEORIE UND CHEMIE

VERLAG VON S. HIRZEL IN LEIPZIG 1928

1928: Quantum Theory and Chemistry

- **London**: Quantum Theory and Chemical Bonding
- **Eucken**: Thermal Conductivity of Nonmetals and Metals
- **Sidgwick**: The Role of Electrons in Chemical Bonding


LEIPZIGER VORTRÄGE 1929

DIPOLMOMENT UND CHEMISCHE STRUKTUR

VERLAG VON S. HIRZEL IN LEIPZIG 1929

1929: Dipole Moments and Chemical Structure

- **Højendahl**: Dielectric Constant of Regular Crystals


LEIPZIGER VORTRÄGE 1930

ELEKTRONEN-INTERFERENZEN

VERLAG VON S. HIRZEL IN LEIPZIG 1930

1930: Electron Interference

- **Rupp**: Internal Potential and Electrical Conductivity of Crystals
- **Mott**: Atomic Form Factors
- **Bloch**: Electrical and Thermal Resistance
- **Peierls**: Metallic Conductors in Strong Magnetic Fields


LEIPZIGER VORTRÄGE 1933

MAGNETISMUS

VERLAG VON S. HIRZEL IN LEIPZIG 1933

1933: Magnetism

- **Kapitza**: Change of Resistance of Metals in Magnetic Fields
- **Kramers**: Paramagnetic Properties of Rare Earth Crystals
- **Bethe**: Theory of Ferromagnetism

Conclusion

- Techniques for handling quantum many-body problem began developing in old quantum theory and were **neither immediately nor fully replaced** by quantum mechanics.
- **Use and physical meaning** of quantum-theoretical concepts (exclusion principle, Bose-Einstein and Fermi-Dirac statistics, spin, superposition of wavefunctions) were **clarified** in context of extending quantum mechanics to solve various many-body problems.
- **New concepts** (resonance and exchange, tunneling) only arose in context of "applications," yet today form an integral part of what we call quantum mechanics.

Conclusion

- Many of the mentioned “applications” have been treated within **disciplinary histories** of, e.g., quantum chemistry, nuclear physics, or solid-state physics.
- In addition, a number of excellent studies focus on history of isolated key **concepts** (Heilbron on Exclusion Principle, Carson on Exchange, Midwinter& Janssen (forthcoming) on electric and magnetic susceptibilities).
- **Our goal:** Contribute to establishing a new **epistemolgical framework** for the study of “applications” of quantum mechanics, taking into account explicitly
    - **continuities** with respect to treatments within frameworks of classical physics and old quantum theory
    - contribution to genesis of quantum mechanics and to clarification of its **meaning**
    - complex **network of interactions** between the different strands of development