

量子論電子工学 講義資料

集積機能工学講座
掛谷一弘

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講義の内容

1. 量子力学の復習
2. 近似法
3. 水素原子
4. 角運動量
5. スピン軌道相互作用
6. 多重項
7. ゼーマン効果
8. ハートリー・フォック方程式
9. 分子モデル
10. 磁性
11. 電子相関

大切なこと

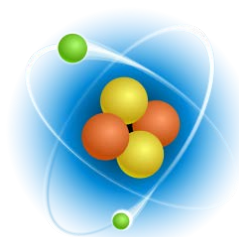
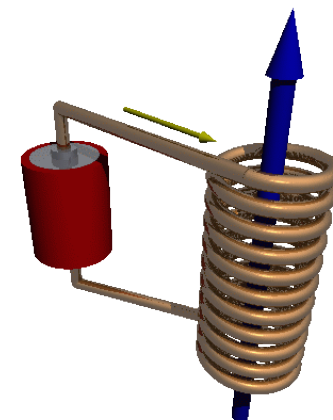
- **単位の認定**
 - 試験
 - レポート (2回)
- **教科書・参考書**
 - 原康夫「量子力学」(岩波書店)
 - 岡崎誠「物質の量子力学」(岩波書店)
 - J. J. Sakurai, “Modern Quantum Mechanics” (Addison-Wesley) 「現代の量子力学」(吉岡書店)
 - 猪木慶治、川合光 共著「量子力学I/II」講談社 (1994)
 - C. Kittel, “Introduction to Solid State Physics” (Wiley)
 - 安達健五「化合物磁性 局在スピン系」(裳華房)
- **Webサイト**
 - sk.kuee.kyoto-u.ac.jp → 講義情報 → 量子論電子工学

Milestones of Quantum mechanics

- 1897 Discovery of electrons: J.J. Thomson
- 1900 Planck's law: Max Planck
- 1904 Saturnian model: H. Nagaoka
- 1905 Photon theory: A. Einstein
- 1909 Elementary charge: R. Millikan
- 1911 Planetary model: E. Rutherford
- 1911 Superconductivity: H.K. Onnes
- 1913 Rutherford-Bohr model: N. Bohr
- 1926 Schrödinger equation: E. Schrödinger
- 1927 Uncertainty principle: W. Heisenberg

長岡半太郎 (1865-1950)

- 長崎県大村市生まれ
- 東京大学理学部卒業
- 東京帝国大学教授
- 大阪帝国大学初代総長
- 磁石の研究
 - 長岡係数
- 土星モデルの提唱
 - 電子が原子核に落ち込まない理由を説明できなかった
 - Rutherfordモデルの着想
- ノーベル賞にも数度推薦
- 弟子：仁科芳雄

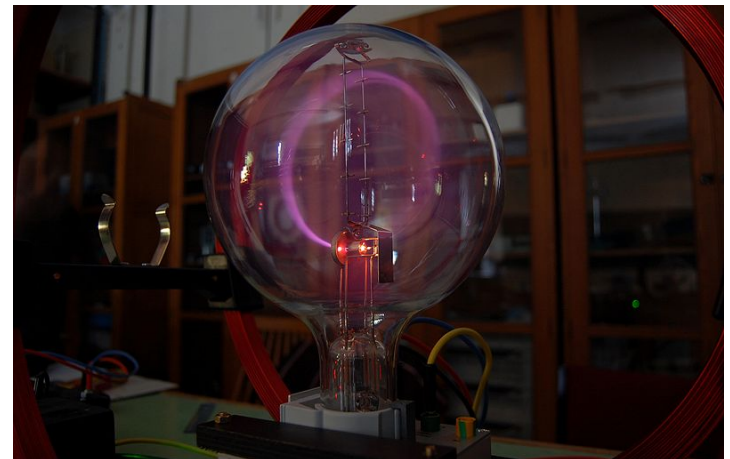
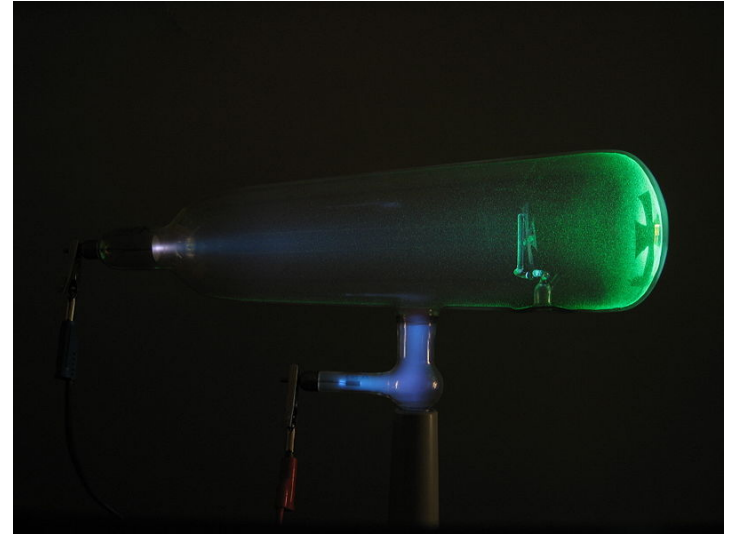


1904
長岡モデル



Discovery of electron

- Charge: recognized since ancient Greeks
- “De Magnete” 1600
- Faraday's laws of electrolysis 1834
- Named by GJ. Stoney 1874
- Cathode rays
- W. Crookes: electron is negatively charged particle
- J.J. Thomson performed experiments



J.J. Thomson (1856-1940)



- Cathode rays
- Mass spectrometer
- Supervisor of Rutherford, Oppenheimer, W.H. Bragg, Born, Langevin, ...
- Nobel prize for physics (1906)



Thomson and Rutherford at Cavendish



1884?

1919?

極低温での金属の電気抵抗に関する論争 (20世紀初頭)

抵抗

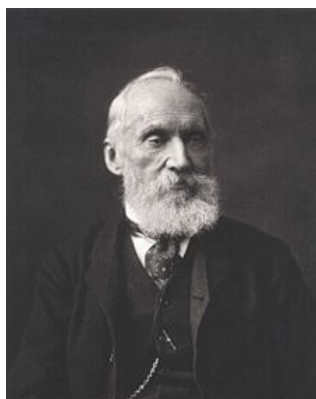
ケルビン卿 1902

電子の熱励起が支配的

マチーセン 1864

デュワー 1904

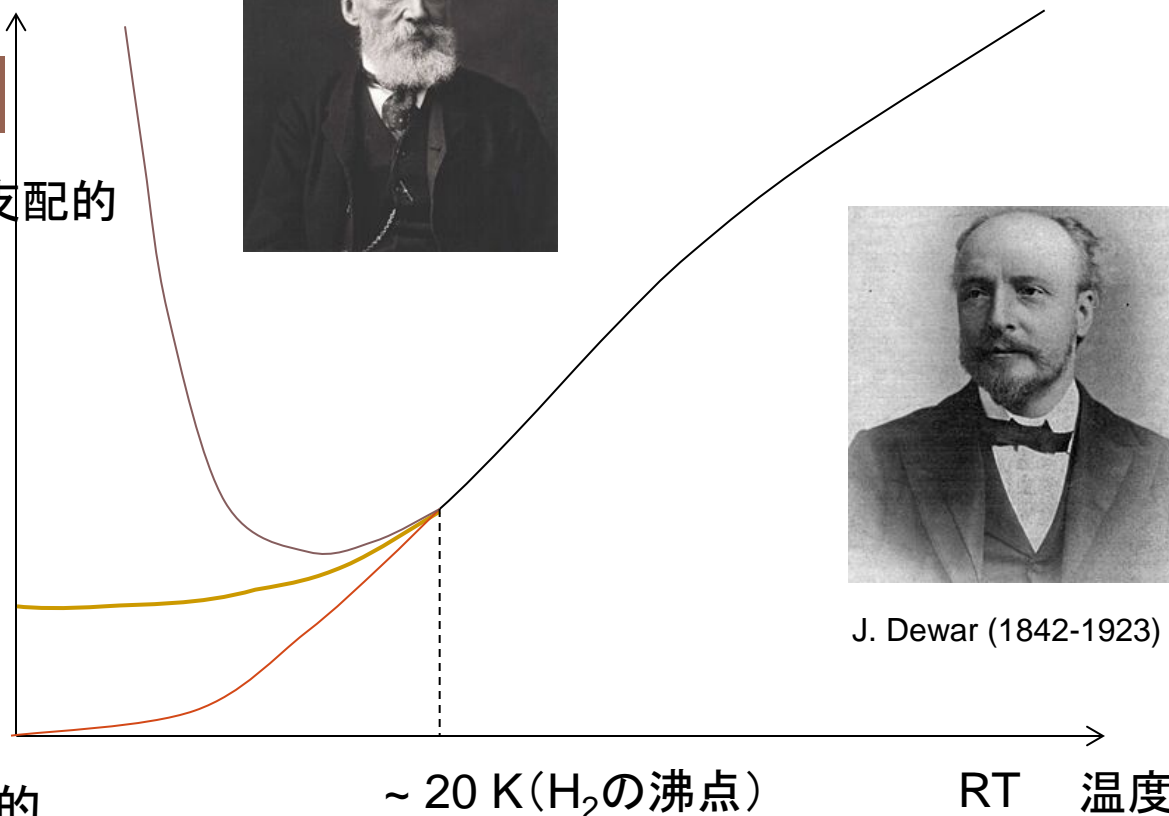
格子振動が支配的



W. Thomson, Lord Kelvin
(1824-1907)



J. Dewar (1842-1923)



低温における電気抵抗の例

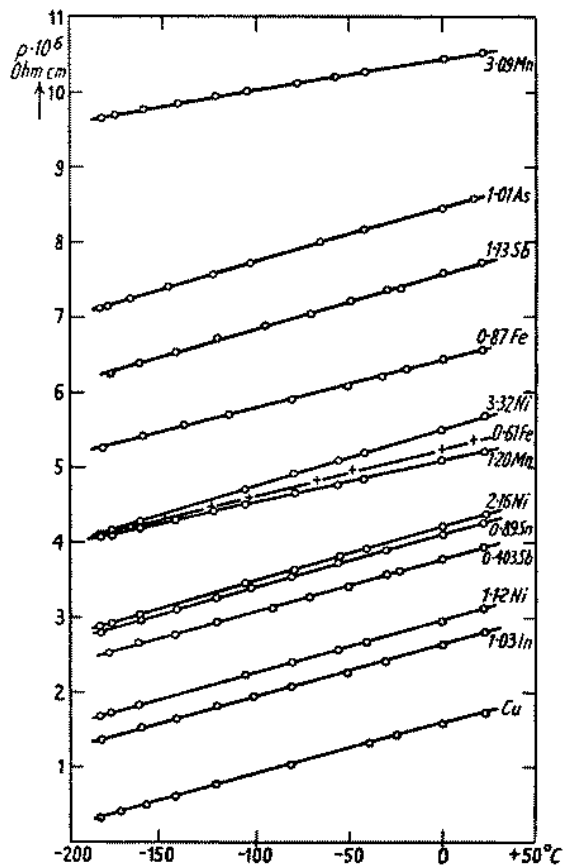
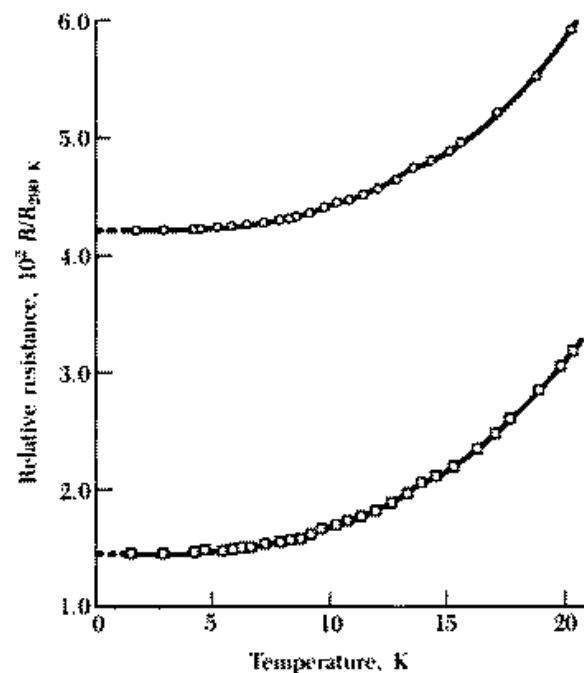


FIG. 100. Resistance-temperature curves of copper alloys; the figures show the atomic percentages of the metal named. (From Linde, *Ann. d. Physik*, 15 (1932), 219.)

銅に様々な不純物を入れたときの電気抵抗の温度依存性。Mott and Jones, "The theory of the properties of Metals and Alloys", 1936

20K以下における2つのカリウムの電気抵抗の温度依存性。極低温で T^2 の温度依存性があることがわかる。0Kとの交点の違いは結晶の不完全性の違いに起因する。C. Kittel, "Introduction to Solid State Physics 7th ed.", 1995

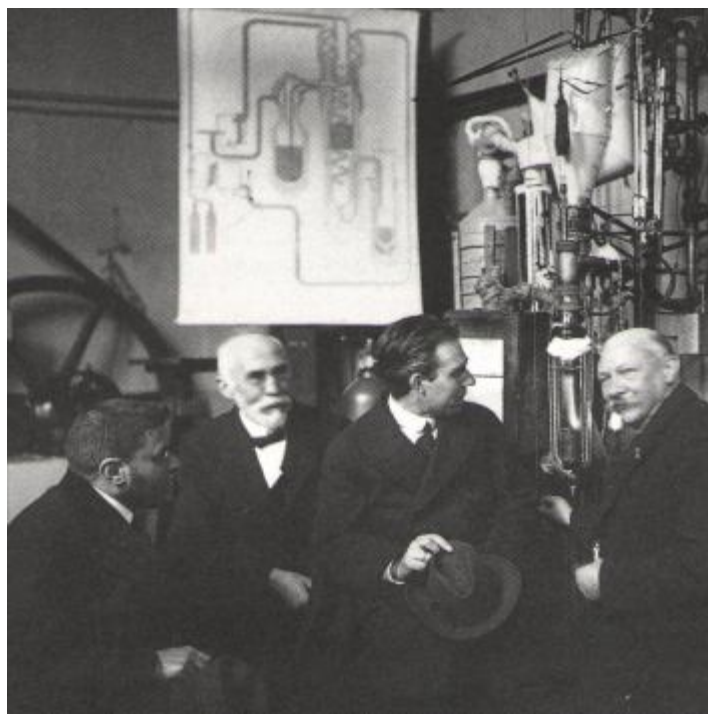


ヘリウムの液化 (1908)

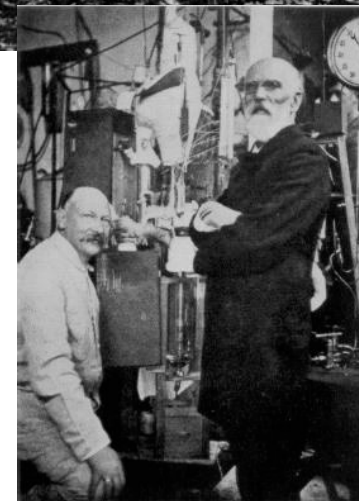


ハイケ・カマリン・オンネス
(H. Kamerlingh Onnes, 1853-1926)

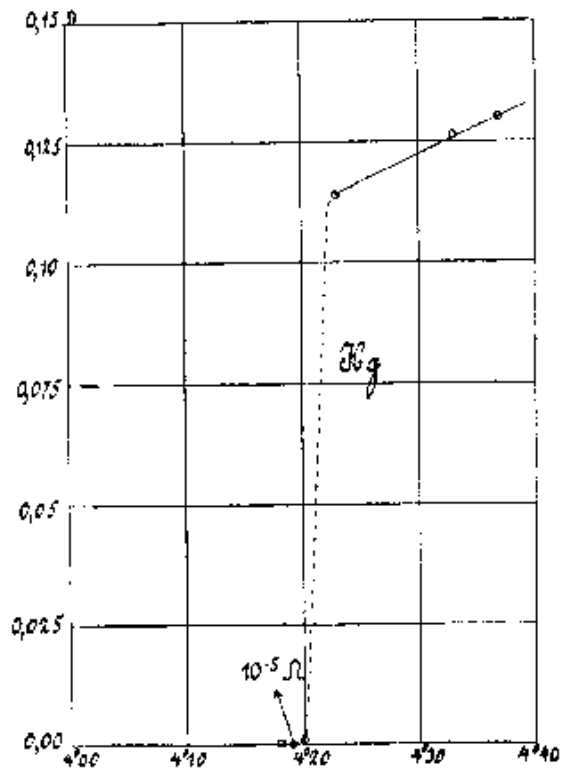
オランダ・ライデン大学で低温物理学を研究。1908年にヘリウムの液化に成功し、減圧により0.8Kを実現。1913年、ノーベル物理学賞を受賞。彼の実験はライデン大学の同僚であるファンデルワールスとローレンツの理論に基づいていた。



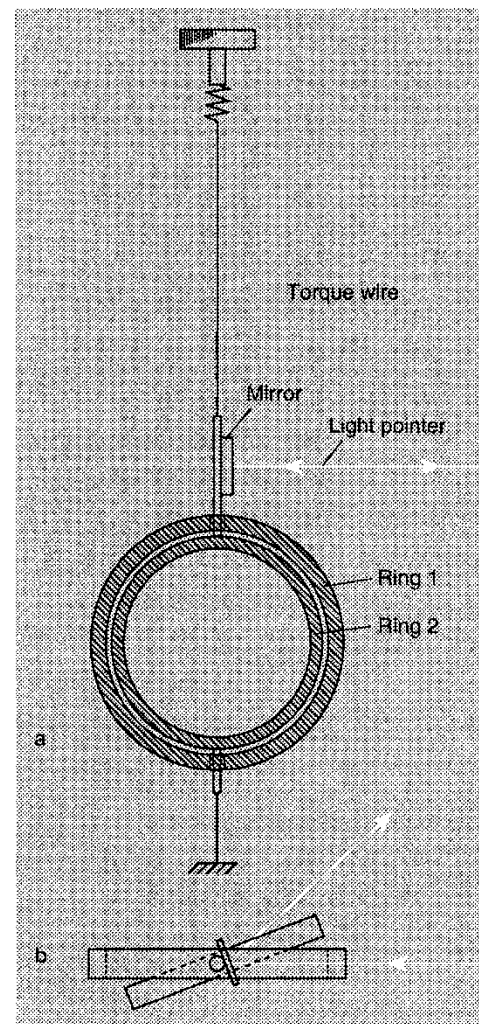
(左) オンネスがヘリウム液化機を示す。左よりアーレンフェスト、ローレンツ、ボーア。(右上)ライデンでの磁性会議の一幕。左からアインシュタイン、アーレンフェスト、ランジュバン、オンネス、ワイス。(右)オンネスとファンデルワールス。



超伝導の発見 (1911)



H. Kamerlingh Onnes, Leiden Comm.
120 b 122b 124c (1911)



10^{-13} オーム以下(Kamerlingh Onnesによる超伝導リングの実験, 1914)

Nobel laureates among SC people



H. K. Onnes

1913

1987



A. Muller, J. G. Bednortz



J. Bardeen, L.N. Cooper, J. R. Schrieffer

1972

2003



A. Abrikosov, V. Ginzburg



I. Giaever, B. D. Josephson

1973

1962

1977

1991

1998

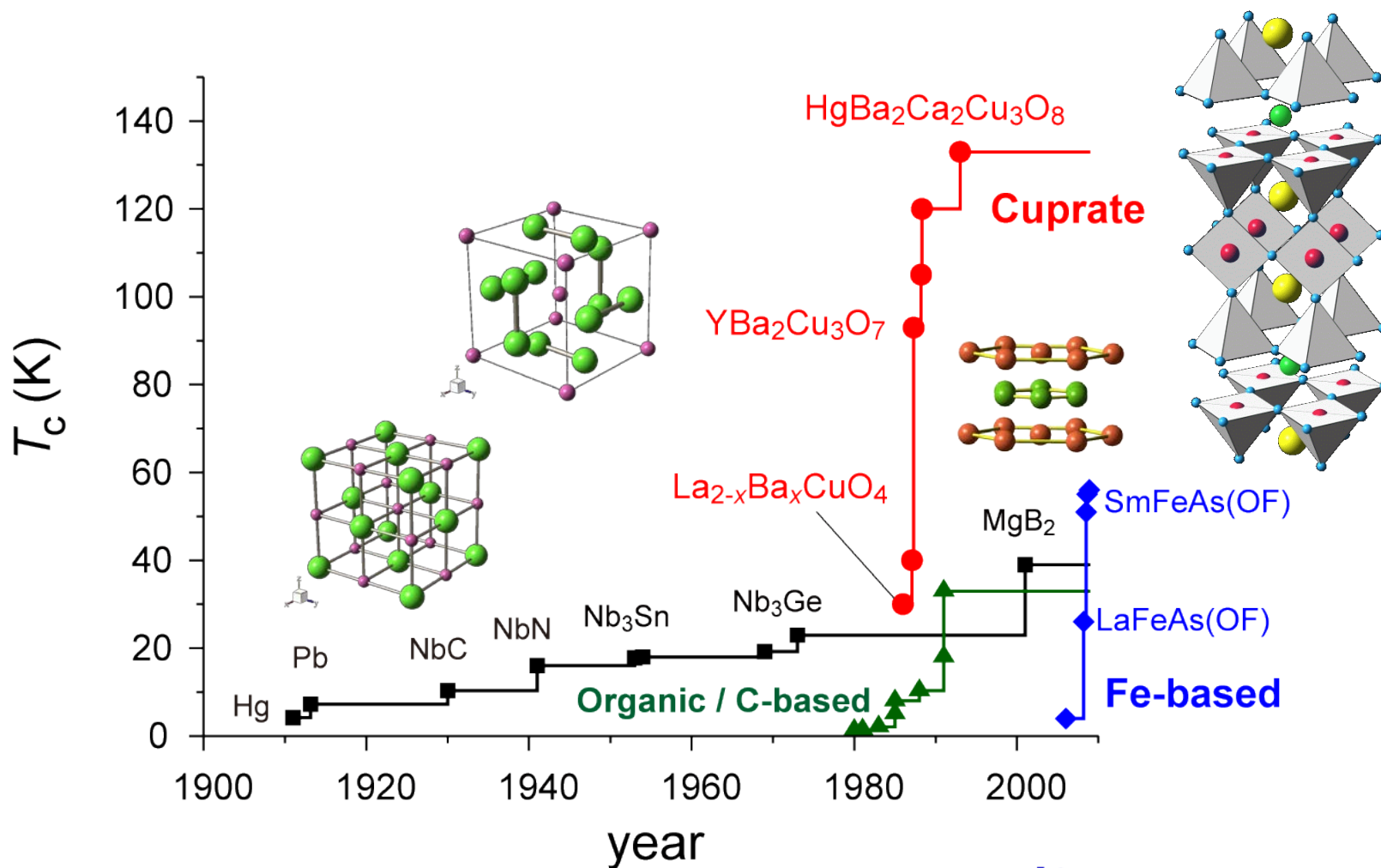
L.D. Landau

P. W. Anderson

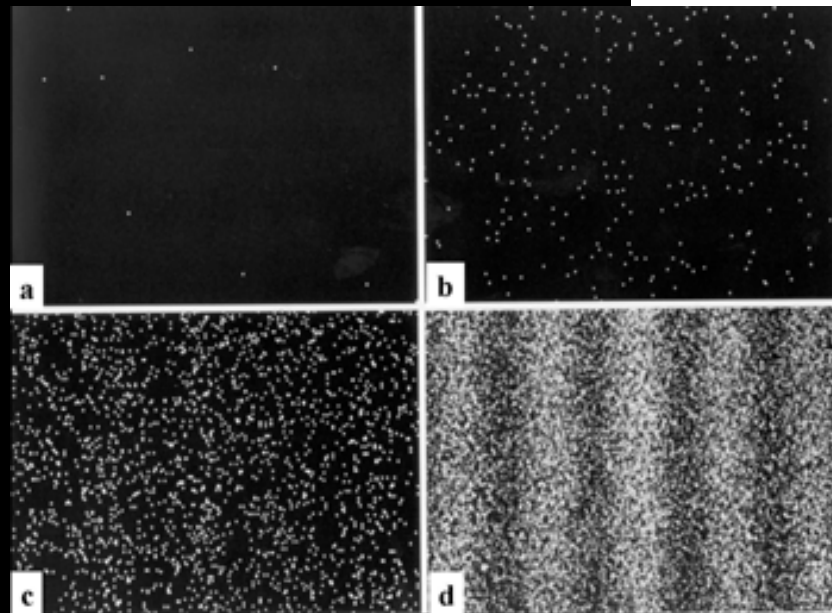
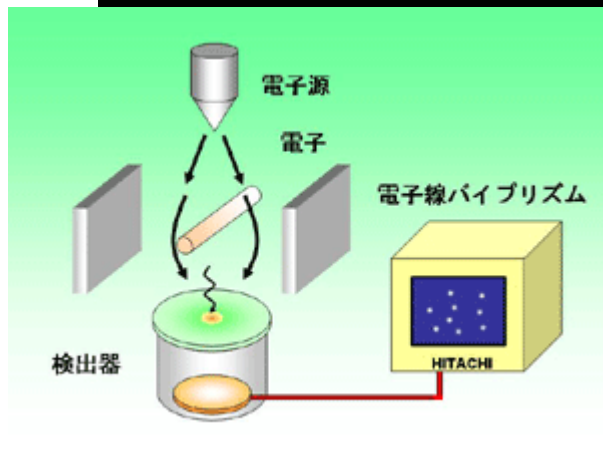
P. G. de Genne

R. B. Laughlin

超伝導転移温度の歴史



二重スリットの実験



C60のヤングの干渉実験

Nature **401** 680 (1999)

Wave-particle duality of C₆₀ molecules

Markus Arndt, Olaf Nairz, Julian Vos-Andreae, Claudia Keller,
Gerbrand van der Zouw & Anton Zeilinger

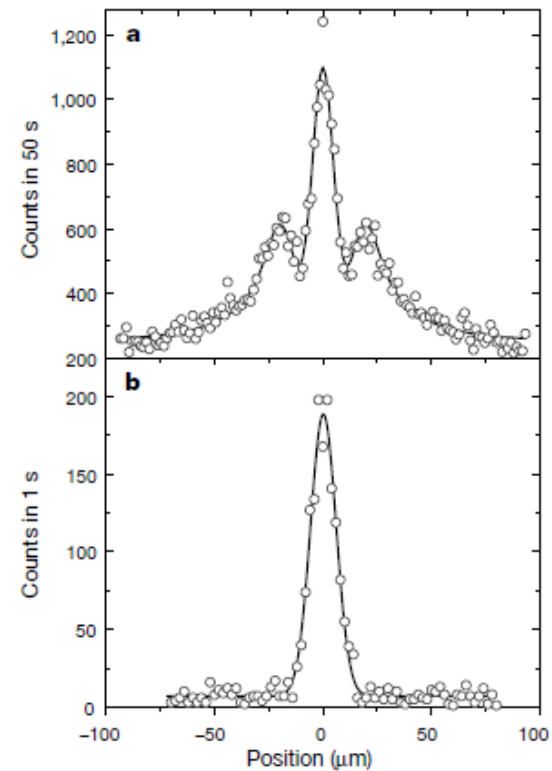
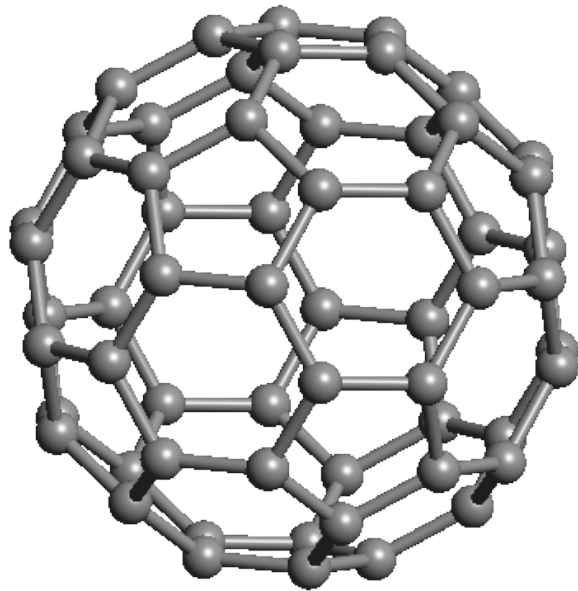


Figure 2 Interference pattern produced by C₆₀ molecules. **a**, Experimental recording (open circles) and fit using Kirchhoff diffraction theory (continuous line). The expected zeroth and first-order maxima can be clearly seen. Details of the theory are discussed in the text. **b**, The molecular beam profile without the grating in the path of the molecules.

後半の内容

5. Zeeman効果

摂動論の一例：スピン自由度の証明

6. Hartree-Fock方程式

変分法：量子力学による化学的性質の説明

7. 分子構造

なぜ分子を構成するか？

8. 磁性

反磁性と常磁性の量子論的取り扱い

Zeeman effect

FEBRUARY 11, 1897]

NATURE

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metals, still 7 cms. apart. We then found the difference of zeros to be -89 sc. divs., or -0.64 of a volt; but instead of seven minutes, scarcely a quarter of a minute was taken to reach the rays-zero after the metallic connection was broken. These results are substantially in accordance with Erskine Murray's §§ 9 of his paper already referred to.

KELVIN.
J. C. BEATTIE.
SMOLUCHOWSKI DE SMOLAN.

THE EFFECT OF MAGNETISATION ON THE NATURE OF LIGHT EMITTED BY A SUBSTANCE.¹

IN consequence of my measurements of Kerr's magneto-optical phenomena, the thought occurred to me whether the period of the light emitted by a flame might be altered when the flame was acted upon by magnetic force. It has turned out that such an action really occurs. I introduced into an oxyhydrogen flame,

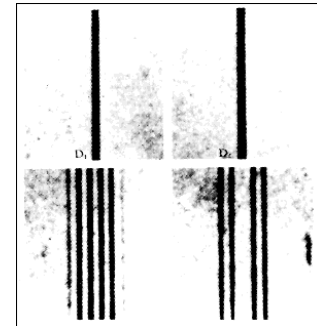
mination of the ratio of the electric charge the ion bears to its mass. We may designate the ratio e/m . I have since found by means of a quarter-wave length plate and an analyser, that the edges of the magnetically-widened lines are really circularly polarised when the line of sight coincides in direction with the lines of force. An altogether rough measurement gives 10^7 as the order of magnitude of the ratio e/m when e is expressed in electromagnetic units.

On the contrary, if one looks at the flame in a direction at right angles to the lines of force, then the edges of the broadened sodium lines appear plane polarised, in accordance with theory. Thus there is here direct evidence of the existence of ions.

This investigation was conducted in the Physical Institute of Leyden University, and will shortly appear in the "Communications of the Leyden University."²

I return my best thanks to Prof. K. Onnes for the interest he has shown in my work.

P. ZEEMAN.
Amsterdam.



Observation of splitting of the D-line from sodium under magnetic fields by Zeeman; *Nature* **55**, 347 1897. [doi:10.1038/055347a0](https://doi.org/10.1038/055347a0)



Pieter Zeeman (1865-1943, Netherlands)

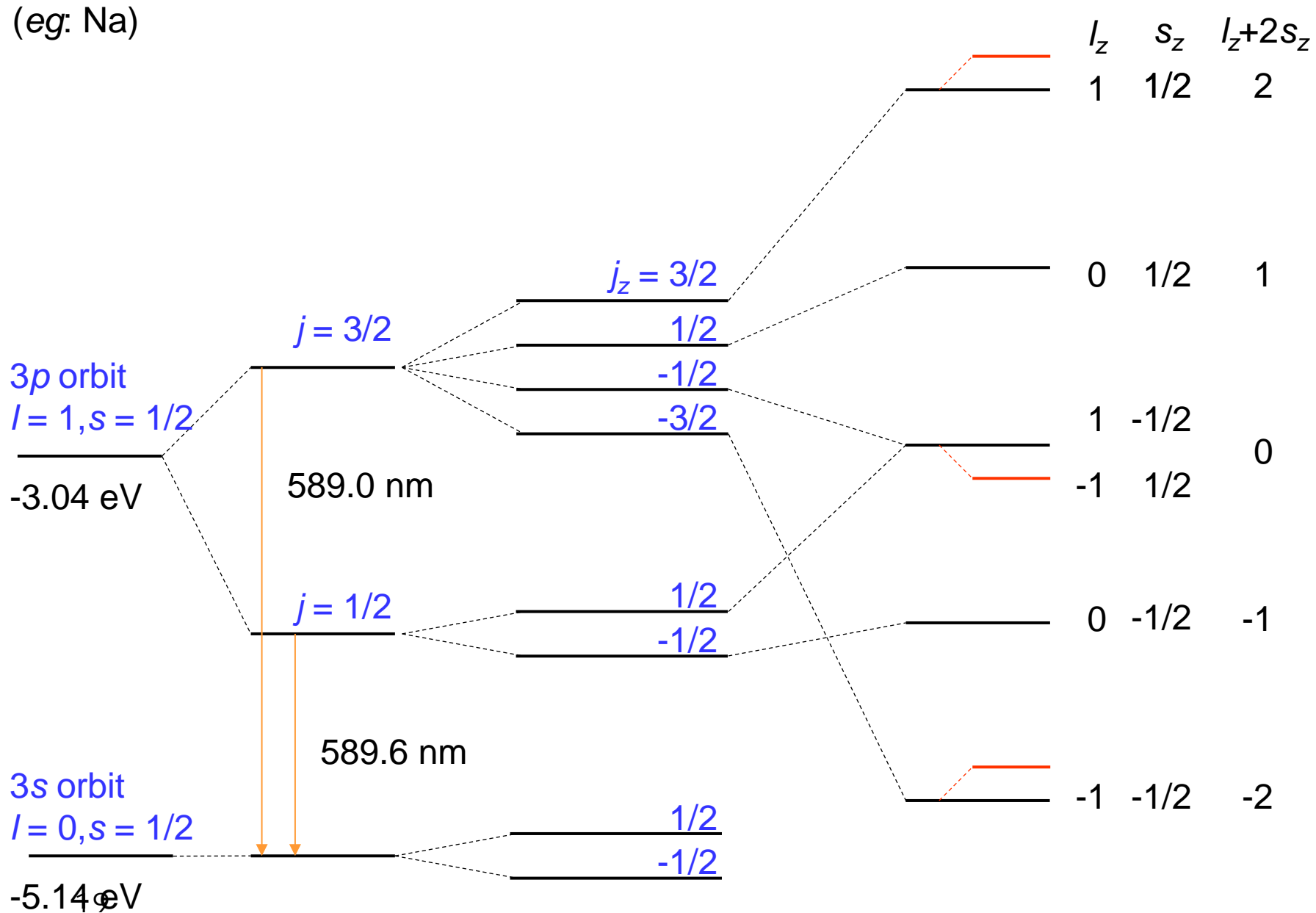
- Supervised by [Heike Kamerlingh Onnes](#)
- [Nobel Prize for Physics](#) (1902) with H. Lorentz
- [Van der Waals-Zeeman Inst. at U. Amsterdam](#)

Free atom
(eg: Na)

Spin-orbit

Zeeman

Paschen-Back



2. Mr. P. Zeeman observed the same phenomenon at Zonnemaire, near Zierikzee ($51^{\circ} 42'$ lat. and $57'$ W. Amsterdam). He wrote me the following on November 19 and 24:—"About 6h. 20m. (I saw) a magnificent, splendid white arch, beginning a little north of east, and prolonging itself to south-west, but in the meantime shortening at the east end and disappearing in a very short time." Mr. Zeeman declares in his second letter that this arch went through Aldebaran, and through α Pegasi. This gives me a horizontal bearing of E. 20° N.-W. 20° S., as the observations of Prof. Cudemans gives also.

May 31, 1883]

NATURE

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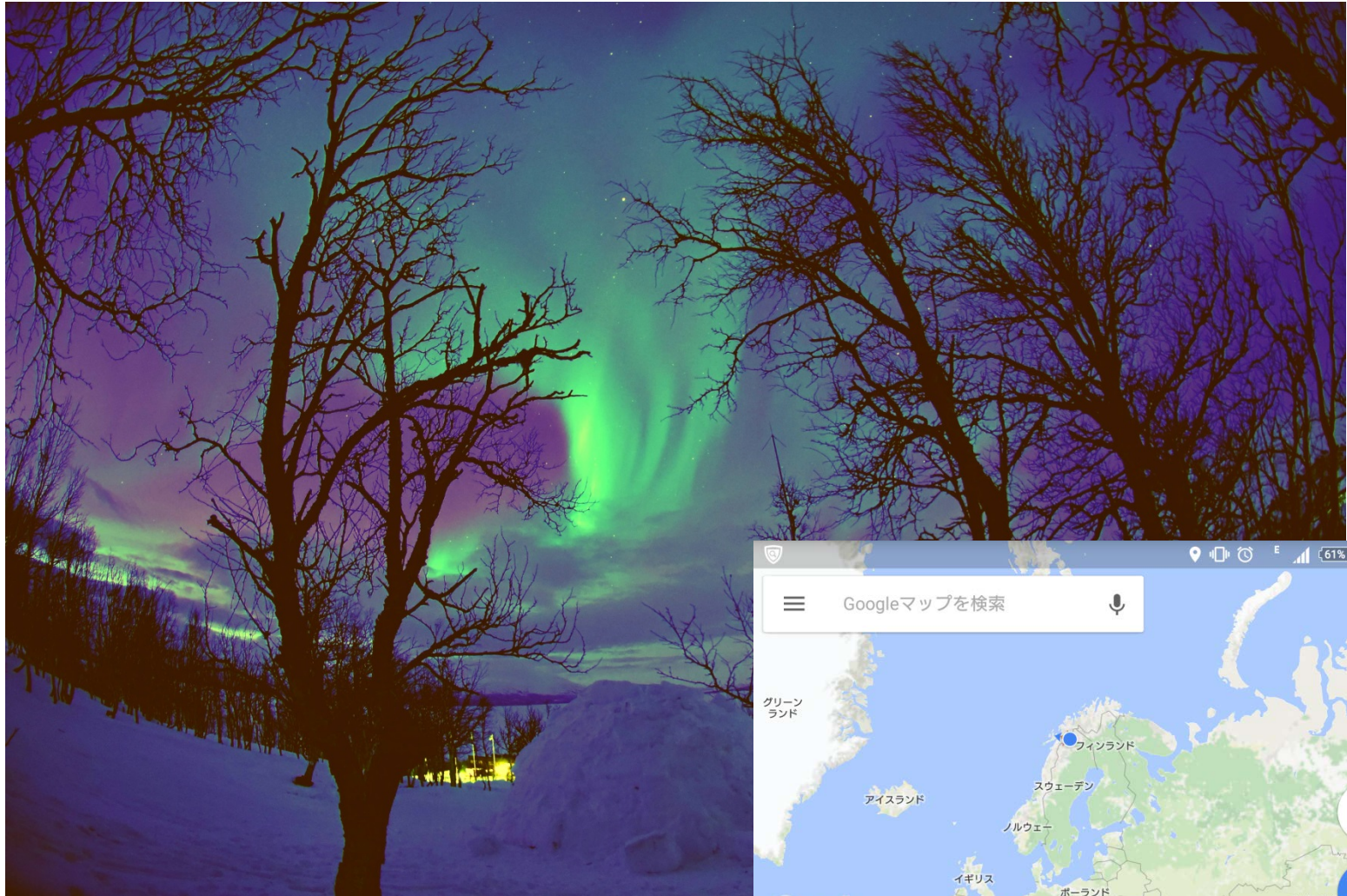
*THE TRUE ORBIT OF THE AURORAL
METEOROID OF NOVEMBER 17, 1882*

AFTER many fruitless efforts to conciliate the apparently widely diverging data, given by the numerous observations of this most interesting phenomenon; and after having been many times on the same point as Mr. H. D. Taylor (vol. xxvii. p. 434), who has

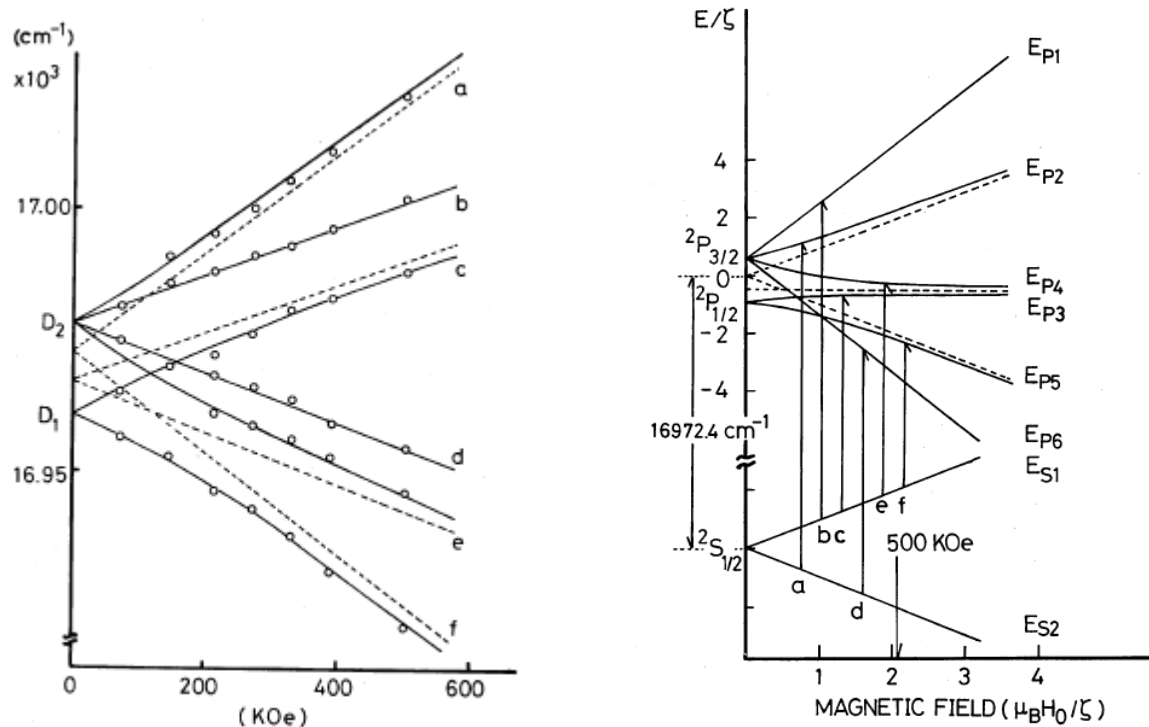
vatoire de Bruxelles, November 18, 1882: "À 6h. 23m. un énorme rayon d'un blanc vif s'éleva à l'horizon E.N.E.; il traversa le ciel en passant le zénith et alla s'éteindre à l'horizon O.S.O." A similar phenomenon has been observed by Dr. F. Terby at Louvain. The great attraction of the Laon observation consisted in the fact that the meteor's apparent path was there seen at the north side of the zenith, this being in harmony with the Brussels zenith observation, and promising a good

Nature 28, 105 - 107 (31 May 1883),

Aurora which I missed

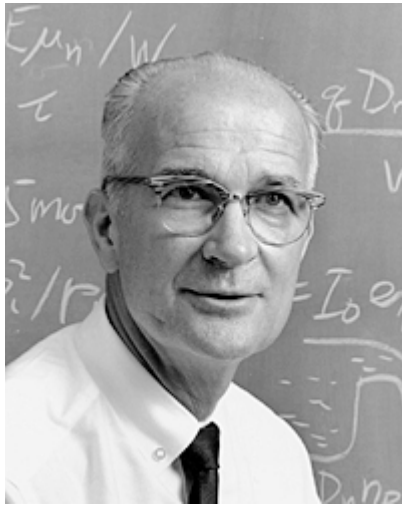


Paschen-Back effect in high magnetic field



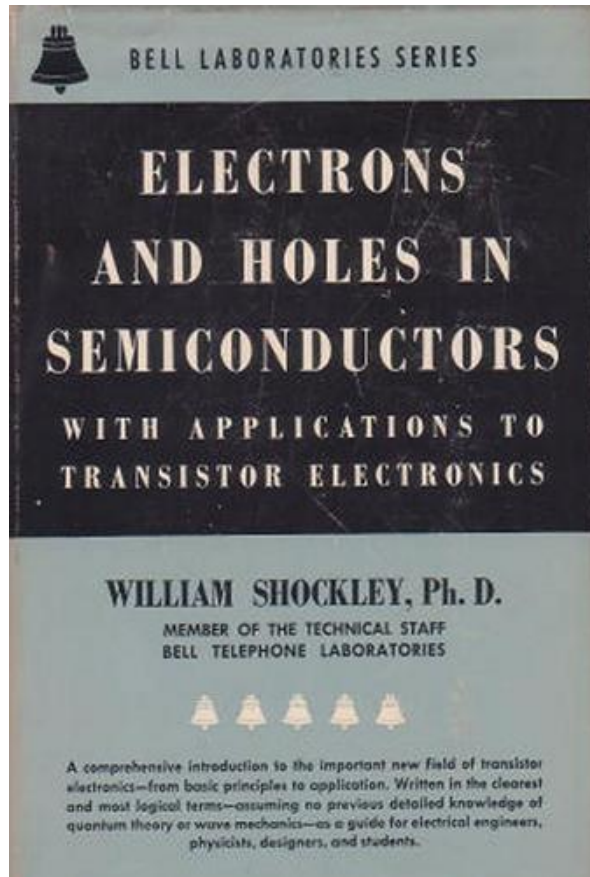
Observation of the Paschen-Back splitting in the D line of Na.
 H. Hori et al., J. Phys. Soc. Jpn, 51 1566 (1982)

W. Shockley (1910-1989)



- Co-inventor of the transistor
- Nobel prize (1956) with J. Bardeen and W. H. Brattain
- Shockley semiconductor Lab.
 - Fairchild semiconductor
 - Intel, National SC, Advanced MD

“Electrons and holes in semiconductors” by W. Shockley



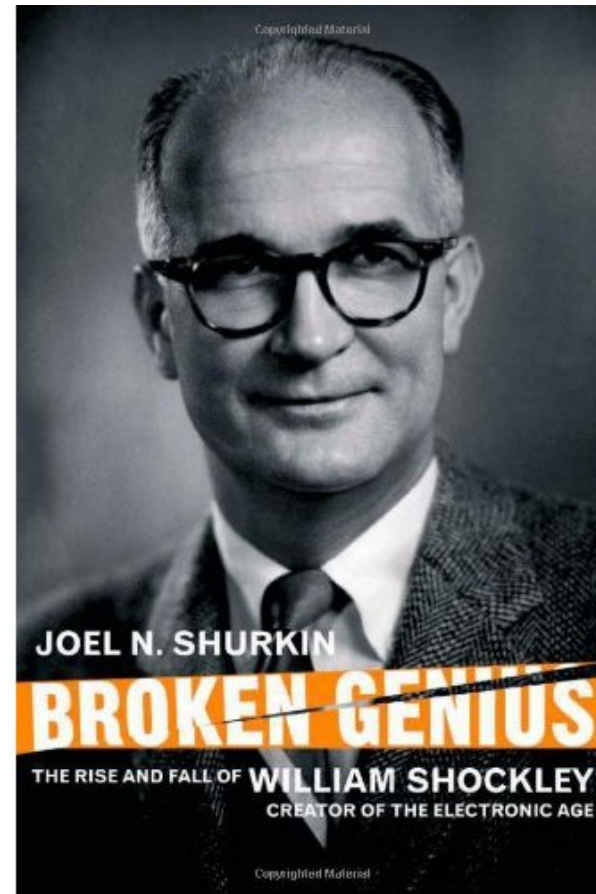
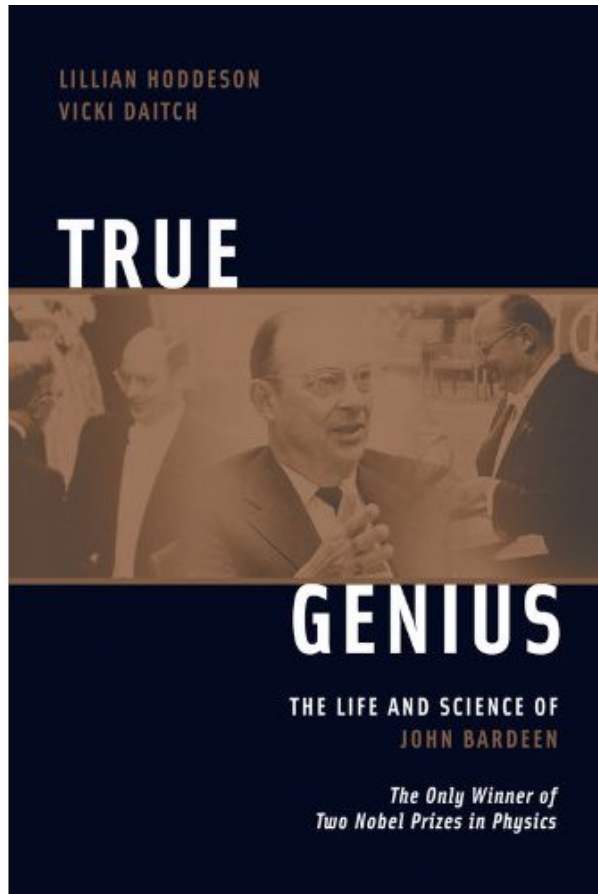
CHAPTER 14

ELEMENTARY QUANTUM MECHANICS WITH CIRCUIT THEORY ANALOGUES

14.1 ON THE NATURE OF AN APPLIED MATHEMATICAL THEORY¹

Quantum mechanics is recognized as one of the more difficult branches of theoretical physics, chiefly because it employs certain abstract mathematical tools which in themselves have no direct physical interpretation. Thus one is told, for example, that applying an operator to a wave function in the proper way will lead to predicting the outcome of an experiment. Neither the operator, the method of applying it, nor the wave function has a direct physical interpretation. This lack of a straightforward interpretation is a definite disadvantage from a pedagogical viewpoint—it makes the theory harder to present—but it does not indicate any lack of validity of the theory in its applications. In so far as its applications are concerned, a mathematical theory of an experimental science must satisfy one supreme requirement: *It must agree with experiment.* Although this requirement can be simply stated, we shall give several examples to illustrate its meaning before discussing the agreement with experiment achieved by quantum-mechanical theory and the procedures used to test it.

Bardeen vs Shockley



原子の量子力学の完成まで



W. Pauli
1900-1958



W. Heisenberg
1901-1976



E. Schrodinger
1887-1961

1924 Pauli's exclusion principle

1924 Matrix dynamics by Heisenberg

1926 Schrödinger eq.

1927 Hartree approx.

1929 Slater Det.

1930 Hartree-Fock

1951 Hartree-Fock-Slater eq.



Douglas Hartree
1897-1958



Vladimir Fock
1898-1974



John C. Slater
1900-1976

Hartree-Fock-Slater Eq.

PHYSICAL REVIEW

VOLUME 81, NUMBER 3

FEBRUARY 1, 1951

A Simplification of the Hartree-Fock Method

J. C. SLATER

Massachusetts Institute of Technology, Cambridge, Massachusetts*

(Received September 28, 1950)

Cited 2,411 times

BCS: 5,513

B&M: 7,697

vKlitzing: 1,647

It is shown that the Hartree-Fock equations can be regarded as ordinary Schrödinger equations for the motion of electrons, each electron moving in a slightly different potential field, which is computed by electrostatics from all the charges of the system, positive and negative, corrected by the removal of an exchange charge, equal in magnitude to one electron, surrounding the electron whose motion is being investigated. By forming a weighted mean of the exchange charges, weighted and averaged over the various electronic wave functions at a given point of space, we set up an average potential field in which we can consider all of the electrons to move, thus leading to a great simplification of the Hartree-Fock method, and bringing it into agreement with the usual band picture of solids, in which all electrons are assumed to move in the same field. We can further replace the average exchange charge by the corresponding value which we should have in a free-electron gas whose local density is equal to the density of actual charge at the position in question; this results in a very simple expression for the average potential field, which still behaves qualitatively like that of the Hartree-Fock method. This simplified field is being applied to problems in atomic structure, with satisfactory results, and is adapted as well to problems of molecules and solids.

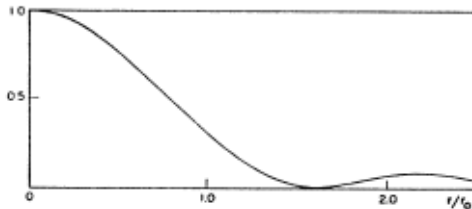


FIG. 2. Exchange charge density (divided by $\rho/2$) plotted as a function of r/r_0 , from Eq. (12), where r_0 is given by Eq. (9).

$$\frac{\rho}{2} \left[\frac{3 \sin(r/d) - (r/d) \cos(r/d)}{(r/d)^3} \right]^2, \quad (12)$$

$$H_1 u_i(x_1) + \left[\sum (k) \int u_k^*(x_2) u_k(x_2) (e^2/4\pi\epsilon_0 r_{12}) dx_2 \right. \\ \left. - 3(e^2/4\pi\epsilon_0) \left\{ \frac{3}{8\pi} \sum (k) u_k^*(x_1) u_k(x_1) \right\}^{\dagger} \right] u_i(x_1)$$

$$= E_i u_i(x_1). \quad (14)$$

Periodicity of elements

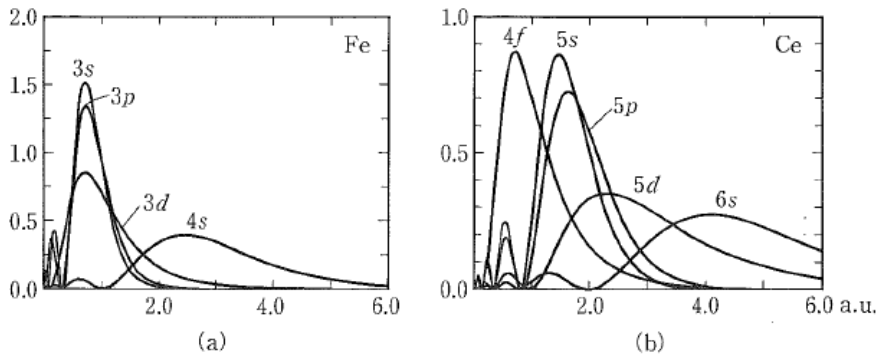
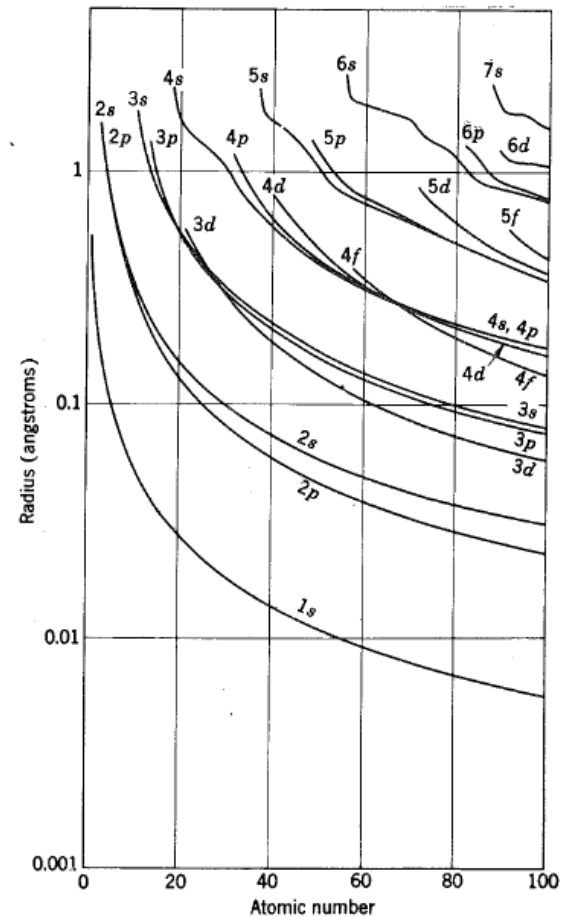


図3-1 外側の軌道の電荷分布

岡崎誠、「物質の量子力学」、岩波書店、1995

H 1	Li 3	Na 11	K 19	Rb 37	Cs 55	Fr 87	s
He 2	Be 4	Mg 12	Ca 20	Sr 38	Ba 56	Ra 88	s ²
	B 5	Al 13	Sc 21	Y 39	La 57	Ac 89	s ² d
	C 6	Si 14	Ti 22	Zr 40	Ce 58	Th 90	s ² df
	N 7	P 15	V 23	Nb 41	Pr 59	Pa 91	s ² df ²
	O 8	S 16	Cr 24	Mo 42	Nd 60	U 92	s ² df ³
	F 9	Cl 17	Mn 25	Tc 43	Pm 61	Np 93	s ² df ⁴
	Ne 10	Ar 18	Fe 26	Ru 44	Sm 62	Pu 94	s ² df ⁵
			Co 27	Rh 45	Gd 64	Cm 96	s ² df ⁷
			Ni 28	Pd 46	Tb 65	Bk 97	s ² df ⁸
			Cu 29	Ag 47	Dy 66	Cf 98	s ² df ⁹
			Zn 30	Cd 48	Ho 67	E 99	s ² df ¹⁰
			Ga 31	In 49	Er 68	Fm100	s ² df ¹¹
			Ge 32	Sn 50	Tu 69	Mv101	s ² df ¹²
			As 33	Sb 51	Lu 70		s ² df ¹³
			Se 34	Te 52	Hf 72		s ² d ²
			Br 35	I 53	Ta 73		s ² d ³
			Kr 36	Xe 54	W 74		sd ⁵
					Re 75		s ² d ⁵
					Os 76		s ² d ⁶
					Ir 77		s ² d ⁷
					Pt 78		s ² d ⁸
					Au 79		sd ¹⁰
					Hg 80		s ²
					Tl 81		s ² p
					Pb 82		s ² p ²
					Bi 83		s ² p ³
					Po 84		s ² p ⁴
					At 85		s ² p ⁵
					Rn 86		s ² p ⁶



QUANTUM THEORY OF MATTER

SECOND EDITION

JOHN C. SLATER

*Graduate Research Professor,
University of Florida*

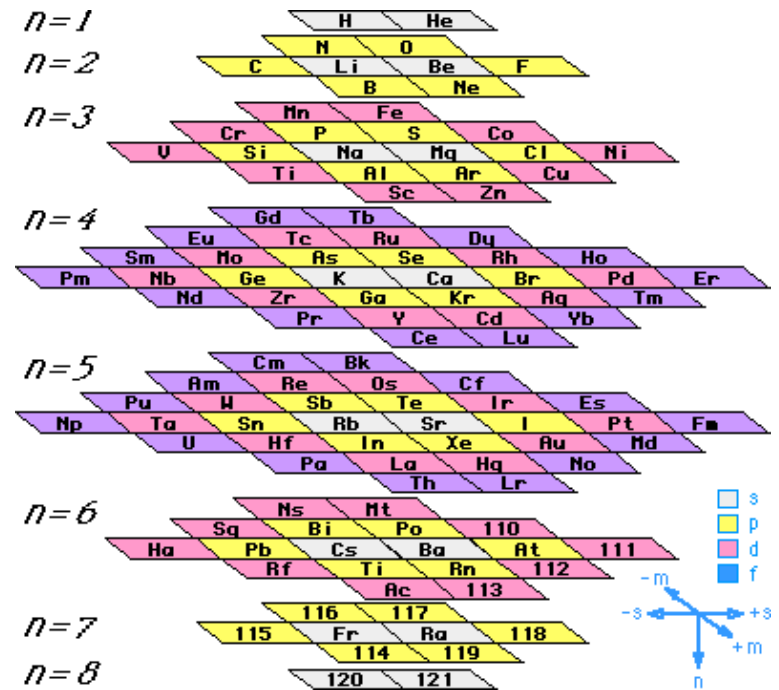
*Institute Professor Emeritus,
Massachusetts Institute of Technology*

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Periodic table of the elements

- Standard type by NIST
- Stowe's table
- Elementouch by Prof. Maeno@Phys.
- Various tables
- 一家に1枚周期律表
(文部科学省)



Magnetism of ions 1

表 2-1 closed shell をもつ原子およびイオンの反磁性帯磁率
(mol 当たり 10^{-6}cm^3 を単位とする)

	実験値	理論値		実験値	理論値
He	-1.9	-1.9	Li ⁺	-0.7	-0.7
Ne	-7.2	-8.6	Na ⁺	-6.1	-5.6
A	-19.4	-20.6	K ⁺	-14.6	-15.3
Kr	-28		Rb ⁺	-22.0	-29.5
Xe	-43		Cs ⁺	-35.1	-47.5
F ⁻	-9.4	-17.0	Mg ⁺⁺	-4.3	-4.2
Cl ⁻	-24.2	-30.4	Ca ⁺⁺	-10.7	-13.1
Br ⁻	-34.5		Sr ⁺⁺	-18.0	
I ⁻	-50.6		Ba ⁺⁺	-29.0	

金森順次郎「磁性」(培風館)より。

遷移金属元素の電子配置によるスピンと軌道の関係。

m_z \ n	0	1	2	3	4	5	6	7	8	9	10
2	—	↑	↑	↑	↑	↑	↑↓	↑↓	↑↓	↑↓	↑↓
1	—	—	↑	↑	↑	↑	↑	↑↓	↑↓	↑↓	↑↓
0	—	—	—	↑	↑	↑	↑	↑	↑↓	↑↓	↑↓
-1	—	—	—	—	↑	↑	↑	↑	↑	↑↓	↑↓
-2	—	—	—	—	—	↑	↑	↑	↑	↑	↑↓
$S = \sum s_z$	—	1/2	1	3/2	2	5/2	2	3/2	1	1/2	—
$L = \sum m_z$	0	2	3	3	2	0	2	3	3	2	0
$J = L \pm S$	0	3/2	2	3/2	0	5/2	4	9/2	4	5/2	0
$p_{\text{eff}}(S)$	—	1.732	2.828	3.873	4.899	5.916	4.899	3.873	2.828	1.732	—
基底状態	¹ S ₀	³ D _{3/2}	³ F ₂	⁴ F _{3/2}	⁵ D ₀	⁶ S _{5/2}	⁵ D ₄	⁴ F _{9/2}	³ F ₄	³ D _{5/2}	¹ S ₀
$\lambda(\text{cm}^{-1})$	—	154	104	87	57	—	-100	-180	-335	-850	
イオン	Sc ³⁺ Ti ⁴⁺	Ti ³⁺ V ⁴⁺	V ³⁺ Ti ²⁺	Cr ³⁺ Mn ⁴⁺	Cr ²⁺ Mn ³⁺	Fe ³⁺ Mn ²⁺	Fe ²⁺ Co ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺

安達健五「化合物磁性 局在スピン系」(裳華房)

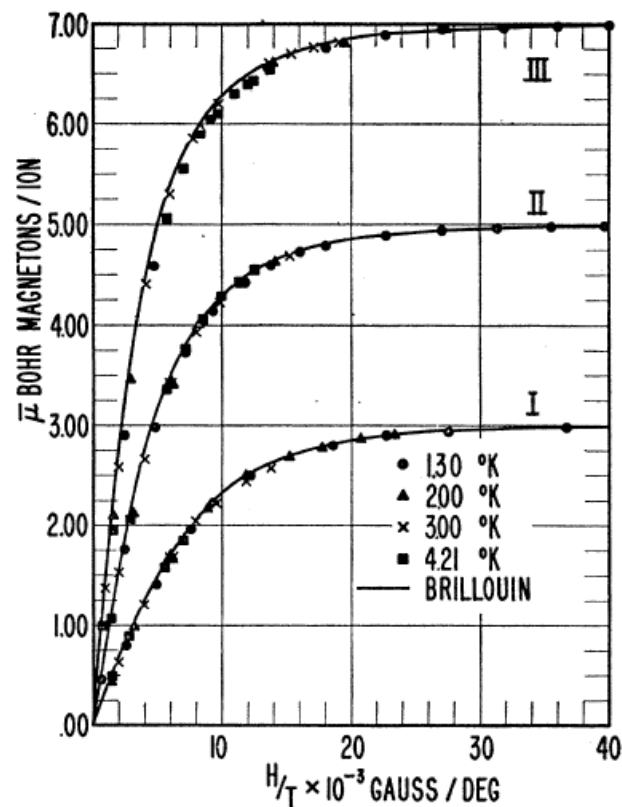
Magnetism of ions 2

イオン	f^n	基底状態	実験値	理論値 1†	理論値 2††
La ³⁺	f^0	$1S$	dia	0.00	0.00
Ce ³⁺	f^1	$2F_{5/2}$	2.5	2.54	2.56
Pr ³⁺	f^2	$3H_4$	3.6	3.58	3.62
Nd ³⁺	f^3	$4I_{9/4}$	3.8	3.62	3.68
Pm ³⁺	f^4	$5I_4$	—	2.68	2.83
Sm ³⁺	f^5	$6H_{5/2}$	1.5	0.84	1.55
Eu ³⁺	f^6	$7F_0$	3.6	0.00	3.40
Gd ³⁺	f^7	$8S_{7/2}$	7.9	7.94	7.94
Tb ³⁺	f^8	$7F_6$	9.7	9.72	9.7
Dy ³⁺	f^9	$6H_{15/2}$	10.5	10.63	10.6
Ho ³⁺	f^{10}	$5I_8$	10.5	10.60	10.6
Er ³⁺	f^{11}	$4I_{15/2}$	9.4	9.59	9.6
Tm ³⁺	f^{12}	$3H_6$	7.2	7.57	7.6
Yb ³⁺	f^{13}	$2F_{7/2}$	4.5	4.54	4.5
Lu ³⁺	f^{14}	$1S$	dia	0.00	0.00

† (2-31) 式から基底状態の g_J を用い $g_J \sqrt{J(J+1)}$ を計算したもの。

†† (2-32) 式を用い常温付近の p (有効ボーア磁子) を計算したもの (Van Vleck-Franck)。

希土類元素の有効ボーア磁子数。金森順次郎「磁性」(培風館)より。



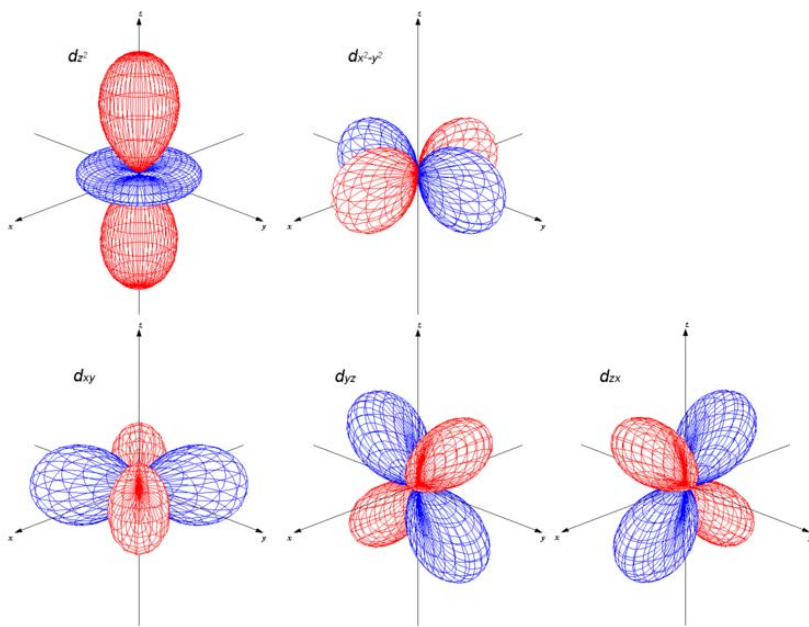
常磁性塩の磁化曲線。I: クロムミョウバン ($J = 3/2$) II: 鉄ミョウバン ($J = 5/2$) III: ガドリニウム炭酸塩 ($J = 7/2$)。W. E. Henry, Phys. Rev. **88** 559 (1952)。

Rear earth ions

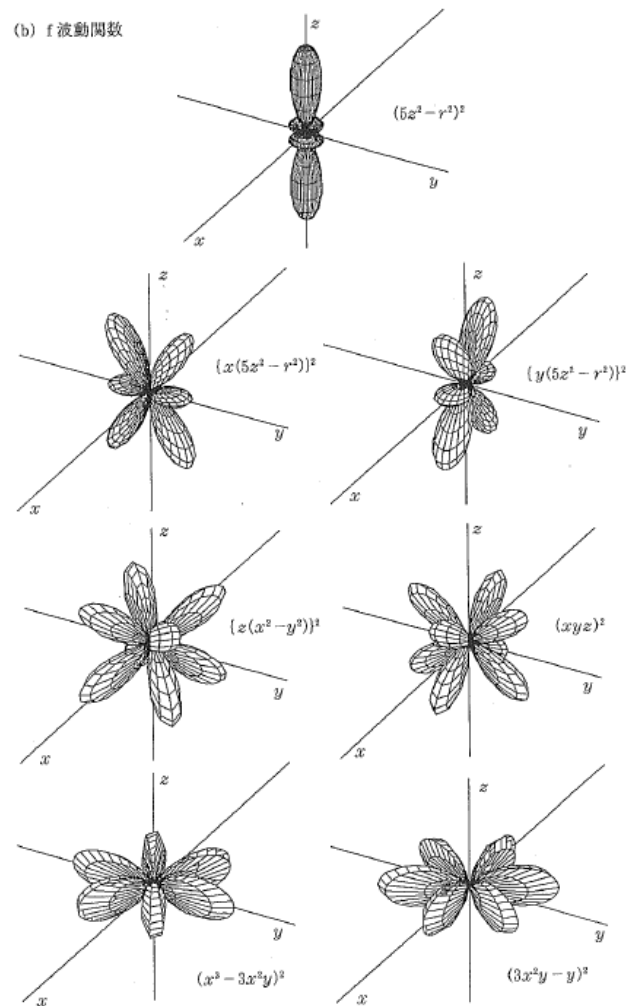
2-2 表 (b) 希土類元素 R^{3+} の $4f^n$ 電子配位におけるスピンと軌道の関係。
Landé 因子 g_J と de Gennes 因子 $dG = (g_J - 1)^2 J(J + 1)$.

$m_z \backslash n$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
3	—	↑	↑	↑	↑	↑	↑	↑	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
2	—	—	↑	↑	↑	↑	↑	↑	↑	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
1	—	—	—	↑	↑	↑	↑	↑	↑	↑	↑↓	↑↓	↑↓	↑↓	↑↓
0	—	—	—	—	↑	↑	↑	↑	↑	↑	↑	↑↓	↑↓	↑↓	↑↓
-1	—	—	—	—	—	↑	↑	↑	↑	↑	↑	↑	↑↓	↑↓	↑↓
-2	—	—	—	—	—	—	↑	↑	↑	↑	↑	↑	↑	↑↓	↑↓
-3	—	—	—	—	—	—	—	↑	↑	↑	↑	↑	↑	↑	↑↓
$S = \sum s_z$	0	1/2	1	3/2	2	5/2	3	7/2	3	5/2	2	3/2	1	1/2	0
$L = \sum m_z$	0	3	5	6	6	5	3	0	3	5	6	6	5	3	0
$J = L + S $	0	5/2	4	9/2	4	5/2	0	7/2	6	15/2	8	15/2	6	7/2	0
p_{eff}	—	2.54	3.58	3.62	2.68	0.845	—	7.94	9.72	10.63	10.58	9.59	7.55	4.54	—
g_J	—	6/7	4/5	8/11	3/5	2/7	—	2	3/2	4/3	5/4	6/5	7/6	8/7	—
$g_J J$	—	15/7	16/5	36/11	12/5	5/7	—	7	9	10	10	9	7	4	—
dG	—	5/28	4/5	81/44	16/5	125/28	—	63/4	21/2	85/12	9/2	51/20	7/6	9/28	—
$\lambda(\text{cm}^{-1})$	0	640	360	290	260	240	230	—	-290	-380	-520	-820	-1290	-2940	—
基底状態	1S_0	$^2F_{5/2}$	3H_4	$^4J_{9/2}$	5I_4	$^6H_{5/2}$	7F_0	$^8S_{7/2}$	7F_6	$^6H_{15/2}$	5I_8	$^4I_{15/2}$	3H_6	$^2F_{7/2}$	1S_0
イオン	La ³⁺	Ce ³⁺	Pr ³⁺	Nd ³⁺	Pm ³⁺	Sm ³⁺	Eu ³⁺	Gd ³⁺	Tb ³⁺	Dy ³⁺	Ho ³⁺	Er ³⁺	Tm ³⁺	Yb ³⁺	Lu ³⁺
							(Sm ²⁺)	(Eu ²⁺)							

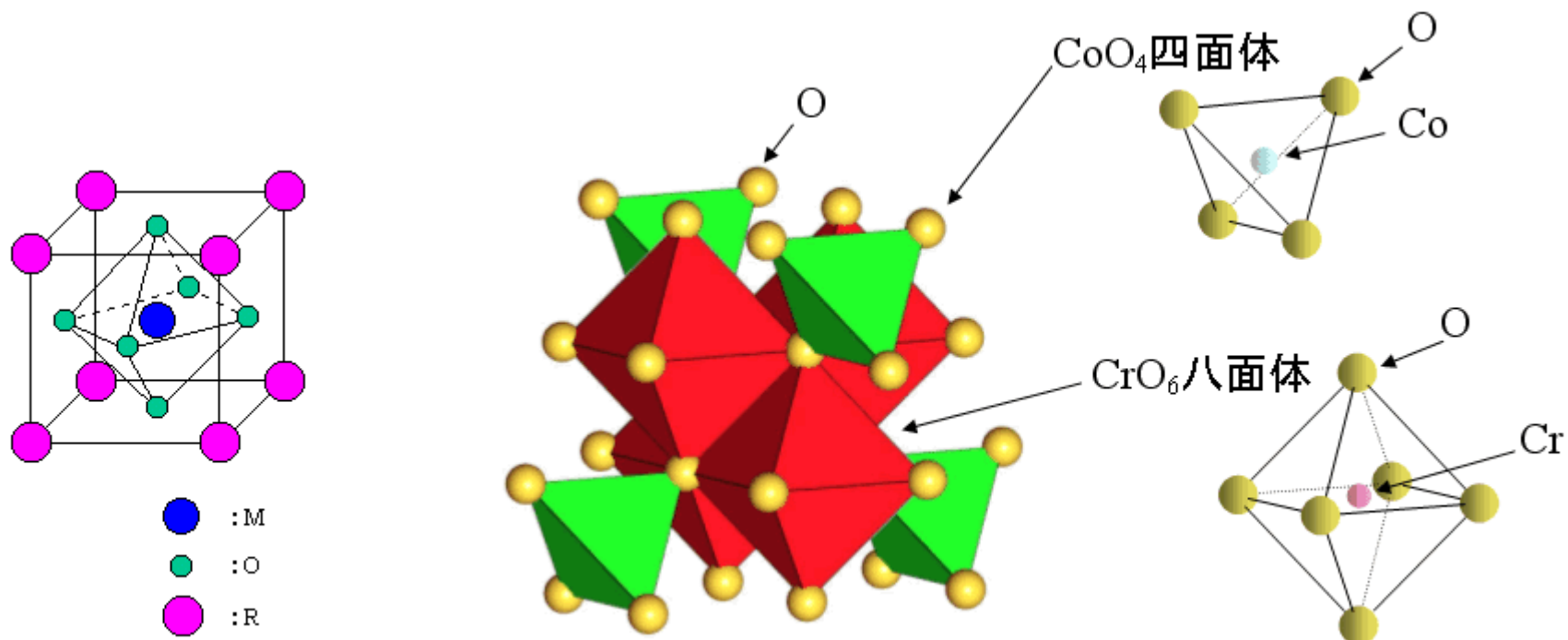
Electron orbits



(b) f 波動関数



ペロブスカイト構造とスピネル構造



もっと勉強したい人のために

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