Cours de

Physique Atomique

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Chapitre 1

Ordres de grandeur

1.1 Introduction

Ce chapitre a comme but d'éviter les grosses erreurs en abordant un nouveau domaine. On y inclut l'analyse dimensionnelle.

Exemple 1

Cherchons à déterminer la dimension de la constante de tension superficielle A, sachant que

$$F = A\ell.$$

On a alors, en utilisant M pour l'unité de masse, L pour celle de longueur et T pour celle de temps

$$[A] = \left[\frac{F}{\ell}\right] = \frac{M \cdot L \cdot T^{-2}}{L} = M \cdot T^{-2}$$

Exemple 2

On prétend que dans l'atome d'hydrogène H, l'électron est lié au proton par la force gravifique (hypothèse avancée entre la fin du XIX$^{\text{e}}$ et le début du XX$^{\text{e}}$ siècle). En posant que la fréquence est

$$\nu = \frac{c}{\lambda} \quad \text{avec } \lambda = 500 \text{ nm}$$

la période de révolution de l'électron vaut alors

$$T = \frac{1}{\nu}.$$

En supposant l'orbite circulaire, on a alors

$$G\frac{m_1 m_e}{R^2} = m_e \omega^2 R \;\Rightarrow\; R = \sqrt[3]{\frac{Gm_1}{4\pi\nu^2}}$$

d'où l'on déduit que $R \simeq 10^{-23}$ m.

Par la diffraction des rayons X, on sait que la dimension des atomes H vaut enciron 10^{-10} m. Ce qui montre que l'hypothèse initiale est fausse.

Exemple 3

Cherchons les fréquences de vibration d'une goutte liquide. On néglige la gravitation (par exemple dans la navette spatiale). On exprime les hypothèses suivantes

1. ρ est constante (liquide incompressible).

2. A, la tension superficielle, joue un rôle important.

Ainsi on suppose, avec d le diamètre de la goutte,

$$\nu = \nu(\rho, d, A)$$

On a

$$\begin{aligned} [\rho] &= M \cdot L^{-3} & [d] &= L \\ [A] &= M \cdot T^{-2} & [\nu] &= T^{-1} \end{aligned}$$

d'où

$$\nu \propto \left(\frac{A}{\rho d^3}\right)^{\frac{1}{2}}.$$

On utilisera alors la relation

$$\nu = \left(\frac{A}{\rho d^3}\right)^{\frac{1}{2}}.$$

1.2 Relations d'éuivalences

1. **Relation de Planck (1900)** : $\Delta E = h\nu$.
   Quand un système isolé voit son énergie varier de ΔE lors d'une transition durant laquelle un photon est émis, la relation de Planck donne la fréquence du rayonnement.
2. **Équivalence entre énergie et température** : La loi de Boltzmann

   $$n(E) = \text{cst} \cdot e^{-\frac{E}{kT}}$$

   T étant la température du système. Á T fixé, il existe une sorte d'énergie "critique", pour laquelle si $E < kT = E_0$ on a une probabilité finie de trouver une particule avec l'énergie E, alors que si $E \gg E_0$ la probabilité devient pratiquement nulle.
3. **Masse-énergie** : On a la relation d'Einstein $E = mc^2$.
4. **Energie-différence de potentiel** : $\Delta E = e\Delta U$.
5. **Relation de de Broglie** : $\lambda = \frac{h}{p}$.
   Cette relation associe une onde de matière à une particule possédant une quantité de mouvement p.

En utilisant ce relations, on peut simplifier les calculs en posant

$$\hbar = c = k = 1$$

avec $\hbar = \frac{h}{2\pi}$ la constante de Planck réduite. On a alors les équivalences suivantes

$$\begin{aligned} 1 \text{ J} &= 6.25 \cdot 10^{18} \text{ eV} \\ 1 \text{ eV} &= 1.6 \cdot 10^{-19} \text{ J} \\ 1 \text{ eV} &= 2.418 \cdot 10^{14} \text{ s}^{-1} \\ 1 \text{ eV} &= 11'605 \text{ K} \\ 1 \text{ kg} &= 5.617 \cdot 10^{35} \text{eV} \end{aligned}$$

1.3 Analyse dimensionnelle en physique atomique

Les constantes à disposition sont

$$e, m_e, m_p, c, \hbar, \epsilon_0, k$$

la charge élémentaire, la masse de l'électron, celle du proton et les constantes usuelles.

— La gravitation est négligée.
— μ_0 est reliée à ϵ_0 par $\epsilon_0 \mu_0 = \frac{1}{c^2}$.
— m_e, m_p, m_n sont ramenées à m_e.

Exemple 4

On a alors les relations dimensionnelles

$$\begin{aligned} [e] &= Q \text{ (charge)} & [\hbar] &= [h] = MLT^{-2}LT \\ & & &= ML^2T^{-1} \text{ (action : énergie·temps)} \\ [m_e] &= M & [c] &= LT^{-1} \\ [k] &= \text{énergie} \cdot T^{-1} & [\epsilon_0] &= Q^2L^{-3}M^{-1}T^2 \end{aligned}$$

Supposons que l'on veuille trouver une longueur sous la forme

$$\ell = e^{n_1} m_e^{n_2} c^{n_3} \hbar n_4 \epsilon_0^{n_5}$$

on obtient alors

$$L = Q^{n_1} M^{n_2} L^{n_3} T^{-n_3} M^{n_4} L^{2n_4} T^{-n_4} Q^{2n_5} L^{-3n_5} M^{-n_5} T^{2n_5}$$

Ainsi

$$n_1 = -2n_5$$

ce qui montre que ϵ_0 n'intervient qu'avec la charge e. On pose alors

$$q_e = \sqrt{\frac{e^2}{4\pi\epsilon_0}} \quad \text{(charge réduite)}$$

Les constantes sont ainsi q_e, m_e, c et $\hbar$ et

$$L = \underbrace{L^{\frac{3}{2}n_1} M^{\frac{n_1}{2}} T^{-n_1}}_{q_e^{n_1}} M^{n_2} L^{n_3} T^{-n_3} M^{n_4} L^{2n_4} T^{-n_4}$$

On obtient alors le système de 3 équations à 4 inconnues suivant

$$\begin{cases} n_2 + n_4 + \frac{n_1}{2} & = 0 \\ n_3 + 2n_4 + \frac{3}{2}n_1 & = 1 \\ -n_3 - n_4 - n_1 & = 0 \end{cases}$$

En prenant $n_2 = -1$ on trouve

$$\begin{aligned} n_4 &= 1 - \frac{n_1}{2} \\ n_3 &= -1 - \frac{n_1}{2} \end{aligned}$$

et n_1 peut être choisi librement. On peut poser $n_1 = 2n$. Il vient alors

$$L = [q_e^{2n} m_e^{-1} c^{-1-n} \hbar^{1-n}] = \left[\left(\frac{q_e^2}{\hbar c} \right)^n \frac{\hbar}{m_e c} \right]$$

La longueur

$$\lambda_C = \frac{\hbar}{m_e c} \simeq 3.867 \cdot 10^{-13} \text{ m}$$

est appelée la *longueur de Compton de l'électron*.

Avec $\alpha = \frac{q_e^2}{\hbar c} = 7.297 \cdot 10{-}3 \simeq \frac{1}{137}$, on a

$$\alpha = \frac{q_e^2}{\frac{\hbar}{m_e c}} \frac{1}{m_e c^2} = \frac{q_e^2}{\lambda_C} \frac{1}{m_e c^2}$$

Le premier rapport est l'énergie électrostatique de deux charges e séparées par une distance λ_C et α est le rapport de cette énergie sur l'énergie de masse de l'électron.

Exemple 5

1. L'énergie de l'électron dans l'atome de Bohr dans son état fondamental vaut

$$E_1 = -\frac{1}{(4\pi\epsilon_0)^2}\frac{m_e e^4}{2\hbar^2} = -m_e c^2 \frac{\alpha^2}{2}$$

2. Le rayon de Bohr vaut

$$a_B = 4\pi\epsilon_0 \frac{\hbar^2}{m_e e^2} = \lambda_C \alpha^{-1} = 0.053 \text{ nm}$$

Remarque 1

Lorsqu'une seule masse est en jeu, en physique atomique, et que l'on désire évoluer une grandeur x quelconque, il est toujours possible d'avoir une relation du type

$$x = (\text{combinaison de constantes de dimension } [x]) \cdot f(\alpha)$$

1.4 L'atome de Bohr

Le modèle de Bohr de l'atome d'hydrogène prend les hypothèses suivantes

- L'électron suit une orbite circulaire selon un mouvement circulaire uniforme autour du noyau sous l'action des forces électrostatiques.
- L'électron n'occuper que des orbites pour lesquelles le moment cinétique est un multiple entier de $\hbar$.
- Sur une telle orbite, l'électron ne rayonne pas Etot $=$ cste.
- Un photon est absorbé ou émis si l'électron passe d'une orbite à une autre avec

$$\nu = \frac{|E_i - E_f|}{h}.$$

On peut décomposer le mouvement en un mouvement du centre de massse (CM) et un mouvement relatif. Dans le mouvement relatif on étudie le mouvement d'une particule réduite de masse

$$m = \frac{m_1 m_2}{m_1 + m_2}, \qquad \text{avec } \frac{m_e}{m_p} = \frac{0.511 \text{ MeV}}{938 \text{ MeV}} = 5.4 \cdot 10^{-4}.$$

Ainsi on peut donc considérer que $m_p \to \infty$ et $m \simeq m_e$.

On obtient alors

1. de la deuxième loi de Newton

$$m_e \omega^2 r_n = \frac{q_e^2}{r_n^2}$$

2. et de la quantification du moment cinétique

$$\oint \vec{p} \cdot d\vec{r} = nh$$

donc

$$m_e v_n r 2\pi = nh$$

soit

$$m_e \omega_n r_n^2 = n\hbar$$

Ainsi, on obtient

$$r_n = \frac{n^2\hbar^2}{m_e q_e^2} = n^2 \lambda_C \alpha^{-1} = n^2 a_B$$

$$\omega_n = \frac{m_e c^2}{n^3 \hbar}\alpha^2$$

L'énergie totale est alors

$$E_n = E_n^{\text{cin}} + E_n^{\text{pot}} = -\frac{q_e^2}{r_n} + \frac{1}{2} m_e v_n^2$$

soit, avec $m_e \frac{v^2}{r} = \frac{q_e^2}{r^2}$

$$E_n = \frac{1}{2} E_n^{\text{pot}} = \frac{1}{2} m_e \omega_n^2 r_n^2 = -\frac{1}{2} \frac{m_e c^2}{n^2} \alpha^2.$$

Pour l'état fondamental on a

$$E_1 = -13.6 \text{ eV} = -R_y$$

où R_y est l'énergie de Rydberg. On définit également la *constante de Rydberg* $R_\infty = \frac{R_y}{hc}$.

1.4.1 Correction pour les masses finies

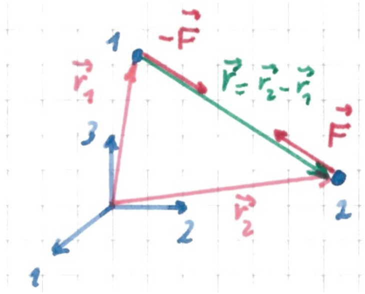
Avec la masse réduite μ on obtient les corrections suivantes

$$r_n = n^2 a_B \frac{m_e}{\mu}$$

et

$$R_\mu = R_\infty \frac{\mu}{m_e}.$$

1.5 La masse réduite



Soit un système mécanique composé de deux corps de masse m_1 et m_2 exer4ant l'un sur l'autre une force $\vec{F}$ centrale. On a

$$\begin{cases} m_1 \ddot{\vec{r}}_1 & = -\vec{F} \\ m_2 \ddot{\vec{r}}_2 & = \vec{F} \end{cases}$$

Prenons

$$\begin{cases} \vec{r} & = \vec{r}_2 - \vec{r}_1 \quad \text{(la position relative)} \\ \mu & = \frac{m_1 m_2}{m_1 + m_2} \quad \text{(la masse réduite)} \end{cases}$$

Il découle alors du premier système

$$m_1 \ddot{\vec{r}}_1 + m_2 \ddot{\vec{r}}_2 = 0.$$

or par définition du centre de masse, avec $M = m_1 + m_2$

$$m_1 \vec{r}_2 + m_2 \vec{r}_2 = M \vec{r}_G$$

donc

$$M \ddot{\vec{r}}_G = 0$$

le centre de masse du système évolue donc librement.

Toujours de

$$m_1 \ddot{\vec{r}}_1 + m_2 \ddot{\vec{r}}_2 = 0.$$

on a

$$m_1 \ddot{\vec{r}}_1 + m_2 \ddot{\vec{r}}_2 + m_1 \ddot{\vec{r}}_2 - m_1 \ddot{\vec{r}}_2 = 0.$$

soit

$$m_1 (\ddot{\vec{r}}_1 - \ddot{\vec{r}}_2) + (m_1 + m_2) \ddot{\vec{r}}_2 = 0$$

ou encore

$$-m_1 \ddot{\vec{r}} + M \ddot{\vec{r}}_2 = 0$$

d'où

$$\ddot{\vec{r}}_2 = \frac{m_1}{M} \ddot{\vec{r}}.$$

On a ainsi

$$m_2\ddot{\vec{r}}_2 = \frac{m_1 m_2}{M}\ddot{\vec{r}} = \mu\ddot{\vec{r}} = \vec{F}.$$

soit

$$\mu\ddot{\vec{r}} = \vec{F}.$$

L'étude du système se ramène donc à étudier l'évolution d'une masse μ sur laquelle s'exerce la force centrale $\vec{F}$.

PHYSICAL CONSTANTS

Reviewed 1991 by B.N. Taylor. Based mainly on the "1986 Adjustment of the Fundamental Physical Constants" by E.R. Cohen and B.N. Taylor, Rev. Mod. Phys. **59**, 1121 (1987). The figures in parentheses after the values give the 1-standard-deviation uncertainties in the last digits; the uncertainties in parts per million (ppm) are given in the last column. The uncertainties of the values from a least-squares adjustment are in general correlated, and the laws of error propagation must be used in calculating additional quantities; the full variance matrix is given in the cited paper. The set of constants resulting from the 1986 adjustment has been recommended for international use by CODATA (Committee on Data for Science and Technology).

Since the 1986 adjustment, new experiments have yielded improved values for a number of constants, including the Rydberg constant R_∞, the Planck constant h, the fine-structure constant α, and the molar gas constant R, and hence also for constants directly derived from these, such as the Boltzmann constant k and Stefan-Boltzmann constant σ. The new results and their impact on the 1986 recommended values are discussed extensively in "Recommended Values of the Fundamental Physical Constants: A Status Report," B.N. Taylor and E.R. Cohen, J. Res. Natl. Inst. Stand. Technol. **95**, 497 (1990). In general, the new results give uncertainties for the affected constants that are 5 to 7 times smaller than the 1986 uncertainties, but the changes in the values themselves are smaller than twice the 1986 uncertainties. Until there are more experiments and a complete readjustment of the constants, the 1986 CODATA set, given (in part) below, remains the set of choice.

Quantity	Symbol, equation	Value	Uncert. (ppm)
speed of light	c	299 792 458 m s^{-1}	(exact)*
Planck constant	h	6.626 075 5(40)$\times10^{-34}$ J s	0.60
Planck constant, reduced	$\hbar \equiv h/2\pi$	1.054 572 66(63)$\times10^{-34}$ J s	0.60
		= 6.582 122 0(20)$\times10^{-22}$ MeV s	0.30
electron charge magnitude	e	1.602 177 33(49)$\times10^{-19}$ C = 4.803 206 8(15)$\times10^{-10}$ esu	0.30, 0.03
conversion constant	$\hbar c$	197.327 053(59) MeV fm	0.30
conversion constant	$(\hbar c)^2$	0.389 379 66(23) GeV^2 mbarn	0.59
electron mass	m_e	0.510 999 06(15) MeV/c^2 = 9.109 389 7(54)$\times10^{-31}$ kg	0.30, 0.59
proton mass	m_p	938.272 31(28) MeV/c^2 = 1.672 623 1(10)$\times10^{-27}$ kg	0.30, 0.59
		= 1.007 276 470(12) u = 1836.152 701(37) m_e	0.012, 0.020
deuteron mass	m_d	1875.613 39(57) MeV/c^2	0.30
unified atomic mass unit (u)	(mass C^{12} atom)/12 = (1 g)/N_A	931.494 32(28) MeV/c^2 = 1.660 540 2(10)$\times10^{-27}$ kg	0.30, 0.59
permittivity of free space	ϵ_0 } $\epsilon_0\mu_0 = 1/c^2$	8.854 187 817 … $\times10^{-12}$ F m^{-1}	(exact)
permeability of free space	μ_0	$4\pi \times 10^{-7}$ N A^{-2} = 12.566 370 614 … $\times10^{-7}$ N A^{-2}	(exact)
fine structure constant	$\alpha = e^2/4\pi\epsilon_0\hbar c$	1/137.035 989 5(61)†	0.045
classical electron radius	$r_e = e^2/4\pi\epsilon_0 m_e c^2$	2.817 940 92(38)$\times10^{-15}$ m	0.13
electron Compton wavelength	$\lambda\!\!\!^{-}_e = \hbar/m_e c = r_e\alpha^{-1}$	3.861 593 23(35)$\times10^{-13}$ m	0.089
Bohr radius ($m_{\text{nucleus}} = \infty$)	$a_\infty = 4\pi\epsilon_0\hbar^2/m_e e^2 = r_e\alpha^{-2}$	0.529 177 249(24)$\times10^{-10}$ m	0.045
wavelength of 1 eV/c particle	hc/e	1.239 842 44(37)$\times10^{-6}$ m	0.30
Rydberg energy	$hcR_\infty = m_e e^4/2(4\pi\epsilon_0)^2\hbar^2 = m_e c^2\alpha^2/2$	13.605 698 1(40) eV	0.30
Thomson cross section	$\sigma_T = 8\pi r_e^2/3$	0.665 246 16(18) barn	0.27
Bohr magneton	$\mu_B = e\hbar/2m_e$	5.788 382 63(52)$\times10^{-11}$ MeV T^{-1}	0.089
nuclear magneton	$\mu_N = e\hbar/2m_p$	3.152 451 66(28)$\times10^{-14}$ MeV T^{-1}	0.089
electron cyclotron freq./field	$\omega^e_{\text{cycl}}/B = e/m_e$	1.758 819 62(53)$\times10^{11}$ rad s^{-1} T^{-1}	0.30
proton cyclotron freq./field	$\omega^p_{\text{cycl}}/B = e/m_p$	9.578 830 9(29)$\times10^{7}$ rad s^{-1} T^{-1}	0.30
gravitational constant	G_N	6.672 59(85)$\times10^{-11}$ m^3 kg^{-1} s^{-2}	128
		= 6.707 11(86)$\times10^{-39}$ $\hbar c$ (GeV/c^2)$^{-2}$	128
standard grav. accel., sea level	g	9.806 65 m s^{-2}	(exact)
Avogadro number	N_A	6.022 136 7(36)$\times10^{23}$ mol^{-1}	0.59
Boltzmann constant	k	1.380 658(12)$\times10^{-23}$ J K^{-1}	8.5
		= 8.617 385(73)$\times10^{-5}$ eV K^{-1}	8.4
Wien displacement law constant	$b = \lambda_{\max}T$	2.897 756(24)$\times10^{-3}$ m K	8.4
molar volume, ideal gas at STP	$N_A k$(273.15 K)/(1 atmosphere)	22.414 10(19)$\times10^{-3}$ m^3 mol^{-1}	8.4
Stefan-Boltzmann constant	$\sigma = \pi^2 k^4/60\hbar^3 c^2$	5.670 51(19)$\times10^{-8}$ W m^{-2} K^{-4}	34
Fermi coupling constant	$G_F/(\hbar c)^3$	1.166 39(2)$\times10^{-5}$ GeV^{-2}	17
weak mixing angle	$\sin^2\theta_W$ ($\overline{\text{MS}}$)	0.2325±0.0008	3441
$W^\pm$ boson mass	m_W	80.22±0.26 GeV/c^2	3241
Z^0 boson mass	m_Z	91.173±0.020 GeV/c^2	219
strong coupling constant	$\alpha_s(m_Z)$	0.1134±0.0035	3.1×10^4

π = 3.141 592 653 589 793 238　　e = 2.718 281 828 459 045 235　　γ = 0.577 215 664 901 532 861

1 in ≡ 0.0254 m　1 barn ≡ 10^{-28} m^2　1 eV = 1.602 177 33(49) × 10^{-19} J　1 gauss (G) ≡ 10^{-4} tesla (T)
1 Å ≡ 10^{-10} m　1 dyne ≡ 10^{-5} newton (N)　1 eV/c^2 = 1.782 662 70(54) × 10^{-36} kg　0° C ≡ 273.15 K
1 fm ≡ 10^{-15} m　1 erg ≡ 10^{-7} joule (J)　2.997 924 58 × 10^9 esu = 1 coulomb (C)　1 atmosphere ≡ 760 torr ≡ 1.013 25 × 10^5 N/m^2

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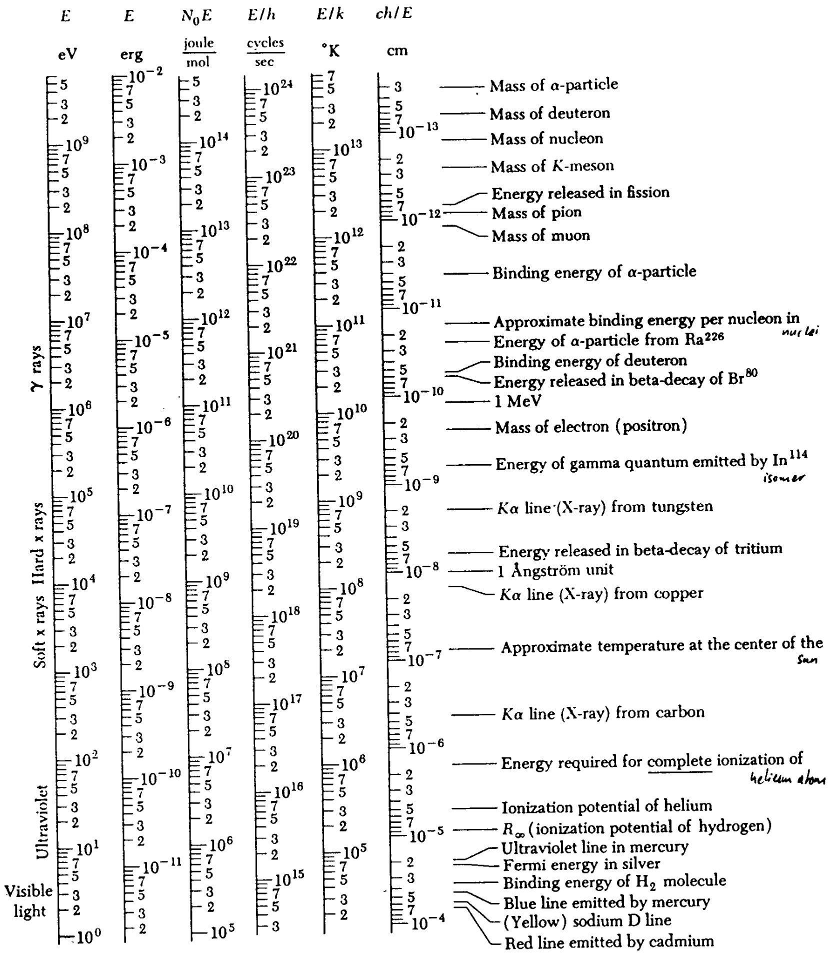
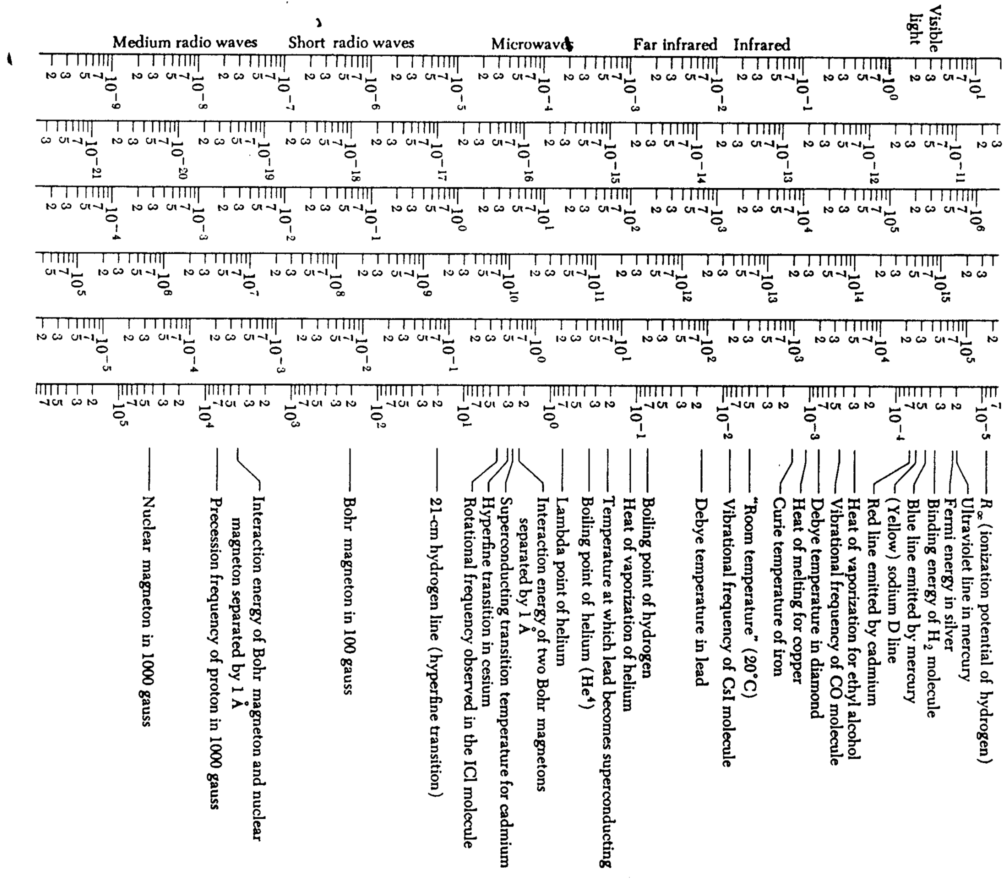
* The meter is now defined to be the length of the path traveled by light in 1/299792458 second. See B.W. Petley, Nature **303**, 373 (1983).

† At $Q^2 = m_e^2$. At $Q^2 \approx m_W^2$ the value is approximately 1/128.

The Energy Spectrum of Physical Phenomena



Characteristic energies of physical phenomena. The selected data on this page and the next are presented to give the reader a general idea of typical energies for various phenomena. The energies are expressed in several commonly used units: see Secs. 14-16 for an explanation.



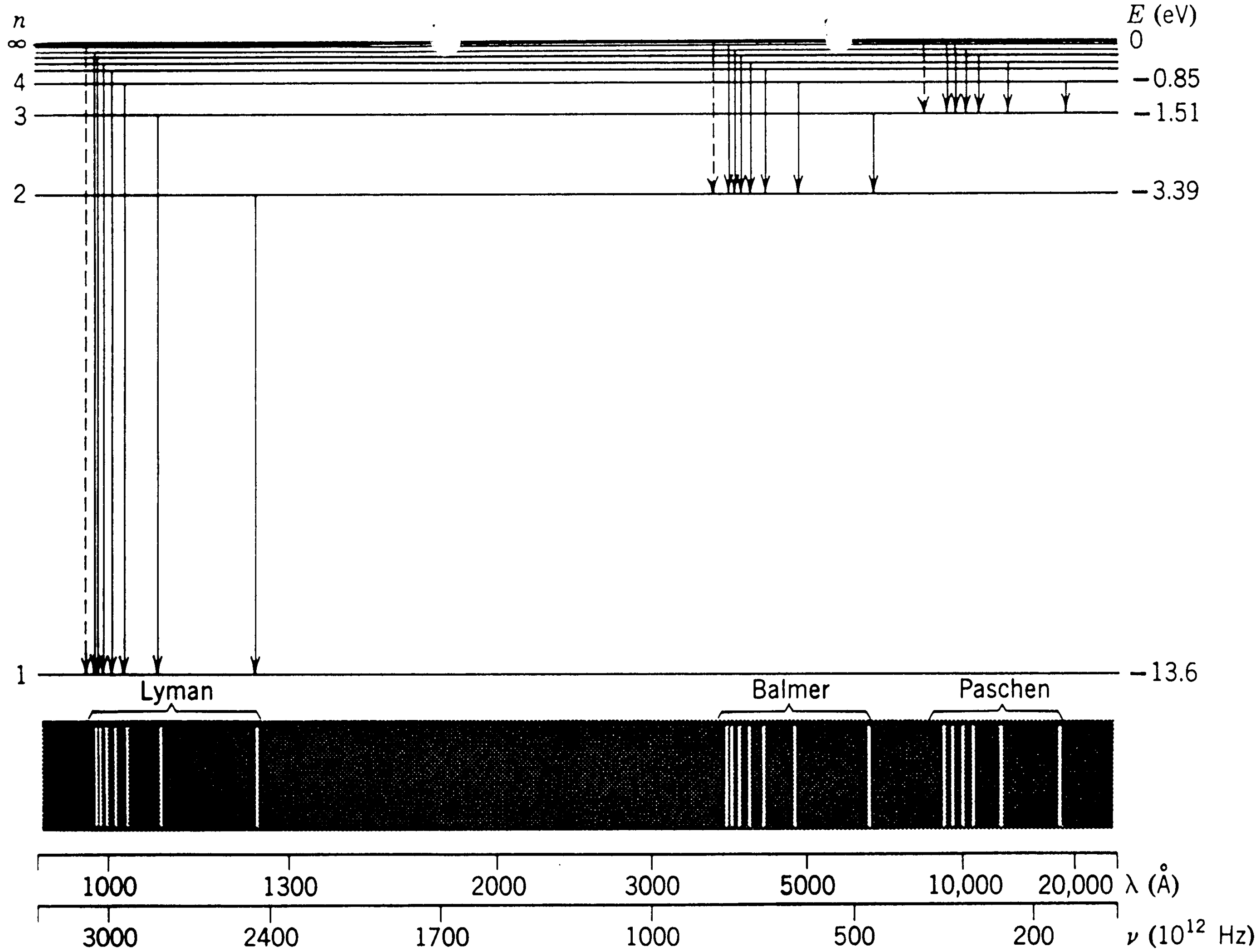


Figure 4-12 *Top:* The energy-level diagram for hydrogen with the quantum number *n* for

Chapitre 2

Spectroscopie

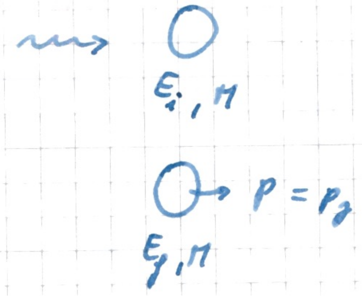
2.1 Spectre discrets

Les systèmes quantiques non élémentaires possèdent un ensemble de niveaux d'énergie (molécules, atomes, noyaux atomiques, ...). Les échelles d'énergies mises en jeu vont de l'IR aux Rγ. La fréquence du rayonnement émis dépend directement des niveaux énergétiques

$$\nu = \frac{|E_i - E_f|}{h}.$$

Lors d'une émission, il y a conservation de la quantité de mouvement $\vec{p}$, de l'énergie E et du moment cinétique $\vec{L}$, ainsi que d'autres grandeurs quantiques. On verra donc apparaître des *règles de sélection.*

Absorption La quantité de mouvement du photon est $p_\gamma = \frac{h\nu}{c} = p$, où p est la quantité de mouvement de l'atome après absorption (on suppose l'atome initialement immobile).



L'énergie finale et initiale de l'atome sont liées par

$$E_i = E_f + \frac{p^2}{2M} - h\nu$$

de sorte que

$$E_i - E_f = h\nu - \frac{p^2}{2M} = h\nu\left(1 - \frac{h\nu}{2Mc^2}\right)$$

d'où

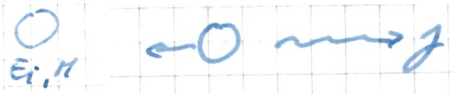
$$h\nu = \frac{E_i - E_f}{1 - \frac{h\nu}{2Mc^2}}$$

et si $h\nu \simeq E_i - E_f << 2Mc^2$, alors

$$h\nu \simeq (E_f - E_i)\left(1 + \frac{E_f - E_i}{2Mc^2}\right)$$

Emission De la même manière

$$h\nu \simeq (E_i - E_f)\left(1 - \frac{E_i - E_f}{2Mc^2}\right).$$



Avec $2Mc^2 \simeq 10^{10}$–10^{11} eV et

$$|E_f - E_i| \simeq 99 \text{ eV} \quad \text{(physique atomique)}$$
$$|E_f - E_i| \simeq 10^6 \text{ eV} \quad \text{(physique nucléaire)}$$

Dans un gaz (par exemple H) la population dans l'état d'énergie E_2 par rapport à celle d'énergie E_1 est donnée par la statistique de Boltzmann

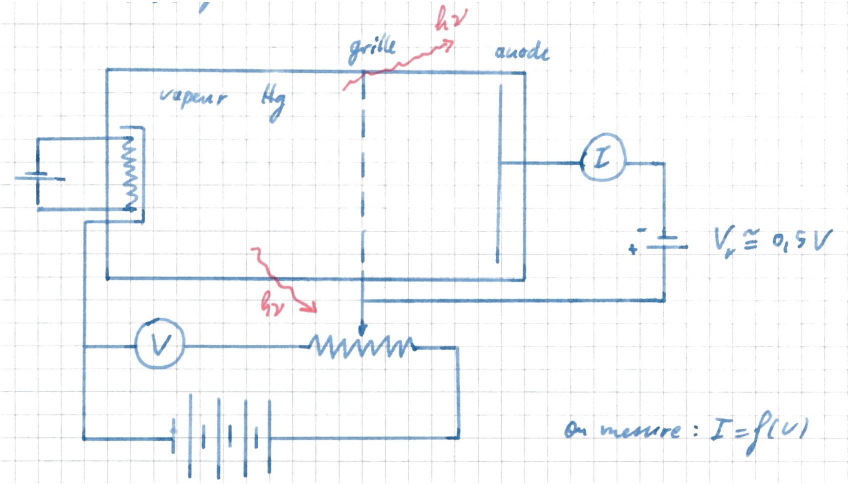
$$\frac{N_2}{N_1} = e^{-\frac{E_2 - E_1}{kT}}$$

On ne peut par voir les raies de Balmer à T_{ambiante}, mais le Soleil ayant une température bien plus élevée, elles deviennent visibles.

On peut exciter des atomes ou molécules à un niveau E supérieur notamment par décharge ou absorption. La particule excitée revient spontanément à son état fondamental par une cascade ou directement. La *fluorescence* est l'émission par cascade. La *phosphorescence* est une émission dans laquelle des règles de sélection ralentissent un état intermédiaire qui reste excité plus longtemps.

2.2 Expérience de Franck et Hertz

Cette expérience met en évidence l'existence de niveaux d'énergie.

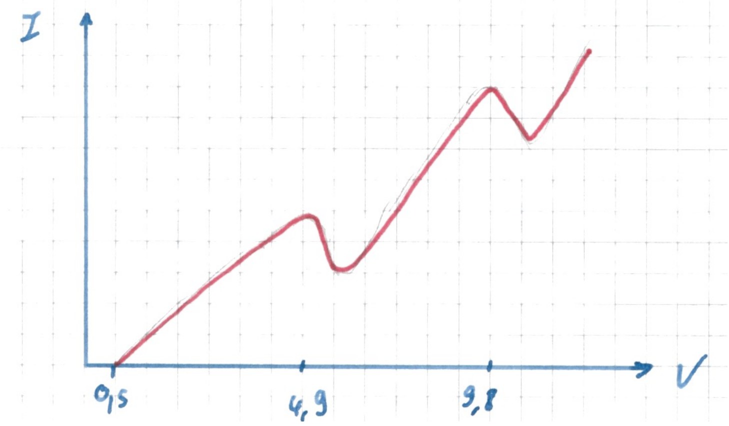


On veut montrer qu'il existe des niveaux d'énergie dans les atomes Hg qui ne peuvent être peuplés que par des collisions inélastiques entre les atomes Hg et les électrons. Lors d'une collision inélastique

$$\frac{1}{2}mv_i^2 \simeq \frac{1}{2}mv_f^2 + (E_2 - E_1) \quad \text{(collision inélastique)}$$

Si $\frac{1}{2}mv_i^2 < (E_2 - E_1)$ les collisions sont uniquement élastiques.

Les mesures donnent le résultat suivant



Des photons sont émis $\lambda = 253.7$ nm, avec $E = \frac{1.23981\cdot 10^{-6}}{253.7\cdot 10^{-9}}$eV $= 4.9$ eV et ne sont observés que si $V > 4.9V$.

Le niveau d'énergie E_2 est peuplé en une seule collision.

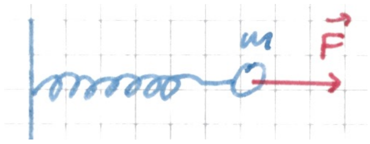
2.2.1 Dissociation-ionisation

Au-delà d'une certaine énergie, l'atome est ionisé. L'électron et le noyau sont libres et toutes les énergies sont possibles. L'effet photoélectrique est l'éjection d'un électron avec une énergie $E_{\text{photon}} - E_{\text{liaison}}$, par absorption d'un photon. Le phénomène existe dans les noyaux (*photodissociation* du deuton $E_\gamma > 2.23$ MeV) et l'inverse est la *capture radiative*.

$$O_3 + h\nu \to O_2 + O \quad \lambda = 240\text{–}360 \text{ nm(UV)}.$$

2.3 Largeurs des niveaux

2.3.1 Oscillateur mécanique forcé



Dans le cas d'un oscillateur mécanique forcé, on a

$$F - kx = ma$$

avec F la force oscillante de fréquence ν, d'où

$$\frac{d^2x}{dt^2} + \frac{k}{m}x = \frac{F}{m} = \frac{F_0}{m}\cos(\omega t)$$

Il s'agit d'une équation linéaire que l'on peut résoudre en posant

$$F = F_0 e^{i\omega t}$$

et

$$x = x_0 e^{i\omega t}.$$

On obtient ainsi

$$(i\omega)^2 x_0 + \frac{k}{m}x_0 = \frac{F_0}{m}$$

d'où

$$x_0 = \frac{F_0}{m(\omega_0^2 - \omega^2)}, \quad \text{ou } \omega_0^2 = \frac{k}{m}.$$

On observe

1. Une résonance à $\omega = \omega_0$.
2. x et F sont en phase.

Il y a toujours un amortissement. Si $F_{\text{frott}} \propto v$, pour v petit

$$m\frac{d^2x}{dt^2} + C\frac{dx}{dt} + kx = F$$

On pose $C = m\gamma$ et $k = m\omega_0^2$

$$\frac{d^2x}{dt^2} + \gamma\frac{dx}{dt} + \omega_0^2 x = \frac{F}{m}.$$

On obtient alors

$$(i\omega)^2 x_0 + (i\omega)\gamma x_0 + \omega_0^2 x_0 = \frac{F_0}{m}$$

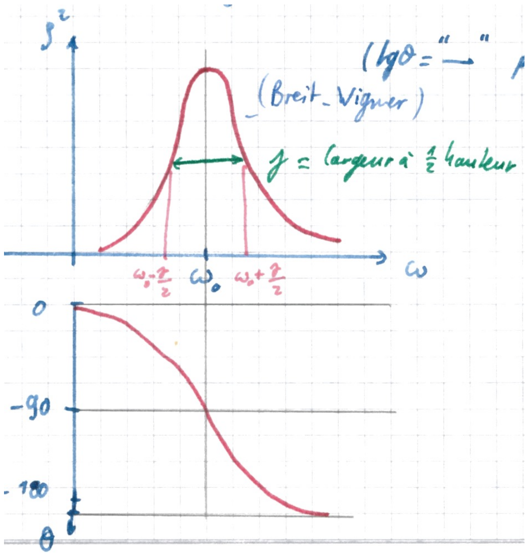
de sorte que

$$x_0 = \frac{F_0}{m(\omega_0^2 - \omega + i\gamma\omega)} = F_0 R = F_0 \rho e^{i\theta}$$

avec

$$\rho = \frac{1}{m^2}\frac{1}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}, \quad \text{et} \quad \tan(\theta) = -\frac{\gamma\omega}{\omega_0^2 - \omega^2}$$

L'expression pour $\tan(\theta)$ reflette la causalité : l'effet suit la cause et θ représente le retard.



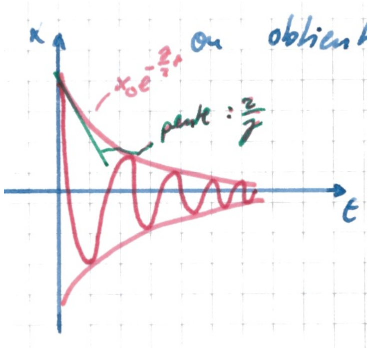
La courbe de ρ est une courbe de *Breit-Wigner* et γ est la valeur de la largeur du pic de la résonance à mi-hauteur.

Si l'on supprime l'excitation F

$$\frac{d^2x}{dt^2} + \gamma\frac{dx}{dt} + \omega_0^2 x = 0$$

on obtient

$$x = x_0 e^{-\frac{\gamma}{2}t} e^{-i\omega_0 t}.$$



Pour le cas $\gamma \ll \omega_0$ (faiblement amorti)

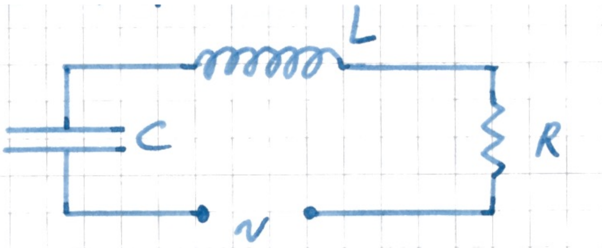
$$\omega_0^2 - \omega \simeq 2\omega_0(\omega_0 - \omega), \qquad i\gamma\omega \simeq i\gamma\omega_0$$

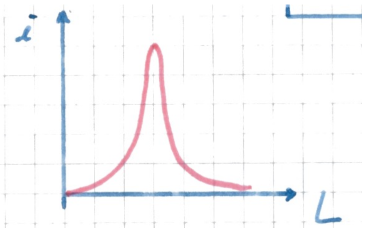
et on obtient

$$\rho = \frac{1}{4m^2\omega_0^2\left[(\omega_0-\omega)^2 + \frac{\gamma^2}{4}\right]}$$

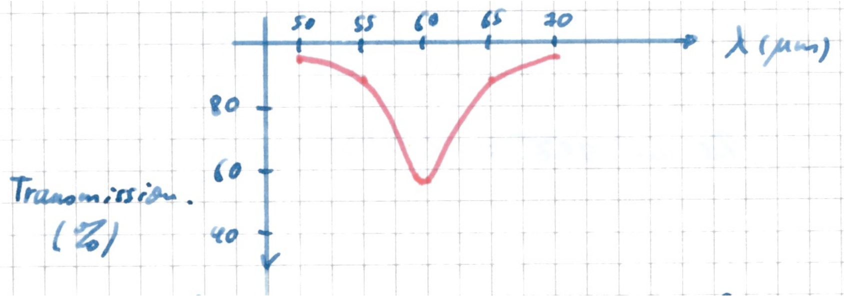
2.3.2 Phénomènes physiques

Circuit RLC Le circuit RLC est une bonne illustration d'un système présentant une résonance.





Absorption de la lumière On prend le modèle mécanique dans lequel les atomes sont liés entre eux (comme par des ressorts). L'excitation est ici une onde é.-m. que l'on fait passer à travers le cristal (R. Barnes, Zeitschrift für Physik, **75** (1932), 723). La transmission de la lumière à travers une couche mince de NaCl varie selon le graphe



L'énergie absorbée par le cristal est transformée en énergie de vibration (production de phonons).

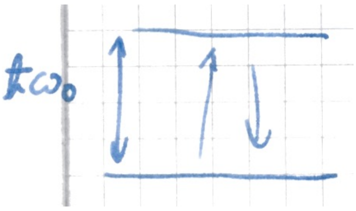
Diffusion Une onde é.-m. est absorbée si $\omega \simeq \omega_0$ et la matière réémet l'onde dans d'autre directions.

Les niveaux d'énergie atomique sont des résonances analogues aux résonances mécaniques. Les niveaux ont des largeurs finies.

Relations d'incertitude

Pour les résonances mécaniques, on peut définir une durée de demi-vie

$$\tau = \left(\frac{\gamma}{2}\right)^{-1}.$$



En physique, la largeur d'un niveau, ΔE, est reliée à la durée de vie de ce niveau τ, par la relation

$$\Delta E = \frac{\hbar}{\tau}$$

qui donne la largeur naturelle de ce niveau.
Cette largeur induit une incertitude sur la longueur d'onde λ[1]

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta\nu}{\nu} \simeq \frac{1}{\nu\tau}$$

Exemple 1

Pour $\lambda = 500$ nm et $\tau = 10^{-7}$ s, on obtient

$$\frac{\Delta\lambda}{\lambda} \simeq 1.67 \cdot 10^{-8}.$$

2.3.3 Effet Doppler

On montre que si un émetteur s'éloigne d'un observateur à la vitesse v

$$\nu_{\text{obs}} = \nu_{\text{em}}\sqrt{\frac{1-\frac{v}{c}}{1+\frac{v}{c}}} \qquad \text{(red shift)}$$

et si l'émetteur se rapproche

$$\nu_{\text{obs}} = \nu_{\text{em}}\sqrt{\frac{1+\frac{v}{c}}{1-\frac{v}{c}}} \qquad \text{(blue shift)}$$

Dans un gaz

$$\langle v^2\rangle \propto \frac{kT}{m}$$

et pour $\nu \ll c$

$$\frac{\Delta\nu}{\nu} \propto \frac{v}{c} \propto \sqrt{\frac{kT}{mc^2}}$$

C'est l'élargissement dû à l'effet Doppler-Fizeau.

2.3.4 L'effet Mössbauer

En guise de rappel
Emission : $h\nu = (E_i - E_f) - \frac{(E_i-E_f)^2}{2Mc^2}$ avec $E_i > E_f$
Absorption : $h\nu = (E_f - E_i) + \frac{(E_f-E_i)^2}{2Mc^2}$ avec $E_f > E_i$
Si la largeur (naturelle + Doppler) du niveau dépasse $\frac{(E_i-E_f)^2}{2Mc^2}$, des photons émis par un système (atome, molécule, noyau,...) peuvent être absorbés par un système identique.

---

[1] De la relation $\lambda = \frac{c}{\nu}$ on obtient

$$\Delta\lambda = \frac{\Delta\nu}{\nu^2}c = \frac{\Delta\nu}{\nu}\lambda$$

d'où

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta\nu}{\nu}.$$

Exemple 2

Pour la raie 4.9 eV du mercure Hg de masse atomique $A = 200$, on a

$$Mc^2 = 200 \cdot 0.93 \cdot 10^9 \text{ eV} = 1.86 \cdot 10^{11} \text{ eV}.$$

et

Recul

$$\frac{(E_i - E_f)^2}{2Mc^2} = 6.5 \cdot 10^{-11} \text{ eV}$$

Largeur naturelle

$$\tau = 10^{-8} \text{ s} \qquad \Delta E = \frac{\hbar}{\tau} = 6.58 \cdot 10^{-8} \text{ eV}$$

Élargissement Doppler

$$\frac{\Delta E}{E_1 - E_2} = \frac{\Delta \nu}{\nu}$$

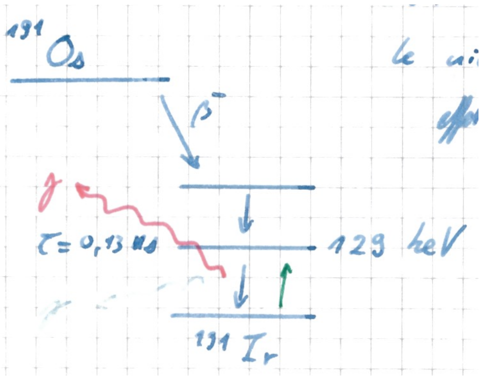
d'où

$$\Delta E = (E_2 - E_1)\sqrt{\frac{kT}{mc^2}} = 1.82 \cdot 10^{-6} \text{ eV}$$

Les recul peut donc être négligé.

Transitions nucléaires

Prenons le cas de l'osmium 131 Os^{131}_{96}. On veut savoir si le γ émis peut servir à repeupler le niveau à 129 keV (en vert).



L'effet de recul vaut

$$\frac{(E_i - E_f)^2}{2Mc^2} = 4.68 \cdot 10^{-2} \text{ eV}$$

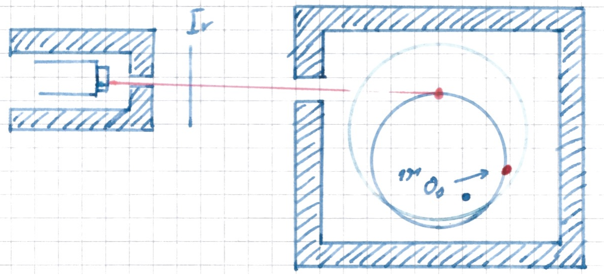
et la largeur naturelle

$$\Delta E = \frac{\hbar}{\tau} = 5.06 \cdot 10^{-6} \text{ eV}.$$

Ce qui montre que ce n'est pas possible.

En 1959 Mössbauer (Z. für Physik, **151**, (1959), 125) proposé une méthode pour mesurer la largeur d'un niveau.

Si les atomes (noyaux) sont pris dans un réseau cristallin, l'effet de recul sera négligeable (en fait le réseau va avoir des modes de vibrations supplémentaires après ce recul (phonons)).

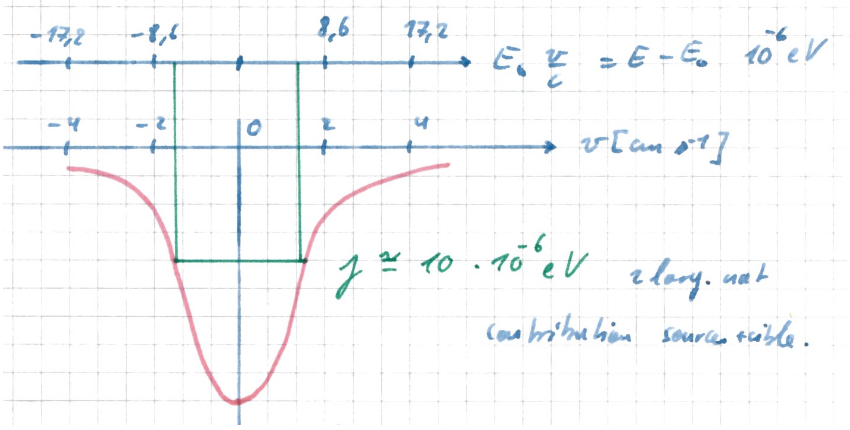


Le but de l'expérience est de balayer la largeur du niveau de 129 keV. L'énergie que verra la cible est

$$E = E_0 \left(1 + \frac{v}{c}\right).$$

Le balayage peut alors être très fin, car v est de l'ordre du $\text{cm}\,\text{s}^{-1}$.

On mesure le nombre de γ transmis au travers de la cible en I_r



En pratique, on emploie la méthode de Mössbauer pour étudier l'environnement de l'absorbeur ou de l'émetteur.

Chapitre 3

Équilibre rayonnement-matière

(Interaction d'un grand nomnre de photons avec la matière)

3.1 Le corps noir

Tout corps en équilibre thermique émet et absorbe des radiations en égales quantités.

L'énergie absorbée ar un corps de surface S pendant un temps Δt vaut

$$aSI\Delta t$$

où

a) I est l'énergie incidente

b) a le coefficient d'absorption ($a < 1$) en $\mathrm{m^{-2}\,s^{-1}}$.

L'énergie émise par ce corps durant ce même intervalle est

$$WS\Delta t$$

où W est l'émittance du corps considéré en $\mathrm{J\,m^{-2}\,s^{-1}}$.

En prenant deux corps de même surface à l'équilibre, on a

$$\begin{aligned} W_1 S\Delta t &= a_1 SI\Delta t \\ W_2 S\Delta t &= a_2 SI\Delta t. \end{aligned}$$

On en déduit

$$\frac{W_1}{W_2} = \frac{a_1}{a_2} \quad \Leftrightarrow \quad \frac{W_1}{a_1} = \frac{W_2}{a_2}$$

autrement dit, plus un corps possède un grand coefficient d'absorption, plus il est un bon émetteur, et inversement. Pour un corps noir, qui est un absorbeur parfait, on a

$$a_{\text{c.n.}} = 1.$$

Une petite ouverture qui donne dans une grande cavité est un bon absorbeur et une bonne approximation d'un corps noir.

Considérons un cube de côté L. On recherche la densité spectrale d'énergie portée par le rayonnement en équilibre à la température T (en particulier la densité d'énergie pour des rayonnements dont la longueur d'onde est comprise entre λ et $\lambda + d\lambda$ par unité de volume). On suppose que le cube est un bon conducteur.

La démarche consiste à

1. dénombrer les ondes stationnaires (de longueur d'onde comprise entre λ et $\lambda + d\lambda$).
2. rechercher de l'énergie moyenne d'une onde stationnaire.

Cas unidimensionnel (Corde fixée à ses extrémités)

On considère un champ électrique de la forme

$$E(x,t) = E_0 \sin(kx)\sin(\omega t)$$

avec

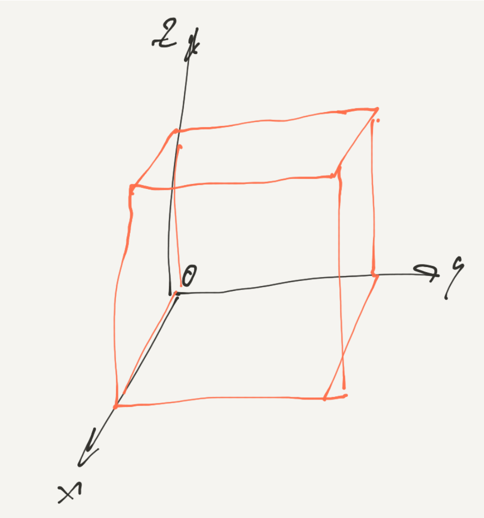
$$
\begin{aligned}
k &= \frac{2\pi}{L} \\
\omega &= 2\pi\nu \\
c &= \lambda\nu = \frac{\omega}{k}
\end{aligned}
$$

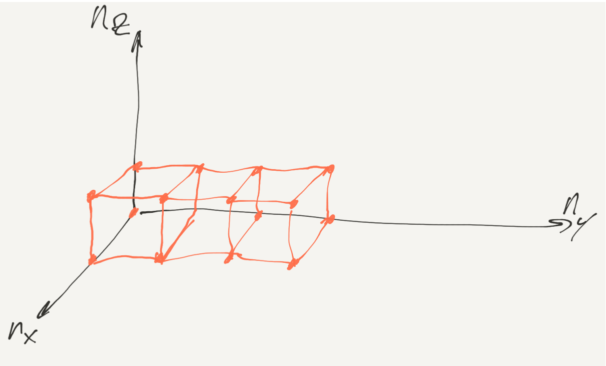
et les conditions aux bords

$$
\begin{aligned}
E(L,t) &= 0 \\
\sin(kL) &= 0 \\
kL &= n\pi \\
dn = \frac{L}{\pi}dk &= \frac{2L}{\lambda^2}d\lambda
\end{aligned}
$$

(ex. : Sur une corde de 10m, il y a 20 modes stationnaires différents pour $\lambda \in [10, 11]$m)

Cas tridimensionnel (Entre faces internes conductrices)





En prenant

$$
\begin{aligned}
E_x &= E_{0x}\cos(k_x x)\sin(k_y y)\sin(k_z z)\sin(\omega t) \\
E_y &= E_{0y}\sin(k_x x)\cos(k_y y)\sin(k_z z)\sin(\omega t) \\
E_z &= E_{0z}\sin(k_x x)\sin(k_y y)\cos(k_z z)\sin(\omega t)
\end{aligned}
$$

et

$$\omega = ck = c\sqrt{k_x^2 + k_y^2 + k_z^2}.$$

Les conditions aux bords imposent

$$
\begin{cases}
k_x L &= n_x \pi \\
k_y L &= n_y \pi \\
k_z L &= n_z \pi
\end{cases}
$$

et

$$\omega = c\frac{\pi}{L}\sqrt{n_x^2 + n_y^2 + n_z^2}$$

où à chaque triplet (n_x, n_y, n_z) correspond une onde stationnaire.

On a

$$n_{\max} = \frac{\omega L}{\pi c} \quad (n \text{ pour } \omega_0 < \omega)$$

et

$$N(\lambda) = \frac{1}{8}\frac{4}{3}\pi\left(\frac{\omega L}{\pi c}\right)^3 = \frac{4}{3}\pi\frac{V}{\lambda^3}$$

et le nombre d'ondes stationnaires différentes de pulsation inférieure à ω dans l'intervalle λ,$\lambda + d\lambda$ et

$$dN = \frac{4\pi V}{\lambda^4}d\lambda.$$

3.1.1 Rayleigh-Jeans

L'énergie moyenne,$\bar{\epsilon}$, d'un mode d'onde stationnaire est égal à l'énergie moyenne des 'oscillateurs' qui constituent la matière des parois. En prenant la distribution de Boltzmann pour l'énergie de ces oscillateurs

$$\bar{\epsilon} = \frac{\int_0^\infty E n_0 e^{-\frac{E}{kT}} dE}{\int_0^\infty n_0 e^{-\frac{E}{kT}} dE} = \frac{e^{-\frac{E}{kT}}\big(-EkT-(kT)^2\big)\Big|_0^\infty}{-(kT)e^{-\frac{E}{kT}}\Big|_0^\infty} = kT$$

d'où l'on déduit la densité spectrale d'énergie

$$I(\lambda)d\lambda = \frac{\bar{\epsilon} dN}{V} = \frac{8\pi}{\lambda^4} kT d\lambda$$

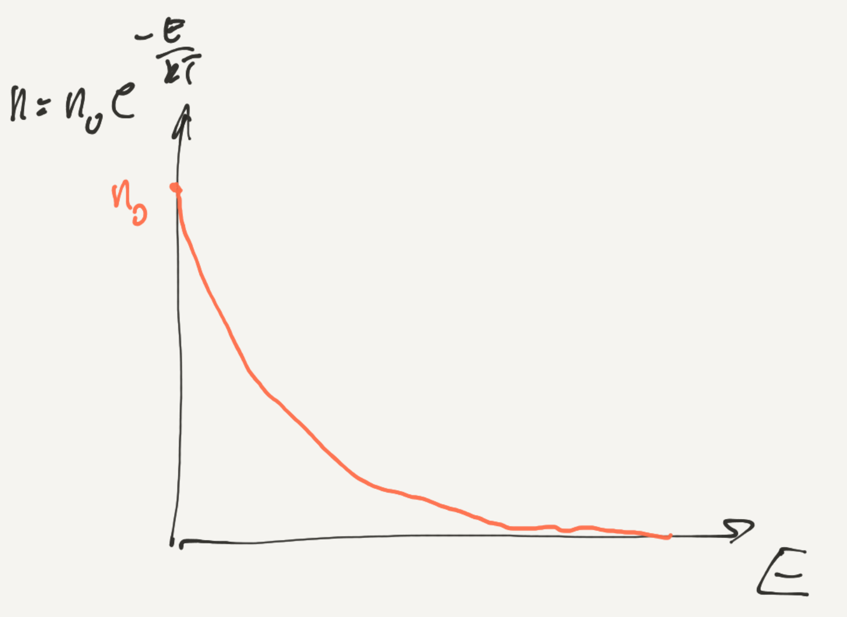
ou encore

$$I(\nu)d\nu = \frac{8\pi\nu^2}{c^3} kT d\nu$$

Ces expressions conduisent à la *catastrophe UV*, à savoir une divergence pour $\nu \to 0$ ou $\lambda \to \infty$.

Critique

1. $\bar{\epsilon}$ est indépendant de la fréquence.
2. Les modes d'excitation à grande énergie sont-ils également probables que les modes à basse énergie ?



3.1.2 Planck (1900)

En équilibre avec le rayonnement, les transferts d'énergie matière-rayonnement se font par sauts discrets de $u, 2u, 3u, \ldots$ petits paquets d'énergie. Ainsi, l'énergie moyenne devient

$$\bar{\epsilon} = \frac{\sum_{m=0}^\infty mu\, n_0 e^{-\frac{mu}{kT}}}{\sum_{m=0}^\infty n_0 e^{-\frac{mu}{kT}}} = \frac{0 + ue^{-\frac{u}{kT}} + 2ue^{-\frac{2u}{kT}} + \ldots}{1 + e^{-\frac{u}{kT}} + e^{-\frac{2u}{kT}} + \ldots}$$

Avec $x = e^{-\frac{u}{kT}} < 1$, on a

$$\bar{\epsilon} = ux\frac{1 + 2x + 3x^2 + \ldots}{1 + x + x^2 + \ldots}$$

Le dénominateur est

$$1 + x + x^2 + \cdots = \lim_{m\to\infty} \frac{1 - x^m}{1 - x} = \frac{1}{1 - x}$$

et le numérateur est la dérivée du dénominateur

$$1 + 2x + 3x^2 + \cdots = \frac{1}{(1 - x)^2}$$

de sorte que

$$\bar{\epsilon} = \frac{ux}{1-x} = \frac{u}{e^{-\frac{u}{kT}} - 1}.$$

Ainsi

$$I(\nu)d\nu = \frac{8\pi\nu^2}{c^3} \frac{u}{e^{-\frac{u}{kT}} - 1} d\nu.$$

En posant $u = h\nu$ on reproduit la distribution $I(\nu)$ à toutes les fréquences

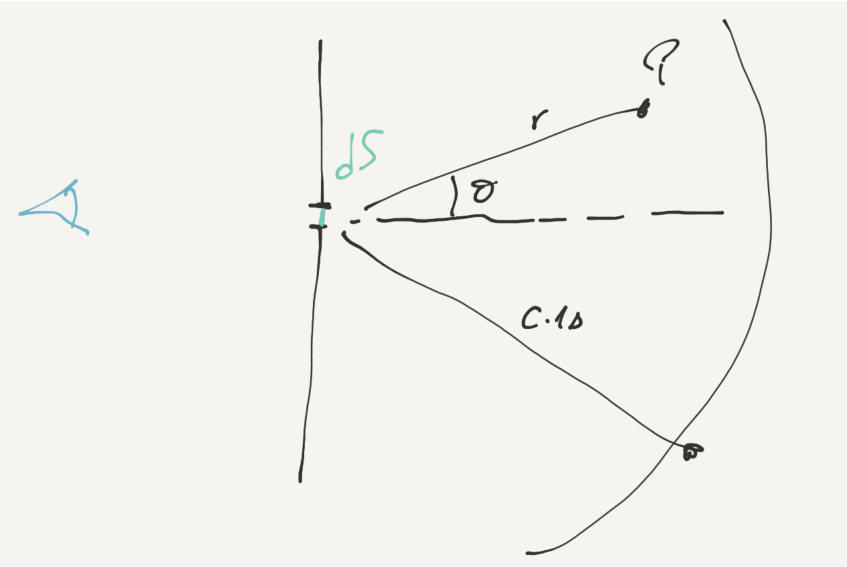
$$I(\nu)d\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{-\frac{h\nu}{kT}} - 1} d\nu \quad (\text{en J m}^{-3})$$

ou

$$I(\lambda)d\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{-\frac{hc}{\lambda kT}} - 1} d\lambda$$

3.2 Radiance spectrale

La radiance spectrale est la quantité d'énergie émise par unité de temps dans $[\nu, \nu + d\nu]$ par une surface unité d'un corps noir à la température T.



$$\begin{aligned} R(\nu)d\nu &= \int_0^c \int_0^{2\pi} \int_0^{\frac{\pi}{2}} \frac{I(\nu)}{4\pi} \frac{dS\cos(\theta)}{r^2} r^2 \sin(\theta) d\theta d\phi dr \\ &= -\frac{I(\nu)dS}{4\pi} \int\int\int \cos(\theta) d(\cos(\theta)) d\phi dr \\ &= \frac{I(\nu)}{4} c dS \end{aligned}$$

3.2.1 Loi de Stefan-Boltzmann

L'énergie totale émise par unité de temps et de surface par un corps noir

$$U_{\text{ray}} = \int_0^\infty R(\nu)d\nu = \frac{c}{4}\int_0^\infty I(\nu)d\nu = \sigma T^4$$

Pour ν petit, la loi de Planck tend vers celle de Rayleigh-Jeans ($e^{\frac{h\nu}{kT}} \simeq 1 + \frac{h\nu}{kT}$)

$$\bar{\epsilon} \simeq kT.$$

3.2.2 Application à l'astrophysique

On retient de l'astrophysique

1. La loi de dilatation $\lambda(t+dt) = \lambda(t) + d\lambda$
2. $R_{\text{univers}} T = \text{cste}$

Soit f le facteur de dilatation

$$f = \frac{R(t')}{R(t)} = \frac{T}{T'} = \frac{\lambda'}{\lambda}$$

Pour l'énergie d'un photon, on a

$$h\nu = \frac{c}{\lambda}$$

qui diminue du facteur f. Concernant la radiance spectrale

$$du = I(\lambda) d\lambda = \frac{c_1 \lambda^{-5} d\lambda}{e^{\frac{c_2}{\lambda T}} - 1}$$

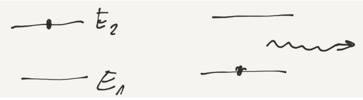
qui diminue du facteur f.

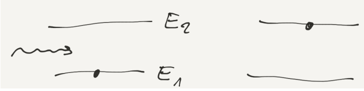
Mais le volume $V = 1$ cm^3 aura augmenté à $f^3 V$. Avec $\lambda = \frac{\lambda'}{f}$ et $T' = \frac{T}{f}$, on a

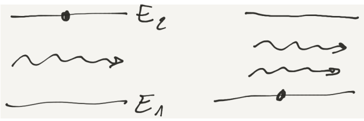
$$du' = \frac{du}{f^4} = \frac{1}{f^4} \frac{c_1 \lambda^{-5} d\lambda}{e^{\frac{c_2}{\lambda T}} - 1} = \frac{c_1 \lambda'^{-5} d\lambda'}{e^{\frac{c_2}{\lambda' T}} - 1}$$

Ainsi, le caractère 'thermique' du rayonnement est conservé en chaque instant dans un Univers en expansion, si ce caractère à existé une fois.

3.3 Transitions radiatives induites et spontanées

émission spontanée : 

absorption induite : 

émission induite : 

On considère l'analogie mécanique

> L'énergie peut être apportée ou retirée à un oscillateur, si on lui applique une force excitatrice de même fréquence mais en ayant une phase 0 ou π par rapport à l'oscillateur.

Les liens quantitatifs entre ces trois phénomènes on été élaborés par Einstein (1916).

1. Soit n_1 et n_2 les populations d'électrons des niveaux d'énergie E_1 et E_2 ($E_1 < E_2$).
2. Soit $\rho(\nu)$ la densité d'énergie portée par le rayonnement dans l'intervalle $[\nu, \nu + d\nu]$, avec $h\nu = E_2 - E_1$.

La variation de la population n_2 est due au peuplement par absorption d'un photon d'un électron de l'état E_1 vers l'état E_2

$$\text{(absorption :)} \quad \frac{dn_2}{dt} = B_{12} \rho(\nu) n_1$$

et pour l'émission, elle dépend de l'émission induite par influencée par la présence de photons déjà présents et par l'émission spontanée (de coefficient A_{21}) du niveau E_2 vers le niveau E_1 qui peut avoir lieu indépendamment de la présence des photons

$$\text{(emission :)} \quad \frac{dn_1}{dt} = n_2 (B_{21} \rho(\nu) + A_{21})$$

Pour l'état d'équilibre, on obtient

$$\rho(\nu) = \frac{\frac{A_{21}}{B_{21}}}{\frac{n_1}{n_2} \frac{B_{12}}{B_{21}} - 1}$$

avec

$$\frac{n_1}{n_2} = e^{\frac{E_2-E_1}{kT}} = e^{\frac{h\nu}{kT}}$$

Ainsi

$$\rho(\nu) = \frac{\frac{A_{21}}{B_{21}}}{\frac{B_{12}}{B_{21}}e^{\frac{h\nu}{kT}} - 1}$$

En prenant $\rho(\nu)d\nu = I(\nu)d\nu$ pour la densité spectrale d'énergie, on en déduit

$$B_{12} = B_{21} \quad \text{et} \quad \frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3\nu}{c^3}$$

Remarque 1

On ne connaît que les rapports des coefficients A et B

$$\frac{dn_1|_{\text{spont}}}{dn_2|_{\text{ind}}} = \frac{A}{B\rho(\nu)} = e^{\frac{h\nu}{kT}-1}$$

1. à T ambiante, $kT \simeq 0.025$ eV, et $h\nu_{\text{visible}} \simeq 2.5$ eV, on obtient

$$\frac{A}{B\rho} = e^{100} - 1$$

Dans le domaine des micro-ondes, $\vec{u} = 24$ GHz ($\lambda = 80$ m), $h\nu = 10^{-4}$ eV et

$$\frac{A}{B\rho} = 0.004$$

2. Rapport entre émission induite et absorption :

$$\frac{B\rho(\nu)n_2}{B\rho(\nu)n_1} = \frac{n_2}{n_1}$$

et à l'équilibre

$$\frac{n_2}{n_1} = e^{-\frac{h\nu}{kT}} < 1.$$

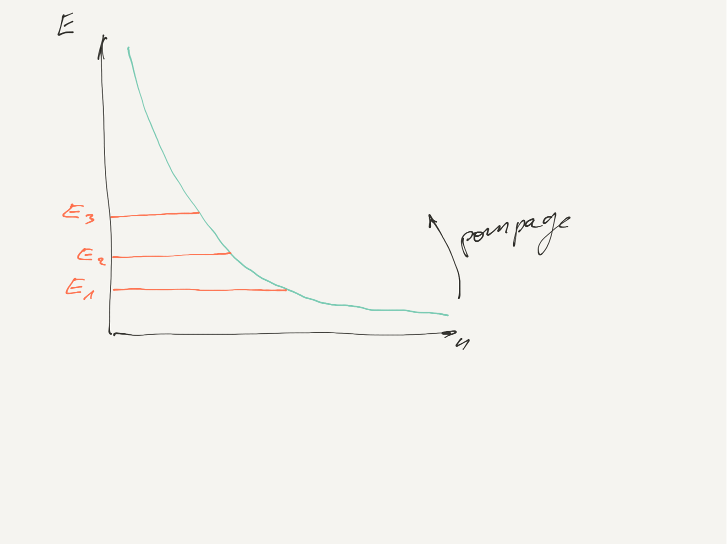
Si l'on parvient à inverser la population, $n_2 > n_1$, l'émission induite sera plus importante que l'absorption et la lumière incidente de fréquence ν sera amplifiée (c'est le principe du LASER).

Le processus d'émission induite va réduiren_2 et faire tendre le système vers l'équilibre, donc il faut maintenir l'inversion de population.

On a les acronymes :
MASER : Microwave Amplification by Stimulated Emission of Radiation
LASER : Light Amplification by Stimulated Emission of Radiation
Pour réaliser ces systèmes, il y a deux points à réaliser

1. L'inversion de population
2. Une amplification aussi efficace que possible.

Pour le premier point, on prend des éléments ou des mélanges ayant trois niveaux ou plus d'énergie. Il faut égaliser les populations des niveaux E_1 et E_3 ($n_1 = n_3$).



Si la durée de vie du niveau E_2, τ_2 est faible, il y a inversion de population entre E_3 et E_2.

Si τ_2 est grand, il aura accumulation sur le niveau E_2 et une inversion de population entre les niveaux E_2 et E_1.

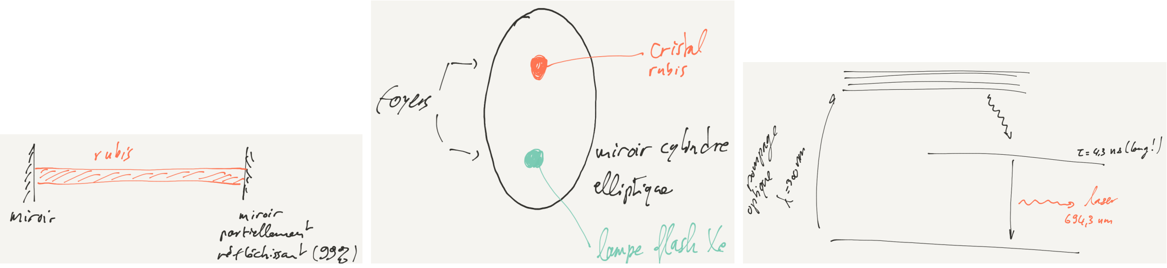


FIGURE 3.1 – Pompage et miroirs du laser à rubis et schéma de placement pour la lampe flash.

Exemple 1 (Le laser à rubis)

Le rubis est de l'alumine Al_2O_3 dans lequel certains ions Al^{+++} sont remplacés par des ions chromes Cr^{+++} (à 0.2 ‰ à quelques pourcent). Les impuretés de chrome ont deux bandes d'absorption dans le vert et le bleu.

Les réflexions sur les faces réfléchissantes induisent la lumière LASER. Les rayons parallèles à l'axe sont ainsi les plus aptes à sortir, pour former un rayon cohérent.

Le pompage est réalisé à l'aide d'une lampe flash au xénon.

Les propriétés principales de la lumière LASER sont

1. Le parallélisme, dans les limites du parallélisme d'un faisceau de section finie.
2. La cohérence de la lumière. Lors de l'émission induite, les ondes électromagnétiques induites sont en phase avec l'onde stimulante (sinon interférence destructive). Le front d'onde résultant est émis en phase avec l'onde stimulante (c'est une réalisation de la construction de Huygens).

Pour le calcul de l'intensité de N ondes de même fréquence et de phase δ_i

$$E(t) = E_0 \sum_{i=1}^{N} e^{i(\omega t + \delta_i)}$$

et

$$|E(t)|^2 = E_0^2 \sum_{ij} e^{i(\delta_i - \delta_j)}$$

Dans la moyenne temporelle, seule la contribution des phases cohérentes $\delta_i = \delta_j$ contribue, les autres s'annulant

$$|E|^2 = E_0^2 < e^{i(\delta_i - \delta_j)} >= E_0^2 \frac{1}{T} \int_0^T \sum_{ij} e^{i(\delta_i - \delta_j)} dt = N E_0^2$$

Chapitre 4

L'atome de Sommerfeld

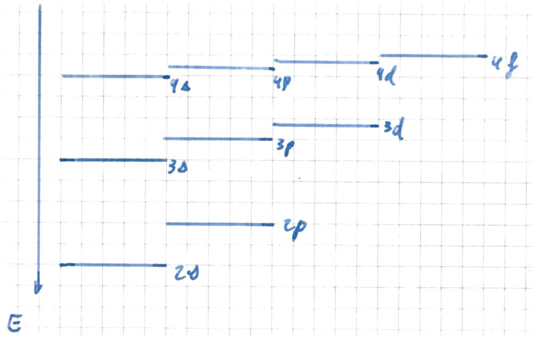
4.1 Nécessité de l'extension du modèle de Bohr

Les métaux alcalins ont la propriété d'être plus gros que le gaz rare qui les précède, ils ont un potentiel d'ionisation très faible et ils sont monovalents.

He	Ne	Ar	Kr	Xe	Rn
–	3.20	3.82	4	4.4	–
3.13	3.83	4.76	5.02	5.4	–
Li	Na	K	Rb	Cs	Fr

Table 4.1 – Dimension atomique en Å de quelques métaux et gaz rares.

Tout se passe comme si les niveaux se sont subdivisés en sous-niveaux d'énergie différentes.



On émet alors l'hypothèse :

> Les orbites elliptiques les plus excentrées auront l'énergie la plus basse, pour une même valeur de n, car l'électron sur cette orbite "voit" le noyau peu écranté.

La quantification de Sommerfeld prend en compte la caractéristique de ces ellipses.

4.2 Parenthèse sur le formalisme de Lagrange et Hamilton

Soit un système avec des coordonnées généralisées q_α, $\alpha \in \{1, \ldots, N\}$, N étant le nombre de degrés de libertés du système.

Les équations du mouvement sont déduites d'une fonction, dite fonction de Lagrange $L = L(q_\alpha, \dot{q}_\alpha, t)$. Pour un système conservatif

$$L = T - V$$

où T est le terme d'énergie cinétique et V le potentiel. Les équations du mouvement sont obtenues par les équations d'Euler-Lagrange

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_\alpha}\right) - \frac{\partial L}{\partial q_\alpha} = 0$$

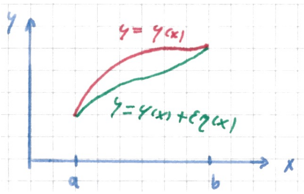
obtenue par un principe variationnel sur l'action

$$S = \int_{t_1}^{t_2} L dt$$

afin de déterminer le chemin qui rend extrémal l'action

$$\delta S = 0.$$

C'est l'expression du principe de Maupertuis-Hamilton, qui s'exprime de manière générale sur une fonctionnelle



$$I[y] = \int_a^b F(x, y, y') dx$$

en demandant que la courbe $y = y(x)$ est celle qui rend extrémale la fonctionnelle I, avec

$$y = y(x), \quad a \leqslant x \leqslant b.$$

Pour une courbe proche de y, on a

$$I_\epsilon = \int_a^b F(x, y + \epsilon\eta, y' + \epsilon\eta') dx$$

et y rend la fonctionnelle I extrémale si

$$\left.\frac{d}{d\epsilon} I_\epsilon\right|_{\epsilon=0} = 0.$$

avec

$$\frac{d}{d\epsilon} I_\epsilon = \int_a^b \left[\frac{\partial F}{\partial y}\eta + \frac{\partial F}{\partial y'}\eta'\right] dx = 0$$

en intégrant le second terme par partie

$$\int_a^b \frac{\partial F}{\partial y'}\eta' dx = \left.\frac{\partial F}{\partial y'}\eta\right|_a^b - \int_a^b \eta \frac{d}{dx}\left(\frac{\partial F}{\partial y'}\right) dx$$

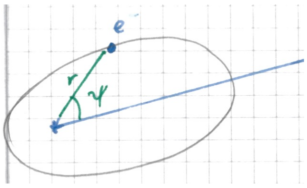
et avec les conditions aux bords $\eta(a) = \eta(b) = 0$, on obtient finalement

$$\int_a^b \left[\frac{\partial F}{\partial y} - \frac{d}{dx}\left(\frac{\partial F}{\partial y'}\right)\right] \eta \, dx = 0$$

et ceci pour tout η arbitrairement choisi, ce qui conduit à l'équation d'Euler-Lagrange.

Exemple 1

Pour un électron dans un champ coulombien



$$V(r) = -Z\frac{q_e^2}{r}.$$

Avec $q_\alpha \in \{r, \psi\}$ on a

$$T = \frac{1}{2}m(\dot{r}^2 + (r\dot{\psi})^2)$$

$$L = T - V = \frac{1}{2}m(\dot{r}^2 + (r\dot{\psi})^2) + Z\frac{q_e^2}{r}$$

et

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{r}}\right)-\frac{\partial L}{\partial r}=0$$

donne

$$m\ddot{r}-(mr\dot{\psi}^2+\frac{Zq_e^2}{r^2})=0$$

d'où

$$m\ddot{r}-mr\dot{\psi}^2=\frac{Zq_e^2}{r^2}$$

et d'autre part

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\psi}}\right)-\frac{\partial L}{\partial \psi}=0$$

donne

$$m\frac{d}{dt}(r^2\dot{\psi})=0$$

4.2.1 Formalisme de Hamilton

On définit l'hamiltonien du système

$$H=\sum_\alpha p_\alpha\dot{q}_\alpha-L,\quad p_\alpha=\frac{\partial L}{\partial \dot{q}_\alpha}$$

p_α est l'impulsion généralisée.

$H=H(p_\alpha,q_\alpha,t)$ et pour un système conservatif

$$H=T+V=E_{\text{totale}}$$

Les équations du mouvement sont les équations de Hamilton

$$\begin{cases}\dot{p}_\alpha &= -\frac{\partial H}{\partial q_\alpha}\\ \dot{q}_\alpha &= \frac{\partial H}{\partial p_\alpha}\end{cases}$$

Pour un lagrangien $L=\frac{1}{2}m(\dot{r}^2+r^2\dot{\psi}^2)-V(r)$, on trouve

$$p_r=\frac{\partial L}{\partial \dot{r}}=m\dot{r},\quad p_\psi=\frac{\partial L}{\partial \dot{\psi}}=mr^2\dot{\psi}$$

d'où l'on obtient

$$\dot{r}=\frac{p_r}{m},\quad \dot{\psi}=\frac{p_\psi}{mr^2}.$$

Ainsi, l'hamiltonien s'écrit

$$H=\frac{p_r^2}{m}+\frac{p_\psi^2}{mr^2}-\left[\frac{1}{2}m\left(\frac{p_r^2}{m^2}+\frac{r^2p_\psi^2}{m^2r^4}\right)+\frac{Zq_e^2}{r}\right]$$

soit

$$H=\frac{1}{2m}\left(p_r^2+\frac{p_\psi^2}{r^2}\right)-\frac{Zq_e^2}{r}.$$

Les équations du mouvement sont ainsi

$$\begin{aligned}\dot{r}&=\frac{p_r}{m}, & \dot{p}_r&=\frac{p_\psi^2}{mr^3}-\frac{Zq_e^2}{r}\\ \dot{\psi}&=\frac{p_\psi}{mr^2}, & \dot{p}_\psi&=0\end{aligned}$$

Une coordonnée qui n'apparaît pas explicitement dans l'hamiltonien entraîne que l'impulsion correspondante est une constante ($\dot{p}_\alpha=-\frac{\partial H}{\partial q_\alpha}=0$).

Il est souvent plus simple de résoudre les équations dans un autre ensemble de coordonnées généralisées q_α, p_α.

Une transformation canonique est une transformation qui conserve les équations de hamilton dans les nouvelles coordonnées Q_α, P_α. On a alors, pour le nouvel hamiltonien $\mathcal{H}$

$$\dot{P}_\alpha = -\frac{\partial \mathcal{H}}{\partial Q_\alpha} \quad \text{et} \quad \dot{Q}_\alpha = \frac{\partial \mathcal{H}}{\partial P_\alpha}$$

Selon le principe de Hamilton, il faut que

$$\delta \int_{t_1}^{t_2} L\,dt = 0 = \delta \int_{t_1}^{t_2} \mathcal{L}\,dt$$

où $\mathcal{L}$ est le nouveau lagrangien dans les nouvelles coordonnées

Cette condition est satisfaite s'il existe une fonction génératrice G telle que

$$\frac{dG}{dt} = L - \mathcal{L}.$$

Supposons que $G = G(q_\alpha, Q_\alpha, t)$ soit une telle fonction génératrice

$$\begin{aligned}\frac{dG}{dt} &= L - \mathcal{L} \\ &= \sum_\alpha p_\alpha \dot{q}_\alpha - H - \left(\sum_\alpha P_\alpha \dot{Q}_\alpha - \mathcal{H}\right) \\ &= \sum_\alpha p_\alpha \dot{q}_\alpha - \sum_\alpha P_\alpha \dot{Q}_\alpha + \mathcal{H} - H\end{aligned}$$

d'où l'on déduit

$$\begin{aligned}dG &= \sum_\alpha p_\alpha dq_\alpha - \sum_\alpha P_\alpha dQ_\alpha + (\mathcal{H} - H)dt \\ &= \sum_\alpha \frac{\partial G}{\partial q_\alpha} dq_\alpha + \sum_\alpha \frac{\partial G}{\partial Q_\alpha} dQ_\alpha + \frac{\partial G}{\partial t} dt.\end{aligned}$$

Ainsi

$$\begin{aligned}p_\alpha &= \frac{\partial G}{\partial q_\alpha}, & \dot{P}_\alpha &= -\frac{\partial \mathcal{H}}{\partial Q_\alpha} \\ P_\alpha &= \frac{\partial G}{\partial Q_\alpha}, & \dot{Q}_\alpha &= \frac{\partial \mathcal{H}}{\partial P_\alpha} \\ \mathcal{H} - H &= \frac{\partial G}{\partial t}\end{aligned}$$

On peut alors écrire

$$dG = \sum_\alpha p_\alpha dq_\alpha - d\left(\sum_\alpha P_\alpha Q_\alpha\right) + \sum_\alpha Q_\alpha dP_\alpha + (\mathcal{H} - H)dt$$

soit

$$d(G + \sum_\alpha P_\alpha Q_\alpha) = \sum_\alpha p_\alpha dq_\alpha + \sum_\alpha Q_\alpha dP_\alpha + (\mathcal{H} - H)dt$$

En posant

$$S = G + \sum_\alpha P_\alpha Q_\alpha, \quad p_\alpha = \frac{\partial S}{\partial q_\alpha}, \quad Q_\alpha = \frac{\partial S}{\partial P_\alpha}$$

alors $S = S(q_\alpha, P_\alpha, t)$ (c'est la transformée de Legendre de G) et

$$\mathcal{H} = \frac{\partial S}{\partial t} + H.$$

Si l'on parvient à trouver une transformation canonique telle que $\mathcal{H} = 0$, alors

$$\dot{P}_\alpha = -\frac{\partial \mathcal{H}}{\partial Q_\alpha} = 0, \quad \text{et} \quad \dot{Q}_\alpha = \frac{\partial \mathcal{H}}{\partial P_\alpha} = 0$$

et P_α et Q_α sont alors des constantes. On obtient ainsi l'équation de Hamilton-Jacobi

$$\boxed{\frac{\partial S}{\partial t} + H\left(\frac{\partial S}{\partial q_\alpha}, q_\alpha, t\right) = 0.}$$

4.2.2 Constantes du mouvement

En dehors de l'équilibre statique, $P_\alpha = 0$, $Q_\alpha = Q_{\alpha 0}$, on ne peut avoir que n constantes du mouvement. Avec

$$S = S(q_1, \ldots, q_n, \beta_1, \ldots, \beta_n, t)$$

On a

$$Q_\alpha = \frac{\partial S}{\partial P_\alpha} = \frac{\partial S}{\partial \beta_\alpha} = \gamma_\alpha = \text{constante}.$$

Par séparation des variables

$$S = S_1(q_1) + \cdots + S_n(q_n) + F(t).$$

et si H ne dépend pas du temps, on a $F(t) = -Et$ (système conservatif) et

$$H\left(\frac{\partial S}{\partial q_\alpha}, q_\alpha\right) = E.$$

4.3 Application au problème de Képler

Pour le problème de Képler de l'électron autour d'un noyau, on a

$$H = \frac{1}{2m}\left(p_r^2 + \frac{p_\psi^2}{r^2}\right) - \frac{Zq_e^2}{r}$$

et on recherche la fonction génératrice

$$S = S_r(r) + S_\psi(\psi) - Et.$$

Posons

$$p_r = \frac{dS_r}{dr}, \qquad p_\psi = \frac{dS_\psi}{d\psi}$$

L'équation de Hamilton-Jacobi donne alors

$$\frac{1}{2m}\left((\frac{dS_r}{dr})^2 + \frac{1}{r^2}(\frac{dS_\psi}{d\psi})^2\right) - \frac{Zq_e^2}{r} = E$$

et en multipliant par $2mr^2$, on peut séparer les variables

$$(\frac{dS_\psi}{d\psi})^2 = r^2\left[2mE + \frac{2mZq_e^2}{r} - (\frac{dS_r}{dr})^2\right] = \text{constante} = \beta^2.$$

On en déduit la constante du mouvement

$$\frac{dS_\psi}{d\psi} = \beta \quad \Rightarrow \quad S_\psi = \beta\psi.$$

De plus

$$\frac{dS_r}{dr} = \sqrt{2mE + \frac{2mZq_e^2}{r} - \frac{\beta^2}{r^2}}$$

d'où

$$S_r = \int \sqrt{2mE + \frac{2mZq_e^2}{r} - \frac{\beta^2}{r^2}} dr$$

de sorte que

$$S = \int \sqrt{2mE + \frac{2mZq_e^2}{r} - \frac{\beta^2}{r^2}} dr + \beta\psi - Et$$

En identifiant P_1 à β et P_2 à E, et avec

$$Q_\alpha = \frac{\partial S}{\partial P_\alpha}$$

on obtient l'équation de la trajectoire

$$Q_1 = \frac{\partial S}{\partial P_1} = \frac{\partial S}{\partial \beta} = \frac{\partial S_r}{\partial \beta} + \psi = \gamma_1 = \text{constante}$$

et l'équation horaire

$$Q_2 = \frac{\partial S}{\partial P_2} = \frac{\partial S}{\partial E} = \frac{\partial S_r}{\partial E} - t = \gamma_2 = \text{constante}$$

$$\psi - \gamma_1 = \int \frac{\frac{2\beta}{r^2}dr}{2\sqrt{2mE + \frac{2mZq_e^2}{r} - \frac{\beta^2}{r^2}}} = \int \frac{\beta}{r^2}\frac{dr}{\sqrt{2mE + \frac{2mZq_e^2}{r} - \frac{\beta^2}{r^2}}}$$

On pose $u = \frac{1}{r}$ et

$$\gamma_1 - \psi = \int \frac{\beta du}{\sqrt{2mE + 2mZq_e^2 u - \beta^2 u^2}} = \arcsin\left(\frac{\beta^2 u - mZq_e^2}{\sqrt{m^2Z^2q_e^4 + 2mE\beta^2}}\right)$$

d'où

$$r = \frac{\frac{\beta^2}{mZq_e^2}}{1 + \sin(\gamma_1 - \psi)\sqrt{1 + \frac{2E\beta^2}{mZ^2q_e^4}}}$$

avec γ_1 comme condition initiale.

Selon les valeurs de E on distingue les trajectoires
$E < 0$ elliptiques.
$E = 0$ paraboliques.
$E > 0$ hyperboliques.

Comme seule la première classe de trajectoire est liée, on ne considérera pas les deux autres dans la suite de la discussion.

4.3.1 Quantification de Bohr-Sommerfeld

Les règles de quantification de Bohr-Sommerfeld sont

$$J_\psi = \oint dS_\psi = \oint p_\psi d\psi = n_\psi h$$

et

$$J_r = \int dS_r = \oint p_r dr = n_r h$$

où h est la constante de Planck.

On a ainsi

$$J_\psi = \oint \frac{\partial S_\psi}{\partial \psi} d\psi = \beta \oint d\psi = 2\pi\beta = n_\psi h$$

d'où

$$p_\psi = \beta = n_\psi \hbar.$$

De plus

$$J_r = \oint \frac{\partial S_r}{\partial r} dr = 2\int_{r_{\min}}^{r_{\max}} \sqrt{2mE + \frac{2mZq_e^2}{r} - \frac{\beta^2}{r^2}}dr = \frac{2\pi mZq_e^2}{\sqrt{-2mE}} - 2\pi\beta$$

d'où, en se rappelant que $E < 0$

$$\frac{2\pi mZq_e^2}{\sqrt{-2mE}} - 2\pi\beta = n_r h$$

De sorte que

$$J_r + J_\psi = (n_r + n_\psi)h = \frac{2\pi mZq_e^2}{\sqrt{-2mE}}$$

soit

$$E = -\frac{Z^2q_e^4 m}{2\hbar^2(n_r + n_\psi)^2} = -\frac{Z^2mc^2}{2(n_r + n_\psi)^2}\alpha^2,$$

où $\alpha = \frac{q_e^2}{\hbar c}$[1] est la *constante de structure fine.* On remarque que

$$p_r = m\dot{r}$$

et donc

$$J_r = m \oint \frac{dr}{dt} dr = n_r h$$

et ce dernier intégrand est positif, donc $n_r > 0$.

De même

$$p_\psi = mr^2\dot{\psi}$$

et donc $n_\psi > 0$.

En posant $n = n_r + n_\psi$, on obtient

$$E = -\frac{Z^2 q_e^4 m}{2\hbar^2 n^2} = -\frac{Z^2 mc^2}{2n^2}\alpha^2.$$

On constate que l'énergie de dépend que de la valeur de n.

Avec cette valeur de l'énergie, on obtient les trajectoires

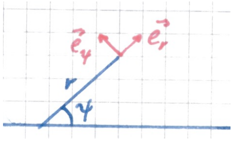
$$r = \frac{a_B}{Z} \frac{(n-n_r)^2}{1 + \sin(\gamma_1 - \psi)\sqrt{1 - \frac{(n-n_r)^2}{n^2}}}$$

où l'on a utilisé le rayon de Bohr

$$a_B = \frac{\hbar^2}{q_e^2 m} \simeq 0.053 \text{ nm}$$

On trouve alors

$$\begin{aligned} \text{grand axe :} \quad & a = a_B \frac{n^2}{Z} \quad \text{(diamètre du cercle dans le modèle de Bohr)} \\ \text{petit axe :} \quad & b = a_B \frac{n n_\psi}{Z} \quad (1 \leqslant n_\psi \leqslant n) \end{aligned}$$



Si $a = b$, on retrouve les orbites de Bohr, alors que si $n_\psi = 0$ on obtient des orbites dégénérées qui forment des segments

.

Le moment p_ψ s'interprète naturellement comme le moment cinétique de l'électron. En effet, avec le lagrangien L, on a

$$p_\psi = \frac{\partial L}{\partial \dot{\psi}} = mr^2\dot{\psi}$$

et le moment cinétique est

$$\begin{aligned} \vec{L} &= \vec{r} \times m\vec{v} \\ &= \vec{r} \times m(\dot{r}\vec{e}_r + r\dot{\psi}\vec{e}_\psi) \\ &= \vec{r} \times mr\dot{\psi}\vec{e}_\psi \end{aligned}$$

et donc la norme du moment cinétique

$$\|\vec{L}\| = mr^2\dot{\psi}.$$

Or $\vec{L} = \vec{p}_\psi$ est une constante du mouvement.

En physique quantique, on définit un nombre quantique de moment cinétique ℓ avec $0 \leqslant \ell \leqslant n-1$. Pour faire le lien avec la mécanique quantique, on remplace n_ψ par $\ell = n_\psi - 1$. On utilise fréquemment l'abus de langage qui consiste à confondre le moment cinétique p_ψ avec le nombre quantique du moment cinétique n_ψ ou ℓ.

---

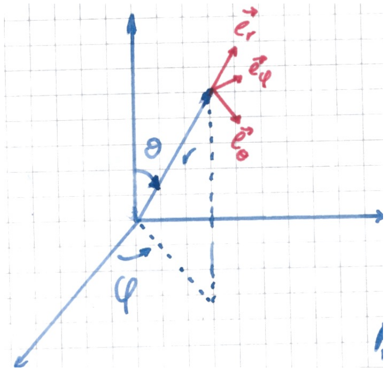
[1] L'expression donnée est en statcoulomb ou esu (système cgs) pour lequel $q_e^2 = \frac{e^2}{4\pi\epsilon_0}$. En unités SI, avec une charge de l'électron en coulomb e on a

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c}.$$

Son inverse vaut approximativement

$$\alpha^{-1} \simeq 137.035999074(44).$$

4.4 Orientation dans l'espace



En coordonnées sphériques on a

$$\vec{v} = \dot{r}\vec{e}_r + r\dot{\theta}\vec{e}_\theta + r\sin(\theta)\dot{\phi}\vec{e}_\phi$$

et l'énergie cinétique s'exprime

$$E_{\text{cin}} = \frac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2(\theta)\dot{\phi}^2)$$

et le potentiel de Coulomb

$$V = -Z\frac{q_e^2}{r}.$$

Avec le lagrangien

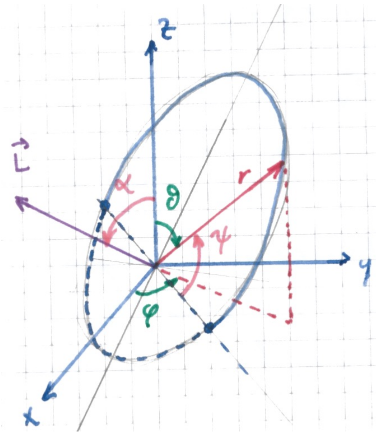
$$L = E_{\text{cin}} - V$$

on a les moment

$$\begin{cases} p_r &= \frac{\partial L}{\partial \dot{r}} = m\dot{r} \\ p_\theta &= \frac{\partial L}{\partial \dot{\theta}} = mr^2\dot{\theta} \\ p_\phi &= \frac{\partial L}{\partial \dot{\phi}} = mr^2\sin^2(\theta)\dot{\phi} \end{cases} \Rightarrow \begin{cases} \dot{r} &= \frac{p_r}{m} \\ \dot{\theta} &= \frac{p_\theta}{mr^2} \\ \dot{\phi} &= \frac{p_\phi}{mr^2\sin^2(\theta)} \end{cases}$$

d'où l'hamiltonien

$$H = E_{\text{cin}} + E_{\text{pot}} = \frac{p_r^2}{2m} + \frac{p_\theta^2}{2mr^2} + \frac{p_\phi^2}{2mr^2\sin^2(\theta)} - Z\frac{q_e^2}{r}$$



La variable r conserve la même signification comparée au traitement à 2 dimensions

$$p_\theta^2 + \frac{p_\phi^2}{\sin^2(\theta)} = p_\psi.$$

$p_\theta = mr^2\dot{\theta}$ est nul pour $\dot{\theta} = 0$, quand $\vec{L}$, Oz et $\vec{r}$ sont dans un même plan.

Dans notre cas

$$\sin^2(\theta) = \cos^2(\alpha) = \frac{p_\phi^2}{p_\psi^2}.$$

Hamilton-Jacobi

Soit

$$S = S_r(r) + S_\theta(\theta) + S_\phi(\phi) - Et$$

l'hamiltonien devient

$$H = E = \frac{1}{2m}\left[\left(\frac{dS_r}{dr}\right)^2 + \frac{1}{r^2}\left(\frac{dS_\theta}{d\theta}\right)^2 + \frac{1}{r^2\sin^2(\theta)}\left(\frac{dS_\phi}{d\phi}\right)^2\right] - Z\frac{q_e^2}{r}$$

En multipliant par $2mr^2$ et en regroupant les termes angulaires, on trouve

$$\left(\frac{dS_\theta}{d\theta}\right)^2 + \frac{1}{\sin^2(\theta)}\left(\frac{dS_\phi}{d\phi}\right)^2 = r^2\left(2mE + \frac{2mZq_e^2}{r} - \left(\frac{dS_r}{dr}\right)^2\right) = \text{cst} = \beta_1$$

on peut ainsi séparer les variables et

$$\left(\frac{dS_\phi}{d\phi}\right)^2 = \beta_1\sin^2(\theta) - \sin^2(\theta)\left(\frac{dS_\theta}{d\theta}\right)^2 = \text{cst} = \beta_2.$$

n	ℓ	m
1	0	0
2	0	0
	1	$-1, 0, 1$
3	0	0
	1	$-1, 0, 1$
	2	$-2, -1, 0, 1, 2$
4	0	0
	1	$-1, 0, 1$
	2	$-2, -1, 0, 1, 2$
	3	$-3, -2, -1, 0, 1, 2, 3$
$\vdots$	$\dots$	$\dots$
	$\vdots$	$\vdots$

Table 4.2 – Structure des nombres quantiques pour les états énergétiques dans le modèle de Sommerfeld.

ℓ	0	1	2	3	4	5
nom	s	p	d	f	g	h

Table 4.3 – Désignation des sous-couches par des lettres. Les lettres pour les sous-couches suivantes suivent l'ordre alphabétique.

Soit une complète séparation des variables. On voit ainsi que

$$\frac{dS_\phi}{d\phi} = p_\phi$$

est une constante du mouvement.

Sommerfeld a également introduit une quantification pour p_ϕ

$$J_\phi = \oint p_\phi d\phi = n_\phi h \;\Rightarrow\; p_\phi = n_\phi \hbar.$$

avec $n_\phi \in \mathbb{Z}$. Or

$$\cos(\alpha) = \frac{p_\phi}{p_\psi} = \frac{L_z}{L}$$

donc

$$L_z = n_\phi \hbar$$

et n_ϕ prend les $2\ell + 1$ valeurs entre $-\ell$ et ℓ.

La projection L_z est prise par rapport à une direction arbitraire Oz que l'on doit néanmoins spécifier par

— une caractéristique du système.

— l'appareillage de mesure.

La projection du moment cinétique est ainsi également quantifiée.

En résumé

n est le nombre quantique principal. Il définit l'énergie

$$E_n = -\frac{Z^2 q_e^4 m}{2\hbar^2} \frac{1}{n^2}$$

Pour $1 \leqslant n_\psi \leqslant n$ ou $0 \leqslant \ell \leqslant n - 1$, on a $2\ell + 1$ valeurs $-\ell \leqslant n_\phi \leqslant \ell$.

ℓ est le nombre quantique de moment cinétique.

$m = n_\phi$ est le nombre quantique magnétique.

Les "sous-couches" ℓ sont désignées par des lettres : $s, p, d, f, \dots$, selon le tableau 4.3 [2]

On parle de *dégénérescence* lorsque des états de nombres quantiques différents ont la même énergie. Pour l'atome H traité jusqu'à maintenant

---

[2] La lettre s vaut pour *sharp*, p pour *principal*, d pour *diffuse* et f pour *faint*.

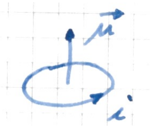
1. pour un même n, les états de ℓ différent ont la même énergie. Il s'agit d'un accident dû au potentiel en $\frac{1}{r}$.
2. pour n et ℓ donnés, il y a une dégénérescence en m.

Toutes les transitions énergétiquement possibles ne sont pas permises. Des règles de sélection déterminent les transitions qui peuvent avoir lieu. Par exemple, il ne peut pas y avoir de transition $2s^0 \to 1s^0$ (notation $n\ell^m$) dans l'atome d'hydrogène. En particulier, dans ce cas, ce sont des règles de sélection qui proviennent de la conservation du moment cinétique.

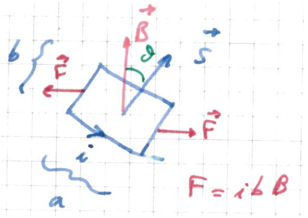
4.5 Le moment magnétique en physique atomique

4.5.1 Moment magnétique orbital

Á une boucle de courant, on peut associer un moment magnétique



$$\boxed{\vec{\mu} = i\vec{S}.}$$



Dans un champ magnétique $\vec{B}$, ce moment magnétique subit un couple

$$|\tau| = ibBa\sin(\theta)$$

ou

$$\vec{\tau} = \mu \times \vec{B}.$$

Selon le principe du travail virtuel

$$dE = \tau d\theta = -dT$$

où T est le travail que l'environnement doit fournir.

On a alors

$$dE = \mu B \sin(\theta) d\theta$$

et en intégrant de 0 à θ

$$\boxed{E = -\mu B \cos(\theta) = -\vec{\mu} \cdot \vec{B}.}$$

Dans un champ magnétique orienté selon z et présentant un gradient selon z

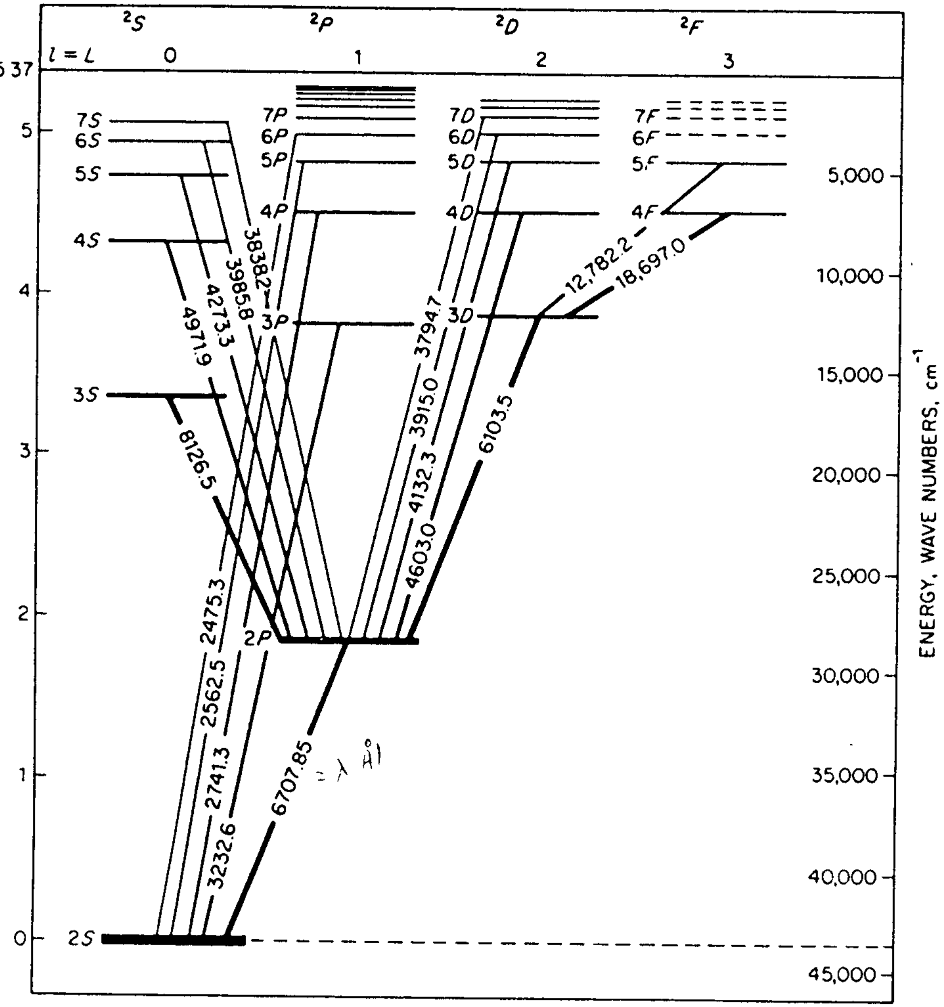
$$E = -\vec{\mu} \cdot \vec{B} = -\mu_z B_z$$

on obtient

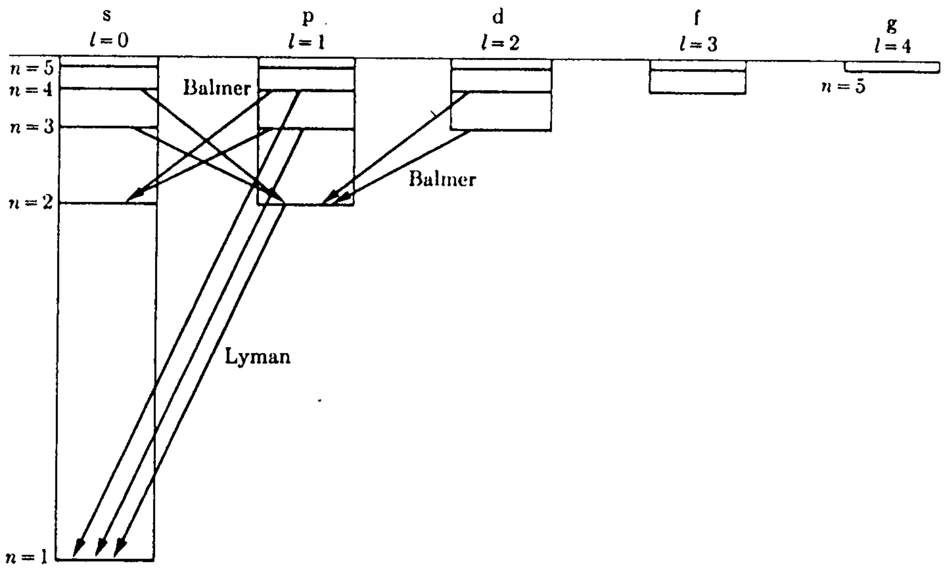
$$dT = F_z dz = -\frac{\partial E}{\partial z} dz = \mu_z \frac{\partial B_z}{\partial z} dz$$

d'où

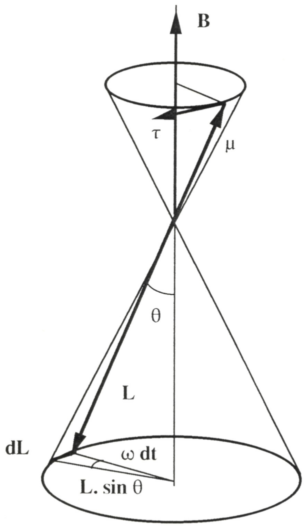
$$F_z = \mu_z \frac{\partial B_z}{\partial z}.$$



Spectre de Li



Spectre H



Pour un électron sur une orbite circulaire

$$i = -e\frac{v}{2\pi r}$$

et

$$\mu = -\frac{ev}{2\pi r}\pi r^2 = -\frac{evr}{2}$$

ou encore

$$\vec{\mu} = -\frac{e}{2}\vec{r}\times\vec{v} = -\frac{2}{2m_e}\vec{r}\times\vec{p} = -\frac{e}{2m_e}\vec{L}.$$

Le rapport

$$\boxed{\frac{\mu}{L} = -\frac{e}{2m_e}}$$

est le *rapport gyromagnétique*.

On peut encore écrire le moment magnétique

$$\mu_z = -\frac{e}{2m_e}L_z = -\frac{e\hbar}{2m_e}m = -\mu_B m$$

où

$$\boxed{\mu_B = \frac{e\hbar}{2m_e}}$$

est le *magnéton de Bohr*.

Dans le cas où la distribution de charge ne coïncide pas avec celle des masse (noyaux) on pose

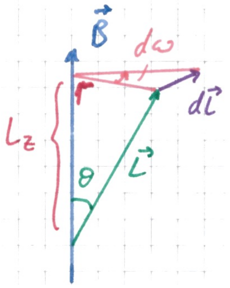
$$\mu_u = -g\mu_B m$$

avec g le *facteur de Landé*.

Pour l'électron, $g = 1$.

Remarque 1

En physique atomique, un champ magnétique $\vec{B}$ n'aligne pas $\vec{\mu}$ avec le champ, mais le fait précesser autour de $\vec{B}$.



Dans un champ $\vec{B}$ uniforme

$$\tau = \frac{d\vec{L}}{dt} = \vec{\mu}\times\vec{B} = -\frac{2}{2m_e}g\vec{L}\times\vec{B}$$

d'où

$$\begin{aligned} dL &= L\sin(\theta)\omega dt = \mu B\sin(\theta)dt \\ &= -\frac{eg}{2m_e}LB\sin(\theta)dt \end{aligned}$$

on obtient

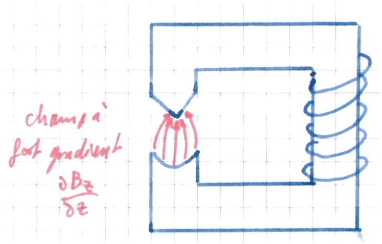
$$L\sin(\theta)\omega dt = -g\frac{\mu_B}{\hbar}LB\sin(\theta)dt$$

d'où

$$\boxed{\omega = g\frac{\mu_B}{\hbar}B = \frac{-eg}{2m_e}B.}$$

C'est la *vitesse de précession de Larmor*. Durant la précession L_z ne change pas.

4.5.2 Expérience de Stern et Gerlach



L'expérience de Stern et Gerlach consiste à faire passer un faisceau d'atomes d'Ag le long d'un champ $\vec{B}$ à fort gradient $\frac{\partial B_z}{\partial z}$.

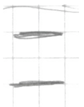
On a alors

$$F_z = \mu_z \frac{\partial B_z}{\partial z}$$

et le faisceau d'atomes peut être analysé selon les valeurs de μ_z. Les résultats attendus de l'expérience de Stern et Gerlach, dans le cadre de la physique classique et dans le cadre de la physique quantique sont résumés dans le tableau suivant.

Physique classique	Physique quantique
On doit observer une distribution continue des impacts sur l'écran puisque L_z peut rendre toutes les valeurs de manière continue $\mu_z \in [-\mu_{\max}, \mu_{\max}]$. 	On doit observer une distribution discrète, car $\mu_z = -\mu_B m$ et que m ne prend qu'un ensemble fini de valeurs entières m : $-\ell, -\ell+1, \dots, 0, \dots, \ell$, soit $2\ell + 1$ valeurs en tout (un nombre impair). 

L'expérience donne 2 raies



Cela signifie que les atomes d'Ag, dans leur état fondamental, on un moment magnétique à 2 composantes selon z.

En 1927, Phipps et Taylor répètent l'expérience avec H dans son état fondamental $n = 1$ et $\ell = 0$. Ils trouvent aussi deux raies.

En 1925 Uhlenbeck et Goudsmitt proposent l'existence d'un moment cinétique intrinsèque de l'électron : le *spin*.

Les projections de ce spin sont $\pm\frac{1}{2}$ en unités de $\hbar$. Aussi obtient-on

$$\vec{\mu} = -\frac{e}{2m_e}(g\vec{L} + g_s\vec{s})$$

avec $g = 1$ et $g_s = 2$ (résultat prévu actuellement à plus de 8 décimales).

Le moment cinétique orbital, $\vec{L}$, est caractérisé par le nombre quantique ℓ

Le moment cinétique de spin $\vec{s}$ est caractérisé par le nombre quantique de spin $s = \frac{1}{2}$.

Le spin n'a pas d'équivalent classique. L'électron, le muon, le proton, le neutron, les neutrinos, notamment, ont un spin $\frac{1}{2}$. Le spin est une conséquence directe des équations de Dirac de l'électron.

4.5.3 Le moment cinétique en physique quantique

Module du moment cinétique

La norme du moment cinétique est calculée par

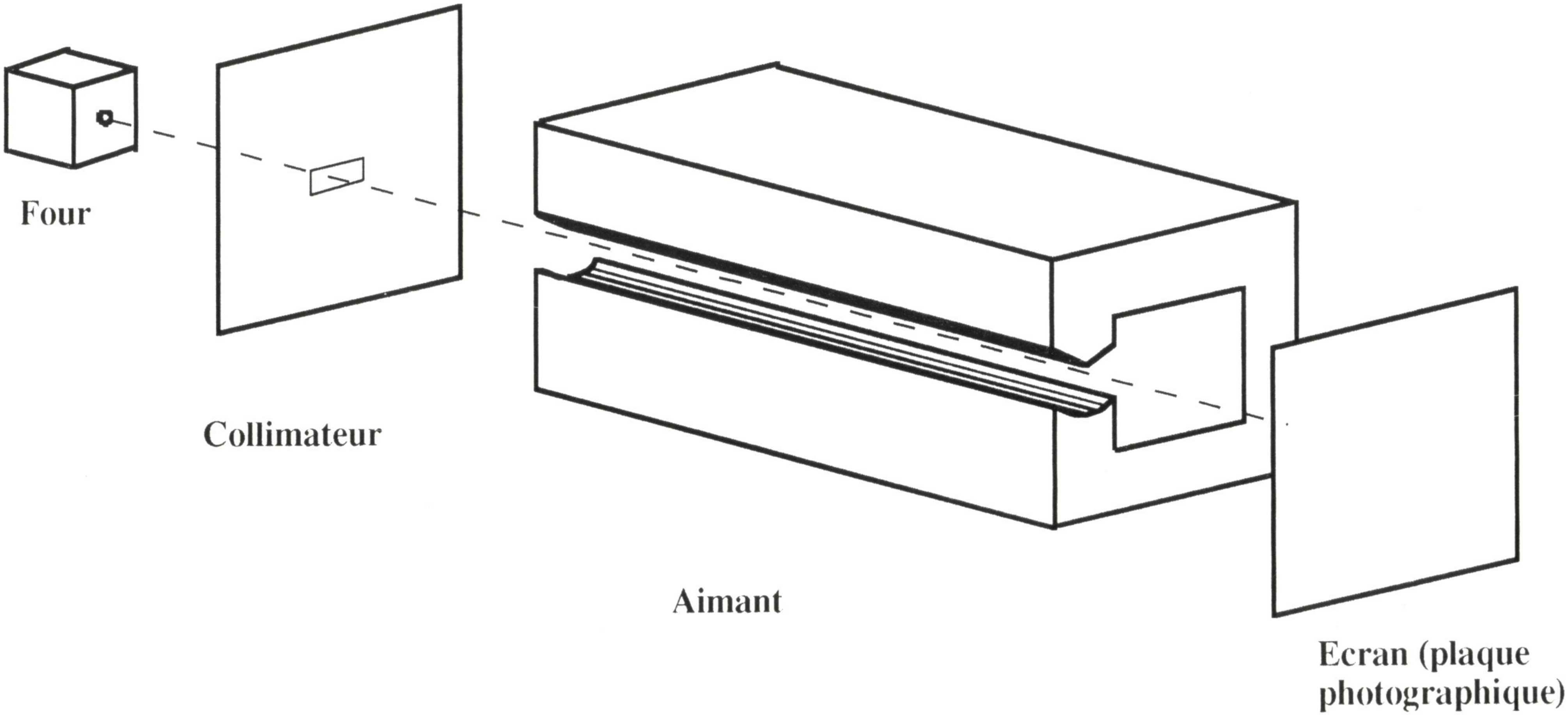
$$\|\vec{L}\|^2 = \vec{L} \cdot \vec{L} = L_X^2 + L_y^2 + L_z^2$$

Si l'on prend un grand nombre d'atomes et que l'on effectue une moyenne d'ensemble

$$\langle \vec{L} \cdot \vec{L} \rangle = 3\langle L_z^2 \rangle.$$

où l'on a supposé qu'il n'y a pas de direction privilégiée dans l'espace. Comme la norme d'un vecteur ne dépend pas de son orientation, on peut écrire

$$\vec{L} \cdot \vec{L} = 3\langle L_z^2 \rangle.$$



Expérience de Stern et Gerlach

On a

$$\begin{aligned}\langle L_z^2\rangle &= \frac{1}{2\ell+1}\left[\ell^2+(\ell-1)^2+\cdots+(-\ell+1)^2+(-\ell)^2\right]\hbar^2\\ &= \frac{2}{2\ell+1}\left[\ell^2+(\ell-1)^2+\cdots+1\right]\hbar\\ &= \frac{1}{3}\ell(\ell+1)\hbar^2\end{aligned}$$

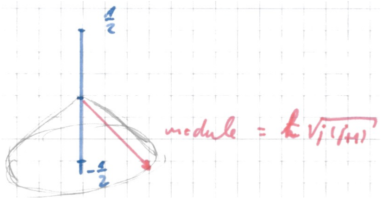
où ℓ est entier et $1+2^2+3^2+\cdots+n^2=\frac{n}{6}(n+1)(2n+1)$. Ainsi,

$$\boxed{L^2=\ell(\ell+1)\hbar.}$$

Pour J^2 avec les projections $+j,\dots,-j$ avec $j=\frac{2n+1}{2}$ demi-entier

$$J^2=j(j+1)\hbar^2.$$

Exemple 2



Pour $s=\frac{1}{2}$ on a

$$s^2=\frac{3}{4}\hbar^2,\qquad s_z=\frac{1}{2}\hbar.$$

Addition de deux moment cinétiques

1. Les projections du moment cinétique s'additionnent.
2. $J_z=m\hbar$ et $-j\leqslant m\leqslant j$.

Exemple 3

Pour $\vec{J}=\vec{L}+\vec{S}$, avec $\ell=3$ et $s=\frac{1}{2}$, on obtient (on recherche les projections maximales possibles de m_j)

σ \ m	-3	-2	-1	0	$+1$	$+2$	$+3$
$+\frac{1}{2}$	$-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$
$-\frac{1}{2}$	$-\frac{7}{2}$	$-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$

Si $\vec{J}=\vec{J}_1+\vec{J}_2$, la projection maximale j de $\vec{J}$ sont

$$|j_1-j_2|\leqslant j\leqslant j_1+j_2.$$

Pour le cas $\vec{J}=\vec{L}+\vec{S}$, on aura
si $\ell\neq 0$ $j\in\{\ell-\frac{1}{2},\ell+\frac{1}{2}\}$.
si $\ell=0$ $j=\frac{1}{2}$.

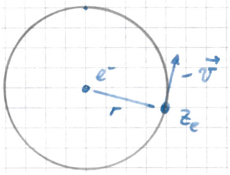
Retour à l'atome H

En notant les niveaux $n\ell$ (par exemple $2p$, pour $n=2$ et $\ell=1$)

n	ℓ	m	σ	dégénérescence
1	0	0	$-\frac{1}{2}, \frac{1}{2}$	2
2	0	0	$-\frac{1}{2}, \frac{1}{2}$	2
	1	$-1, 0, 1$		6
				total : 8
3	0	0	$-\frac{1}{2}, \frac{1}{2}$	2
	1	$-1, 0, 1$		6
	2	$-2, -1, 0, 1, 2$		10
				total : 18

4.5.4 Interaction spin-orbite

Le spin peut jouer un rôle dynamique en ce sens qu'il est à l'origine du dédoublement des niveaux d'énergie : la *structure fine*.



On considère l'électron sur une orbite circulaire et on se place sur l'électron. Le courant est alors dû au noyau

$$\vec{j} = -Ze\vec{v}.$$

Selon la loi de Biot-Savart

$$\vec{B} = \frac{\mu_0}{4\pi}\frac{\vec{j} \times \hat{r}}{r^2} = -\frac{Ze\mu_0}{4\pi}\frac{\vec{v} \times \vec{r}}{r^3}$$

et le champ électrique

$$\vec{E} = \frac{Ze}{4\pi\epsilon_0 r^2}\frac{\vec{r}}{r}$$

qui induit un champ magnétique

$$\vec{B} = -\epsilon_0\mu_0\vec{v} \times \vec{E} = -\frac{1}{c^2}\vec{v} \times \vec{E}$$

Pour obtenir l'expression relativiste, on corrige par le facteur $\gamma = \frac{1}{\sqrt{1-\frac{v^2}{c^2}}}$.

La vitesse pour un atome de Bohr est de l'ordre

$$\vec{v}_n = \frac{q_e^2}{n\hbar} = 2.6 \cdot 10^6 \frac{1}{n} \text{ m s}^{-1}.$$

Dans le référentiel de l'électron, ce dernier voit son énergie varier de

$$\Delta E = -\vec{\mu}_s \cdot \vec{B} = g_s \frac{\mu_B}{\hbar}\vec{S} \cdot \vec{B}$$

avec $g_s \simeq 2$.

Dans le référentiel du laboratoire

$$\Delta E = \frac{1}{2}\frac{g_s\mu_B}{\hbar}\vec{S} \cdot \vec{B}$$

le facteur $\frac{1}{2}$ venant de la précession de Thomas (cf. 4.5.7).

Avec

$$\vec{B} = \frac{1}{c^2}\vec{E} \times \vec{v} = \frac{1}{c^2}\frac{Ze}{4\pi\epsilon_0 r^3}\vec{r} \times \vec{v}$$

soit

$$\boxed{\vec{B} = \frac{1}{c^2}\frac{Ze}{4\pi\epsilon_0 r^3 m_e}\vec{L}}$$

Avec $\mu_B = \frac{e\hbar}{2m_e}$ on obtient

$$\Delta E = \frac{1}{4}\frac{Zq_e^2}{m_e^2c^2}\frac{g_s}{r^3}\vec{L}\cdot\vec{S}$$

soit

$$\boxed{\Delta E = \frac{g_s}{4}a\vec{L}\cdot\vec{S},}$$

où $a = \frac{Zq_e^2}{m_e^2c^2r^3}$.

Ordre de grandeur

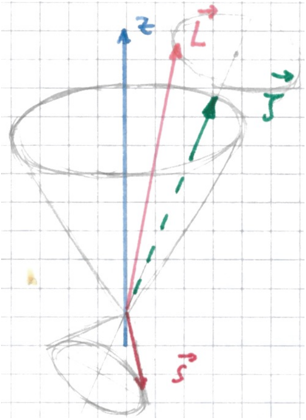
On a

$$a = \frac{Zq_e^2}{m_e^2c^2r^3} = \frac{Zq_e^2}{2r_n}\frac{2}{m_e^2c^2r_n^2} = -E_n\frac{2\alpha^2}{\hbar^2}\frac{Z^2}{n^4}$$

où $\alpha = \frac{q_e^2}{\hbar c} \simeq \frac{1}{137}$ est la constante de structure fine. On trouve alors

$$\frac{\Delta E}{E} \propto \alpha^2 \simeq 10^{-5}.$$

Dédoublement des niveaux



S'il n'y avait pas de couplage spin-orbite, $\vec{L}$ et $\vec{s}$ seraient indépendants l'un de l'autre.

Vu de l'extérieur, aucun couple ne s'exerce, donc le moment cinétique total est conservé : $\vec{J} = \vec{L} + \vec{s}$.

Ainsi $\vec{L}$ et $\vec{s}$ ont un mouvement de précession autour de $\vec{J}$, de sorte que leur projection autour de $\vec{J}$ soit constante.

Avec $\vec{J} = \vec{L} + \vec{S}$

$$\begin{aligned}\vec{L}\cdot\vec{S} &= \frac{1}{2}\left[\vec{J}\cdot\vec{J} - \vec{L}\cdot\vec{L} - \vec{S}\cdot\vec{S}\right]\\ &= \frac{\hbar^2}{2}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right]\\ &= \frac{\hbar^2}{2}\left[j(j+1) - \ell(\ell+1) - \frac{1}{2}\frac{3}{2}\right]\end{aligned}$$

Si $\ell \neq 0$, pour
$j = \ell + \frac{1}{2}$ on obtient $\vec{L}\cdot\vec{S} = \frac{\hbar^2}{2}\ell$.
$j = \ell - \frac{1}{2}$ on obtient $\vec{L}\cdot\vec{S} = -\frac{\hbar^2}{2}(\ell+1)$.
L'écart en énergie entre ces deux états donne la *structure fine* du spectre et vaut

$$\boxed{\Delta E_{\text{SF}} = g_s\frac{a\hbar^2}{8}(2\ell+1).}$$

Si $\ell = 0$ alors $j = \frac{1}{2}$ et il n'y a pas de dédoublement.
L'écart d'énergie ΔE_{SF} dépend clairement de ℓ, mais également de n à cause du facteur $\frac{1}{r_n^3}$.

Application

La raie H_α de l'hydrogène appartient à la série de Balmer $n = 3 \to n = 2$.

On note les niveaux nL^j. Il y a 7 transitions possibles, en utilisant les règles de sélection $\Delta j \in \{0, -1, +1\}$ et $\Delta \ell \in \{-1, +1\}$.

1. $3s^{\frac{1}{2}} \to 2p^{\frac{3}{2}}$
2. $3d^{\frac{3}{2}} \to 2p^{\frac{3}{2}}$
3. $3d^{\frac{5}{2}} \to 2p^{\frac{3}{2}}$
4. $\begin{cases} 3s^{\frac{1}{2}} & \to 2p^{\frac{1}{2}} \\ 3p^{\frac{1}{2}} & \to 2s^{\frac{1}{2}} \end{cases}$
5. $\begin{cases} 3p^{\frac{3}{2}} & \to 2s^{\frac{1}{2}} \\ 3d^{\frac{3}{2}} & \to 2p^{\frac{1}{2}} \end{cases}$

On ne trouve pas que pour une même valeur de n, ΔE_{SF} augmente avec ℓ. En mécanique quantique, il faut calculer la moyenne de $\frac{1}{r^3}$ qui elle dépend également de ℓ

$$\langle \frac{1}{r^3} \rangle = \frac{1}{a_B^3 n^2 \ell(\ell+1)(\ell+\frac{1}{2})}$$

4.5.5 La structure hyperfine

On appelle *structure hyperfine* (SHF) de nombreux spectres atomiques, la propriété de certains niveaux de se décomposer en multiplets séparés par des longueurs d'onde λ entre 10^3 et 1 cm ($10^7 < \nu < 10^{10}$ Hz).

On remarque que cette propriété ne se manifeste que pour les éléments dont les noyaux ont un spin nucléaire.

Comme pour la structure fine, il s'agit de l'interaction entre le champ magnétique $\vec{B}$ créé par μ_e (le moment cinétique et intrinsèque) et le moment magnétique de spin du noyau

$$\vec{\mu}_e = -\frac{e}{2m_e}(\vec{L} + g_s \vec{S})$$

On montre en magnétostatique qu'un moment magnétique $\vec{\mu}$ crée un potentiel vecteur $\vec{A}$, donné par

$$\vec{A} = \frac{\mu_0}{4\pi} \frac{\mu \times \vec{r}}{r^3}$$

d'où l'on tire

$$\vec{B} = \nabla \times \vec{A} \propto \frac{1}{r^3}$$

et

$$\begin{cases} B_x & \propto \frac{\mu 3xy}{r^5} \\ B_y & \propto \frac{\mu 3yz}{r^5} \\ B_z & \propto \mu \left(\frac{1}{r^3} - \frac{3z^2}{r^5} \right) \end{cases}$$

Limitons-nous au cas de l'atome H dans l'état $1s$ ($n = 1$, $\ell = 0$).

On a

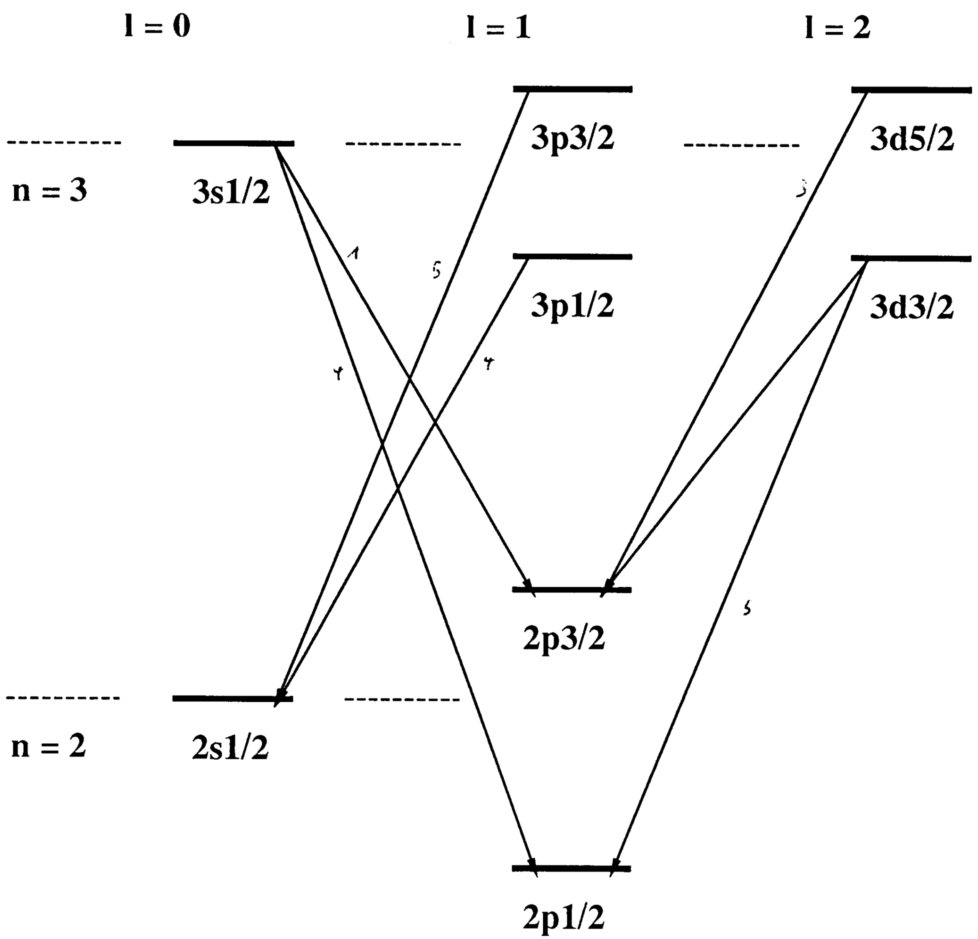
$$\Delta E_{SHF} = -\vec{\mu}_{\text{spin nucl.}} \cdot \vec{B}_e$$

avec

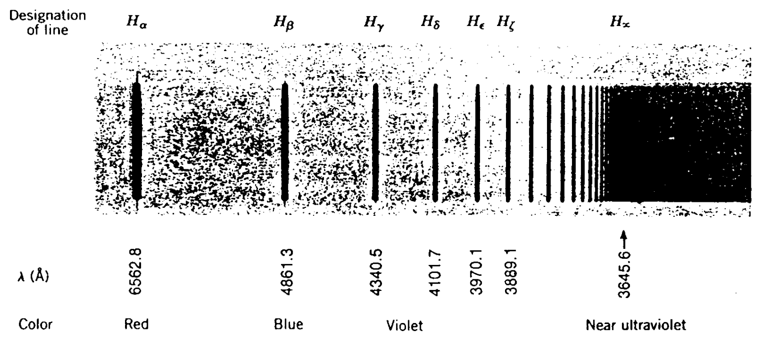
$$B_e \propto \frac{\mu_0}{4\pi} \mu_{\text{spin élect.}} \frac{1}{r^3} = \frac{\mu_0}{4\pi} \frac{e g_s}{2m_e} s \frac{1}{r^3} \simeq \frac{e\hbar}{4\pi\epsilon_0 c^2 m_e} \frac{1}{a_B^3}$$

d'où

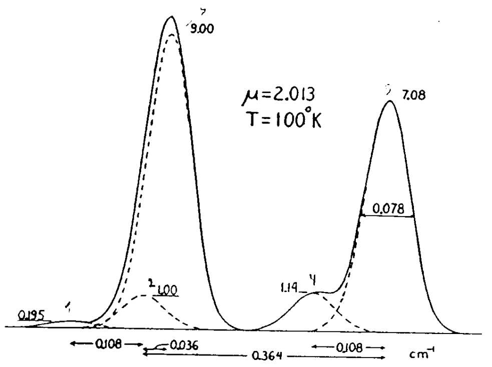
$$|\Delta E_{SHF}| \simeq \frac{e\hbar}{2m_p} B_e = \frac{e^2\hbar^2}{4\pi\epsilon_0} \frac{1}{m_e^2 c^2} \frac{1}{a_B^3} \frac{m_e}{m_p}.$$



Les écarts en énergie des différents niveaux ne sont pas respectés !



Partie visible du spectre de l'hydrogène



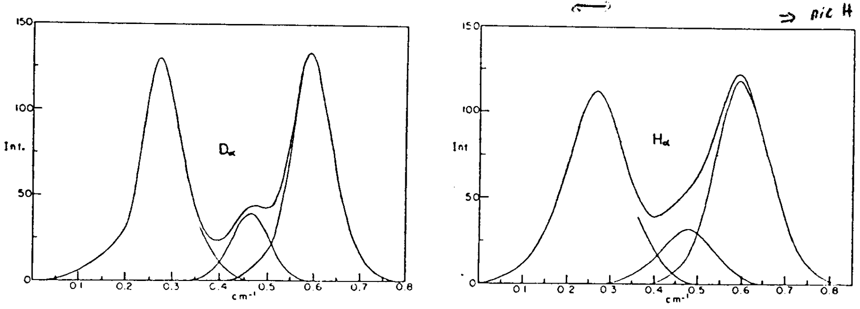
$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{M_{H_{noyau}}}$

"Structure fine" de la raie D_α à 100K. calculé

Réf. : R.C. Williams Phys. Rev. **54** (1938) 558

élargissement des raies → Doppler $\frac{\Delta\nu}{\nu} = \sqrt{\frac{3T}{Mc^2}}$

⇒ pic H = $\sqrt{2}$ (+ large de D)



pour n = l
(2p → 3p)
l'élargissement
est + important
pour n − l + petit

FIG. 5. Typical intensity curves obtained for Hα and Dα.

Du modèle de Bohr

$$E = \frac{q_e^2}{2a_B} \qquad a_B = \frac{\hbar}{m_e c}\frac{1}{\alpha}$$

Ainsi

$$\frac{\Delta E_{SHF}}{E} \simeq \frac{\hbar^2}{m_e^2 c^2}\frac{m_e}{m_p}\frac{1}{a_B^2} = \alpha \frac{m_e}{m_p}$$

(pour rappel $\frac{\Delta E_{SF}}{E} \simeq \alpha^2$).

La correction énergétique est donc environ $2'000$ plus faible que dans le couplage spin-orbite.

$$\Delta E_{SHF} = -\vec{\mu}_{\text{spin nucl.}} \cdot \vec{B}_e$$

avec

$$\vec{\mu}_{\text{spin nucl.}} = \frac{e}{2m_p} g_n \vec{s}_n, \qquad \vec{B}_e \propto \vec{s}_e$$

et $s_e^2 = \frac{1}{2}(\frac{1}{2}+1) = \frac{3}{4}$. Ainsi

$$\begin{aligned}\Delta E_{SHF} &= \frac{a'}{\hbar^2}[(\vec{s}_n + \vec{s}_e)^2 - (s_n)^2 - (s_e)^2] \\ &= \frac{a'}{\hbar^2}[(\vec{s}_n + \vec{s}_e)^2 - \frac{3}{2}]\end{aligned}$$

La physique quantique permet de calculer a'

$$a' = \frac{e}{2m_p} g_n \frac{e}{4\pi\epsilon_0 c^2 m_e r^3}.$$

Posons $\vec{F} = \vec{s}_n + \vec{s}_e$. Alors les états propres de F se décomposent en un état singulet $f = 0$ et un état triplet $f = 1$

	$-\frac{1}{2}$	$\frac{1}{2}$
$-\frac{1}{2}$	-1	0
$\frac{1}{2}$	0	1

états $f = 1$

états $f = 0$

Pour $f = 1$, c'est un état trois fois dégénéré

$$\Delta E_{SHF} = -a'\frac{1}{2}$$

Pour $f = 0$

$$\Delta E_{SHF} = -a'\frac{3}{2}$$

La transition $f = 1 \to f = 0$ ($\lambda = 21$ cm) signale la présence d'atome H neutre dans notre galaxie.

Connaissant la vitesse des différentes parties de la galaxie, on peut en déduire la densité d'hydrogène neutre dans ces parties.

4.5.6 Règles de sélection

Lors d'une émission ou absorption, les grandeurs suivantes doivent être conservées

1. L'énergie
2. La quantité de mouvement
3. Le moment cinétique

Le photon a un moment cinétique qui vaut $1\hbar$

Pour une transition $\ell_1 \to \ell_2$ on a alors

$$|\ell_2 - 1| \leqslant \ell_1 \leqslant \ell_2 + 1$$

Pour le moment cinétique total $\vec{J} = \vec{L} + \vec{S}$

$$|\ell - \frac{1}{2}| \leqslant j \leqslant \ell + \frac{1}{2}$$

et si $\vec{J} = \vec{J}_1 + \vec{J}_2$

$$|j_1 - j_2| \leqslant j \leqslant j_1 + j_2$$

Les règles de sélection sont alors

$$\Delta\ell = \pm 1$$

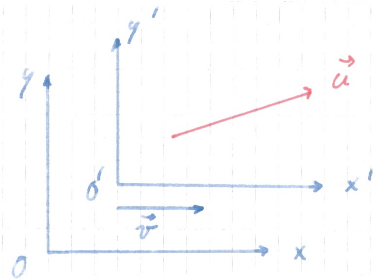
et

$$\Delta j = 0, \pm 1.$$

Ainsi, ce n'est pas seulement la conservation du moment cinétique qui impose les règles de sélection, mais aussi la *parité*.

4.5.7 La précession de Thomas

Rappel de relativité restreinte



Les transformations de Lorentz relient les référentiels $\mathcal{R}$ et $\mathcal{R}'$, ce dernier en mouvement relatif à la vitesse $\vec{v}$ selon l'axe commun Ox, Ox' par rapport à $\mathcal{R}$:

$$x' = \frac{x - vt}{\sqrt{1 - \frac{v^2}{c^2}}}$$

$$t' = \frac{t - \frac{vx}{c^2}}{\sqrt{1 - \frac{v^2}{c^2}}}$$

La vitesse $\vec{v}$ mesurée dans $\mathcal{R}$, dans le référentiel $\mathcal{R}'$ s'obtient en calculant

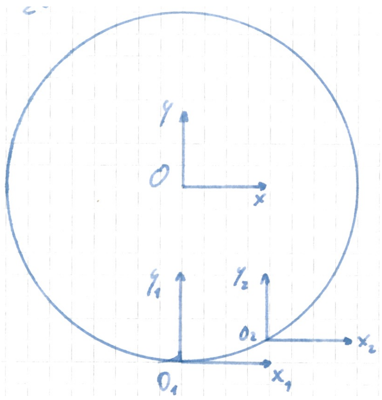
$$dx' = \frac{dx - vdt}{\sqrt{1 - \frac{v^2}{c^2}}}, \quad dt' = \frac{dt - \frac{vdx}{c^2}}{\sqrt{1 - \frac{v^2}{c^2}}}$$

d'où

$$u'_x = \frac{dx - vdt}{dt - \frac{vdx}{c^2}} = \frac{u_x - v}{1 - \frac{vu_x}{c^2}}$$

$$u'_y = \sqrt{1 - \frac{v^2}{c^2}} \frac{dy}{dt\left(1 - \frac{vdx}{c^2}\right)} = \sqrt{1 - \frac{v^2}{c^2}} \frac{u_y}{1 - \frac{vu_x}{c^2}}$$

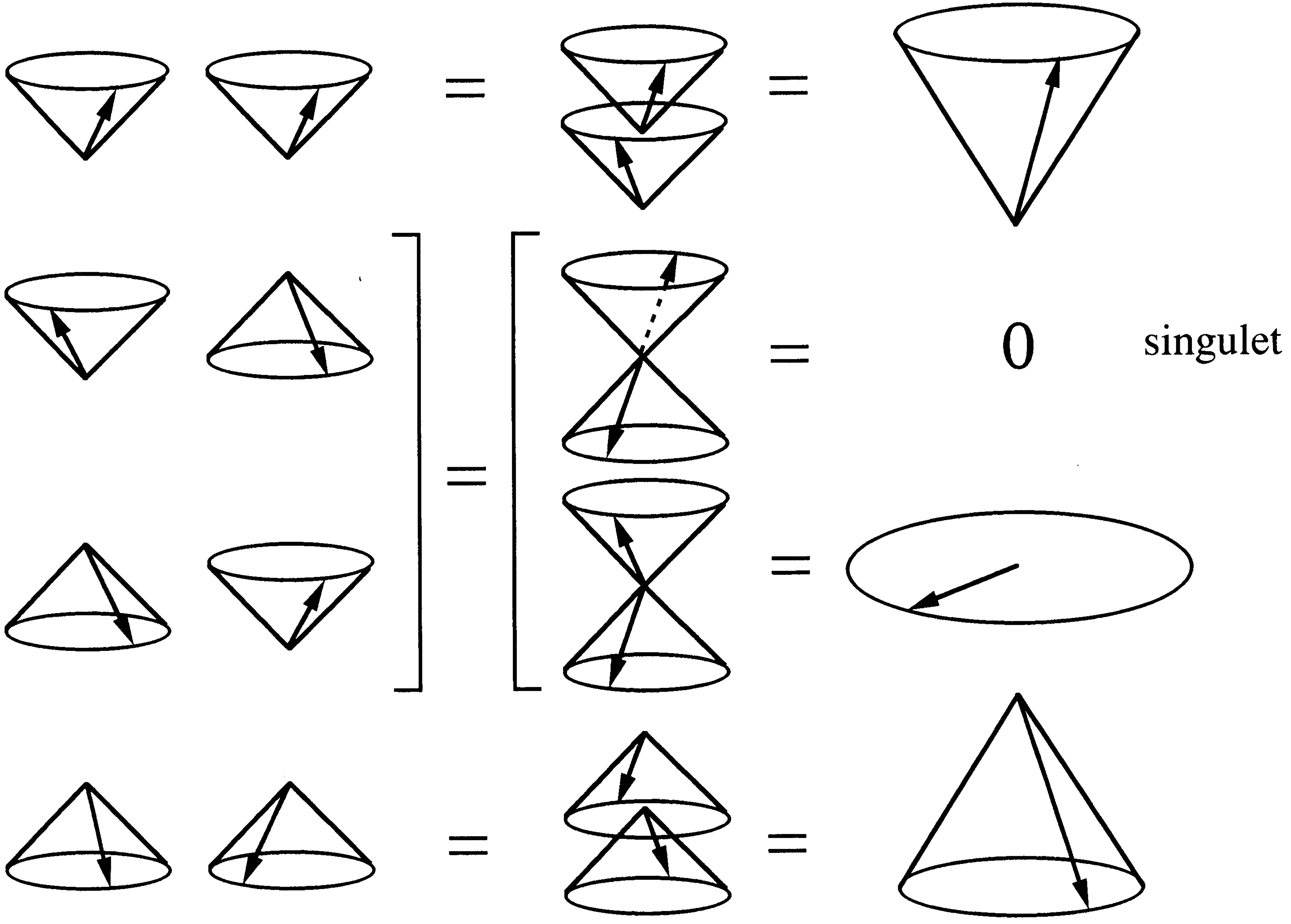
Retour à l'atome H



Dans le modèle de Bohr, posons $\mathcal{R}_0$ le référentiel lié au noyau, $\mathcal{R}^1$ le référentiel dans lequel l'électron est immobile en t_1 (avec une vitesse instantanée nulle, mais avec une accélération non nulle) et enfin le référentiel $\mathcal{R}^2$ similaire, mais en $t_2 > t_1$.

Depuis $\mathcal{R}^1$ on voit le noyau en O aller à la vitesse $-\vec{v}$. Depuis $\mathcal{R}^1$ l'électron est accéléré vers le noyau avec une accélération $\vec{a} \parallel Oy_1$.

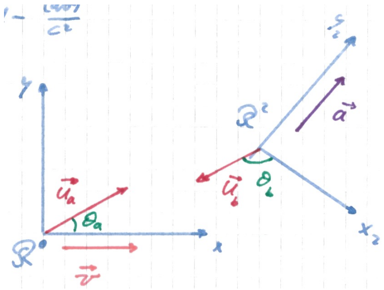
$\mathcal{R}^2$ est en mouvement avec une vitesse $d\vec{v} = a(t_2 - t_1) = \vec{a}dt$ parallèle à Oy_1 par rapport à $\mathcal{R}^1$. $\mathcal{R}_0$ possède une vitesse $-\vec{v}$ par rapport à $\mathcal{R}^1$.



Composition de deux spins 1/2

La vitesse de $\mathcal{R}^2$ par rapport à $\mathcal{R}^0$ est $\vec{u}_a$

$$u_{ax} = \frac{0-(-v)}{1-\frac{v}{c^2}0} = v$$
$$u_{ay} = \sqrt{1-\frac{v^2}{c^2}}\frac{dv}{1-\frac{v}{c^2}0} = \sqrt{1-\frac{v^2}{c^2}}dv$$



La vitesse de $\mathcal{R}^0$ relativement à $\mathcal{R}^2$ est $\vec{u}_b$

$$u_{bx} = \sqrt{1-\frac{dv^2}{c^2}}\frac{-v}{1-\frac{dv}{c^2}0} = -v\sqrt{1-\frac{dv^2}{c^2}}$$
$$u_{by} = \frac{-dv}{1-\frac{dv}{c^2}0} = -dv$$

On a alors $\vec{u}_a = -\vec{u}_b$. De plus les angles des vitesses selon Ox sont

$$\theta_a = \frac{u_{ay}}{u_{ax}} = \frac{dv}{v}\sqrt{1-\frac{v^2}{c^2}}$$
$$\theta_b = \frac{u_{by}}{u_{bx}} = \frac{dv}{v}\frac{1}{\sqrt{1-\frac{dv^2}{c^2}}}$$

Soit une différence d'orientation

$$d\theta = \theta_b - \theta_a = \frac{dv}{v}\left(\frac{1}{\sqrt{1-\frac{dv^2}{c^2}}} - \sqrt{1-\frac{v^2}{c^2}}\right) \simeq \frac{dv}{v}\left(1-\sqrt{1-\frac{v^2}{c^2}}\right)$$

soit

$$d\theta \simeq \frac{dv}{v}\frac{1}{2}\frac{v^2}{c^2} = \frac{v}{2c^2}dv = \frac{va}{2c^2}dt$$

On définit alors la vitesse angulaire de précession de Thomas

$$\omega_T = \frac{d\theta}{dt} = \frac{av}{2c^2}$$

qui donne sous forme vectorielle

$$\vec{\omega}_T = \frac{1}{2c^2}\vec{a}\times\vec{v}.$$

Dans le référentiel $\mathcal{R}^2$, le spin de l'électron précesse à la vitesse angulaire

$$\vec{\omega}_s = \frac{g_s\mu_b}{\hbar}\vec{B}$$

où $\vec{B}$ est le champ créé par le mouvement orbital

$$\vec{B} = -\frac{1}{c^2}\vec{v}\times\vec{E}$$

et

$$g_s \simeq 2, \qquad \mu_B = \frac{e\hbar}{2m_e}$$

soit

$$\vec{\omega}_2 = -\frac{e}{m_e c^2}\vec{v}\times\vec{E}.$$

Mais $\mathcal{R}_2$ précesse à la vitesse angulaire $\vec{\omega}_T$, et donc $\vec{\omega}_0 = \vec{\omega}_2 + \vec{\omega}_T$. Avec l'accélération

$$\vec{a} = -e\frac{\vec{E}}{m}$$

on obtient

$$\vec{\omega}_T = \frac{e}{2m_e c^2}\vec{v} \times \vec{E},$$

ce qui donne

$$\vec{\omega}_0 = -\frac{e}{2m_e c^2}\vec{v} \times \vec{E} = \frac{1}{2}\vec{\omega}_2.$$

Concernant le facteur g_s, l'étude est réalisée sur le demi écart à 2

$$a = \frac{1}{2}(g_s - 2).$$

La théorie donne

$$a_e = 1'159'652'140.7 \cdot 10^{-12},$$

et l'expérience

$$a_{e^-} = 1'159'652'188.4 \cdot 10^{-12},$$

et

$$a_{e^+} = 1'159'652'187.8 \cdot 10^{-12}.$$

Chapitre 5

Atomes à plusieurs électrons

Il n'est pas possible de résoudre analytiquement le problème à N corps de façon exacte. On procède alors à des approximations

- potentiel du noyau
- effet des autres électrons (répulsion) de symétrie sphérique (force centrale → moment cinétique est un bon nombre quantique → $\vec{L}$ est conservé)

Comme conséquence, on observe que

- Chaque électron occupe un état caractérisé par $(n, \ell, m.\sigma)$. Il n'y a pas d'autre caractéristique complémentaire.
- États d'énergie (n, ℓ) avec $2(2\ell + 1)$ états possibles pour les électrons. On dit que les états sont $2(2\ell + 1)$ fois dégénérés.

5.1 Principe de Pauli

Principe de Pauli

Si N particules de spin $\frac{1}{2}$-entier se répartissent sur un ensemble d'états à 1 particule, chacun de ces états ne peut être occupé que par 0 ou 1 particule [1].

Diagramme d'énergie (cf. feuille suivante)

On utilise une méthode itérative (cf. Hartree (1928) et R. Latter, Phys.Rev.,**99**, 510 (1955))

On part d'un potentiel V_0 et on considère un électron dans ce potentiel, ce qui donne une fonction d'onde (dont le module au carré donne la densité de probabilité de trouver la particule dans la position $\vec{r}$).

La probabilité de trouver Z électrons s'obtient en effectuant une combinaison linéaire des ψ_i obéissant au principe de Pauli.

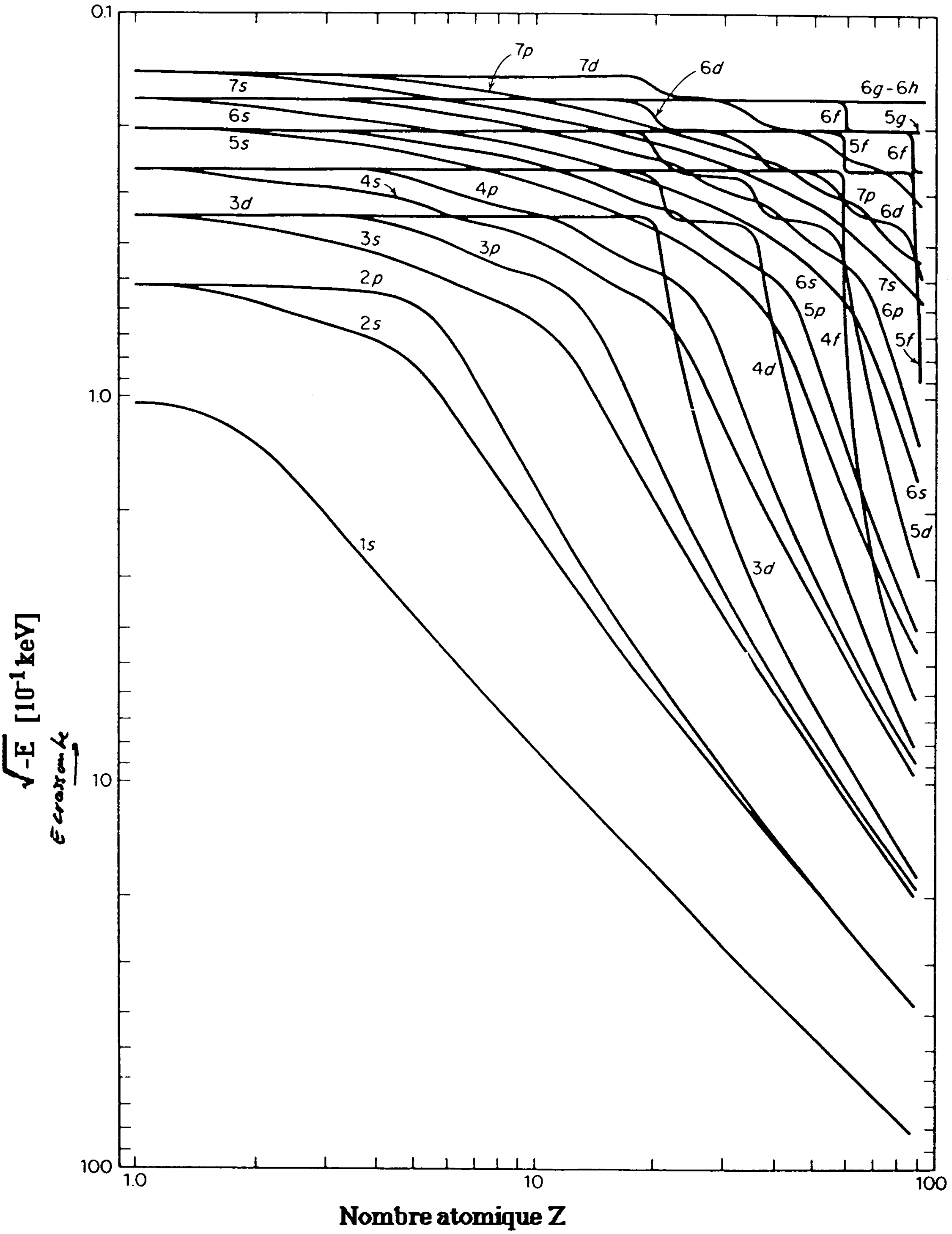
Par le théorème de Gauss on tire alors $\vec{E}(\vec{r})$, soit le potentiel V_1 et on remplace V_0 par V_1 et on recommence jusqu'à ce que $V_j \simeq V_{j+1}$. On en définit ainsi les énergies des électrons.

En résumé

1. $$V_0(r) \to \begin{cases} \frac{e^2}{r} & \text{pour } r \to \infty \\ \frac{Ze^2}{r} & \text{pour } r \to 0 \end{cases}$$
2. On résout l'équation de Schrödinger pour ce potentiel pour obtenir les états ψ_i
3. Antisymétrisation (Pauli) pour Z électrons
$$\psi_{\text{tot}} = \mathcal{A}(\prod \psi_i).$$
4. On calcule le champ électrique produit par ces électrons et on définit un nouveau potentiel. On recommence le processus avec le nouveau potentiel.

---

[1] Les particules à spin demi-entier sont dénommées *fermions*.



Walter J. Moore, *Physical Chemistry*, Ed. Longmans

Pour obtenir l'énergie d'un niveau, on divise par 10 la valeur obtenue, puis on élève au carré. On obtient alors $-E$ en keV.

Exemple 1

Pour le niveau $1s$ de H, on trouve 1.17 ainsi on prend 0.117 ce qui donne $E = -0.0136$ keV.

Pour les Z petits, les sous-couches ayant la même valeur de n ont à peu près la même énergie.
Pour les Z grands, les sous-couches internes ayant même n on environ la même énergie.

Définition 1

couche : ensemble de niveaux compris entre deux sauts d'énergie.
sous-couche : ensemble de niveaux $2(2\ell + 1)$ fois dégénérés correspondants à une valeur du couple (n, l).

5.2 Désignation des niveaux et structures

Une configuration est donnée par la liste des états électroniques, dont on ne donne que le couple (n, ℓ).

Exemple 2

Pour les états fondamentaux, on a

H	$1s^1$	
He	$1s^2$	
Li	$1s^2$	$2s^1$

L'état fondamental de Li s'écrit également

$$[\mathrm{He}]2s^1$$

Pour l'atome dans un ensemble, on peut donner la structure de cet atome par le spin total

$$\vec{S}_{\text{tot}} = \sum_i \vec{S}_i$$

Le moment cinétique

$$\vec{L}_{\text{tot}} = \sum_i \vec{L}_i$$

et le moment cinétique total

$$\vec{J}_{\text{tot}} = \vec{S}_{\text{tot}} + \vec{L}_{\text{tot}}$$

On note alors un état particulier

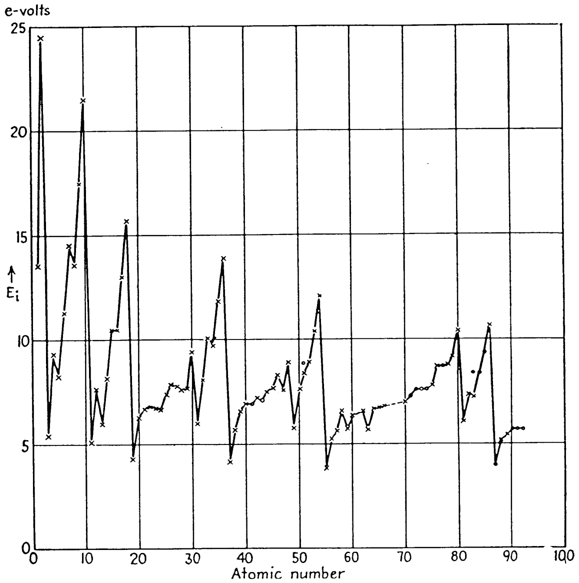
$$L_{\text{tot}}^{2S_{\text{tot}}+1}, \qquad \text{ou} \qquad J_{\text{tot}}^{2S_{\text{tot}}+1}$$

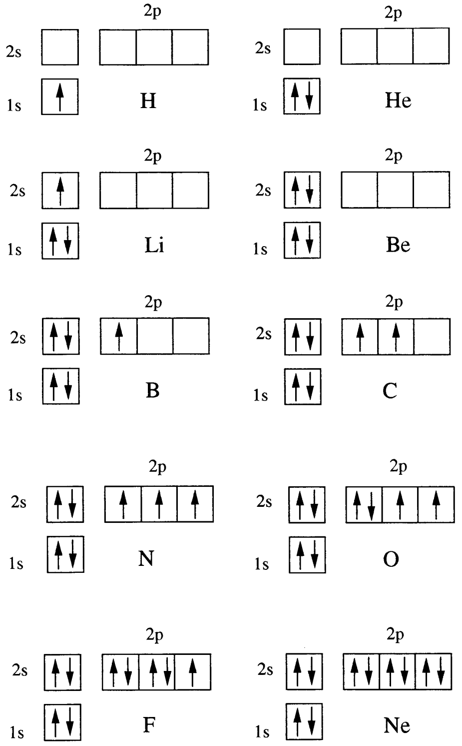
Stabilité d'une couche complète

Une couche complète est caractérisée par
- Une grande valeur du potentiel de 1$^{\text{re}}$ ionisation.
- inertie chimique (gaz rares ou nobles).

Autres conséquences

- Les alcalins ont tendance à céder leur électron qui se trouve au-dessus de la couche complète.
- les halogènes on tendance à prendre un électron pour former une couche complète.





Configuration électronique des dix premiers éléments dans leur état fondamental

Occupation des sous-couches

(par ordre de décroissance de l'énergie en valeur algébrique)

Nombre quantique n, l	désignation de la sous-couche	Nombre d'électrons au maximum 2(2l+1)	Σ
--	--	--	
--	--	--	
6, 2	6d	10	
5, 3	5f	14	
7, 0	7s	2	
6, 1	6p	6	86
5, 2	5d	10	
4, 3	4f	14	
6, 0	6s	2	
5, 1	5p	6	54
4, 2	4d	10	
5, 0	5s	2	
4, 1	4p	6	36
3, 2	3d	10	
4, 0	4s	2	
3, 1	3p	6	18
3, 0	3s	2	
2, 1	2p	6	10
2, 0	2s	2	
1, 0	1s	2	2

5.3 Règle de Hund

Une fois le recensement des configurations possibles effectué, il s'agit de déterminer comment se répartissent les électrons sur ces configurations.

Exemple 3

Pour le carbone

$$1s^2\ 2s^2\ 2p^2$$

Règle de Hund

Dans l'état fondamental, le spin total $\vec{S}_{\text{tot}} = \sum \vec{S}_i$ a la plus grande valeur compatible avec le principe d'exclusion.

Exemple 4

Pour le carbone $n = 2$ $\ell = 0$ ($m = 0$ 1 case) et $\ell = 1$, on a $m = -1, 0, 1$ (donc 3 cases)

$$2s : \boxed{\uparrow\downarrow}, \quad 2p : \boxed{\uparrow}\boxed{}\boxed{\uparrow}$$

et pour $n = 1$ et $\ell = 0$

$$1s : \boxed{\uparrow\downarrow}$$

Explication

Qualitativement, un ensemble d'électrons ayant leur spin parallèles auront forcément (Pauli) leurs autres nombres quantiques différents (leur fonction d'onde seront différentes, autrement dit, la probabilité de les trouver en un endroit de l'espace). En fait, ils auront tendance à se trouver éloignés les uns des autres, d'où une diminution de la répulsion coulombienne.

La règle est aussi valable pour plusieurs sous-couches non-complètes

Exemple 5

Pour le chrome

$$\text{Cr} : \quad [\text{Ar}]\ 3d^5\ 4s$$

soit

$$4s : \boxed{\uparrow}$$
$$3d^5 : \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$$

et le niobium

$$\text{Nb} : \quad [\text{Kr}]\ 4d^4\ 5s$$

soit

$$5s : \boxed{\uparrow}$$
$$4d^4 : \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{}$$

5.4 Étude de la table périodique

Dans le modèle de Sommerfeld, les orbites circulaires : $3d, 4f, 5g$ sont écrantées par les couches inférieures, d'où une inversion dans l'ordre de remplissage.

Exemple 6

La couche $4s$ est remplie avant la couche $3d$.

Le béryllium, Be, possède une couche $2s^2$ complète, mais ce n'est pas un gaz rare comme He ($2s^2$), car il existe une sous-couche toute proche : $2p$. Il en va de même pour tous les alcalino-terreux (colonne 2 du tableau périodique).

La première série de transition, après le Ca, est due à l'inversion $3d$–$4s$ qui sont très proches (quelques eV). Il en découle des propriétés optiques notables, en particulier ce sont des éléments très colorés.

- Fe : le fer a des degrés de valence variés.
- Cu : le cuivre, [Ar] $3d^{10}\ 4s^1$, est bivalent
- Après Ba, le baryum, il y a une seconde inversion. La charge du noyau est devenue tellement grande que la sous-couche $4f$ a une énergie inférieure à celle $5d$. Ce sont les terres rares, les lanthanides et actinides.

Exemple 7

Le cérium

$$\text{Ce :}\quad [\text{Xe}]\ 4f^2\ 5d^0\ 6s^2$$

Les sous-couches internes sont incomplètes ($\vec{L} \neq 0$ d'où $\vec{\mu} \neq 0$). Ce sont des éléments paramagnétiques.

5.5 Spectroscopie d'un atome à plusieurs électrons

5.5.1 Les interactions entre les électrons

Méthode de Hartree : L'électron se meut dans un potentiel moyen décrivant l'attraction du noyau et la répulsion des autres électrons supposée de symétrie sphérique.

correction Corrections aux niveaux d'énergie dues à la brisure de la symétrique sphérique
- couplage entre les spins des électrons.
- couplage entre les moments cinétiques orbitaux
- couplage spin-orbite.

Atomes alcalins

C'est l'électron périphérique qui intervient dans les transitions : c'est l'électron optiquement actif.

Il n'y a pas d'autre correction que le couplage spin-orbite. Le traitement est identique à celui de l'atome H, d'hdrogène.

Exemple 8

Le dédoublement de la ligne jaune du sodium

$$\text{Na :}\quad [\text{Ne}]\ 3s^1$$

le niveau $3p$ ($n=3$, $\ell=1$), avec $s=\frac{1}{2}$, est dédoublé $3p_{\frac{3}{2}}$ et $3p_{\frac{1}{2}}$, car $j=\frac{1}{2}$ ou $j=\frac{3}{2}$.

5.5.2 Atomes à plusieurs électrons optiquement actifs

Exemple 9

Le carbone dans son état fondamental

$$\text{C :}\quad 1s^1\ 2s^2\ 2p^2$$

a deux électrons optiquement actifs.

L'azote

$$\text{N :}\quad 1s^2\ 2s^2\ 2p^3$$

en a 3. Cela ne signifie pas pour autant que tous participent à des transitions.

Les corrections à apporter au modèle de Hartree sont

- Couplage entre spins : comme on l'a vu avec la règle de Hund, ce couplage tend à minimiser[2] la répulsion coulombienne (interaction résiduelle coulombienne : c'est une petite correction à la méthode de Hartree) Les spins des électrons optiquement actifs se combinent et le spin total de l'atome
$$\vec{S}_{\text{tot}} = \sum \vec{S}_i$$
aura son module maximum (en conséquence du principe de Pauli).
- interaction résiduelle coulombienne entre les moments cinétiques.
Classiquement, deux électrons sur une orbite de Bohr sont situés sur les extrémités d'un diamètre. Chaque électron exerce sur le moment cinétique de l'autre un couple, ce qui entraine une précession des moments cinétiques autour de leur somme qui est constante.
Á chaque électron est associé une fonction d'onde, donc une distribution de charge dépendant de n et ℓ.
En résumé $\vec{S}_{\text{tot}} = \sum \vec{S}_i$ et $\vec{L}_{\text{tot}} = \sum \vec{L}_i$. Les interactions résiduelles minimisent la répulsion coulombienne et sont des conséquences du principe de Pauli.

Les couches internes complètes ne contribuent pas au moment cinétique de l'atome (la somme des spins $\boxed{\uparrow\downarrow}$ vaut 0 et la somme des m aussi), donc le spin et $\vec{L}$ de l'atome est de total de ceux des électrons optiquement actifs.

$\vec{S}_{\text{tot}}$ et $\vec{L}_tot$ sont reliés à des moments magnétiques et vont interagir, il y a un couplage entre eux (ils ne vont pas être indépendants). c'est le mécanisme de *couplage L–S* ou *couplage Russel-Saunders.*

$$\vec{J}_{\text{tot}} = \vec{S}_{\text{tot}} + \vec{L}_{\text{tot}}, \qquad \text{(couplage spin-orbite).}$$

C'est valable pour les atomes à Z moyen (jusqu'à Zn, Hg).

Pour les atomes lourds, l'interaction spin-orbite pour 1 électron

$$\Delta E = \frac{g_s}{4} a \vec{L}_i \cdot \vec{S}_i$$

avec

$$a \simeq -E_n \frac{2\alpha^2}{\hbar^2} \frac{Z^2}{n^4}$$

où, à cause de Z^2, devient rapidement grand et ne peut plus être négligé. On a alors, avec $\vec{J}_i = \vec{L}_i + \vec{S}_i$ un *couplage J–J* avec

$$\vec{J}_{\text{tot}} = \sum \vec{J}_i.$$

5.6 Un exemple : l'atome d'azote

L'azote dans son état fondamental a la structure

$$\text{N :} \quad 1s^2\ 2s^2\ 2p^3$$

Les trois électrons de la sous-couche $2p$ vont se répartir sur les $2(2\ell+1) = 6$ états possibles.

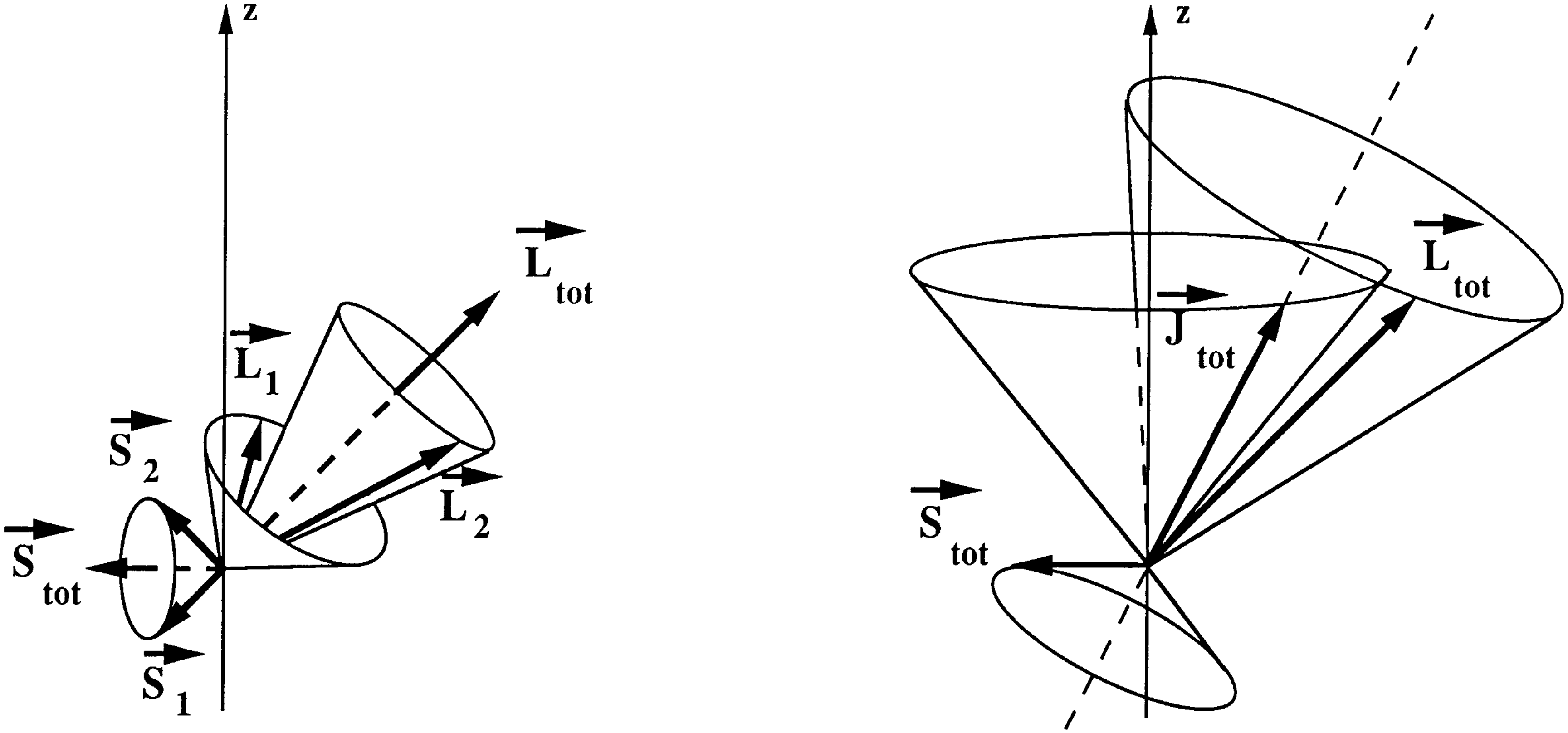
Concernant le couplage L–S on a (avec + pour $\sigma = \frac{1}{2}\hbar$ et − pour $\sigma = -\frac{1}{2}\hbar$)

m \ état	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
+1	+	+	+	+	+			±	±	−
0	+	+	−	±		+	±	+		+
−1	+	−	+		±	±	+		+	+

Ainsi, pour la colonne
(1) : $\sigma_{\text{tot}} = \frac{3}{2}$ et $m_{\text{tot}} = 0$
(5) : $\sigma_{\text{tot}} = \frac{1}{2}$ et $m_{\text{tot}} = -1$
(6) : $\sigma_{\text{tot}} = \frac{1}{2}$ et $m_{\text{tot}} = -2$

---

[2] On minimise quelque chose de positif, donc également l'énergie du système.



Le couplage L-S (Russell-Saunders)

Pour le moment cinétique total on trouve

m_{tot} \ σ_{tot}	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$
$+2$		1	1	
$+1$		2	2	
0	1	3	3	1
-1		2	2	
-2		1	1	

Avec σ_{tot} la projection de S_{tot}

— pour $\ell_{\text{tot}} = 0$ et $s_{\text{tot}} = \frac{3}{2}$ on a

$$\sigma_{\text{tot}} = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}, \quad m_{\text{tot}} = 0.$$

Ainsi $j_{\text{tot}} = \frac{3}{2}$ c'est l'état[3]

$${}^4S_{\frac{3}{2}}.$$

— pour $\ell_{\text{tot}} = 1$ et $s_{\text{tot}} = \frac{1}{2}$ on a

$$\sigma_{\text{tot}} = \frac{1}{2}, -\frac{1}{2}, \quad m_{\text{tot}} = 1, 0, -1.$$

Alors $j_{\text{tot}} = \frac{3}{2}, \frac{1}{2}$ et ce sont les états

$${}^2P_{\frac{1}{2}}, \quad {}^2P_{\frac{3}{2}}.$$

— pour $\ell_{\text{tot}} = 2$ et $s_{\text{tot}} = \frac{1}{2}$ on a

$$\sigma_{\text{tot}} = \frac{1}{2}, -\frac{1}{2}, \quad m_{\text{tot}} = -2, -1, 0, 1, 2.$$

et $j_{\text{tot}} = \frac{5}{2}, \frac{3}{2}$ pour les états

$${}^2D_{\frac{5}{2}}, \quad {}^2D_{\frac{3}{2}}.$$

Sur le plan énergétique on observe que par ordre d'importance

1. plus S_{tot} augmente, plus les électrons sont liés.
2. plus ℓ_{tot} augmente, plus les électrons sont liés.
3. plus j_{tot} diminue, plus les électrons sont liés.

Aussi, par ordre d'énergie décroissante, on a

$${}^4S_{\frac{3}{2}}, \ {}^2D_{\frac{3}{2}}, \ {}^2D_{\frac{5}{2}}, \ {}^2P_{\frac{1}{2}}, \ {}^2P_{\frac{3}{2}}$$

On a 20 possibilités différentes de caser les électrons dans les états quantiques en respectant le principe de Pauli. En effet, il y a 6 cases différentes, dans lesquelles ranger 3 électrons, soit $\binom{6}{3} = 20$.

Pour 1 électron, la règle de sélection résultant de la conservation d moment cinétique et de la parité

$$\Delta\ell = \pm 1, \quad \Delta j = 0, \pm 1.$$

Pour un atome dans son état fondamental, satisfaisant au couplage L–S

$$\Delta\ell_{\text{tot}} = 0, \pm 1, \quad \Delta j_{\text{tot}} = 0, \pm 1, \quad \Delta m_{\text{tot}} = 0, \pm 1.$$

Il faut encore prendre en compte l'absence de transition $0 \to 0$

$$\Delta m_{\text{tot}} = 0, \text{ si } \Delta j_{\text{tot}} = 0 \text{ est interdit.}$$

---

[3] La notation de la structure atomique est

$${}^{2S_{\text{tot}}+1}L_{\text{tot}\,S_{\text{tot}}}.$$

5.7 Effet Zeeman

En 1896 Zeeman observe la décomposition du spectre de Na (obtenu par une flamme) dans un champ magnétique.

Nous avons vu que le déplacement des raies dans l'interaction spin-orbite était proportionnel à $\alpha^2 E$ et de l'ordre de 10^{-4} eV.

Ceci résulte de l'interaction entre $\vec{\mu}_s$ et le champ $\vec{B}$ résultant du mouvement orbital de l'électron, $\|\vec{B}\|$ allant de quelques gauss à 1 T.

Le champ extérieur appliqué dans l'efet Zeeman est faible (environ 1 kGauss). Il s'agit d'une petite perturbation, qui ne couvre pas le couplage spin-orbite.

L'énergie de l'interaction est

$$\Delta E = -\vec{\mu} \cdot \vec{B}$$

où $\vec{\mu}$ résulte de $\vec{\mu}_L = -\frac{e}{2m_e}\vec{L}_{\text{tot}}$ et $\vec{\mu}_s = -g_s \frac{e}{2m_e}\vec{S}_{\text{tot}}$, avec $g_s \simeq 2$

$$\vec{\mu}_{\text{tot}} = \vec{\mu}_L + \vec{\mu}_s.$$

En général $\vec{\mu}_{\text{tot}}$ ne sera pas colinéaire avec $\vec{J}_{\text{tot}}$.

Ainsi

$$\Delta E = -(\mu_{Lz} + \mu_{sz})B$$

où (cf. schéma pour les définition des angles)

$$\mu_{Lz} = -\frac{e\hbar}{2m_e}\sqrt{\ell_{\text{tot}}(\ell_{\text{tot}}+1)}\cos(\theta_L)\cos(\theta)$$

et

$$\mu_{Lz} = -\frac{e\hbar}{m_e}\sqrt{s_{\text{tot}}(s_{\text{tot}}+1)}\cos(\theta_s)\cos(\theta)$$

et

$$\cos(\theta) = \frac{m_{\text{tot}}}{\sqrt{j_{\text{tot}}(j_{\text{tot}}+1)}}; \quad \vec{J}_{\text{tot}} = \vec{L}_{\text{tot}} + \vec{S}_{\text{tot}}.$$

On a alors (par le théorème du cosinus)

$$s_{\text{tot}}(s_{\text{tot}}+1) = j_{\text{tot}}(j_{\text{tot}}+1) + \ell_{\text{tot}}(\ell_{\text{tot}}+1) - 2\sqrt{j_{\text{tot}}(j_{\text{tot}}+1)\ell_{\text{tot}}(\ell_{\text{tot}}+1)}\cos(\theta_L)$$

et de même pour ℓ

$$\ell_{\text{tot}}(\ell_{\text{tot}}+1) = j_{\text{tot}}(j_{\text{tot}}+1) + s_{\text{tot}}(s_{\text{tot}}+1) - 2\sqrt{j_{\text{tot}}(j_{\text{tot}}+1)s_{\text{tot}}(s_{\text{tot}}+1)}\cos(\theta_S)$$

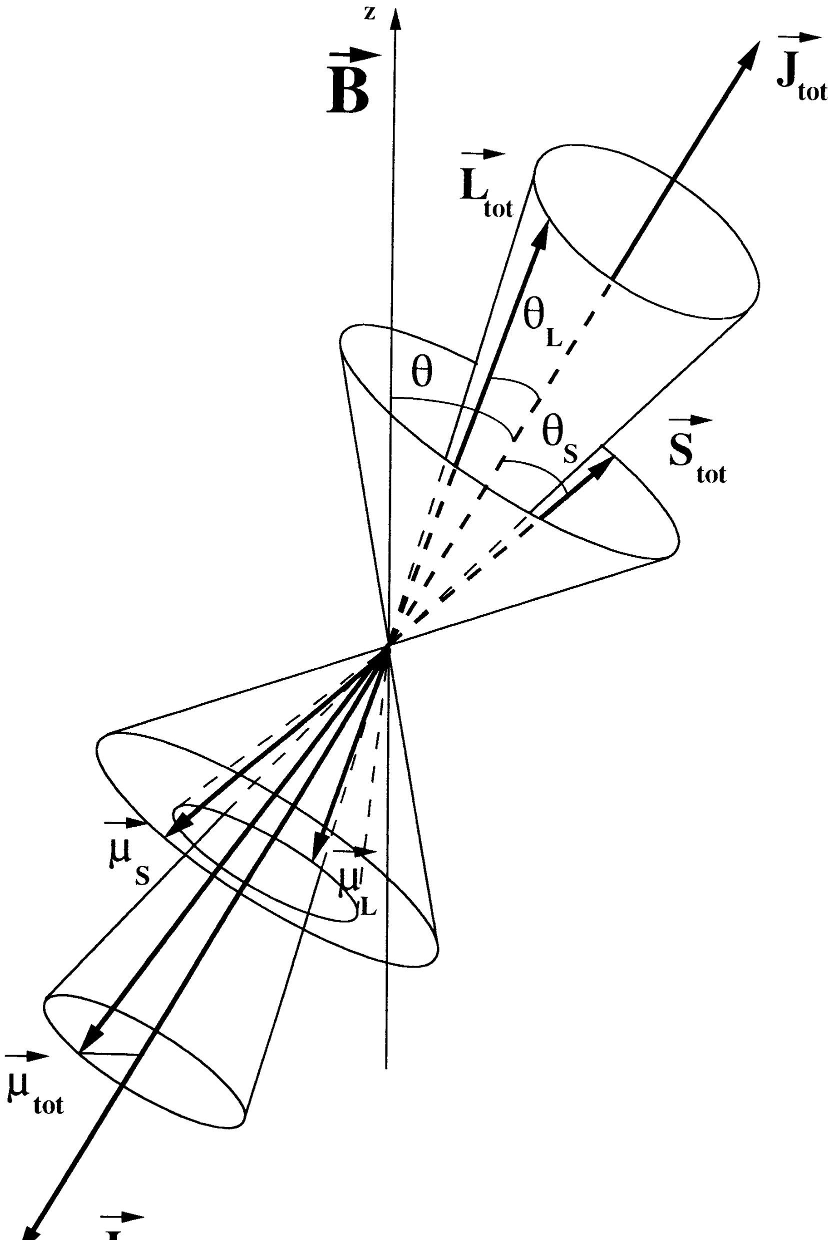
avec $\cos(\theta)$, $\cos(\theta_L)$ et $\cos(\theta_S)$ on a

$$\Delta E = \frac{e\hbar}{2m_e} m_{\text{tot}} g B = \mu_B m_{\text{tot}} g B$$

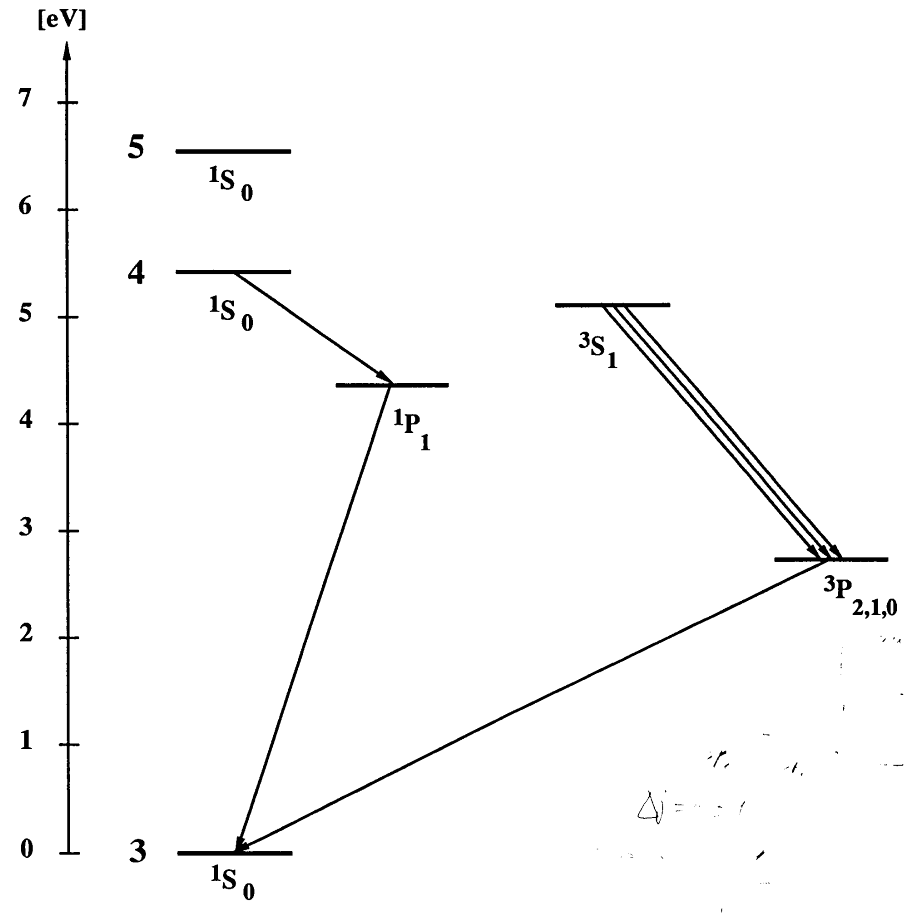
où g est le facteur de Landé. Une approximation de g est donnée par l'expression

$$g = 1 + \frac{j_{\text{tot}}(j_{\text{tot}}+1) + s_{\text{tot}}(s_{\text{tot}}+1) - \ell_{\text{tot}}(\ell_{\text{tot}}+1)}{2j_{\text{tot}}(j_{\text{tot}}+1)}$$

Si $\ell_{\text{tot}} = 0$, alors $j_{\text{tot}} = s_{\text{tot}}$ et $g = 2$.



L'effet Zeeman et le couplage L-S



Les premiers niveaux excités de l'atome de Mg

Exemple 10

La configuration d'un alcalino-terreux (colonne II) est celle du gaz rare qui le précède avec ns^2

$$[\text{gaz rare}]\ ns^2.$$

Si $n = 3$ c'est Mg et si $n = 4$ c'est Ca.

Prenons le cas de Mg

$$\text{Mg :}\quad [\text{Ne}]\ 3s^2.$$

Excitation : Un électron est amené de $3s^2$ à $3p$ ou à $4s$

1. [Ne] $3s^1$ $3p^1$ état excité avec $\ell = 0$ et $\ell = 1$. Alors

$$\begin{aligned} \ell_{\text{tot}} &= 1 \\ s_{\text{tot}} &= 0, 1 \\ j_{\text{tot}} &= 0^-, 0, 1, 2, \text{ soit } {}^1P_1, {}^3P_0, {}^3P_1, {}^3P_2 \end{aligned}$$

σ_{tot} \ m	1	0	-1
1	2	1	0
0	1	0	-1
-1	0	-1	-2

Addition :

$$\begin{aligned} \ell_{\text{tot}} &= 1 \\ s_{\text{tot}} &= |\ell_{\text{tot}} - s_{\text{tot}}| < j_{\text{tot}} < \ell_{\text{tot}} + s_{\text{tot}} \end{aligned}$$

2. [Ne] $3s^2$ $4s^1$ état excité avec $\ell = 0$ et $\ell = 0$ Ainsi

$$\begin{aligned} \ell_{\text{tot}} &= 0 \\ s_{\text{tot}} &= 0, 1 \end{aligned}$$

soit

$${}^1S_0, {}^3S_1.$$

On a alors

$$\ell_{\text{tot}} = s_{\text{tot}} = j_{\text{tot}} = 0$$

ou

$$\ell_{\text{tot}} = 0,\ s_{\text{tot}} = 1,\ j_{\text{tot}} = 1$$

L'état fondamental est

$$[\text{Ne}]\ 3s^2 :\quad {}^1S_0.$$

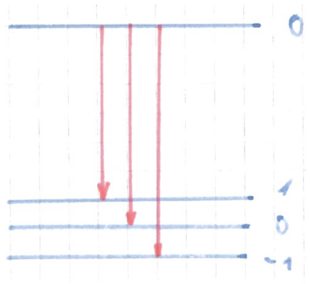
En général, on a

$$\Delta S_{\text{tot}} = 0$$

bien que ce soit une règle mal observée.

Effet Zeeman

1. ${}^1S_0 \to {}^1P_1$



C'est l'effet Zeeman *normal* (i. e. explicable classiquement, et dont l'explication classique a été donnée au début du XX^e siècle)

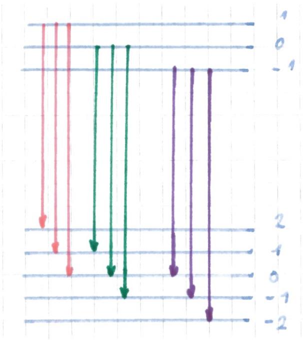
2. $^3S_1 \rightarrow {}^3P_2$

$$^3S_1 \;\rightarrow\; g = 1 + \frac{1(1+1)+1(1+1)-0}{2(1+1)} = 2$$

et

$$^2P_2 \;\rightarrow\; g = 1 + \frac{2(2+1)+1(1+1)-1(1+1)}{2\cdot 2(2+1)} = 1.5$$

Or le facteur de Landé caractérise l'écart entre les raies (écart plus grand dans le premier cas que dans le second).



On a 9 raies : c'est l'effet Zeeman *anormal*.

Remarque 1

L'effet *Paschen-Back* dans un champ magnétique très intense. $\vec{L}$ et $\vec{S}$ sont alors découplés et précessent indépendamment autour de $\vec{B}$.

Chapitre 6

Courte introduction à la physique quantique

6.1 Effet Compton

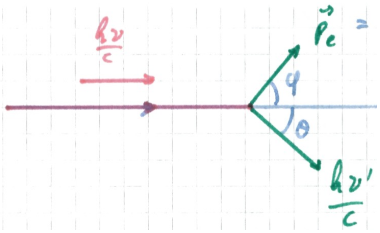
En 1923 Compton irradie un bloc de graphite avec des rayons X. En mesurant la longueur d'onde des rayons X diffusés λ', il obtint les résultats suivants

- λ' dépend de l'angle θ de diffusion.
- λ' ne dépend pas du matériau choisi.
- $\Delta\lambda = \lambda' - \lambda_0$ ne dépend que de l'angle θ.

Classiquement, $\Delta\lambda$ ne doit pas dépendre de l'angle.

Si les photons sont des particules, ils vont avoir des diffusions élastiques sur les électrons.

Le fait que $\Delta\lambda$ ne dépend pas du matériau, suggère que la diffusion se fait sur les électrons, dont on peut négliger l'énergie de liaison.



$\vec{p}_e$ est la quantité de mouvement de l'électron de recul (particule de recul). La quantité de mouvement du photon diffusé (particule diffusée) est $\frac{\hbar\nu'}{c}$.

La conservation de l'énergie

$$E_{\text{tot}} = h\nu + m_e c^2 = h\nu' + c\sqrt{m_e^2 c^2 + p_e^2}$$

où l'on a utilisé l'expression relativiste $E = c\sqrt{m_e^2 c^2 + p^2}$.

La conservation de la quantité de mouvement

$$\begin{cases} \frac{h\nu}{c} &= \frac{h\nu'}{c}\cos(\theta) + p_e\cos(\phi) \\ 0 &= \frac{h\nu'}{c}\sin(\theta) - p_e\sin(\phi) \end{cases}$$

donne

$$\nu - \nu' = \frac{h\nu\nu'}{m_e c^2}(1 - \cos(\theta))$$

soit

$$\begin{aligned} \Delta\lambda &= \lambda' - \lambda \\ &= \frac{h}{m_e c}(1 - \cos(\theta)) \\ &= 2\pi\lambda_C(1 - \cos(\theta)) \end{aligned}$$

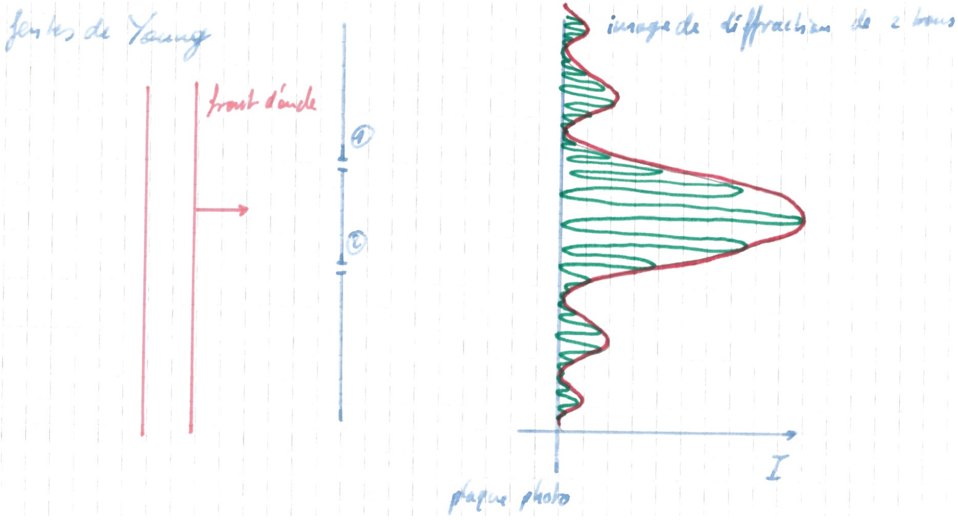
où l'on a définit la *longueur d'onde de Compton*

$$\lambda_c = \frac{\hbar}{m_e c}.$$

Le premier pic de la figure constitue la diffusion de Rayleigh sur l'atome C pris dans son entier ($M(C) \gg 20'000\, M(e^-)$, cf. feuille polycopiée).

6.2 Onde ou corpuscule

Fentes de Young Image de diffraction de deux trous.



Les photons impressionnent les grains etet donnent la mesure de l'intensité (bonne localisation du photon). Mais si une fente est fermée, on obtient la courbe rouge. La figure de diffraction devient celle formée par une seul trou.

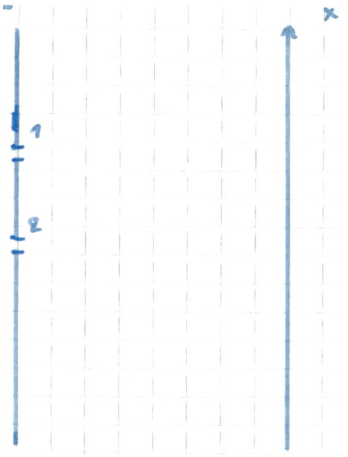
Le photon passant dans le trou 1 interfère-t-il avec un autre photon passant par 2 ?

Si nous baissons l'intensité de la source et laissons les deux fentes ouvertes, la figure d'interférence réapparaît.

On en vient à la conclusion que le photon est à la fois onde <u>et</u> corpuscule.

Chaque fois que l'on veut détecter la lumière expérimentalement, on fait appel à son aspect corpusculaire et on détruit l'aspect ondulatoire.

Avec des ondes



Soit deux ondes

$$\psi_1 = \psi_{01} e^{i(\omega_1 t + \delta_1)}$$

et

$$\psi_2 = \psi_{02} e^{i(\omega_2 t + \delta_2)}$$

Alors si une des fentes est fermée

$$I_k(x) = |\psi_k(x)|^2 = |\psi_{0k}|^2, \quad k \in \{1, 2\}.$$

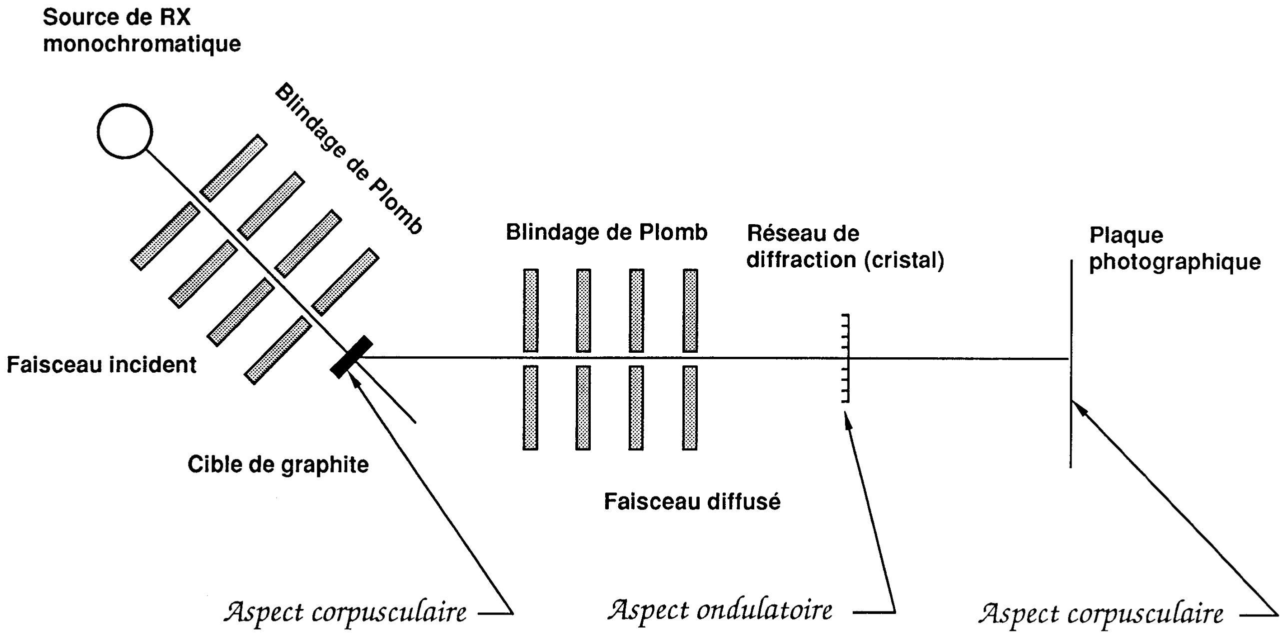
Alors que si les deux fentes sont ouvertes, on a

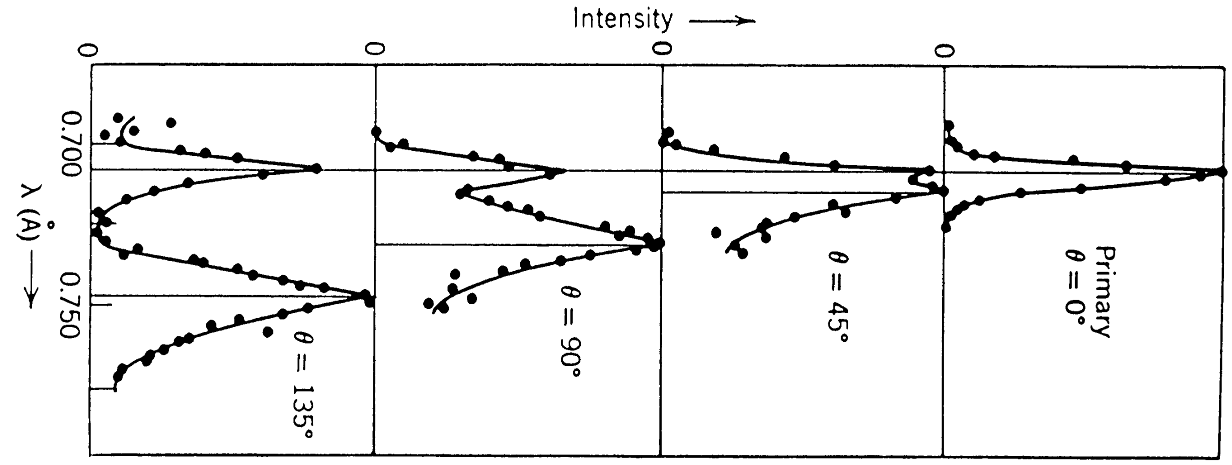
$$\begin{aligned} I_{1+2}(x) &= |\psi_1 + \psi_2|^2 \\ &= \psi_{01}^2 + \psi_{02}^2 + 2|\psi_{01}||\psi_{02}| \cos(\delta_1 - \delta_2) \\ &= I_1 + I_2 + 2\sqrt{I_1 I_2} \cos(\delta_1 - \delta_2) \end{aligned}$$

Le dernier terme représente le terme d'interférence.

$I_{1,2}$ et I_{1+2} sont les intensités mesurées en x sur l'écran. Ce sont les probabilités de trouver le photon entre x et $x + dx$.

L'effet Compton

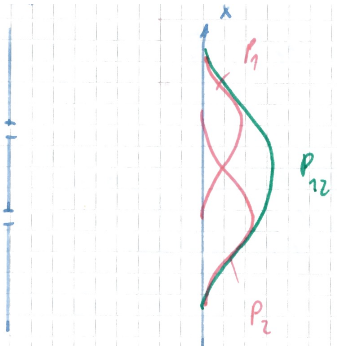




RX Mo 17,44 keV

λ = 0,711 Å

Avec des particules

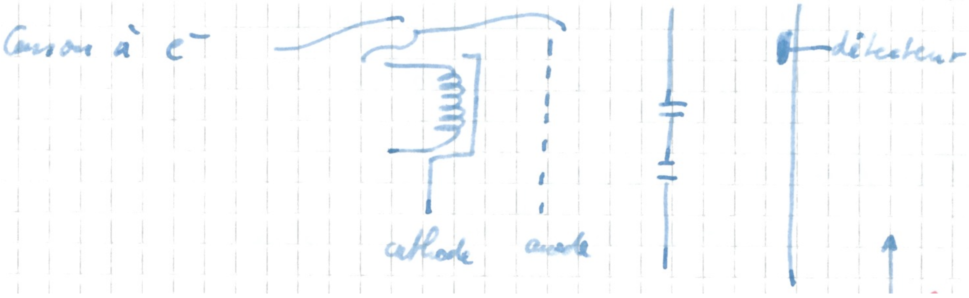


Soit $P_1(x)dx$ la probabilité de trouver les grains entre x et $x+dx$ avec le trou 2 fermé. et $P_2(x)dx$ la probabilité de trouver les grains entre x et $x+dx$ avec le trou 1 fermé.

On observe alors

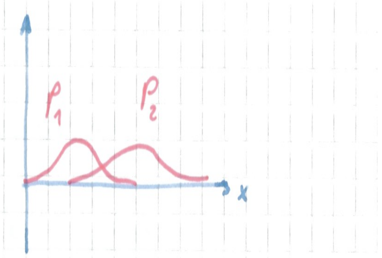
$$P_{12}(x) = P_1(x) + P_2(x).$$

Canon à électron

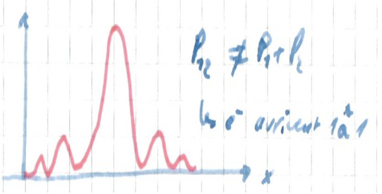


Résultat :

- Avec une des deux fentes fermée



- Avec les deux fentes ouvertes



Conclusion : La proposition « Chaque électron passe par la fente 1 ou par la fente 2 »est fausse

$$P_i(x) = |\psi_i(x)|^2, \quad i \in \{1, 2\}$$

mais

$$P_{1+2}(x) = |\psi_1(x) + \psi_2(x)|^2.$$

Les électrons (des particules) et les photons (des bosons d'interaction) arrivent individuellement comme des particules classiques, mais la probabilité de les trouver se comporte de manière ondulatoire.

6.3 L'observation perturbe

On peut imaginer un dispositif pour "voir" l'électron (expérience de pensée de Bohr, cf. feuille suivante).

On voit qu'en faisant diffuser des photons, l'électron et le photon diffusé vont partir dans des directions que l'on ne peut pas maîtriser. On ne peut pas mesurer précisément à la fois la position x et la quantité de mouvement p_x à mieux que

$$\Delta x \Delta p_x \geqslant \frac{\hbar}{2}$$

c'est la *relation d'incertitude de Heisenberg.*

Exemple 1

La vitesse d'une balle de fusil est de l'ordre de 300 $\mathrm{m\,s^{-1}}$ avec une précision de mesure de 10^{-4}.

Un neutron thermique (à Grenoble à l'institut Laue-Langevin ILL) est produit avec la même vitesse et la même précision.

neutron : La masse du neutron est $m_n = 1.6748 \cdot 10^{-27}$ kg. Alors

$$p = mv = 5.02 \cdot 10^{-25}\ \mathrm{kg\,m\,s^{-1}}$$
$$\Delta p = m\Delta v = 5.02 \cdot 10^{-29}\ \mathrm{kg\,m\,s^{-1}}$$
$$\Delta x \geqslant \frac{\hbar}{2\Delta p} = 1.05 \cdot 10^{-6}\ \mathrm{m}$$

balle de fusil : $m = 50$ g, et on obtient

$$\Delta x \geqslant 3 \cdot 10^{-32}\ \mathrm{m}$$

à comparer avec la taille d'un proton d'environ 10^{-15} m (soit 1 fm).
Ainsi, pratiquement, il n'y a pas vraiment de limite de précision imposée aux objets macroscopiques.

Retournons à l'expérience de pensée de Bohr. Après diffusion des photons, l'électron n'est plus dans l'état initial, mais si on ne l'illumine pas, on ne le voit pas.

On a ainsi une indétermination de la composante x de la quantité de mouvement

$$\Delta p_x = \frac{2h}{\lambda}\sin(\theta')$$

(En toute rigueur il aurait fallu utiliser $\lambda' = \lambda + \frac{h}{m_e c}(1-\cos(\theta))$).

Dans les instruments d'optique, l'image d'un point est une tache due à la diffraction

$$\Delta x = \frac{\lambda}{\sin(\theta')}$$

et on obtient

$$\Delta x \cdot \Delta p_x = 2h.$$

En physique classique

$$\vec{F} = \frac{d\vec{p}}{dt} = S\vec{\omega}$$

où $\vec{\omega}$ est la pression de radiation et $\omega = \mu\cos(i)$ avec μ la densité d'énergie, proportionnelle à l'intensité de la radiation, et i l'angle d'incidence.

On peut baisser à volonté

— l'intensité de l'onde, afin d'obtenir une meilleure précision sur p_x.

— λ, pour obtenir une meilleure précision sur Δx.

En physique quantique, on ne peut pas diminuer λ pour augmenter la précision sur x sans détériorer celle sur p_x. En effet, le photon porte une quantité de mouvement $p = \frac{h}{\lambda}$ et est insécable (on ne peut pas baisser l'intensité d'un seul photon).

Pour les particules, on a la relation de de Broglie

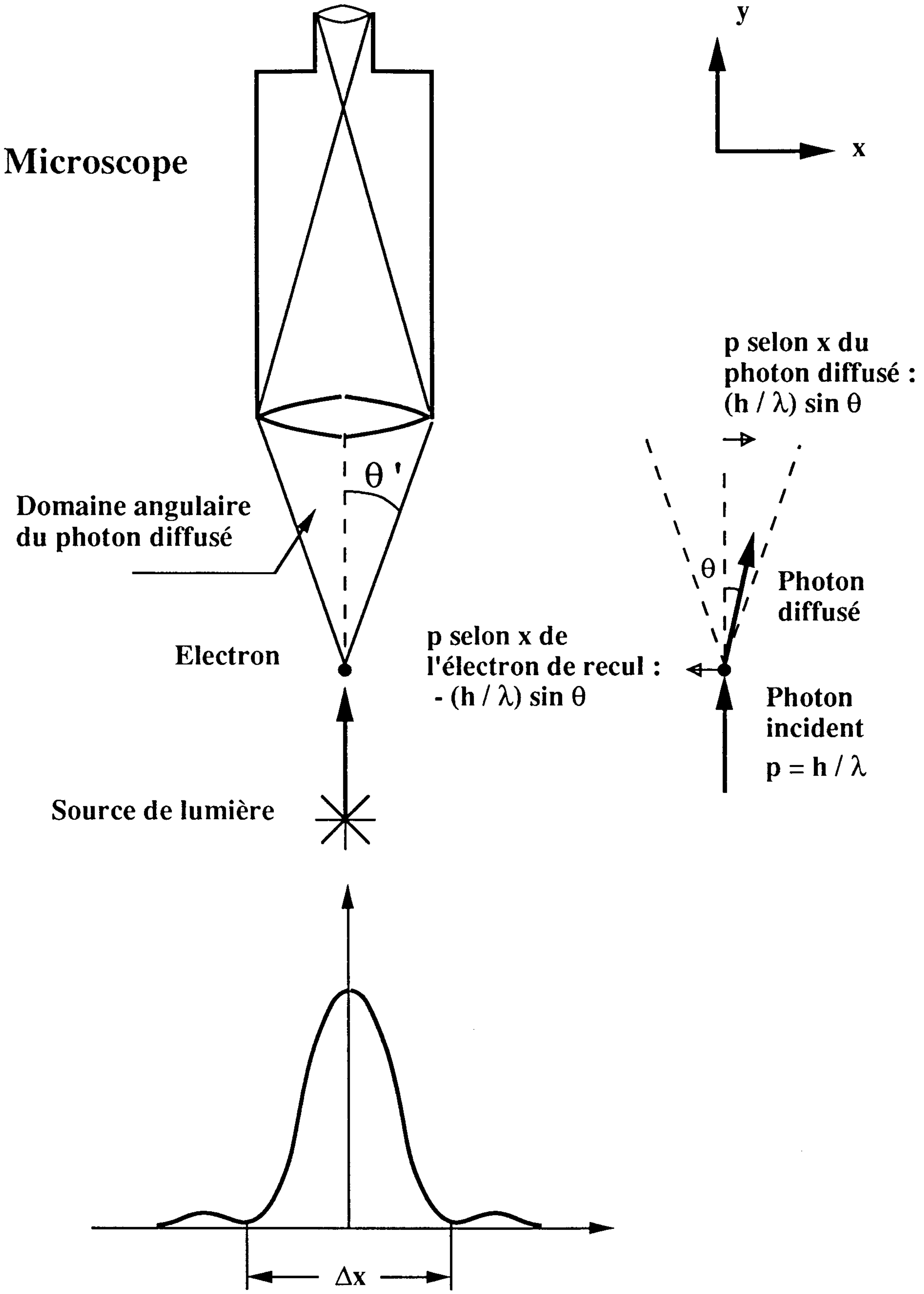
$$\lambda = \frac{h}{p}.$$

λ est la longueur d'onde de l'onde à partir de laquelle on détermine la densité de probabilité

$$\psi(x) = Ae^{i(kx+\omega t)}$$

pour une onde plane, λ est bien définie et donc p est bien déterminé. Mais dans ce cas

$$|\psi(x)|^2 = A^2 = \text{constante}.$$



Expérience de pensée de Bohr

Si l'on veut avoir une particule un tant soit peu localisée, il faut superposer des ondes planes

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{ikx} dx.$$

C'est une transformée de Fourier, dont la transformée inverse donne

$$A(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x) e^{-ikx} dk.$$

On a alors

$$k = \frac{2\pi}{\lambda} = \frac{p}{\hbar}.$$

Dans ces cas, la précision des mesures et donnée par

$$\begin{aligned} \Delta x = \sigma_x &= \sqrt{\overline{x^2} - \bar{x}^2} \\ \Delta p = \sigma_p &= \sqrt{\overline{p^2} - \bar{p}^2} \end{aligned}$$

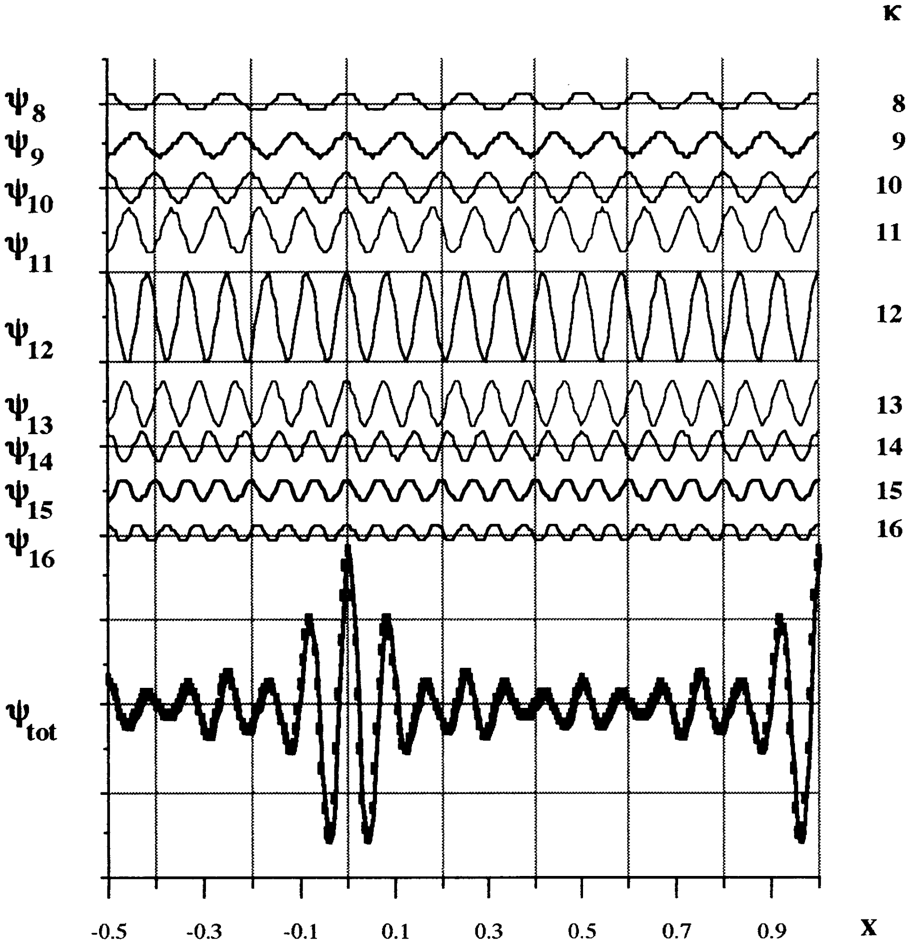
Or

$$\begin{aligned} \sigma_x^2 &= \int_{-\infty}^{\infty} (x - \bar{x})^2 |\psi(x)|^2 dx \\ &= \int_{-\infty}^{\infty} x^2 |\psi(x)|^2 dx - (\bar{x})^2 \\ &= \overline{x^2} - \bar{x}^2 \end{aligned}$$

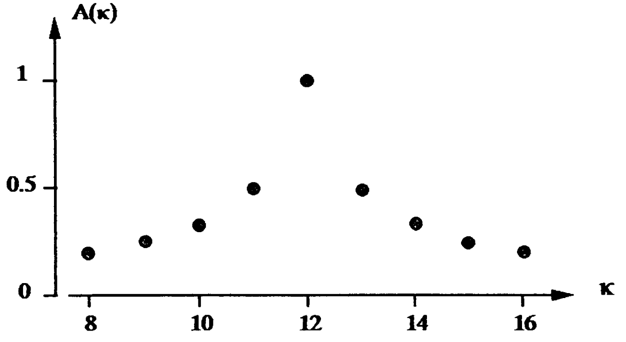
et

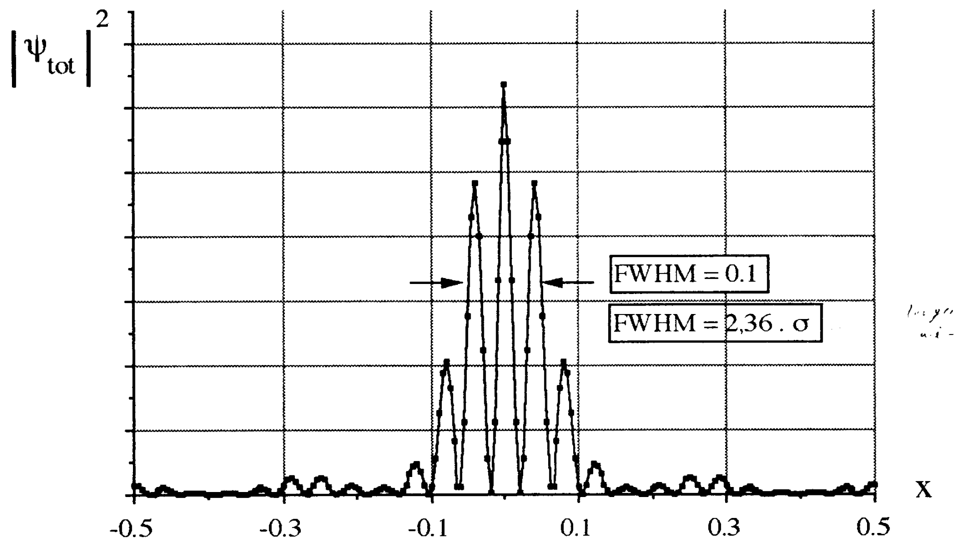
$$\sigma_p^2 = \int_{-\infty}^{\infty} (p - \bar{p})^2 |A(p)|^2 dp$$

La relation d'incertitude résulte du fait que $\psi(x)$ et $A(p)$ sont transformée de Fourier l'un de l'autre.



$\psi_{tot} = \sum_i A(\kappa_i) \cos[2\pi \kappa_i x]$ $\kappa_i = \frac{1}{\lambda_i}$

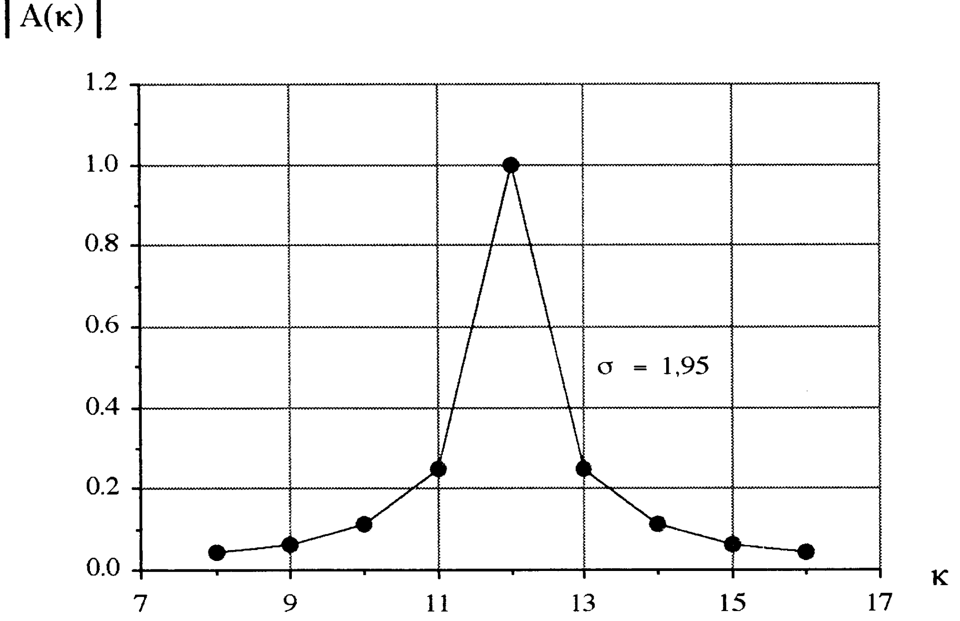




[illegible]

$$\sigma(x) \bullet \sigma(\kappa) \approx 0{,}0826 \approx \frac{1}{4\pi}$$

$\Rightarrow$ [illegible] λ



Annexe A

Exercices

Exercices de Physique IV

Série 1 16 avril 1993

1) Un atome de Fer est 25 fois ionisé. Calculez :

a) l'énergie du niveau fondamental de l'ion Fe $^{25+}$

b) l'énergie des photons émis lors des transitions de n = 2 à n = 1.

2) On peut former des "atomes d'hydrogène muonique" en faisant en sorte qu'un muon négatif (μ^-) soit capturé par un noyau d'hydrogène, prenant ainsi la place de l'électron.

a) Calculer la constante de Rydberg pour cet atome muonique $m_\mu = 207\, m_e$

b) Calculer le rayon de l'orbite de Bohr de cet atome $m_p = 1836\, m_e$

c) Calculer l'énergie des photons émis lors de la transition de n = 2 à n = 1.

3) On considère l'annihilation d'un électron et d'un positon au repos. Le positon est un "anti-électron", de charge + e et de même masse exactement que l'électron. L'annihilation se fait dans un référentiel S au repos et deux photons sont émis.

Donner l'énergie et la longueur d'onde des photons en fonction de la masse m_0 de l'électron.

L'annihilation se fait maintenant dans un référentiel S' en mouvement rectiligne uniforme à la vitesse **v** par rapport au référentiel au repos S. Calculer la quantité de mouvement et la longueur d'onde des photons tels que les verrait un observateur dans S.

[Remarque : Pour des particules sans masse, donc forcément relativistes, comme les photons, la quantité de mouvement est égale à $p = E / c$ et est reliée à la longueur d'onde par la relation de de Broglie $p = h / \lambda$]

Données numériques :

charge du noyau de Fer :	26
masse de l'électron :	0.511 MeV
masse du muon :	105.658 MeV
masse du proton :	938.272 MeV

Exercices de Physique IV

Série 2 23 avril 1993

1) La cavité d'un corps noir a la forme d'un cube de 2 cm de côté et le corps noir est à 1500 K.

a) Trouver le nombre de modes de vibrations par unité de volume dans la bande de longueurs d'onde de 499,5 nm à 500,5 nm.

b) Calculer l'énergie portée par le rayonnement dans cette bande de longueurs d'onde pour la cavité toute entière

- en assignant une valeur moyenne de kT à chacun des modes de vibration (Rayleigh-Jeans)
- en utilisant la loi de Planck.

2) Une bille de Tungstène de 2.3 cm de diamètre est chauffée à 2000 K, température à laquelle le W ne rayonne qu'environ 30% de l'énergie que rayonnerait un corps noir de même dimension et porté à la même température. Quelle serait la température d'un corps noir de même dimension qui rayonnerait la même quantité d'énergie que la bille de W ?

$T = (0,3)^{1/4} T_0 = 1480$ K

3) Une masse de 10 g est attachée à un ressort sans masse dont la constante est $k = 25\,\mathrm{N.m^{-1}}$. Supposons que cet oscillateur soit quantifié comme le sont les oscillateurs émettant des rayonnements.
Quelle serait le minimum d'énergie qui pourrait être absorbé par la masse de 10 g ?
Si la masse était initialement au repos et qu'elle absorbait cette quantité d'énergie, quelle serait le déplacement du ressort ?
Combien de quanta d'énergie la masse devrait-elle absorber pour que l'on puisse observer une élongation du ressort de 10 cm ?

On donne :

Constante de Boltzmann :	$k = 1.381\ 10^{-23}$ Joule/°K
Constante de Planck :	$h = 6.626\ 10^{-34}$ Joule.sec

Exercices de Physique IV

Série 3 30 avril 1993

1) Quelles sont les dimensions des paramètres A et B d'Einstein ?

2) A quelle longueur d'onde le nombre d'émissions spontanées serait-il égal au nombre d'émissions induites à température ambiante ?

3) Un laser est constitué d'une cellule amplificatrice terminée à ses extrémités par des miroirs plans. Cet ensemble constitue un résonateur à l'intérieur duquel la lumière ne peut avoir que des modes bien définis. Pour un laser He-Ne dont la longueur d'onde est de 632.8 nm, quel doit être la distance entre les miroirs pour que, avec un élargissement Doppler de la raie de 1000 MHz, on n'ait qu'un seul mode de vibration ?

$\Delta\nu = \frac{c}{2l}$

$l = \frac{c}{\Delta\nu} =$ [illegible]

Exercices de Physique IV

Série 4 7 mai 1993

1) Trouver l'équation horaire de l'oscillateur harmonique à une dimension par

a) l'équation de Lagrange

b) les équations canoniques de Hamilton

c) l'équation de Hamilton-Jacobi.

Dans la résolution de l'équation de Hamilton-Jacobi, interpréter les constantes qui apparaissent.

Exercices de Physique IV

Série 5   14 mai 1993

1) Montrer avec des arguments classiques que le module~~s~~ au carré du vecteur moment cinétique total , J^2, est égal à $j(j+1)$ en unités de h^2; dans cette expression, j est la valeur, en unité de h, de la plus grande projection de $\vec{J}$ sur un axe et prend des valeurs demi-entières.

2) Un faisceau d'atomes d'hydrogène, émis d'un four chauffé à 400K, est envoyé à travers un aimant de type "Stern-Gerlach" ayant un gradient de champ de 10 Tesla/m. Estimer la déviation de chaque atome à la sortie de l'aimant, déviation due à la force exercée sur son moment magnétique de spin.
[L' énergie cinétique d'un faisceau d'atomes, dans le cas d'une collimation, est en moyenne de 2kT, où k est la constante de Boltzmann].

3) Peut-on envisager faire l'expérience de Stern et Gerlach avec des ions ?

Exercices de Physique IV

Série 6 21 mai 1993

1) Considérez les états atomiques l = 4 , s= 1/2. Pour l'état avec la plus grande valeur de la projection du moment cinétique total $\vec{J}$, et la plus grande valeur possible du module de $\vec{J}$, calculez

a) l'angle entre les vecteurs $\vec{L}$ et $\vec{S}$

b) l'angle entre les vecteurs $\vec{\mu}_L$ et $\vec{\mu}_S$

c) l'angle entre le vecteur $\vec{J}$ et l'axe Oz.

2) Dans le spectre d'émission de l'hydrogène, on trouve une raie à 486.13 nm. En vous aidant des règles de sélections, trouvez les états entre lesquels la transition s'est faite. Tracez un diagramme des niveaux d'énergie en incluant le couplage spin orbite; désignez les niveaux par leur notation spectroscopique (ex : $1s_{1/2}$...)

Exercices de Physique IV

Série 7 28 mai 1993

1) Calculez le déplacement du niveau d'énergie $n = 2, l = 1$ dans le couplage spin-orbite de l'atome d'hydrogène, en utilisant comme rayon moyen celui de l'orbite de l'atome de Bohr.
Quel devrait être le champ magnétique extérieur que l'on devrait appliquer pour que, agissant sur un moment magnétique de spin, ce champ produise le même déplacement du niveau d'énergie ?

On donne : magnéton de Bohr

$$\mu_B = \frac{e\hbar}{2.\, m_e} = 5{,}788\,382\; 10^{-11}\ \text{MeV}.\,\text{T}^{-1}$$

2) Trois électrons sont sur une sous-couche $l = 1$. Quelles sont les projections possibles σ_{tot} du spin total $\vec{S}_{tot}$ et m_{tot} du moment cinétique orbital total $\vec{L}_{tot}$?

Exercices de Physique IV

Série 9 11 juin 1993

1) Nous aimerions mesurer simultanément la position et la longueur d'onde d'un photon. La mesure donne $\lambda = 600$ nm et nous utilisons un appareillage qui nous permet d'atteindre une précision de 10^{-6} dans cette mesure. Quelle serait l'incertitude minimale que nous pourrions atteindre dans la détermination de la position du photon ?

2) On fait diffuser par effet Compton les faisceaux de photons suivants sur un bloc de graphite :

- Rayons gamma du ^{137}Cs , énergie de 662 keV,
- Rayons X du Molybdène, énergie de 17.44 keV,
- Lunière visible, $\lambda = 500$ nm.

On détecte les photons diffusés à 90° par rapport à la direction des photons incidents. En faisant l'hypothèse que l'énergie de liaison des électrons dans le Carbone peut être négligée, calculer la différence relative ($\Delta\lambda$ / λ) entre la longueur d'onde des photons diffusés et des photons incidents. Supposons que l'énergie de liaison de l'électrons dans le Carbone est de 4 eV, que pourrait-on dire de la faisabilité de l'expérience pour les trois faisceaux de photons précédents ?

Annexe B

Historic Papers

The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part I. Theory and Methods. By D. R. HARTREE, Ph.D., St John's College.

[*Received* 19 November, *read* 21 November, 1927.]

§ 1. *Introduction.*

On the theory of atomic structure proposed by Bohr, in which the electrons are considered as point charges revolving in orbits about the nucleus, the orbits being specified by quantum conditions, it is well known that both a qualitative and an approximate quantitative explanation of many features of the simpler optical spectra and of X-ray spectra of atoms with many electrons (e.g. Rydberg sequences in optical spectra, term magnitudes in both X-ray and optical spectra) can be given, if the assumption is made that the effects of the electrons on one another can be represented by supposing each to move in a central non-Coulomb field of force*; further, the additional concept of a spinning electron provides a similar explanation of other features of these spectra† (e.g. doublet structure of terms and magnitude of doublet separation, anomalous Zeeman effect). This assumption of a central field was admittedly a rough approximation made in the absence of any detailed ideas about the interaction between the different electrons in an atom, but in view of its success as a first approximation for the orbital atom model, the question arises whether the same simple approximations may not give useful results when applied to the new formulation of the quantum theory which has been developed in the last two years.

The wave mechanics of Schrödinger‡ appears to be the most suitable form of the new quantum theory to use for this purpose, and will be adopted throughout. Further, if ψ is a solution of the wave equation (suitably normalised), the suggestion has been made by Schrödinger, and developed by Klein§, that $|\psi|^2$ gives the volume density of charge in the state described by this ψ; whether this interpretation is always applicable may be doubtful, but for the wave functions corresponding to closed orbits of electrons in an atom, with which alone this paper will be concerned, it has the advantage that it gives something of a model both of the stationary states (if ψ only contains one of the characteristic functions) and of the process of radiation (if ψ is the sum of

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* See, for example, M. Born, *Vorlesungen über Atommechanik* (or the English translation, *The Mechanics of the Atom*), Ch. III.

† For a general review, see R. H. Fowler, *Nature*, Vol. CXIX, p. 90 (1927); for a more detailed treatment, F. Hund, *Linienspektren*, Ch. III.

‡ E. Schrödinger, *Ann. der Phys.*, Vol. LXXIX, pp. 361, 489; Vol. LXXX, p. 437; Vol. LXXXI, p. 109 (1926); *Phys. Rev.*, Vol. XXVIII, p. 1049 (1926).

§ F. Klein, *Zeit. f. Phys.*, Vol. XLI, p. 432 (1927).

a number of characteristic functions), and gives a simple interpretation of the formula of the perturbation theory, namely, that the change in the energy is the perturbing potential averaged over the distribution of charge. Also in considering the scattering of radiation of wave length not large compared to atomic dimensions, the coherent radiation scattered by a hydrogen atom is given by treating the scattering as classical scattering by the distribution of charge given by Schrödinger's suggestion (if the wave length is not too short)*, and this is probably true for any atom. For the purpose of this paper the suggestion will be adopted literally; the charge distribution for an atom in a stationary state is then static (it does not necessarily follow that the charge itself is static).

Further, the distribution of charge for a closed n_k group of electrons is centrally symmetrical†, which suggests that on the wave mechanics the assumption of a central field may give results more satisfactory in detail than could be expected on the older form of quantum theory.

Schrödinger's suggestion concerning the interpretation of ψ affords a hope that it may be possible to consider the internal field of the atom as being due to the distribution of charge given by the characteristic functions for the core electrons; we may, in fact, attempt to find a field of force such that the total distribution of charge, given by the characteristic functions in this field (taken in suitable multiples corresponding to the numbers of electrons in different n_k groups), reproduces the field. The solution of this problem, or rather a refinement of it, is, indeed, the main object of the quantitative work to be considered here.

One point of contrast between the old 'orbital' mechanics and the new wave mechanics may be emphasised here at once. On the orbital mechanics the motion of an electron in an orbit lies wholly between two radii (the potential energy and so the total energy depends on the field at distances greater than the maximum radius, but this does not affect the motion); on the wave mechanics the solution of the wave equation is different from zero at all but a finite number of values of the radius, and depends on the field at all distances (though certainly the solution is very small, and depends on the field to an extent negligible in practice, at very large radii and usually at very small radii).

It will be seen later (§ 2) that, for a given characteristic function, it is possible to specify two points which may to a certain extent be considered to mark the apses of the corresponding orbit in the orbital atom model, but the characteristic function is not zero

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* I. Waller, *Nature*, Vol. cxx, p. 155 (1927); *Phil. Mag.* Nov. 1927 (Supplement).

† See A. Unsöld, *Ann. der Phys.*, Vol. LXXXII, p. 355, §§ 5 and 6. Unsöld proves this by considering the energy of an indefinitely small charge in the field of a closed group; it also follows directly for the charge distribution from Unsöld's formulae (67), (69).

outside them; as a consequence, it is not possible to make a strict separation between 'penetrating' and 'non-penetrating' solutions of the wave equation as it was possible to divide orbits into two such classes. This suggests that it would be interesting to enquire what occurs in the wave mechanics in cases when on the orbital mechanics an atom may have a 'penetrating' and a 'non-penetrating' orbit with the same quantum numbers* n_k, and also whether the comparatively large doublet separations of some terms corresponding to orbits classed as 'non-penetrating' can be explained by the non-zero fraction of the total charge which must, on the wave mechanics, lie inside the core.

Associated with this question is that of the assignment of the principal quantum number n to a solution of the wave equation in a non-Coulomb field; in the orbital mechanics this was assigned in a perfectly definite way, to which there is no direct analogy on the wave mechanics. In this paper l will be written for the subsidiary quantum number, taking integer values from zero upwards, which is less by unity than Bohr's azimuthal quantum number k; this follows the practice adopted by various writers†; to avoid altering a notation which has become familiar, k will be retained as a suffix in referring to the quantum numbers of an electron, so that $l=k-1$. It seems best to define n such that $n-k=n-l+1$ is the number of values of the radius r for which $\psi=0$, excluding $r=0$ (if it is a root) and $r=\infty$; $n-l$ is then the number of values of r for which $|\psi|^2$ is a maximum. This agrees with Bohr's principal quantum number n for the hydrogen atom.

Both in order to eliminate various universal constants from the equations and also to avoid high powers of 10 in numerical work, it is convenient to express quantities in terms of units, which may be called 'atomic units.' defined as follows:

Unit of length, $a_H=h^2/4\pi^2me^2$, on the orbital mechanics the radius of the 1-quantum circular orbit of the H-atom with fixed nucleus.

Unit of charge, e, the magnitude of the charge on the electron.

Unit of mass, m, the mass of the electron.

Consistent with these are:

Unit of action, $h/2\pi$.

Unit of energy, e^2/a = potential energy of charge e at distance a from an equal charge $=2hcR=$ *twice* the ionisation energy of the hydrogen atom with fixed nucleus.

Unit of time, $1/4\pi cR$.

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* For example, on the orbital mechanics, Rb, Cu, Ag, Au, have 3_3 X-ray orbits, and for the neutral atoms of these elements the first d term corresponds to a non-penetrating 3_3 orbit.

† See, for example, F. Hund, *op. cit.*, *passim*.

These units being consistent, the ordinary equations of classical and wave mechanics hold in them; in particular Schrödinger's wave equation for the motion of a point electron with total energy E, in a static field in which its potential energy is V, becomes

$$\nabla^2\psi + 2(E - V)\psi = 0. \qquad \text{......(1·1)}$$

For an attractive field, V is always negative; it is convenient to write

$$V = -v, \qquad \text{......(1·2)}$$

so that the quantity v calculated in numerical work is usually positive.

For terms of optical and X-ray spectra, E is always negative. It is convenient to write

$$E = -\tfrac{1}{2}\epsilon, \qquad \text{......(1·3)}$$

the factor $\frac{1}{2}$ being introduced in order that ϵ shall be the energy as a multiple of the ionisation energy of the hydrogen atom; if a characteristic value of the solution of the wave equation gives directly a spectral term, of wave number ν, then

$$\epsilon = \nu/R. \qquad \text{......(1·4)}$$

The wave equation in terms of v and ϵ is

$$\nabla^2\psi + (2v - \epsilon)\psi = 0. \qquad \text{......(1·5)}$$

The present paper is divided into two parts; this, the first, deals with the methods used for solving this equation for a given non-Coulomb central field, and with the relevant theory; the second with the question of the determination of the potential v, and with an account and discussion of the results for some actual atoms.

§ 2. *Theory.*

When the field is spherically symmetrical so that v is a function of the radius r only, and spherical polar coordinates r, θ, ϕ are used, ψ separates into a product of a function $\chi(r)$ of r only, and a surface spherical harmonic $S(\theta, \phi)$; if l is the order of the spherical harmonic, the function χ satisfies the equation

$$\frac{d^2\chi}{dr^2} + \frac{2}{r}\frac{d\chi}{dr} + \left[2v - \epsilon - \frac{l(l+1)}{r^2}\right]\chi = 0 \qquad \text{......(2·1)}$$

or, writing

$$P = r\chi \qquad \text{......(2·2)}$$

and using dashes to denote differentiation with respect to r,

$$P'' + [2v - \epsilon - l(l+1)/r^2]P = 0. \qquad \text{......(2·3)}$$

This is the form in which the wave equation is used in the greater part of this paper.

There are three advantages in working with P rather than with χ; first, the differential equation is simpler, secondly, P^2 gives the *radial* density of charge if P is suitably normalised (i.e. $P^2 dr \Big/ \int_0^\infty P^2 dr$ is the charge lying between radii r and $r+dr$)*, and this is the quantity often required in applications, thirdly, as a consequence of this, P^2 is the weighting function for the perturbing potential at different radii, in the case of a perturbation which is centrally symmetrical.

If we recall that the wave equation is derived from the classical Hamiltonian equation of the problem by the substitution

$$p_x = i \frac{\partial}{\partial x}, \text{ etc.}$$

(in atomic units), and also that on the orbital mechanics the radial momentum p_r in an orbit of angular momentum k (in atomic units $h/2\pi$) is given by

$$p_r^2 = 2v - \epsilon - k^2/r^2,$$

equation (2·3) suggests that as far as we can picture an orbit corresponding to a given solution of the wave equation, its angular momentum in atomic units is given by $k^2 = l(l+1)$ (l integral), and that its apses are given by the roots of

$$2v - \epsilon - l(l+1)/r^2 = 0, \qquad \ldots\ldots(2{\cdot}4)$$

i.e. by the points of inflexion of P other than those which occur at the points where $P = 0$. Usually this expression has two roots, between which it is positive; between them P has an oscillatory character, outside them it has an exponential character; it may have one root only (in the case $l = 0$) or four (for $l > 0$ only). On the orbit model of the atom, when four roots occur they give the apses of an internal and an external orbit with the same energy†; what then happens on the wave mechanics will be discussed in the second part of this paper.

The first requirement is a method for finding values of ϵ for which, given v as a function of r, the solution P of (2·3) is zero at $r = 0$ and ∞ (Schrodinger's condition is that ψ should be finite

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* According to Schrödinger's interpretation of ψ (§ 1) the charge lying in an element of volume defined by $dr\,d\theta\,d\phi$ is $\psi^2 r^2 \sin^2\theta\, dr\,d\theta\,d\phi / \int \psi^2 r^2 \sin^2\theta\, dr\,d\theta\,d\phi$, the integral being over all space, so that the charge lying between radii r and $r+dr$ is

$$\psi^2 r^2 dr \Big/ \int_0^\infty \psi^2 r^2 dr = P^2\,dr \Big/ \int_0^\infty P^2 dr,$$

the integration of the spherical harmonic factor cancelling out.

† In general the internal and external orbits with the same energy will not both be quantum orbits, but when they occur it is usually possible (always if integral quantum numbers are used) to obtain an internal and an external quantum orbit with the same quantum numbers.

everywhere; since $P = r\chi$, P must be 0, not only finite, at $r = 0$), and the solution for each value of ϵ. The value of ϵ then gives a spectral term for the motion of an electron in the field v, and, with the arbitrary multiplying constant adjusted so that $\int_0^\infty P^2 dr = 1$, P^2 gives the radial density of charge. In this part of the paper we shall consider the solution of (2·3) for a given v subject to the necessary boundary conditions, and in the second consider how v may itself be related to the solutions of (2·3).

For any value of ϵ, we can find a solution of (2·3) which is zero at $r = 0$ and a solution which is zero at $r = \infty$. Except for certain values of ϵ, these solutions are independent, and the one zero at $r = 0$ is infinite at $r = \infty$ and vice versa, but for certain values of ϵ the two solutions (apart from an arbitrary multiplying constant in each) are the same. These are the values of ϵ and the solutions required, and this aspect of them suggests the following method of determining them, viz. integrate the equation* outwards from $P = 0$ at $r = 0$, and inwards from $P = 0$ at $r = \infty$, and by trial find a value of ϵ for which these solutions meet at some convenient intermediate radius r; since each solution contains an arbitrary multiplying constant, P'/P rather than P itself has to be the same in both solutions. This is in effect the method adopted in the numerical work (for an example see § 10), and it has proved very satisfactory in practice. In finding the required value of ϵ, it is not necessary to integrate from the beginning for each value of ϵ; it is possible to calculate directly (and accurately, not only to the first order) the variation in the solution for a variation in the value of ϵ, and this can be used to shorten the numerical work considerably. A general variation equation of which this is a special case will be given in § 4.

Over most of the range of r for which P is appreciable, equation (2·3) as it stands is in a suitable form for numerical integration; but for small values of r (out to or a little beyond the first maximum of $|P|$) and for large values (from about the last maximum of $|P|$ outwards) other forms are more suitable, and will now be considered.

If we write $$\eta = -P'/P, \qquad \text{......(2·5)}$$ equation (2·3) reduces to a non-linear first order equation in η, viz.

$$\eta' = \eta^2 + 2v - \epsilon - l(l+1)/r^2, \qquad \text{......(2·6)}$$

and it might seem that this equation, being of the first order so that one of the integrations for P is reduced to a simple quadrature, would be more suitable for numerical work than the equation for P

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* An outline of the method used for the practical numerical integration of the equation for P is given in § 9.

itself, but the zeros of P give rise to infinities in η and η' which make numerical work with this equation impracticable except in certain regions. For large values of r (as specified above) it is, however, very suitable.

§ 3. *Form of Solution for Small Values of r.*

When r is small the substitution of

$$P = r^c(1 + a_1 r + \ldots) \qquad \ldots\ldots(3{\cdot}1)$$

provides the indicial equation

$$c(c-1) - l(l+1) = 0,$$

of which the positive root is $c = l + 1$, so that for small r the solution remaining finite at $r = 0$ behaves as r^{l+1}.

In the neighbourhood of $r = 0$ it is therefore convenient to work with

$$Q = Pr^{-(l+1)} \qquad \ldots\ldots(3{\cdot}2)$$

rather than with P, or with

$$-Q'/Q = \xi = \eta + (l+1)/r \qquad \ldots\ldots(3{\cdot}3)$$

rather than with η. The equation for ξ is

$$\xi' = \xi^2 - 2(l+1)\xi/r + 2v - \epsilon, \qquad \ldots\ldots(3{\cdot}4)$$

and is the most convenient one to use up to or a little beyond the first maximum of $|P|$; the only difficulty is at $r = 0$ itself, where the second and third terms of this expression for ξ' become infinite. This difficulty is avoided by the use of the solution in series to give values of ξ and ξ' at $r = 0$.

For an atom of atomic number N we certainly have, in the neighbourhood of $r = 0$,

$$v = N/r + v_0 + o(1) \qquad \ldots\ldots(3{\cdot}5)$$

(v_0 is the potential at the nucleus of the negative distribution of charge due to the outer electrons, and is of course negative), and the series solution of the equation for ξ (or of that for P) gives

$$\xi = N/(l+1), \quad \xi' = [N^2/(l+1)^2 + 2v_0 - \epsilon]/(2l+3), \text{ at } r = 0. \qquad \ldots\ldots(3{\cdot}6)$$

With these initial values, the numerical integration can be begun without difficulty.

§ 4. *Variation Equations.*

It may happen that for a certain range of r a solution of the equation for P has been found for a certain potential function v and a certain value of ϵ, and that the solution for a different function v or a different value of ϵ, or both, is required. [This is more general than the 'perturbation theory' of wave mechanics, for which the original solution must be a characteristic solution of the differential equation, and the variation of ϵ is connected in a definite way with the variation of v.] The difference in the solution for a change of value of ϵ is required, for example, in the process of finding by trial a value of ϵ which is a characteristic value for any particular field.

Let P be the solution of

$$P'' + [2v - \epsilon - l(l+1)/r^2]\,P = 0, \qquad \ldots\ldots(4{\cdot}1)$$

which has already been found, and let the solution be required of

$$P_1'' + [2v_1 - \epsilon_1 - l(l+1)/r^2]\,P_1 = 0. \qquad \ldots\ldots(4{\cdot}2)$$

Writing Δ for the variation of a quantity *at given* r, i.e.

$$v_1 - v = \Delta v, \quad \epsilon_1 - \epsilon = \Delta\epsilon, \quad P_1 - P = \Delta P,$$

and subtracting, we have

$$(\Delta P)'' + [2v_1 - \epsilon_1 - l(l+1)/r^2]\,\Delta P + [2\Delta v - \Delta\epsilon]\,P = 0, \qquad \ldots\ldots(4{\cdot}3)$$

which is an exact (not only first order) equation for ΔP, and it is usually easier to solve this equation numerically than to work through a solution of (4·2) independent of the solution of (4·1).

In the particular case $\Delta v = 0$, $\Delta\epsilon \to 0$, we have

$$\left(\frac{\partial P}{\partial\epsilon}\right)'' + [2v - \epsilon - l(l+1)/r^2]\left(\frac{\partial P}{\partial\epsilon}\right) - P = 0 \qquad \ldots\ldots(4{\cdot}4)$$

(the differentiation with respect to ϵ being for r constant), for which a formal solution in quadratures can be found, but on account of the zeros of P this formal solution is more trouble for numerical work than the integration of the equation as it stands.

It is interesting to note that a simple derivation of the formula for the first order perturbation in ϵ for a central perturbing field can be found from (4·3).

For this purpose, suppose the value of ϵ in (4·1) to be a characteristic value for the field v, and P to be the corresponding characteristic function. Consider first order variations only, i.e. write v and ϵ for v_1 and ϵ_1 in the coefficient of ΔP in (4·3), giving

$$(\Delta P)'' + [2v - \epsilon - l(l+1)/r^2]\,\Delta P + [2\Delta v - \Delta\epsilon]\,P = 0. \qquad \ldots\ldots(4{\cdot}5)$$

Knowing the solution P of (4·1), adopt the standard method for the solution of (4·5), i.e. write

$$\Delta P = PR; \qquad \ldots\ldots(4{\cdot}6)$$

the terms in R disappear on substituting, leaving

$$PR'' + 2P'R' + [2\Delta v - \Delta\epsilon]\,P = 0$$

whence, multiplying by P and integrating,

$$\Big[P^2R'\Big]_0^\infty + \int_0^\infty [2\Delta v - \Delta\epsilon]\, P^2 dr = 0.$$

Also from (4·6) $\quad P^2R' = P(\Delta P)' - P'(\Delta P).$

Now if P and P_1 are characteristic solutions of (4·1) and (4·2) respectively, P, P', P_1 and P'_1 (and so ΔP and $\Delta P'$) must all be zero at $r=\infty$, and also at $r=0$ except for $l=0$, while, for $l=0$, P and P_1 (and so ΔP) are zero at $r=0$ and P', $\Delta P'$ are finite. Thus in all cases P^2R' is zero at both limits, whence

$$\int_0^\infty [2\Delta v - \Delta\epsilon]\, P^2 dr = 0,$$

$$\Delta\epsilon = \left[\int_0^\infty 2\Delta v P^2 dr\right] \Big/ \left[\int_0^\infty P^2 dr\right] \qquad \text{......(4·7)}$$

which is the form Schrödinger's perturbation equation* takes for a central perturbation of a central field (it must be remembered that ϵ is defined as *twice* the negative energy in atomic units).

Equations for the variation of ξ or η due to difference of potential function or of ϵ can be obtained in the same way as (4·3) for the variation of P. The equation for $\Delta\eta$ is

$$(\Delta\eta)' = 2\eta\Delta\eta + (\Delta\eta)^2 + 2\Delta v - \Delta\epsilon, \qquad \text{......(4·8)}$$

and since Δ indicates a variation for a given value of r, it follows from the definition of ξ (3·4) that $\Delta\xi = \Delta\eta$.

To find ΔP, we have by definition of η

$$\eta = -d(\log P)/dr,$$

so that $\quad \Delta\eta = -d(\Delta \log P)/dr = -d[\log(P_1/P)]/dr.$

For the solution P which is zero at the origin, it is most convenient to choose the arbitrary multiplying constants so that $P_1/P = 1$ at $r=0$; if this is done, then

$$P_1/P = \exp\left[-\int_0^r \Delta\eta\, dr\right]$$

(exactly, not only to the first order).

§ 5. *Form of Solution in Region where Deviation from Coulomb Field is Inappreciable.*

As already explained, for large values of r the solution used in the numerical work is that which is zero at $r=\infty$; in the region where the field can be taken to be that of a point charge equal to the core charge C, certain relations between different solutions can be used to shorten the numerical work by avoiding the numerical integration in each particular case.

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* *Ann. der Phys.*, Vol. LXXX, p. 443, equation (7').

It is most convenient for work with these solutions to use as independent variable not r but

$$\rho = Cr/n^*, \qquad \text{......(5·1)}$$

the 'effective quantum number' n^* of a term being defined in the usual way,

$$\epsilon = C^2/(n^*)^2. \qquad \text{......(5·2)}$$

For the field of a point charge C, for which $v = C/r$, the equation (2·3) for P becomes, with ρ as independent variable,

$$\frac{d^2P}{d\rho^2} + \left[\frac{2n^*}{\rho} - 1 - \frac{l(l+1)}{\rho^2}\right] P = 0, \qquad \text{......(5·3)}$$

for which the solution is a confluent hypergeometric function†

$$P = W_{n^*,\, l+\frac{1}{2}}(2\rho),$$

as pointed out by Eddington‡ and Sugiura§. From the asymptotic formula for the confluent hypergeometric function|| it follows that for large ρ the solution of (5·3) which is zero at $\rho = \infty$ behaves like $\rho^{n^*} e^{-\rho}$ as $\rho \to \infty$, so, in order to work with a function which remains finite, we define M by

$$P = \rho^{n^*} e^{-\rho} M \qquad \text{......(5·4)}$$

(apart from an arbitrary multiplying constant); an asymptotic series for M in inverse powers of ρ can be written down from that for the confluent hypergeometric function, but for values of ρ which are practically interesting the series diverges too early to be of much value, and M is best found by numerical integration of the appropriate equation (except of course for integral values of n^*, for which M is a polynomial of degree $n^* - l - 1$ in $1/\rho$).

In integration inwards from $r = \infty$, r is clearly an unsuitable independent variable; the most suitable one appears to be $1/\rho$ (rather than $1/r$), and with this independent variable M satisfies

$$u^2 \frac{d^2M}{du^2} - 2[(n^* - 1)u - 1]\frac{dM}{du} + (n^* - l - 1)(n^* + l)M = 0; \qquad \text{......(5·5)}$$

we will write $M(n^*, l)$ for the solution of this equation with given values of n^* and l, and take the dependent variable u as understood.

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† E. T. Whittaker and G. N. Watson, *Modern Analysis*, Ch. XVI.

‡ A. S. Eddington, *Nature*, Vol. CXX, p. 117 (1927).

§ Y. Sugiura, *Phil. Mag.*, Ser. 7, Vol. IV, p. 498 (1927).

|| Whittaker and Watson, *op. cit.*, § 16·3.

As with the equation for P, it is convenient to work with the logarithmic derivative of M when u is much smaller than the first zero of M. The equation for

$$\zeta = -d(\log M)/du \qquad \text{......(5·6)}$$

is found to be

$$u^2 \frac{d\zeta}{du} = (n^* + l)(n^* - l - 1) - 2\zeta[1 - (n^* - 1)u] + \zeta^2 u^2. \qquad \text{......(5·7)}$$

A solution in series provides the initial values

$$\zeta = \tfrac{1}{2}(n^* + l)(n^* - l - 1), \quad \frac{d\zeta}{du} = (n^* - l)\,\zeta, \text{ at } u = 0. \qquad \text{......(5·8)}$$

The relations referred to between different solutions of the wave equation take the form of recurrence relations between the values for a given u (or ρ, not r) of the functions M for values of n^* and l differing by integers.

Epstein† has given such recurrence relations for the function $\rho^{n^*} M$, using the fact that the series for this function, for the solution of the wave equation finite at $r = 0$, is a limiting form of the hypergeometric series; recurrence formulae for M can be derived from the formulae given by Epstein, but in the present case we are interested in the solutions for which M is finite at $r = \infty$, and it is most convenient to choose the arbitrary constants in the solutions for different n^*, l so that

$$M(n^*, l) = 1 \text{ at } u = 0 \text{ for all } n^*, l, \qquad \text{......(5·9)}$$

which is a different choice from that adopted in the relations given by Epstein, so that the coefficients in the relations used here and in those derived from Epstein's are not the same; the relations will here be derived direct from the differential equation.

§ 6. *Recurrence Relations between functions M for values of n^* and l differing by integers.*

Using D to denote differentiation with respect to u and writing for shortness

$$F(n^*, l, D) = u^2 D^2 - 2[(n^* - 1)u - 1]D + (n^* - l - 1)(n^* + l), \qquad \text{......(6·1)}$$

equation (5·4) for $M(n^*, l)$ becomes

$$F(n^*, l, D)\, M(n^*, l) = 0. \qquad \text{......(6·2)}$$

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† P. Epstein, *Proc. Nat. Acad. Sci.*, Vol. XII, p. 629 (1926).

Since the function F contains u as well as the operator D, it is not commutative with D, but it is easily verified that

$$D \, . \, F(n^*, l, D) = F(n^* - 1, l, D) \, . \, D,$$

so that, differentiating (6·2),

$$D \, . \, F(n^*, l, D) \, M(n^*, l) = F(n^* - 1, l, D) \, . \, DM(n^*, l) = 0,$$

i.e. $DM(n^*, l)$ satisfies the differential equation for $M(n^* - 1, l)$. Since, apart from an arbitrary multiplying constant, this equation has only one solution finite at $u = 0$, it follows that

$$DM(n^*, l) = aM(n^* - 1, l), \qquad \text{......(6·3)}$$

a being a constant for a given n^*, l which must be determined to fit the initial condition (5·9).

Now at $u = 0$

$$\zeta(n^*, l) = -DM(n^*, l)/M(n^*, l) = \tfrac{1}{2}(n^* + l)(n^* - l - 1)$$

by (5·8), so, to satisfy (5·9), (6·3) must become

$$DM(n^*, l) = -\tfrac{1}{2}(n^* + l)(n^* - l - 1) \, M(n^* - 1, l). \qquad \text{......(6·4)}$$

Given $M(n^* - 1, l)$, $M(n^*, l)$ can thus be found by quadrature from the initial condition $M(n^*, l) = 1$ at $u = 0$; by further quadratures $M(n^* + 1, l)$, $M(n^* + 2, l)$ and so on, can be found in succession, but the integration is not necessary as a purely algebraical expression can be found between the functions M for three values of n^* increasing by unity.

Substituting $n^* + 1$ for n^* in (6·4), we have

$$DM(n^* + 1, l) = -\tfrac{1}{2}(n^* + l + 1)(n^* - l) \, M(n^*, l); \qquad \text{......(6·5)}$$

differentiation and substitution of (6·4) gives an expression for $D^2M(n^* + 1, l)$ and substitution of this and (6·5) in the differentiation equation for $M(n^* + 1, l)$ gives

$$M(n^* + 1, l) = [1 - n^* u] \, M(n^*, l) - \tfrac{1}{4}u^2 (n^* + l)(n^* - l - 1) \, M(n^* - 1, l). \qquad \text{......(6·6)}$$

This, it must be emphasised, is a relation between the different functions M for the same value of $u = n^*/Cr$, not for the same value as r.

For the relations between solutions for different values of l, it can be verified by substitution in the differential equation

$$y = [-(n^* - l) + uD] \, M(n^* + 1, l)$$

satisfies

$$F(n^* + \tfrac{1}{2}, l + \tfrac{1}{2}, D) \, y = 0,$$

and since, apart from an arbitrary multiplying constant, this equation has only one solution $M(n^*+\frac{1}{2},\,l+\frac{1}{2})$ which is finite at $u=0$, we can put

$$M(n^*+\tfrac{1}{2},\,l+\tfrac{1}{2})=b\,[-(n^*-l)+uD]\,M(n^*+1,\,l),$$

or substituting (6·5), and taking $b=-1/(n^*-l)$ in order to make $M(n^*+\frac{1}{2},\,l+\frac{1}{2})=1$ at $u=0$ in accordance with (5·9),

$$M(n^*+\tfrac{1}{2},\,l+\tfrac{1}{2})=M(n^*+1,\,l)+\tfrac{1}{2}(n^*+l+1)\,uM(n^*,\,l). \quad \text{......(6·7)}$$

For the purposes of the present paper we are only interested in the solutions for integer values of l; by successive use of (6·7) and substitution of (6·6) we obtain

$$M(n^*,\,l+1)=[1+(l+1)\,u]\,M(n^*,\,l) + \tfrac{1}{2}(n^*+l)(l+1)\,u^2M(n^*-1,\,l). \quad \text{......(6·8)}$$

With these relations between the values of the function M in a Coulomb field, for values n^* and l differing by integers, it is only necessary to find M by numerical integration of the differential equation for one value of l and a set of values for n^* covering a range of unity closely enough to allow of interpolation to the accuracy required; the functions M for other values of n^* and l can then be built up, using first (6·4), then (6·6) and (6·8); the results apply to any atom with a positive core charge.

The numerical integration of equation (5·7) for

$$\zeta=-d\,(\log M)/du$$

has actually been carried out for $l=0$ and n^* at intervals of 0·1 from 0·6 to 1·5 (for $l=0$, the solution for $n^*=1$ is $\zeta=0$, and, for neighbouring values of n^*, ζ and $\frac{d\zeta}{du}$ are small over a large range of u). The results as immediately obtained are in terms of $u=n^*/Cr$ as independent variable, for practical application they must be expressed in terms of r. The method adopted is to find ζ for a given value of Cr for each value of l and n^*, and from these values of ζ to calculate

$$\frac{\eta}{C}=-\frac{1}{CP}\frac{dP}{dr}=\frac{1}{n^*}-\frac{n^*}{Cr}\left(1+\frac{\zeta}{Cr}\right), \quad \text{.........(6·9)}$$

which follows by differentiating (5·4) and using (5·1). For each value of l, the values of η/C so obtained, which refer to the solution zero at $r=\infty$, are plotted against n^*; the intersection of the curve so obtained with the curve of η/C against n^* for the solution which is zero at $r=0$ then gives the values of n^* for the characteristic values of the wave equation.

§ 7. *General Formula for the Normalisation Integral for the Series Electron.*

The normalisation integral $\int_0^\infty P^2 dr$ is required in calculation of perturbations; for the series electron the main contribution to this integral is from values of r where the field is effectively that of a point charge C; using some of the results of the previous section an approximate recurrence formula for this integral can be found, and from it an approximate formula for the integral itself.

We consider the arbitrary constant chosen so that

$$P = e^{-\rho}\rho^{n^*}M;\quad M\to 1,\ \rho\to\infty \qquad \ldots\ldots(7{\cdot}1)$$

(cf. formula 5·4). Using a dash to indicate differentiation with respect to ρ (not r), as will be done throughout this section, the recurrence formulae (6·4), (6·6) then give respectively

$$\rho P'(n^*, l) = -(\rho - n^*)P(n^*, l) + \tfrac{1}{2}(n^* + l)(n^* - l - 1)P(n^* - 1, l), \qquad \ldots\ldots(7{\cdot}2)$$

$$\begin{aligned} P(n^* + 1, l) &= (\rho - n^*)P(n^*, l) \\ &\quad - \tfrac{1}{4}(n^* + l)(n^* - l - 1)P(n^* - 1, l), \end{aligned} \qquad \ldots\ldots(7{\cdot}3)$$

from which elimination of $P(n^* - 1, l)$ gives

$$P(n^* + 1, l) = \tfrac{1}{2}[(\rho - n^*)P(n^*, l) - \rho P'(n^*, l)]. \qquad \ldots\ldots(7{\cdot}4)$$

By subtracting the square of (7·3) from twice the square of (7·4), and then using (7·2) to substitute for $P(n^* - 1, l)$ in the product term $P(n^*, l)P(n^* - 1, l)$, we obtain

$$\begin{aligned} P^2(n^* + 1, l) &= \tfrac{1}{2}[(\rho - n^*)^2 P^2(n^*, l) + \rho^2 P'(n^*, l)^2] \\ &\quad - [\tfrac{1}{4}(n^* - l - 1)(n^* + l)]^2 P^2(n^* - 1, l). \end{aligned}$$

The required recurrence relation for $\int P^2 d\rho$ is obtained by integrating this. For the second term on the right we have, on integrating by parts,

$$\int \rho^2 (P')^2 d\rho = [\rho^2 P P'] - \int P \frac{d}{d\rho}(\rho^2 P')\, d\rho;$$

expansion of the differential coefficient under the integral, followed by substitution for P'' from the differential equation for P (5·3) and integration of the remaining term by parts gives finally

$$\int \rho^2 (P')^2 d\rho = [\rho^2 P P'] - [\rho P^2] - \int [\rho^2 - 2n^*\rho + l(l + 1) - 1] P^2 d\rho,$$

so that altogether

$$\begin{aligned} \int P^2(n^* + 1, l)\, d\rho &= \tfrac{1}{2}[\rho^2 P P'] - \tfrac{1}{2}[\rho P^2] \\ &\quad + \tfrac{1}{2}[(n^*)^2 - l(l + 1) + 1]\int P^2(n^*, l)\, d\rho \\ &\quad - [\tfrac{1}{4}(n^* - l - 1)(n^* + l)]^2 \int P^2(n^* - 1, l)\, d\rho, \end{aligned}$$

the function P in the integrated terms being $P(n^*, l)$. These terms vanish at the upper limit $\rho = \infty$; if the field were a Coulomb field for all r, they would become infinite at the lower limit except for integral values of n^*. But for the actual wave functions corresponding to optical terms the part which would give the infinite contribution in a Coulomb field is replaced by a part in a non-Coulomb field which gives a contribution small compared to the total value of the integral, so that for an approximate result for these wave functions we may omit the integrated terms and write

$$\int_0^\infty P^2(n^*+1, l)\,d\rho = \tfrac{1}{2}\left[(n^*)^2 - l(l+1) + 1\right]\int_0^\infty P^2(n^*, l)\,d\rho$$

$$-\left[\tfrac{1}{4}(n^* - l - 1)(n^* + l)\right]^2 \int_0^\infty P^2(n^* - 1, l)\,d\rho. \quad \ldots\ldots(7{\cdot}5)$$

For integer values of n^*, and the choice of the arbitrary constants in the solutions P for different values of n^* here made (see 7·1), we have from a formula given by Waller†

$$\int_0^\infty P^2(n, l)\,d\rho = 2^{-2n} n\,(n+l)!\;(n-l-1)!.$$

This satisfies the recurrence relation (7·5), and suggests for a general value of n^*

$$\int_0^\infty P^2(n^*, l)\,d\rho = 2^{-2n^*} n^*\,\Gamma(n^* + l + 1)\,\Gamma(n^* - l), \quad \ldots\ldots(7{\cdot}6)$$

which also satisfies it. In applying this result it must be remembered that the integral is taken with respect to $\rho = Cr/n^*$, not with respect to r, and that the arbitrary constant in P has been chosen according to (7·1), i.e. so that

$$P/\rho^{n^*} e^{-\rho} = M \to 1, \quad \rho \to \infty.$$

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† I. Waller, *Zeit. f. Phys.*, Vol. XXXVIII, p. 635. Using atomic units and the notation of this paper, let P be defined as $2C/n$ times Waller's $rX_{n,l}$, i.e.

$$P = (2\rho)^{l+1} e^{-\rho}\,L^{(2l+1)}_{n+l}(2\rho) \qquad (\rho = Cr/n = \text{half Waller's } \xi);$$

then it follows from Waller's formulae (32′), (33), (34) that

$$\int P^2\,d\rho = n\,[(n+l)!]^3/(n-l-1)!$$

Now the highest power of x in $L^{(2l+1)}_{n+l}(x)$ is $\frac{(n-l-1)!}{(n+l)!}x^{n-l-1}$, so that, for large r, P as defined behaves like $\frac{(n-l-1)!}{(n+l)!}(2\rho)^n e^{-\rho}$. Hence if, instead, the arbitrary constant in P is to be chosen so that $P/\rho^n e^{-\rho} \to 1$ as $\rho \to \infty$ (see 7·1), $\int P^2\,d\rho$ must have the value given here.

As explained at the end of the last section, solutions of the equations for M with different values of n^* and l satisfying this condition have been calculated, so that from the values of P at a comparatively small radius (only large enough for the deviation from a Coulomb field to be inappreciable) the value of the normalisation integral can be found from (7·6), thus avoiding the numerical evaluation of the integral in each particular case.

This formula has been tested on the first s and the first p term of Rb, and the errors are about $2\frac{1}{2}\%$ and 2% respectively; they would presumably be less for higher terms of the series, since the larger n^* is, the larger is the proportional contribution to the integral from the range of r where the field is effectively a Coulomb field.

§ 8. *Perturbations.*

The general first order formula for central perturbations has already been found (see § 4, formula 4·7). If $\Delta\epsilon$ is the change in characteristic value of the wave equation due to a change Δv in the potential function v, then

$$\Delta\epsilon = \int_0^\infty 2\Delta v \, P^2 \, dr \Big/ \int_0^\infty P^2 dr\,;$$

this mean value of $2\Delta v$ weighted by P^2 corresponds to the time average of the perturbing potential in the classical perturbation theory.

Apart from the use of this formula to estimate the alteration in ϵ due to a trial change in the field of force, there are two particular perturbations to which it can be applied, viz. the 'relativity' correction and the 'spinning electron' correction.

The relativity perturbation term in the classical Hamiltonian is (in ordinary units) $-(1/2mc^2)(E-V)^2$†, or in atomic units

$$\Delta v = \tfrac{1}{2}\alpha^2(\epsilon/2 - v)^2 \qquad [\alpha^2 = (2\pi e^2/ch)^2 = 1/18800],$$

so that
$$\Delta\epsilon = (\alpha^2/4)\int_0^\infty (\epsilon - 2v)^2 P^2 \, dr \Big/ \int_0^\infty P^2 dr.$$

If Z is the effective nuclear charge at any radius (the charge which, placed at the nucleus, would give the same *field* as the actual field at that radius), and **l** and **s** are the orbital and spin angular momentum vectors, the spinning electron perturbation term in the classical Hamiltonian is (in ordinary units) $\frac{1}{2}(eh/2\pi mc)^2(Z/r^3)\,\mathbf{l}\mathbf{s}$‡, or in atomic units $\frac{1}{2}\alpha^2(Z/r^3)\,\mathbf{l}\mathbf{s}$, so that

$$\Delta\epsilon = \alpha^2\,\mathbf{l}\mathbf{s}\int_0^\infty (Z/r^3)\,P^2 dr \Big/ \int_0^\infty P^2 dr.$$

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† See, for example, M. Born, *op. cit.*, p. 234 (English translation, p. 204).

‡ See, for example, F. Hund, *op. cit.*, p. 74, formula (1).

According to Heisenberg and Jordan*, on the new quantum mechanics the scalar product **ls** must, in the case of a Coulomb field, be given the values

$$\mathbf{ls} = \tfrac{1}{2}[j(j+1) - l(l+1) - s(s+1)],$$
$$j = l \pm \tfrac{1}{2}, \text{ except that } j = \tfrac{1}{2} \text{ only when } l = 0,$$
$$s = \tfrac{1}{2}.$$

There is no reference to a Coulomb field in these results, so that, at any rate provisionally, they may be taken to apply also to an atom with a non-Coulomb field.

If, as is convenient in the numerical work, the arbitrary constant in P is taken so that, for small r, P is the same for all solutions with the same l (strictly, so that the limit of P/r^{l+1} as $r \rightarrow 0$ is the same for all solutions), and the main part of the perturbation arises from small values of r (as is the case for the two special perturbations considered), then $\int_0^\infty 2vP^2 dr$ will be approximately the same for all solutions with the same l, so that approximately

$$\Delta\epsilon \propto \left[\int_0^\infty P^2 dr\right]^{-1}.$$

§ 9. *Method of Integrating the Differential Equations.*

An outline of the method used for the numerical integration of the differential equations will now be given.

Suppose that a function f is tabulated at equal intervals δx of the independent variable x, and the integral $y = \int f dx$ is required; using central differences†

$$\delta f_{\frac{1}{2}} = f_1 - f_0, \quad \delta f_{1\frac{1}{2}} = f_2 - f_1, \ \ldots,$$
$$\delta^2 f_0 = \delta f_{\frac{1}{2}} - \delta f_{-\frac{1}{2}} = f_1 - 2f_0 + f_{-1}, \ \ldots,$$

the contribution δy to y from an interval δx is

$$\delta y = \bar{f}\,\delta x,$$

the mean value $\bar{f}$ being‡

$$\bar{f} = f_0 + \tfrac{1}{2}(\delta f)_{\frac{1}{2}} - \tfrac{1}{12}(\delta^2 f)_0 - \tfrac{1}{24}(\delta^3 f)_{\frac{1}{2}} + \tfrac{11}{720}(\delta^4 f)_0 + \ldots \qquad \ldots\ldots(9{\cdot}1)$$

$$= f_0 + \tfrac{1}{2}(\delta f)_{\frac{1}{2}} - \tfrac{1}{12}(\delta f')_{\frac{1}{2}}\,\delta x \qquad + \tfrac{1}{720}(\delta^4 f)_0 + \ldots \qquad \ldots\ldots(9{\cdot}2)$$

$(f' = df/dx)$.

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* W. Heisenberg and Jordan, *Zeit. f. Phys.*, Vol. xxxvii, p. 263 (1926).

† See, for example, E. T. Whittaker and G. Robinson, *Calculus of Observations*, p. 35.

‡ For the first formula see Whittaker and Robinson, *op. cit.*, p. 147 (put $r=1$ and express the result in central differences); the second follows directly from the Euler-Maclaurin formula (Whittaker and Robinson, *op. cit.*, p. 135) on putting $r=1$ and expressing the differential coefficients in central differences. I am indebted to Mr C. H. Bosanquet for pointing out the advantage of (9·2), involving differences of the derivative of the integrand, with its small fourth order term.

The integration is carried out by one or other of these formulae applied to a series of equal intervals δx, an equation of the second order being reduced to a pair of the first order by the use of the first differential coefficient as a subsidiary dependent variable. Usually the first three orders of difference are taken into account, the fourth order term being an error term.

In the simple evaluation of integrals, the integrand f is known throughout the whole range of x before the integration is begun, but in the integration of a differential equation f for one at least of the first order equations is an explicit function of the integral of one or more of them, so that the integration has to be carried out by a step-by-step process.

Further, if the integration has been carried out up to the values $x = x_0$, only the backward differences $(\delta f)_{-\frac{1}{2}}$, $(\delta f)_{-1}$, ... are directly available, and in terms of these the formula for f converges much more slowly than formula (9·1) in the central differences (the coefficient of the fourth order difference is $-\frac{231}{720}$ instead of $\frac{11}{720}$); if, however, a value of f_1 and hence the differences

$$(\delta f)_{\frac{1}{2}},\ (\delta^2 f)_0,\ (\delta^2 f)_{-\frac{1}{2}},\ \dots$$

are available, the use of $(\delta^3 f)_{-\frac{1}{2}}$ in (9·1) only alters the coefficient of the fourth order term, which is the error term of the method employed, from $\frac{11}{720}$ to $-\frac{19}{720}$. An essential point of the method of integration actually used is the estimation of f_1 when the integration has been carried to the point x_0; this estimation depends on the extrapolation, not of f_1 itself, but of the quantities of which it is given as an explicit function, and this estimation is particularly easy to do satisfactorily in the case of the second order equation with the first derivative absent, which is just the type of the equation for P in the particular problem with which this paper is concerned.

Consider as an example this equation

$$\frac{d^2P}{dr^2} = -\left[2v - \epsilon - \frac{l(l+1)}{r^2}\right] P,$$

already integrated through a series of equal intervals δr up to $r = r_0$; we have the values P up to P_0 and the backward differences from them. dP/dr, which is the subsidiary dependent variable used to reduce the second order equation to two first order ones, does not occur, so that the estimation of d^2P/dr^2 (which is the integrand f for the evaluation of $\dfrac{dP}{dr} = \int f dr$) at $r = r_1$ depends on the estimate of P only, and this is made as follows.

In terms of P'' and its differences, the second difference of P is

$$(\delta^2 P)_0 = (\delta r)^2 \left[P_0'' + \tfrac{1}{12}(\delta^2 P'')_0 + \dots\right], \quad \dots\dots\dots(9·3)$$

and by definition of the second difference $(\delta^2 P)_0$,

$$(\delta P)_{\frac{1}{2}} = (\delta P)_{-\frac{1}{2}} + (\delta^2 P)_0.$$

Now at the stage which the calculation is supposed to have reached, P_0 and so $(\delta P)_{-\frac{1}{2}}$ and P_0'' are known; $(\delta^2 P'')_0$ can be extrapolated from previous values (great accuracy is not needed since its coefficient is small), so that, using (9·3), $(\delta^2 P)_0$ can be estimated, and from it $(\delta P)_{\frac{1}{2}}$ and finally P_1. With this value of P_1, P_1'' is calculated from the differential equation; and then $(\delta P')_{\frac{1}{2}}$ from the integration formula (9·1) with $f = P''$; for the integration of P' to give P, the differences of P'', the derivative of the integrand, are available, so that the formula (9·2), which is the most satisfactory on account of the small coefficient of the fourth order term, can be used.

The differences, tabulated as the work proceeds for use in the integration formulae, also provide a close check on the numerical work, a very important consideration indeed when such work on a large scale is being carried out, especially when a serious mistake at one stage may vitiate all subsequent work.

The intervals δr are kept of such a size that the fourth order difference terms in the integration formulae in any one interval do not affect the last significant figure retained. With intervals of the size so determined, it is only rarely that the method of estimating P_1 described gives a value so different from the value finally obtained by integration that the calculation for the interval has to be repeated with a fresh estimate. The integration formulae depend on the use of a series of intervals of the same size, but it is not necessary to use the same size throughout; the most convenient change is to double the size of interval (in the case of the particular equation considered, the permissible length increases as r increases), the procedure is then quite straightforward; of the values of P'' and P already calculated, alternate values are taken to provide a set of differences to give a start to the calculation with intervals of the double length. For numerical reasons, however, it is preferable to take intervals of 1, 2, or 5 times a power of 10; the change of interval length by a factor of $2\frac{1}{2}$ involves some simple interpolation to provide the initial set of differences, but is otherwise straightforward.

Doubtless it would be possible to derive formulae for integration over longer intervals with adequate accuracy, but the writer's experience in other similar work is that simple formulae and a large number of intervals are much preferable to complicated formulae and a small number of intervals. Apart from the ease of working with simple formulae, the important question of keeping an adequate check on the numerical work is a difficult one unless the intervals are small, so that the successive differences converge rapidly enough to provide one. From the point of view of simplicity it may be mentioned that, in the case of the differential equation for P here considered, only one calculation in each interval requires a slide rule (or logs), namely, that of P'' from the differential equation; the rest involve only additions and subtractions, largely of numbers with one or two significant figures, and multiplications by 2, $\frac{1}{2}$, $\frac{1}{8}$, $\frac{1}{12}$, $\frac{1}{24}$ (the last three always of numbers of few significant figures), which can be done mentally.

For the first order equations for ξ, η and ζ the process is much the same, except that a cruder method has to be used for estimating the value of the integral at the end of the interval in order to obtain a value of the integrand, as the derivative of the integrand is not calculated.

§ 10. *Practical Determination of Characteristic Values and Functions.*

As already explained (see § 2) the characteristic values of ϵ are determined by integrating the wave equation (or some equation derived from it) outwards from $r = 0$ and inwards from $r = \infty$, and choosing the value of ϵ to make the solutions fit at some intermediate radius.

For the electrons with $n = l + 1$ (giving the 'circular orbits' of the Bohr theory) P has no intermediate zeros, and it is convenient to use the ξ equation (3·4) for the integration outwards to rather beyond the first maximum of P, and the η equation (2·6) for the integration inwards. A trial value of ϵ is taken and the values of η at the common value of r for the two solutions are found by numerical integration of the respective equations by the method outlined in the previous section. The solution of the variation equations (see § 4) then gives the changes in these values of η for a given change in ϵ, and the value of ϵ required to make them the same is found by interpolation (inspection of the square terms in the solution of the variation equations shows whether linear interpolation is valid). An example will make the process clearer.

Example.

Rb atom with a certain trial field. 3_3 electron ($n=3$, $l=k-1=2$).

$$\text{At } r=0{\cdot}6 \left\{\begin{array}{llll} \text{Integration outwards} & \epsilon=7{\cdot}0, & \eta=1{\cdot}87\,; & \Delta\epsilon=+1{\cdot}0,\ \Delta\eta=-0.54 \\ \text{Integration inwards} & \epsilon=7{\cdot}0, & \eta=\underline{1{\cdot}35}\,; & \Delta\epsilon=+1{\cdot}0,\ \Delta\eta=\underline{+0{\cdot}27} \\ & & \quad\ 0{\cdot}52 & \qquad\qquad\qquad\qquad\ \ -0{\cdot}81 \end{array}\right.$$

Linear interpolation for the same value of η at $r=0{\cdot}6$ in both integrations gives $\epsilon=7{\cdot}64$ (in this case inspection of square terms in the variation equation showed that error of linear interpolation was probably less than 0·03).

It will be noted that $\Delta\eta$ is of opposite sign for the two integrations; this is always the case, and gives a good intersection for the determination of the characteristic value ϵ. This being found, it is a simple matter to calculate the values of ξ or η for the other values of r, and from them to calculate P^2 from either

$$\log_{10} P^2 = 2\,(l+1)\log_{10} r - 2M\int_0 \xi\,dr \quad (M = \log_{10} e),$$

or

$$\log_{10} P^2 = \log_{10}[P(r_0)]^2 - 2M\int_{r_0} \eta\,dr,$$

according as ξ or η is given (as P^2 is required to give the charge density and for perturbation calculations, it is usually best to calculate it directly).

For X-ray electrons with $n > l+1$ (corresponding to the 'elliptical orbits') it has been found best to integrate equation (3·4) for ξ from $r = 0$ out to about the first maximum of P, and equation (2·3) for P from there to a point rather beyond the last maximum of P; the η equation is integrated inwards to the same point and the estimation of ϵ made as already explained.

It is not in practice necessary to integrate the η equation all the way in from $r = \infty$. Beyond the 'outer apse' (i.e. the greater root of $2v - \epsilon - 1\,(l+1)/r^2 = 0$, see § 2) the integration outwards is highly unstable*, so that if we begin an outwards integration of the η equation from a radius outside the range where P is appreciable (and so well outside the outer apse), the behaviour of the solution is very sensitive to the value of η at this radius chosen to start the integration, and from a very few intervals of integration (2 and 3 in practice) a good estimate can be obtained for the value of η at this radius for the solution required, for which η remains finite at $r = \infty$. The integration inwards being correspondingly highly stable, a small error in the value of η at this radius will cancel itself almost entirely in the process of integration inwards to the point where the join is made with the integration outwards from $r = 0$. This integration outwards is highly stable as far as the inner apse, and stable as far as the outer apse.

The method of determining the characteristic values for the optical terms has been given at the end of § 6.

In the following paper the results of some calculations on these lines will be given and discussed.

§ 11. *Summary.*

The paper is concerned with the practical determination of the characteristic values and functions of the wave equation of Schrödinger for a non-Coulomb central field, for which the potential is given as a function of the distance r from the nucleus.

The method used is to integrate a modification of the equation outwards from initial conditions corresponding to a solution finite

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* It is convenient to speak of the process of the numerical integration of a differential equation as 'stable' if a small change in the solution at one point (for example, a numerical slip) does not produce greater changes in later values as the integration proceeds, and as 'unstable' when the opposite is the case.

at $r = 0$, and inwards from initial conditions corresponding to a solution zero at $r = \infty$, with a trial value of the parameter (the energy) whose characteristic values are to be determined; the values of this parameter for which the two solutions fit at some convenient intermediate radius are the characteristic values required, and the solutions which so fit are the characteristic functions (§§ 2, 10).

Modifications of the wave equation suitable for numerical work in different parts of the range of r are given (§§ 2, 3, 5), also exact equations for the variation of a solution with a variation in the potential or of the trial value of the energy (§ 4); the use of these variation equations in preference to a complete new integration of the equation for every trial change of field or of the energy parameter avoids a great deal of numerical work.

For the range of r where the deviation from a Coulomb field is inappreciable, recurrence relations between different solutions of the wave equations which are zero at $r = \infty$, and correspond to terms with different values of the effective and subsidiary quantum numbers, are given and can be used to avoid carrying out the integration in each particular case (§§ 6, 7).

Formulae for the calculation of first order perturbations due to the relativity variation of mass and to the spinning electron are given (§ 8).

The method used for integrating the equations numerically is outlined (§ 9).

The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part II. Some Results and Discussion. By D. R. HARTREE, Ph.D., St John's College.

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§ 1. *Introduction.*

In the previous paper an account has been given of the theory and methods used for determining the characteristic values and functions of Schrödinger's wave equations for a non-Coulomb central field of force whose potential v is given. In this paper some results of the application of these methods will be given and discussed; references to the previous paper will be prefixed by a I. Atomic units (see I, § 1) will be used throughout this paper.

There are two different objects which one may have in view in doing numerical work of this kind.

First, the object may be to find an empirical field of force for a given atom, for which the characteristic values of the wave equation give as closely as possible the terms of the optical and X-ray spectra of that atom.

Secondly, as suggested in I, § 1, it may be to find a field of force such that the distribution of charge given by the wave functions for the core electrons shall reproduce the field[*].

Certainly these are not altogether independent; in the first case, one may hope that the empirical field may be expressible as the sum of contributions from the different core electrons[†], and in the second case, one may hope that the characteristic values in the field so found will give approximately the term values of the spectra of that atom. Nevertheless they are distinct in that in one case the atomic field may be chosen without reference to the characteristic functions themselves, and in the other case depends essentially on them, so that they involve rather different procedure in the numerical work. The first would be the more appropriate if the results were to be used to find the relative intensities of lines in the spectrum, and some work from this point of view has already

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[*] Corresponding work for the orbital atomic model has been done from the first point of view by E. Fues, *Zeit. f. Phys.*, Vol. XI, p. 364 (1922); Vol. XII, p. 1; Vol. XIII, p. 211 (1923); Vol. XXI, p. 265 (1924); D. R. Hartree, *Proc. Camb. Phil. Soc.*, Vol. XXI, p. 265 (1923) and Y. Sugiura and H. C. Urey, *Det Kongel. Danske Videnskab. Selskab., Math.-Phys. Medd.*, Vol. VII, No. 13 (1926), and from the second by R. B. Lindsay, *Publ. Mass. Inst. Technology*, Series II, No. 20 (1924).

[†] For the orbital atomic model the writer has tried to obtain such results, but without success.

been done by Sugiura[*], the second, if the distribution of charge were required[†] and further results were to be based on it (for example X-ray scattering factors F).

The work here described was done with the second as its main object, and this demands consideration of the appropriate field of force to use for the core electrons.

§ 2. *The Field of Force for a Core Electron.*

Consider an atom such as the neutral atom of an alkali metal, consisting of closed n_k groups and a series electron. The potential v for the series electron is that of the field of the centrally symmetrical distribution of charge of the closed groups; but just as in the theory of the hydrogen atom the field acting on the electron is that of the nucleus only, not that of the nucleus and its own distributed charge, so here the field for a core electron is the total field of the nucleus and all the closed groups, less its own contribution to that field. Now except for an electron with $l=0$, its own contribution to the field is not centrally symmetrical, so that it would seem that the assumption of a central field is not applicable to it; on the other hand, the structure of the X-ray terms is that of terms due to a spinning electron in a central field.

It is just here that we meet the most serious doubts concerning the replacement of the actual many-body problem by a one-body problem with a central field for each electron, even as a first approximation.

A doublet term of an X-ray spectrum is due not to the presence of a single definite electron, but to the absence of one from an otherwise complete n_k group; the presence of this last electron gives the single ^1S term characteristic of a complete group. Now it is only through operation of Pauli's exclusion principle[‡] that an n_k group lacking one electron to make it complete gives only a spectral term of the same type (multiplicity and l-value) as would be given by that electron alone in a central field of other complete groups, and that the complete group gives only a ^1S term; this principle is essentially an expression of the behaviour of a number of electrons with the same n_k, whose mutual interactions may be considerable, and this involves developments of quantum mechanics beyond those applied in this paper.

In order to make headway at all without departing from the simple idea of a central field for each electron, a simplifying assump-

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[*] Y. Sugiura, *Phil. Mag.*, Ser. 7, Vol. IV, p. 495 (1927).

[†] The determination of the distribution of charge directly from a potential or field given as a function of the radius involves numerical differentiation, which is an unsatisfactory process, especially in this case, when it is possible to make a small increase of the field at one radius and a small decrease at another without appreciably affecting the fit between calculated and observed term values.

[‡] See, for example, F. Hund, *Linienspektren*, p. 114 *et seq.*

tion is necessary here in dealing with core electrons, and in this paper it will be assumed that the appropriate potential to take in working out the characteristic value and function for a core electron is the total potential of the nucleus and of the whole electronic distribution of charge, less the potential of the centrally symmetrical field calculated from the distribution of charge of that electron, *averaged over the sphere for each radius*; the radial density of this averaged distribution of charge is just the normalised value of P^2 (i.e. the charge between radii r and $r+dr$ is $P^2\,dr\Big/\int_0^\infty P^2\,dr$) or, for a complete n_k group consisting of s electrons, it is $1/s$ of the contribution to the radial density from this whole group.

It would of course be possible in most cases to carry out the work for the core electrons without taking into account at all the fact that the distributed charge of a core electron does not contribute to the field acting on it, but it seems probable that a better approximation to the actual distribution of charge will be obtained by making some correction, even if it is only a crude one. Besides, in treating the outer electrons of negative ions, some such correction is necessary in order to make the work possible at all.

For numerical work we have to start from a field which will be called the 'initial field'; for each n_k corresponding to a group of core electrons the field is corrected, as explained above, for the fact that the distributed charge of an electron must be omitted in finding the field acting on it, and for the field so corrected the part of the solution of the wave equation depending on r is found by the methods given in I; then from the solutions for all groups of core electrons a distribution of charge can be calculated (if the n_k groups are all complete, this distribution of charge will be centrally symmetrical), and then the field of the nucleus and this distribution of charge can be found; this may be called the 'final field.' The process may be expressed briefly in diagrammatic form:

Initial Field
↓
Initial Field corrected for each core electron
↓
Solutions of Wave Equation for core electrons
↓
Distribution of Charge
↓
Final Field.

If the final field is the same as the initial field, the field will be called 'self-consistent,' and the determination of self-consistent fields for various atoms is the main object of this paper. The self-consistent field so found is a characteristic of the particular atom in the particular state of ionisation considered; it involves no arbitrary functions or constants whatever.

It is thought that the distribution of charge in the self-consistent field is probably the best approximation to the actual distribution of charge in the atom which can be obtained without very much more elaborate theoretical and numerical work, and so is the most suitable to use in any problems involving this distribution of charge; also it is hoped that when the time is ripe for the practical evaluation of the exact solution of the many-electron problem, the self-consistent fields calculated by the methods given here may be helpful as providing first approximations.

For each solution of the wave equation in the self-consistent field (corrected as already explained) in the case of a core electron there will be a characteristic value of the energy parameter ϵ; it is a further question whether these values of ϵ are directly related to the optical and X-ray term values by the relation

$$\epsilon = \nu / R.$$

For the core electrons, this again depends on the details of the mutual interaction of the electrons in a closed group, and on the effect of the removal of one on the remainder; the simplest case, that of the normal state of neutral helium, has been worked out, and suggests that this relation may be expected to hold closely for the X-ray terms (see § 4).

§ 3. *Some Practical Details.*

The determination of the self-consistent field for any atom is a matter of successive approximation. Fortunately this process is 'stable' in that change of the initial field, of the same sign throughout, gives a change of the final field of the opposite sign. Consider, for example, an increase in the initial (positive) field; this pulls the whole distribution of charge further in, so that the negative charge inside a given radius is greater and the final field at each radius less than it was without the increase in the initial field.

For the first atom tried the initial field for the first approximation was obtained by Thomas' method*; in this case preliminary solutions of the wave equations have to be found with the same initial field for all core electrons, without the correction referred to above, in order to estimate the correction. It is better to build up an initial field as the sum of estimated contributions from the different groups of core electrons, so that the corrected field for each can be used even in the first approximation; when the calculations for two or three atoms have been completed this building up of the initial field can be done quite satisfactorily by interpolation or extrapolation.

* L. H. Thomas, *Proc Camb. Phil. Soc.*, Vol. XXIII, p. 542 (1927). It is necessary to extrapolate the field empirically beyond the range to which Thomas' results apply.

Since a given change in Z means a smaller *proportional* change in the field at small radii than at large radii, it might be expected that the final field would be more sensitive to changes in Z of the initial field at large radii than at small. This proves to be the case, and, with the stability of the process of successive approximation to a self-consistent field, suggests that the initial field at any stage should be taken between the initial and final fields of the previous approximation, nearer the final field at small r and nearer the initial field at large r. This general rule is justified by experience*.

For a central field of potential v, which is a function of r only,

$$Z = -r^2 dv/dr = dv/d(1/r)$$

is the point charge which, placed at the nucleus, would give the same *field* at radius r as the actual field; it is often called the 'effective nuclear charge' and this name will be used here. The quantity

$$Z_p = rv$$

is the point charge, which, placed at the nucleus, would give the same *potential* at radius r as that of the actual field; it may be called the 'effective nuclear charge for potential†.' It is usually convenient to work with Z and Z_p rather than with the field and the potential themselves, since Z and Z_p vary over a much smaller range. Differentiating $Z_p/r = v$ and substituting for dv/dr we have

$$-\frac{dZ_p}{dr} = \frac{Z - Z_p}{r},$$

and when Z is given as a function of r it has proved more satisfactory to find Z_p by numerical integration of this equation (which is very easy) than by direct integration of $v = -\int Zr^{-2}dr$‡.

In the numerical work, two places of decimals have usually been kept in Z in the initial and final fields, and the successive approximations towards a self-consistent field have been continued until the maximum difference in Z between the initial and final fields became less than 0·1.

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* The process of successive approximation by taking the initial field always equal to the final field of the previous approximation is not always convergent, though perhaps it usually is. Even when it is, a more rapid convergence to the self-consistent field is obtained by the rule given here.

† The large difference between Z and Z_p is not always realised; for Rb the maximum value of Z/Z_p is over 2 and that of $Z - Z_p$ is over 13, so that Z and Z_p cannot be considered as even approximately equal for a non-Coulomb field.

‡ The reason is that Z is known at equal intervals of r, and for the direct integration unduly small intervals would have to be used in some regions, in order to keep down the higher orders of difference due to the r^{-2} factor; the formula for the mean value $\bar{Z}$ for $\delta v = \bar{Z}\delta(1/r)$, when Z is known at equal intervals of r not of $1/r$, is more trouble to use than the differential equation.

§ 4. *The Normal State of Neutral Helium.*

The simplest case of an atom with more than one electron to which the idea of the self-consistent field is applicable is that of the normal state of neutral helium. In this case we consider the motion of one electron in the field of the nucleus and the second electron, and try to determine this field so that the 1_1 wave function for the first electron gives a charge distribution for which the field is the same as that assumed for the second electron.

The numerical work went so easily that an extra decimal place was kept in Z, and the successive approximation was carried to a point where the maximum difference between the values of Z for the initial and final fields was 0·002.

The value of Z and the radial charge density $-dZ/dr$ for this field are given in Table I.

TABLE I.

Neutral Helium, Normal State. Self-Consistent Field and Distribution of Charge

r atomic units	Z	$-dZ/dr$ electrons per atomic unit	r atomic units	Z	$-dZ/dr$ electrons per atomic unit
0	2·000	0·00	1·6	0·239	0·48
0·1	1·988	0·30	1·8	0·159	0·33
0·2	1·932	0·83	2·0	0·105	0·22
0·3	1·826	1·28	2·2	0·068	0·15
0·4	1·682	1·57	2·4	0·044	0·10
			2·6	0·028	0·06
0·6	1·344	1·73	2·8	0·018	0·04
0·8	1·013	1·55	3·0	0·011	0·026
1·0	0·733	1·25			
1·2	0·515	0·94	3·5	0·003	0·009
1·4	0·354	0·68	4·0	0·001	0·003

The most interesting point about the calculation is the value of the energy parameter ϵ, which was found to be $\epsilon = 1{\cdot}835$ (24·85 volts), while the observed term value for the normal state of neutral helium gives $\nu/R = 1{\cdot}81$ (24·6 volts). Now the calculated value of ϵ is found by considering the wave equation for one electron in the field of the nucleus and the distributed charge of the other, without taking into account the effect of the removal of one on the energy or distribution of charge of the other, while in the actual removal of one the change of charge distribution of the other is quite appreciable. Until it can be shown that the calculated energy parameter of the wave equation, for one electron in the self-consistent field of the nucleus and the other, would be expected to agree well with the energy required to remove one electron, the other adjusting its charge distribution to the change of field caused by that removal, the very close agreement actually found must be taken as an empirical justification of the simple approximations used to represent the interactions of electrons with the same n_k, and of the general idea underlying the work, rather than as a notable success of the method. But it does suggest that in general for core electrons the energy parameter of the wave equation for the self-consistent field, corrected as already explained, may be expected to be a good approximation to the value of ν/R for the corresponding X-ray term *.

§ 5. *Rubidium.*

These methods were first applied to the Rb atom, and more extensive work has been done for it than for any other atom. This choice was made because it seemed interesting to examine what happened on the wave mechanics when on the orbital model an internal and an external orbit of the same n_k were possible, and this does not occur for elements of too low atomic number [Cu (N = 29) is the first such atom which also gives an optical spectrum which can be dealt with by a central field]; for Rb it does occur, and at the same time the atomic number is small enough for the effects of the relativity variation of mass and of the spinning electron to be dealt with adequately as independent first order perturbations (except perhaps for $l = 0$); also for Rb, the writer had fairly extensive results worked out for the orbital model, and it seemed likely that these would be interesting for comparison.

The work for the core electrons was carried out for the ion Rb$^+$. For the first approximation the initial field was calculated by Thomas' method already mentioned, without the correction for the fact that a core electron is not acted on by its own distribution of charge; the final field for the first approximation was taken as the initial field for the second, and the correction was applied. Some trial changes in the field were then made to give an idea of the sensitivity of the final field to a change in the initial field, and a third initial field was built up from estimates of the contributions to Z from the different groups of core electrons. The maximum difference between this initial field and the final field calculated from it was 0·08 in Z; this was within the limit of disagreement (0·1 in Z) which had been previously laid down, so that the process

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* Actually the work was done in the inverse order; the application of the method to helium as an experiment was suggested by the good agreement between values of ϵ so calculated and the observed X-ray term values for more complicated atoms.

of approximation was not carried further. Fig. 1* shows the process of successive approximation to a self-consistent field; for the three approximations the difference between the values of Z for the initial and the final field is plotted as a function of r.

The effective nuclear charge Z and the radial charge density $-dZ/dr$ of the final field† of the third approximation is given in Table II: the values of Z probably differ from those of the self-consistent field by less than 0·05 throughout.

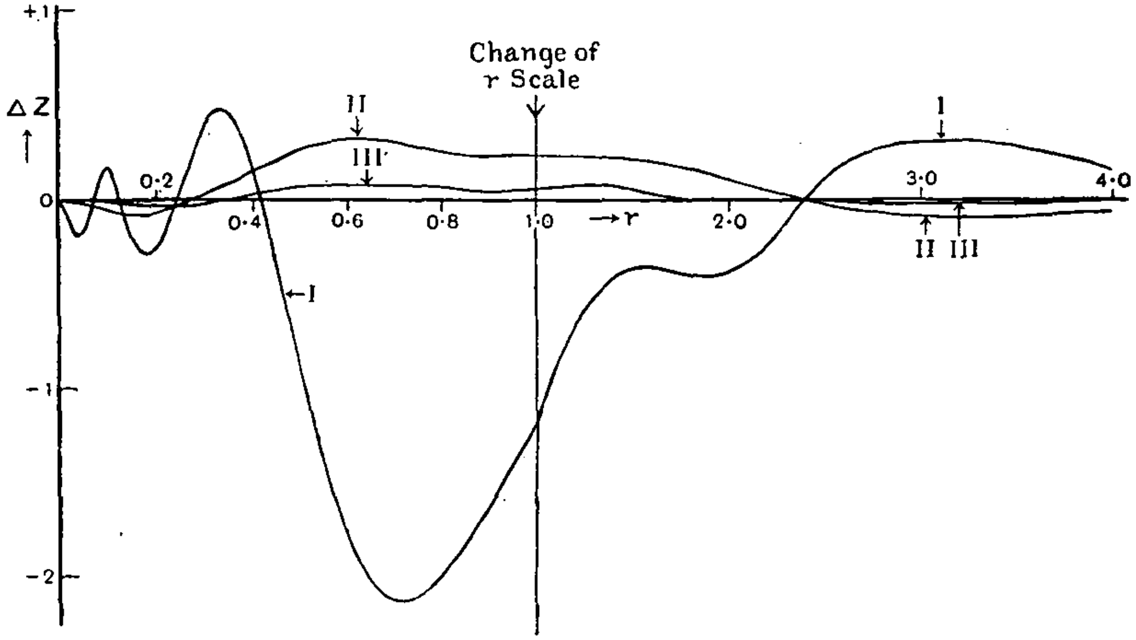

Fig. 1. Showing successive approximations to self-consistent field.
Difference ΔZ between effective nuclear charge of initial and final field plotted against r for the three approximations (Curves I, II, III) made in the calculations for Rb.

§ 6. *Rubidium. Comparison of Charge Distribution Calculated by Different Methods.*

In Fig. 2* the separate contributions to the radial charge density from the different groups of core electrons are shown, also the total radial density; the regions of maximum charge density corresponding to the K, L, M 'shells' will be noticed, but there is no peak, only a flattening out of the curve, for the N 'shell,' as the contribution from the M electrons is still appreciable and decreases more quickly than the contribution from the N electrons increases. In Fig. 3 the charge distribution curve (Curve I) thus calculated is compared with those calculated by other methods, viz.:

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[*] In Figs. 1, 2, 3 a different scale of r is used for $r<1$ and $r>1$. A scale open enough to show the detail of the curves for large r is unnecessarily open for larger r; the use of two uniform scales has seemed preferable to the continuous distortion introduced, for example, by a logarithmic scale of r.

[†] The charge density is calculated from the wave functions from which the final field is built up, not by numerical differentiation of Z.

(1) By the general method of Thomas* (Curve II). In effect, Thomas' work deals with the solution in classical mechanics of the problem investigated here on the basis of the wave mechanics. In the notation of this paper, Thomas' equation (1·2) gives

$$-dZ/dr=(8\sqrt{2}/3\pi)\,r^2v^{\frac{3}{2}}=(8\sqrt{2}/3\pi)\sqrt{(rZ_p{}^3)}.$$

The potential v (or preferably $Z_p=rv$, which varies more slowly and thus is easier to interpolate) can be calculated from the table at the end of Thomas' paper and the radial charge density follows directly from this equation.

TABLE II.

Rubidium$^+$. *Approximate Self-Consistent Field and Distribution of Charge.*

r atomic units	Z	$-dZ/dr$ electrons per atomic unit	r atomic units	Z	$-dZ/dr$ electrons per atomic unit
0	37·00	0	0·40	21·56	37·3
0·005	36·99	7·6	0·45	19·68	37·5
0·01	36·92	21·0	0·50	17·85	35·2
0·02	36·60	40·8	0·6	14·71	26·9
0·03	36·16	45·6	0·7	12·45	18·5
0·04	35·71	42·6	0·8	10·93	12·5
0·05	35·30	39·0	0·9	9·89	8·9
0·06	34·92	37·5	1·0	9·09	7·05
0·07	34·53	38·9			
0·08	34·14	41·8	1·2	7·81	6·08
			1·4	6·60	5·90
0·10	33·23	49·3	1·6	5·44	5·47
0·12	32·20	54·0	1·8	4·43	4·69
0·14	31·12	54·1	2·0	3·60	3·82
0·16	30·06	50·2			
0·18	29·11	44·6	2·5	2·21	2·08
0·20	28·29	39·2	3·0	1·52	0·90
			3·5	1·21	0·38
0·25	26·52	31·0	4·0	1·09	0·16
0·30	25·02	31·2	4·5	1·04	0·06
0·35	23·36	34·8	5·0	1·01	0·02

(2) From the orbital atomic model, with half integer values of k (Curve III). This curve is approximate only†.

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* *loc. cit.*

† For simplicity it has been assumed that all orbits of the same n have the same inner apsidal distance and that all of the same k have the same outer apsidal distance, both of which assumptions are approximately but not accurately true. The orbital model has not been worked out completely for half integer values of k, but the curve is drawn from data estimated from the work with integer values.

(3) From the approximate application of the wave mechanics suggested by Pauling* (Curve IV), in which the radial distribution

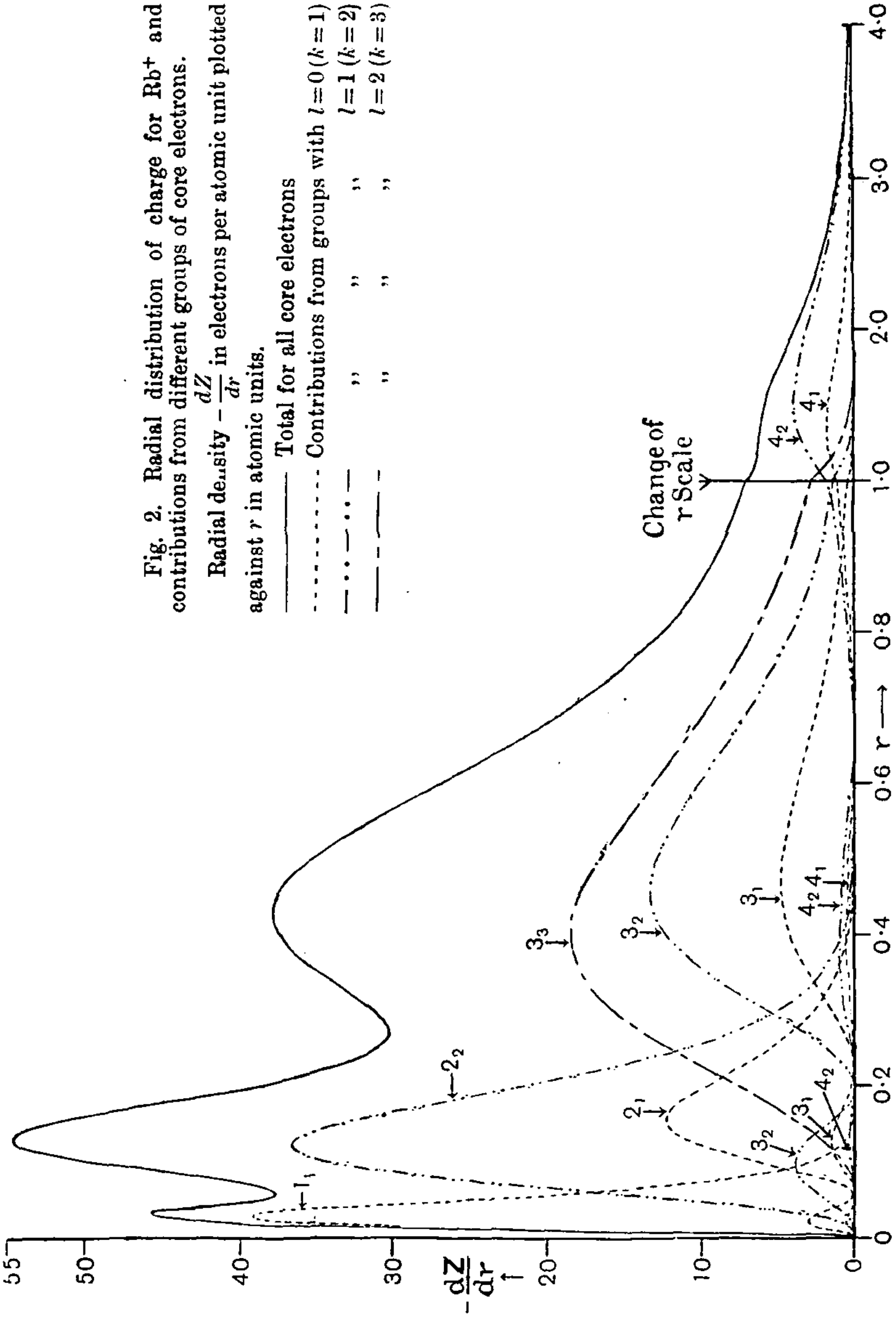

Fig. 2. Radial distribution of charge for Rb^+ and contributions from different groups of core electrons.

Radial density $-\frac{dZ}{dr}$ in electrons per atomic unit plotted against r in atomic units.

——— Total for all core electrons

· · · · · · Contributions from groups with $l=0\ (k=1)$

—·—·— " " " $l=1\ (k=2)$

— — — " " " $l=2\ (k=3)$

of charge for an electron is taken to be that for an electron with the same n_k in a certain Coulomb field, the nuclear charge for this

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* L. Pauling, *Proc. Roy. Soc.*, Vol. cxiv, p. 181 (1927).

Coulomb field, different for each group of core electrons, being given by an empirical table.

It will be seen that the distribution given by Thomas' method is a good smoothed-out approximation to the distribution giving the self-consistent field; the curves intersect several times, as do also the curves for Z, the integrated charge density, as can be seen roughly from the curve in Fig. 1 for the first approximation, for which the initial field was calculated by Thomas' method. The

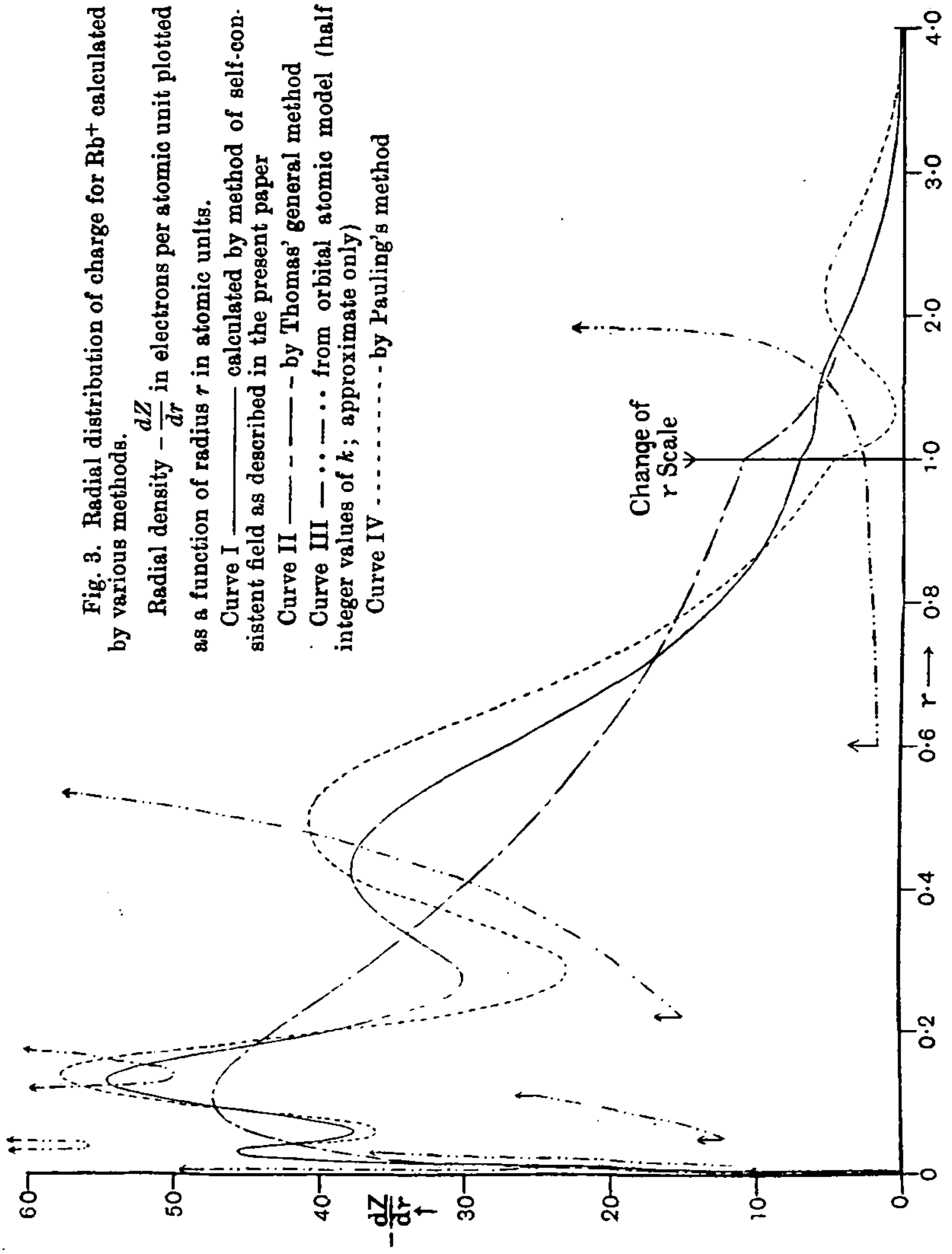

Fig. 3. Radial distribution of charge for Rb^+ calculated by various methods.

Radial density $-\frac{dZ}{dr}$ in electrons per atomic unit plotted as a function of radius r in atomic units.

Curve I ———— calculated by method of self-consistent field as described in the present paper

Curve II — — — — by Thomas' general method

Curve III —··—·· from orbital atomic model (half integer values of k; approximate only)

Curve IV ·········by Pauling's method

maximum difference in Z between the self-consistent field and Thomas' field is just less than 2.

If the details of the field or charge distribution are unimportant for any application, it seems very possible that Thomas' field or distribution might very well be accurate enough. If it is used, however, one point should be kept in mind, namely that it gives a radial charge density which for small r is proportional to $r^{\frac{1}{2}}$, while on the wave mechanics the radial density for small r is proportional to r^2; this may cause apparently large divergences in results involving, for example, $r^{-1}dZ/dr$, such as arise in calculating the charge distribution in plane sheets.

A glance at Fig. 3 shows that the charge distribution calculated from the wave mechanics and from the orbit model of the atom are entirely different in character. For the orbit model the contribution from a group of core orbits to the radial density near the outer apse, of radius r_0, becomes infinite like $(r_0 - r)^{\frac{1}{2}}$ as $r \rightarrow r_0$ from below, and falls discontinuously to zero as r passes through r_0, and there is similar distribution outside the inner apse, so that the radial density curve for the whole atom has infinite discontinuities at the apsidal distances of all the orbits*. The distribution according to the wave mechanics remains always finite and continuous; a particular point to notice about it is that it tends asymptotically to zero (roughly exponentially) as r increases, so that it is not possible to assign a definite size to the atom. Another point is that the successive maxima in the radial density curve (for $n > l + 1$) calculated by the wave mechanics have no analogy whatever on the orbital model.

For small radii the distribution calculated by Pauling's method agrees well with that calculated from the self-consistent field, as would be expected, since Pauling's method is based on the wave functions in a Coulomb field, and for small radii the main contribution to the radial density is from electrons for which the proportional deviation of the field from a Coulomb field is small over the range where the wave function is appreciable. For large radii, however, the difference between the two distributions increases, till for the outermost electrons there is little agreement between them.

There are two reasons for this. First, the scale of the distribution of charge as given by Pauling is too large (i.e. the 'size screening constant' given by Pauling's Table VIII is too large†), the error in scale increasing with n (the principal quantum number) and being quite large for the outermost groups of core electrons

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* With the half integer values of k there are no circular orbits. The curve for the orbital model is really much more broken than as shown in Fig. 3 (see second footnote on page 119).

† The effect of Pauling's correcting factor ΔS_S is small in this case, so that the errors lie in the values of S_{s_0}.

($n = 4$ in this case). Secondly, Pauling takes the radial distribution for any one group of electrons to be proportional to that of an electron in a certain Coulomb field; the actual deviation from a Coulomb field is always such that the effective nuclear charge decreases with increasing r, and the effect of this is to make the peaks of the radial density curve lower and less sharp than they are for a Coulomb field, and particularly to decrease the rate at which the radial density beyond the outermost maximum falls off with increasing r. These two effects combine to make the maxima and minima of the radial distribution curve calculated by Pauling's method too pronounced; in particular with Pauling's distribution of charge the contribution to the radial density from the M electrons has become small before that due to the N electrons has begun to increase up to its outermost maximum, so that the radial density drops to a very small value at about $r = 1{\cdot}3$; with the self-consistent distribution of charge the contribution from the M electrons falls off more slowly, and the increase of that from the N electrons begins at a smaller radius, so that there is actually no minimum between the M and N 'shells'.

The comparison between the distribution of charge calculated in different ways has been based on the results for Rb, but, with appropriate alterations in details, most of it would apply to any atom.

§ 7. *Rubidium. Comparison of Calculated and Observed Term Values.*

The characteristic values of the energy parameter ϵ for the different solutions of the wave equation in the self-consistent field may be compared with the terms of the X-ray and optical spectra.

We consider first the X-ray terms; for these, the removal of one electron is presumably accompanied by some readjustment of the remainder of the atom, but the results for helium suggest that without taking this into account, the values of ϵ so calculated from the self-consistent field (corrected for the fact that the distributed charge of a core electron does not contribute to the field on itself) may be in good agreement with the X-ray term values. A comparison is given in Table III; the effects of the relativity variations of mass and of the spinning electron were calculated as first order perturbations by the formulae given in I, § 8. The agreement is strikingly good, especially when it is remembered that there is no arbitrary function or constant available to be adjusted to bring calculated results into agreement with the observations. The calculated term values refer to the Rb^+ ion; those for the neutral atom would probably be smaller by about $0{\cdot}4$ on account of the effect of the distributed charge of the series electron in decreasing the potential inside the core; the field and so the distribution of charge of the core electrons would not be altered appreciably. The observed

4_1 and 4_2 terms are probably somewhat uncertain apart from this effect, which is relatively largest for them.

TABLE III.

Rubidium. Comparison of Observed X-Ray Term Values and Energy Parameters for Core Electrons.

n_k	ν/R obs.*	ϵ calc. for Rb$^+$ ion					ν/R obs. $-\epsilon$ calc. for orbit model
		Final approximation to self-consistent field	Spin Correction	Relativity Correction	Total	ν/R obs. $-\epsilon$ calc.	
1_1 K	1119·1	1103	−100	+113	1116	−3	0
2_1 L_{I}	152·3	144·5	−9·8	+15·1	149·8	−2·4	−0·6
$2_2\begin{cases}L_{\text{II}}\\L_{\text{III}}\end{cases}$	137·6 133·2	132·3	+2·8 −1·4	+2·4	137·5 133·3	−0·1 +0·1	0
3_1 M_{I}	24·1	21·24	−1·56	+2·51	22·19	−1·9	−0·0
$3_2\begin{cases}M_{\text{II}}\\M_{\text{III}}\end{cases}$	18·2 17·6	16·55	+0·44 −0·22	+0·44	17·43 16·77	−0·8 −0·8	−0·1
$3_3\begin{cases}M_{\text{IV}}\\M_{\text{V}}\end{cases}$	8·4 unresolved	8·28	+0·12 −0·08	+0·08	8·48 8·28	(0)	0
4_1 N_{I}	(2·4)	2·964	−0·198	+0·322	3·088	(+0·7)	
$4_2\begin{cases}N_{\text{II}}\\N_{\text{III}}\end{cases}$	(1·3)	1·557	+0·040 −0·020	+0·041	1·638 1·578	(+0·3)	

* The observed values for all terms but the K term have been taken from a paper by D. Coster and F. P. Mulder, *Zeit. f. Phys.*, Vol. XXXVIII, p. 264 (1926). The value for the K term is from M. Siegbahn, *Spectroscopy of X-rays.*

For comparison, the differences between the observed and calculated term values on the orbital model are also given, the field used in these calculations being chosen to give as good a fit as possible. Compared with these differences, those between term values observed and calculated by the methods of this paper look rather large, but it must be remembered the latter calculated values depend on the self-consistent field and do not involve even one adjustable constant, so that they could be calculated without knowledge of the observed term values, while for the orbit model the calculated values depend on a whole adjustable function, the field, which is chosen empirically to give the best fit to the observed terms. When we come to consider the optical term, it will be seen that even so the advantage lies with the wave mechanics.

The agreement between the calculated and observed spin doublets is very satisfactory; for the L spin doublet the separation deduced from direct observations is 4·4, the value calculated from the general empirical (first order) formula $(\alpha^2/16)(N-3{\cdot}5)^4$ is 4·19, and the value calculated by the perturbation formula (also first order) is 4·20. The calculated M doublet separation agrees with that observed within the limits of observational error. It seems possible that first order relativity and spin corrections may not be adequate for the terms with $l=0$ $(k=1)$, for which the first order corrections separately are about 10 per cent. of the total term value; for these terms also the difference between observed and calculated term values is largest.

As an example of the magnitude of the correction for the fact that the distributed charge of a core electron does not contribute to the field acting on itself, it may be mentioned that for the 2_2 term this correction is about 12, so that if it were not taken into account the agreement between observed and calculated term values would be entirely lost.

For the optical terms, the quantum defect $q=n-n^*$, i.e. the difference between the principal and effective quantum numbers, is the most suitable quantity to use in making a comparison of the results of calculation with observation. Such a comparison is given in Table IV, in which the calculated values are for the final approximation to a self-consistent field, the observed values are calculated from the terms given in Fowler's table[†], and for comparison the differences between observed and calculated values of the quantum defect are given for the orbital atomic model, with the field found to give about the best general agreement between the calculated and observed optical and X-ray terms[‡]. The differences of quantum defect between observation and calculation on the wave mechanics appear at first sight rather large, but they are all positive and of about the same magnitude, which is very satisfactory as will be seen shortly. The corresponding differences on the orbit model show a very much wider range of variation and the largest is

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[†] A. Fowler, *Report on the Series in Line Spectra*, p. 104. The first d term has been given the principal quantum number $n=4$ in accordance with § 8 of the present paper. The doublet separation for this term has not been observed and the value given is estimated from the value observed for the second d term.

[‡] Integer values of k were used in these calculations. The writer has tried some work with half integral values of k, but without any very marked improvement in the general agreement between observed and calculated values.

greater than the largest with the wave mechanics; moreover, this is the best agreement attained with a whole arbitrary function available for adjustment.

It was one of the unsatisfactory points about the results for the orbit model that the calculated variation of the quantum defect within a sequence of terms of the same k (i.e. the deviation from a simple Rydberg formula) was very much larger than the observed variation (larger by a factor from 2 to 3 for the s terms and from $1\frac{1}{2}$ to $2\frac{1}{2}$ for p terms, the error for the first term being relatively the largest). This was found to be the case for all atoms for which calculation was done, and could not be avoided by using half-integer values of k. For the results according to the wave mechanics considered here the calculated variation is actually less than the observed, and this is satisfactory as will appear shortly.

TABLE IV.

Rubidium. Comparison of Observed and Calculated values of Quantum Defect for Optical Terms.

n_k	$q=n^*-n$ obs.	q calculated				q obs. $-q$ calc.	q obs. $-q$ calc. orbit model
		Calc. final approx.	Spin Correction	Relativity Correction	Total		
5_1	3·195	2·986	−·034	·056	3·008	+·187	−·224
6_1	3·153	2·964	−·034	·057	2·987	·166	−·160
7_1	3·146	2·960	−·034	·057	2·983	·163	−·130
5_2	2·707 2·720	2·519	−·007 +·014	·015	2·527 2·548	·180 ·172	−·010
6_2	2·670 2·683	2·494	−·007 +·014	·015	2·502 2·523	·168 ·160	+·058
4_3	0·233 $\Delta\nu=(7)$	0·028	Doublet $\Delta\nu=3·3$	·000	0·028	·205	

The reasons why the differences between the observed quantum defect and that calculated on the wave mechanics are more satisfactory than they appear at first sight is this. The series electron when outside the core presumably polarises it, and the resultant polarisation gives rise to an attractive force on the series electron, always central, in addition to the field due to the unperturbed distribution of charge†. The additional field would act on the series

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† In the case of He (terms other than s terms) the core consists of a hydrogen-like system, for which the second order Stark effect, on which the polarisability depends, can be worked out exactly for a uniform perturbing field. This has already been treated on the wave mechanics by I. Waller, *Zeit. f. Phys.*, Vol. XXXVIII, p. 635 (1926); see particularly § 3.

electron as a central perturbing field having an inverse fourth power potential at large distances. It would certainly increase all calculated values of the quantum defect, and from the effect of such a perturbing field on the orbit model it may be expected that for the s and p terms it would increase the calculated quantum defect somewhat more for the first term or two of each sequence than for the rest, and would affect the two sequences about equally; this is just what is required to improve the agreement between calculated and observed values, both for the individual terms and for the variation of quantum defect within each sequence. How the d terms would be affected is not so easy to say.

This effect has not been calculated as it is not yet clear how the perturbing field may be expected to vary when the distance of the series electron from the core is not large compared with the dimensions of the latter, and this is the important part of the range for application to these terms. It would seem necessary at present to use an empirical perturbing field with a potential proportional to r^{-4} for large r, the behaviour for small r being chosen to give—in combination with the self-consistent field due to the unperturbed core—the best fit for the observed terms.

One unsatisfactory point about the results for the optical terms is the magnitude of the p spin doublet, the calculated separation being about $1\frac{1}{2}$ times that observed. A numerical mistake is a possible explanation, but the work has been thoroughly checked and it seems very unlikely that a mistake anything like big enough to explain the discrepancy could have escaped detection. Another possible explanation is this. The magnitude of the spin doublet on the new quantum mechanics was worked out by Heisenberg and Jordan for a Coulomb field using the matrix method. It seems just possible, though unlikely, that the formula is not applicable to an electron in a field differing widely from a Coulomb field and that in such cases the scalar product $\mathbf{ls}$ which occurs in the formula has a value different from $\frac{1}{2}[j(j-1)+l(l+1)-s(s+1)]$, which it has in a Coulomb field. If this were the case, the central field result would be expected to apply still to the core electrons (especially to the L doublet) for which the proportional deviation from a Coulomb field is not large, but not to the series electron.

Apart from this point, the general agreement of X-ray and optical term values calculated by the methods here given with those observed is very satisfactory.

§ 8. *Solution on Wave Mechanics for the Case when the Equation for Apsidal Distances has four Roots.*

As already mentioned, Rb was chosen as the first atom for which to do numerical work, partly in order to examine what happened on the wave mechanics in the case in which the equation

$$2v-\epsilon-l(l+1)/r^2=0$$

(I, 2·4), giving the apses for the orbital atomic model, has four roots, which for Rb occurs when $l = 2$.

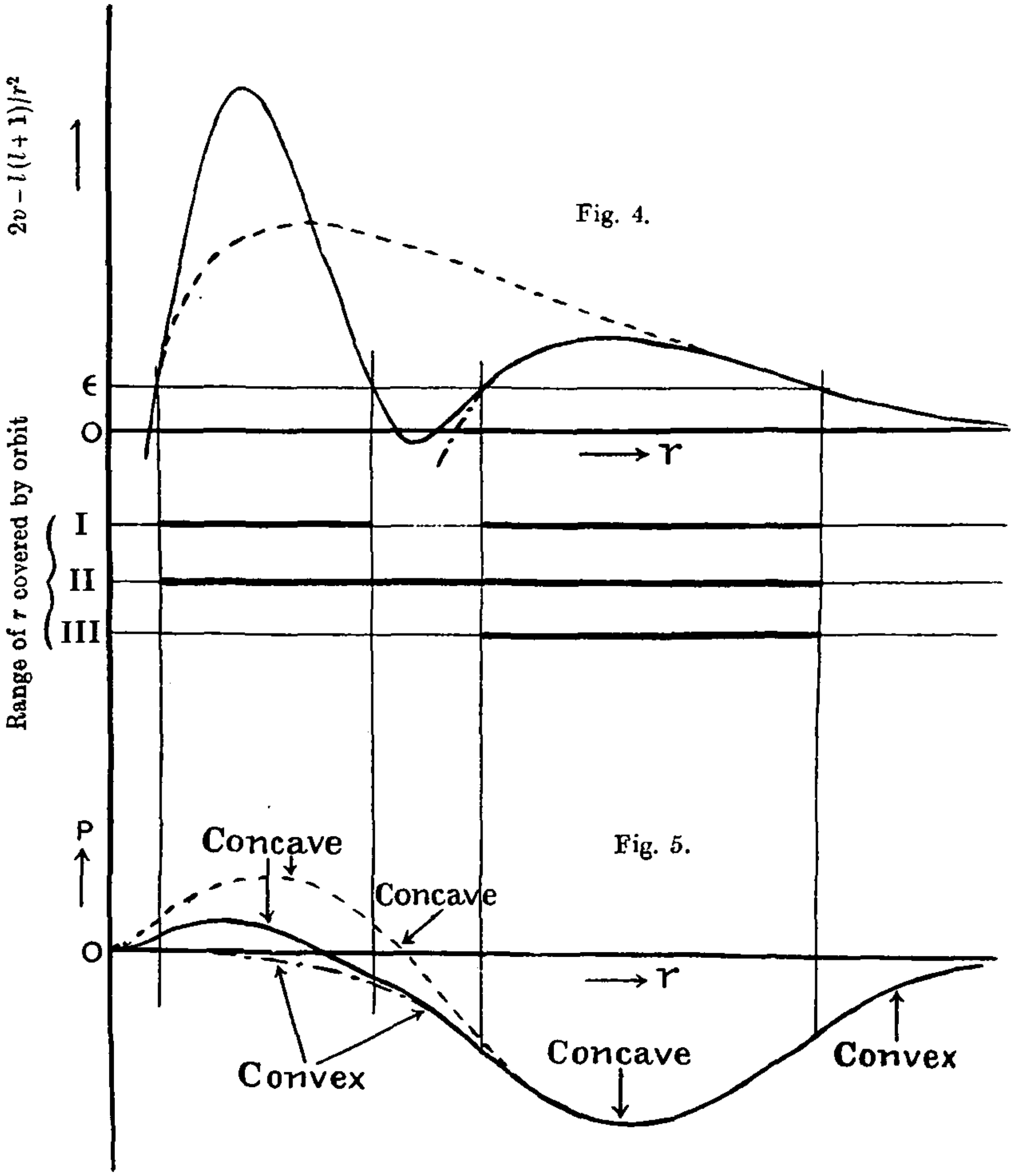

Fig. 4. Curves of $2v - l(l+1)/r^2$ as function of r.
Case I (Internal and external orbit of same energy) ————
Case II (Penetrating orbit) - - - - - - - - -
Case III (Non-penetrating orbit) — · — · —

Fig. 5. Wave function corresponding to curves in Fig. 4 above. 'Convex' and 'concave' refer to curvature with respect to r axis.

Figs. 4 and 5 to illustrate behaviour of wave function for field which gives *separate internal and external orbits of same energy on orbital atomic model.*

In Fig. 4 are shown three curves of $2v - l(l+1)/r^2$ as a function of r for different possible fields, a horizontal line being drawn at height ϵ, which is supposed to be a characteristic value for all three fields.

The usual curve of $2v - l(l+1)/r^2$ has one maximum, which may lie inside or outside the core; a horizontal line can then only cut it at two points, giving the apses of the corresponding orbit which is penetrating or non-penetrating respectively in the two cases. But the curve may have two maxima, in which case a horizontal line can cut it in four places, giving the apses of an internal and external orbit of the same energy. The curve for this case is drawn full, that for a penetrating orbit is drawn broken, and that for a non-penetrating orbit dot-and-dash. The ranges covered by the orbits in the various cases are marked below.

In Fig. 5 the curves of P against r are drawn to correspond with the curves in Fig. 4, the arbitrary constant being chosen so that the outer part of the curve in Fig. 5 is the same in all three cases. (The curves are diagrammatic only.)

From the differential equation for P (I, 2·3),

$$P'' + [2v - \epsilon - l(l+1)/r^2]\,P = 0,$$

it follows that when $2v - \epsilon - l(l+1)/r^2$ (i.e. the ordinate of the curve of $2v - l(l+1)/r^2$ above the line at height ϵ in Fig. 4) is positive, which is the case when r lies between the apses of the corresponding orbit, then the (P, r) curve is concave to the r axis, and when $2v - \epsilon - l(l+1)$ is negative the (P, r) curve is convex to the r axis.

In the case of four roots, the internal and external orbits with the same energy are quite separate mechanically possible orbits (they would in general not both be quantum orbits), whereas on the wave mechanics both are included in a single solution of the wave equation, the complete separation being replaced by a range for r for which the (P, r) curve is convex to the r axis. The effect of this convex piece is that, for the same outer part, P inside—and so the fraction of the total charge lying inside—is smaller than it is when the two intermediate roots of the equation for the apses are absent, so that the corresponding orbit penetrates. On the other hand, when only a non-penetrating orbit is possible, the (P, r) curve must always be convex to the r axis for r smaller than the inner apse of the corresponding orbit, so that P^2 can have no maximum inside the core such as it has in the case of four roots.

Thus the solution on the wave mechanics in the case of four roots is intermediate between those corresponding to penetrating and non-penetrating orbits on the orbital model, and may be expected to give some properties of both, e.g. approximately hydrogen-like terms and at the same time comparatively large doublet separations (as shown, for example, by the d terms of Cu I, Ag I, Au I), the latter being due to the maximum of P inside the core. According to the convention already mentioned (I, § 1), the principal quantum number must be assigned as if the corresponding orbits penetrated.

On the orbital mechanics, if $2v - l(l+1)/r^2$ had two maxima and the intermediate minimum were positive, then the orbits of the series electron whose energy was greater than this minimum would correspond to non-penetrating orbits, and those whose energy was less would correspond to penetrating orbits, and quite a sharp break in the progression of the quantum defect along the sequence of terms would be expected in such a case*. On the wave mechanics, where the sharp separation between internal and external orbits of the same energy in the case of four roots has disappeared, no such sharp break in a sequence of terms would be expected. As the energy decreased, the range of r for which (P, r) curve is convex to the P axis would shrink and disappear, but that is all; an abnormal increase in quantum defect throughout the sequence, and possibly in doublet separation for the first few terms, would be expected, just as observed, for example, in the *d* terms of Al I, but no sharp break.

TABLE V.

Sodium$^+$. *Approximate Self-Consistent Field and Distribution of Charge.*

r atomic units	Z	$-dZ/dr$ electrons per atomic unit	r atomic units	Z	$-dZ/dr$ electrons per atomic unit
0·00	11·00	0·0	0·5	7·15	8·8
0·02	10·98	2·8	0·6	6·26	9·0
0·04	10·90	7·0	0·7	5·37	8·5
0·06	10·72	10·2	0·8	4·55	7·6
0·08	10·49	11·9	0·9	3·84	6·5
0·10	10·25	12·1	1·0	3·25	5·39
0·12	10·02	11·4	1·2	2·39	3·47
0·14	9·80	10·5	1·4	1·82	2·16
0·16	9·61	9·3	1·6	1·47	1·31
0·18	9·43	8·2	1·8	1·27	0·77
0·20	9·27	7·3	2·0	1·16	0·45
0·25	8·94	6·0	2·5	1·04	0·12
0·30	8·64	6·0	3·0	1·01	0·03
0·35	8·33	6·6			
0·40	7·98	7·4			

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* See G. Wentzel, *Zeit. f. Phys.*, Vol. xix, p. 52 (1923).

§ 9. *Sodium and Chlorine.*

Approximations to the self-consistent field have been worked out for the ions Na^+ and Cl^- in a similar way to that for Rb^+, the immediate object being to determine the charge distribution, from which to calculate the functions F entering in the formula for the intensity of reflection of X-rays from crystals, in connection with recent experimental work on rocksalt. A comparison of the results of this work with the results of calculation, using the charge distribution found by the method discussed in this paper, will be given elsewhere, but it may be mentioned here that the result of the comparison is very satisfactory indeed.

TABLE VI.

Chlorine⁻. Approximate Self-Consistent Field and Distribution of Charge.

r atomic units	Z	$-dZ/dr$ electrons per atomic unit
0·00	17·00	0·0
0·01	16·99	2·8
0·02	16·95	8·0
0·03	16·84	13·2
0·04	16·69	16·7
0·06	16·32	19·6
0·08	15·93	18·7
0·10	15·58	16·2
0·12	15·28	14·0
0·14	15·01	12·9
0·16	14·76	12·7
0·18	14·47	13·3
0·20	14·19	14·3
0·25	13·42	17·0
0·30	12·51	18·8
0·35	11·57	18·7
0·40	10·67	17·2
0·5	9·16	12·5
0·6	8·15	8·0
0·7	7·50	5·1
0·8	7·08	3·6
0·9	6·76	3·2
1·0	6·43	3·27
1·2	5·72	3·90
1·4	4·91	4·21
1·6	4·08	4·06
1·8	3·30	3·72
2·0	2·61	3·25
2·5	1·30	2·05
3·0	0·50	1·26
3·5	0·00	0·80
4·0	−0·33	0·52
5	−0·69	0·23
6	−0·85	0·11
7	−0·93	0·05
8	−0·97	0·02

In Tables V and VI the values of Z and the radial charge density $-dZ/dr$ for Na^+ and Cl^- are given for the final field of the last approximation made, for which the maximum difference between initial and final field was 0·05 for Na^+ and 0·08 for Cl^-. The values for Cl^- for $r > 1$ are somewhat uncertain, as the main contribution is from the outermost group of electrons, which is very sensitive to the changes in the initial field. This sensitiveness is a result of the negative charge on the ion, and made the work much more troublesome than for neutral atoms or positive ions. For a multiply charged negative ion, for which there is a repulsive field on one electron when far enough removed from the rest, the distribution of charge for the outer electrons would be still more sensitive to the initial field, and the calculations would probably become unmanageable.

§ 10. *Summary.*

The methods of solution of the wave equation for a central field given in the previous paper are applied to various atoms. For the core electrons, the details of the interaction of the electrons in a single n_k group are neglected, but an approximate correction is made for the fact that the distributed charge of an electron does not contribute to the field acting on itself (§ 2).

For a given atom the object of the work is to find a field such that the solutions of the wave equation for the core electrons in this field (corrected as just mentioned for each core electron) give a distribution of charge which reproduces the field. This is called the self-consistent field, and the process of finding it is one of successive approximation (§ 3).

Approximations to the self-consistent field have been found for He (§ 4), Rb^+ (§ 5), Na^+, Cl^- (§ 9). For He the energy parameter for the solution of the wave equation for one electron in the self-consistent field of the nucleus and the other corresponds to an ionisation potential of 24·85 volts (observed 24·6 volts); this agreement suggests that for other atoms the values of the energy parameter in the self-consistent field (corrected for each core electron) will probably give good approximations to the X-ray terms (§ 4).

The most extensive work has been carried out for Rb^+. The distribution of charge given by the wave functions in the self-consistent field is compared with the distribution calculated by other methods (§ 6). The values of X-ray and optical terms calculated from the self-consistent field show satisfactory agreement with those observed (§ 7).

The wave mechanical analogue of the case in which on the orbital model an internal and an external orbit of the same energy are possible is discussed (§ 8).

Näherungsmethode zur Lösung des quantenmechanischen Mehrkörperproblems *).

Von **V. Fock** in Leningrad.

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Das Variationsprinzip $\int \delta \overline{\Psi} (L - E) \Psi d\tau = 0$ (L = Energieoperator) liefert bekanntlich die Wellengleichung im Konfigurationsraum. Es wird gezeigt, daß der Ansatz $\Psi = \psi_1(x_1)\psi_2(x_2) \ldots \psi_N(x_N)$ (N = Anzahl der Elektronen) zu den Gleichungen der Hartreeschen Theorie des „selfconsistent field" führt. Dieser Ansatz hat aber nicht die richtige Symmetrie. In dem wichtigen Spezialfall der „völligen Entartung des Termsystems" kann aber Ψ durch ein Produkt zweier Determinanten [Formel (50) des Textes] approximiert werden. Die entsprechende Rechnung wird durchgeführt. Die Gleichungen, die sich für $\psi_i(x)$ ergeben, enthalten „Austauschglieder" und können als Eulersche Gleichungen eines dreidimensionalen Variationsproblems mit der Energie als Wirkungsintegral [Formel (93)] aufgefaßt werden. Die Gleichungen sind nicht wesentlich komplizierter als die von Hartree, dürften aber viel genauere Resultate ergeben. Zum Schluß wird eine Formel für die Intensitäten angegeben, die Glieder enthält, welche einer „Umgruppierung" der inneren Elektronen bei einem Quantensprung entsprechen.

1. Das nichtrelativistische quantenmechanische Mehrkörperproblem hat bereits in den ersten Arbeiten von E. Schrödinger** seine mathematische Formulierung gefunden. Eine exakte Lösung der Schrödingerschen Wellengleichung im 3 N-dimensionalen Konfigurationsraum (N = Anzahl der Elektronen) bietet aber unüberwindliche mathematische Schwierigkeiten, und bei der Behandlung dieses Problems ist man auf Näherungsmethoden angewiesen.

Eine geistreiche Näherungsmethode ist von D. R. Hartree*** vorgeschlagen worden. Die Ableitung der Wellengleichung von Hartree beruht aber auf physikalischen Betrachtungen, deren Beziehung zur Schrödingerschen Wellengleichung nicht von vornherein klar ist und erst nachträglich durch eine besondere Untersuchung**** aufgestellt werden mußte.

In der Methode von Hartree (method of selfconsistent field) wird der klassische Begriff der Bahn (in sinngemäßer quantenmechanischer

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* Vorgetragen in der Russischen Physikalisch-Chemischen Gesellschaft am 17. Dezember 1929.

** E. Schrödinger, Quantisierung als Eigenwertproblem I, II, III und IV. Ann. d. Phys. 1926.

*** D. R. Hartree, The wave mechanics of an atom with a non-Coulomb central field. Proc. Cambr. Phil. Soc. **24**, 89, 111, 1928.

**** J. A. Gaunt, A Theory of Hartrees atomic fields. Proc. Cambr. Phil. Soc. **24**, 328, 1928.

Deutung) beibehalten, was der gesamten Methode eine große physikalische Anschaulichkeit verleiht. Daß der Begriff der Bahn auch in der Quantenmechanik in weitgehendem Maße brauchbar ist, wird durch die Möglichkeit bestätigt, die Atomspektren auf Grund der alten Bohrschen Theorie zu klassifizieren. Es entsteht nun die Frage, ob die Methode von Hartree auch wirklich das Optimum leistet, das mit der Beschreibung des Zustandes eines Atoms durch Angabe der Bahnen (Wellenfunktionen) einzelner Elektronen verträglich ist.

In der vorliegenden Arbeit wollen wir zeigen, daß dieses Optimum in der Hartreeschen Methode noch nicht erreicht wird. Mit Hilfe des Variationsprinzips wollen wir für dreidimensionale Wellenfunktionen ein Gleichungssystem aufstellen, das genauer ist als dasjenige von Hartree. In unserem Gleichungssystem treten Glieder auf, die den sogenannten „Austausch“ repräsentieren; die Vernachlässigung der Austauschglieder führt zu dem Gleichungssystem von Hartree zurück.

In unserer Theorie wird der Spin nur insofern berücksichtigt, als es erforderlich ist, dem Pauliprinzip Rechnung zu tragen; der Spin tritt also nur implizite auf, indem er die Symmetrieeigenschaften der Wellenfunktion beeinflußt. Die Spinglieder im Energieoperator werden dagegen vernachlässigt. Eine solche Betrachtungsweise ist aber wohl berechtigt, denn die Spinkorrektionen sind jedenfalls kleiner als die, welche durch den „Austausch“ verursacht werden.

2. Die Schrödingersche Wellengleichung ist bekanntlich die Eulersche Gleichung des Variationsproblems

$$\delta \int \overline{\psi} (L - E) \psi \, d\tau = 0, \tag{1}$$

wo L der Energieoperator ist. Wegen der Selbstadjungiertheit von L kann die Gleichung (1), wie leicht zu beweisen ist, durch

$$\int \delta \overline{\psi} (L - E) \Psi \, d\tau = 0 \tag{2}$$

ersetzt werden.

Wir wollen im folgenden die drei Koordinaten x_k, y_k, z_k eines Elektrons durch ein Zeichen x_k andeuten.

Ferner ist es zweckmäßig, mit Hartree sogenannte „atomare“ Maßeinheiten zu benutzen, nämlich

Länge:	$a_H = \frac{h^2}{4\pi^2 m e^2} = 0{,}529 \cdot 10^{-8}\,\mathrm{cm}$,	Radius des ersten Bohrschen Kreises,
Ladung:	$e = 4{,}77 \cdot 10^{-10}\,\mathrm{CGS}$,	Ladung eines Elektrons,
Masse:	$m = 9{,}00 \cdot 10^{-28}\,\mathrm{g}$,	Masse eines Elektrons.

In diesen Einheiten ist der numerische Wert von $h/2\pi$ gleich 1 und derjenige der Lichtgeschwindigkeit gleich 137 (reziproker Wert der Sommerfeldschen Feinstrukturkonstante).

In atomaren Einheiten ausgedrückt lautet der Energieoperator für das N-Elektronenproblem:

$$\left.\begin{aligned} L &= \sum_{k=1}^{N} H_k + \sum_{i>k=1}^{N} \frac{1}{r_{ik}}, \\ H_k &= -\frac{1}{2}\Delta_k - \frac{N}{r_k}. \end{aligned}\right\} \tag{3}$$

Hier bezeichnet Δ_k den auf die Koordinaten des k-ten Elektrons angewandten Laplaceschen Operator, r_k die Entfernung des k-ten Elektrons vom Kern, r_{ik} den Abstand zwischen den Elektronen i und k.

Im Variationsproblem (1) oder (2) können wir nun für Ψ verschiedene Ansätze machen. Suchen wir Ψ in Form einer endlichen Summe von Produkten von Funktionen $\psi_i(x_i)$ der Koordinaten je eines Elektrons, so können wir sagen, daß im betrachteten Zustand des Atoms bestimmte Bahnen vertreten und mit einer bestimmten Zahl von Elektronen besetzt sind. Die betreffende Beschreibung des Atomzustandes kann daher als mit der Bahnvorstellung verträglich angesehen werden.

Verschiedenen Ansätzen für die Wellenfunktion entsprechen verschiedene Gleichungssysteme für die einzelnen Funktionen ψ_i. Wie sich zeigen wird, führt der Ansatz

$$\Psi = \psi_1(x_1)\,\psi_2(x_2)\cdots\psi_N(x_N) \tag{4}$$

zu den Gleichungen von Hartree. Das einfache Funktionenprodukt (4) hat aber (mit Ausnahme des Heliumatoms im Grundzustand) nicht die richtigen Symmetrieeigenschaften, die durch die Gruppentheorie gefordert werden; deshalb stellen auch die Hartreeschen Gleichungen nur eine ziemlich grobe Näherung dar. Diese Näherung entspricht einer Vernachlässigung der sogenannten Austauschenergie.

Man kann aber eine bessere Näherung erhalten, wenn man für Ψ einen Ausdruck wählt, der als eine richtige Eigenfunktion nullter Näherung betrachtet werden kann und die richtige Symmetrie hat; dann enthalten die aus dem Variationsprinzip folgenden Gleichungen Glieder, welche den sogenannten Austausch repräsentieren. Der Ausdruck für Ψ ist ein Produkt zweier Determinanten mit den Elementen $\psi_i(x_k)$ oder eine Summe solcher Determinantenprodukte*. Der einfachste und wichtigste Spezialfall, wo die Wellenfunktion sich als ein einziges Determinantenprodukt darstellen läßt (das ist der Fall der „völligen Entartung des Termsystems“ nach Heitler), wird in dieser Arbeit durchgerechnet.

3. Um den Gang der Rechnungen klarzumachen, wollen wir mit dem einfachsten Beispiel anfangen, nämlich mit dem Heliumatom.

Der Energieoperator für das Zweielektronenproblem lautet:

$$L = H_1 + H_2 + \frac{1}{r_{12}}\cdot \tag{5}$$

Das Variationsprinzip (2) schreiben wir in der Form:

$$\iint \delta\,\overline{\psi}\,(L - E)\,\psi\, d x_1\, d x_2 = 0. \tag{6}$$

Für den Grundzustand des Heliumatoms machen wir für Ψ den Ansatz

$$\Psi = \psi(x_1)\,\psi(x_2). \tag{7}$$

Diesen Wert von Ψ führen wir in (2) ein. Wir erhalten

$$\iint [\delta\,\overline{\psi}\,(x_1)\,\overline{\psi}\,(x_2) + \overline{\psi}\,(x_1)\,\delta\,\overline{\psi}\,(x_2)]\,(L - E)\,\psi\,(x_1)\,\psi\,(x_2)\,d x_1\, d x_2 = 0.$$

Wegen der Symmetrie von L und Ψ in bezug auf x_1 und x_2 liefern die beiden Glieder in der eckigen Klammer einen gleich großen Beitrag und man erhält

$$\int d x_1\, \delta\,\overline{\psi}\,(x_1) \int \overline{\psi}\,(x_2)\left(H_1 + H_2 + \frac{1}{r_{12}} - E\right)\psi\,(x_1)\,\psi\,(x_2)\,d x_2 = 0. \tag{8}$$

Das innere Integral ist gleich

$$H_1\,\psi(x_1) + G(x_1)\,\psi(x_1 - E_0\,\psi(x_1),$$

wo

$$G\,(x_1) = \int \frac{|\,\psi\,(x_2)\,|^2\, d x_2}{r_{12}} \tag{9}$$

und

$$E_0 = E - \int \overline{\psi}\,(x_2)\,H_2\,\psi\,(x_2)\,d x_2 \tag{10}$$

gesetzt ist. Wir haben also

$$\int d x\, \delta\,\overline{\psi}\,(x)\,[H + G\,(x) - E_0]\,\psi\,(x) = 0 \tag{11}$$

und erhalten für $\psi(x)$ die Gleichung

$$[H + G(x) - E_0]\,\psi(x) = 0, \tag{12}$$

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* Siehe z. B. W. Heitler, Störungsenergie und Austausch beim Mehrkörperproblem. ZS. f. Phys. **46**, 47, 1927; I. Waller und D. R. Hartree, On the Intensity of Total Scattering of X-Rays, § 3. Proc. Roy. Soc. London (A) **124**, 119, 1929.

die genau mit der Hartreeschen übereinstimmt. Der Eigenwert E des Energieoperators ist mit dem Parameter E_0 durch die Relation (10) verbunden, die sich auch mit Hilfe von (12) in der Form

$$E = 2 E_0 - \int G(x) \, | \psi(x) |^2 \, dx \tag{13}$$

schreiben läßt. Die letztere Gleichung fällt mit der von Gaunt (l. c.) angegebenen zusammen. Die beiden Gleichungen (12) und (13) von Hartree und Gaunt folgen hier ganz automatisch aus dem Variationsprinzip.

Man kann die weitere Annahme machen, daß $\psi(x) = \psi(x, y, z)$ nur vom Abstand r vom Kern abhängen soll. Die Funktion $G(xyz)$ ist dann auch eine Funktion von r allein, so daß man in der Gleichung (12) die kugelsymmetrische Lösung aufzusuchen hat.

Für das angeregte Heliumatom hat man

$$\Psi = \psi_1(x_1) \psi_2(x_2) + \psi_1(x_2) \psi_2(x_1) \tag{14}$$

zu setzen und für Parhelium

$$\Psi = \psi_1(x_1) \psi_2(x_2) - \psi_1(x_2) \psi_2(x_1). \tag{15}$$

Im letzteren Falle darf man annehmen, daß ψ_1 und ψ_2 orthogonal sind; wir nehmen sie auch als normiert an. Geht man mit (15) in (6) ein, so bekommt man das Gleichungssystem:

$$\left.\begin{aligned} H \psi_1(x) + G_{22}(x) \psi_1(x) - G_{21}(x) \psi_2(x) & \\ = E - H_{22}) \psi_1(x) + H_{21} \psi_2(x), & \\ H \psi_2(x) + G_{11} \psi_2(x) - G_{12} \psi_1(x) = H_{12} \psi_1(x) + (E - H_{11}) \psi_2(x). & \end{aligned}\right\} \tag{16}$$

Hier bezeichnet

$$\left.\begin{aligned} G_{ik}(x) &= \int \frac{\overline{\psi}_i(x') \psi_k(x')}{r} \, dx', \\ H_{ik} &= \int \overline{\psi}_i(x) H \psi_k(x) \, dx. \end{aligned}\right\} \tag{17}$$

Wir setzen noch zur Abkürzung

$$\left.\begin{aligned} (ik \,|\, G \,|\, lm) &= \iint \overline{\psi}_i(x') \overline{\psi}_k(x) \psi_l(x') \psi_m(x) \frac{dx \, dx'}{r} \\ &= \int \overline{\psi}_i(x) \psi_l(x) G_{km}(x) \, dx \\ &= \int \overline{\psi}_k(x) \psi_m(x) G_{il}(x) \, dx. \end{aligned}\right\} \tag{18}$$

Im Gleichungssystem (16) repräsentieren $G_{12}(x)$ und $G_{21}(x)$ sowie H_{12} und H_{21}, also die Koeffizienten mit verschiedenen Indizes, den Austausch. Die Größen G_{12} und G_{21} sind zwar im allgemeinen kleiner als G_{11} und G_{22}, aber immerhin so beträchtlich, daß sie nicht vernachlässigt werden dürfen*.

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* Vgl. J. A. Gaunt, Anmerkung auf S. 331, l. c.

Multiplizieren wir die erste der Gleichungen (16) mit $\overline{\psi}_1(x)$ und integrieren, so erhalten wir den folgenden Ausdruck für die Energie des Atoms:

$$E = H_{11} + H_{22} + (12|G|12) - (12|G|21). \tag{19}$$

Dieser Ausdruck läßt sich in einer anderen Form schreiben, die eine anschauliche Deutung zuläßt. Setzt man

$$\varrho(x, x') = \overline{\psi}_1(x)\,\psi_1(x') + \overline{\psi}_2(x)\,\psi_2(x'), \tag{20}$$

$$\varrho(x) = \varrho(x, x), \tag{21}$$

so wird

$$E = H_{11} + H_{22} + \frac{1}{2}\iint \frac{\varrho(x)\,\varrho(x') - |\varrho(x, x')|^2}{r}\,dx\,dx'. \tag{22}$$

Hier stellen die beiden ersten Glieder H_{11} und H_{22} die Energie der einzelnen Elektronen dar und das Integral ist die Wechselwirkungsenergie der Elektronen. *Zu beachten ist, daß im Zähler des Integranden nicht einfach* $\varrho(x)\varrho(x')$ (Produkt der Ladungsdichten), sondern $\varrho(x)\varrho(x') - |\varrho(x, x')|^2$ steht, ein Ausdruck, der für $x = x'$ verschwindet. Diese Tatsache kann dahin gedeutet werden, daß das Elektron nicht auf sich selbst wirkt.

Mit dem Ansatz (14) für angeregtes Orthohelium gelangt man zu Gleichungen, die den Gleichungen (16) analog sind; nur haben die Austauschglieder G_{12}, H_{12} usw. ein entgegengesetztes Vorzeichen und es treten einige weitere Glieder auf, die davon herrühren, daß die Funktionen ψ_1, ψ_2 nicht mehr orthogonal angenommen werden dürfen.

4. Wir gehen nun zum N-Elektronenproblem über und machen zunächst für Ψ den Ansatz (4):

$$\Psi = \prod_{q=1}^{N} \psi_q(x_q). \tag{23}$$

Wie erwähnt, besitzt diese Funktion Ψ nicht die nötigen Symmetrieeigenschaften; wir wollen aber die Rechnung durchführen, um zu zeigen, daß der Ansatz (23) zu den Gleichungen von Hartree führt. Das Pauliprinzip kann hier nur dadurch berücksichtigt werden, daß man unter den Funktionen ψ_q höchstens zwei gleiche zuläßt.

Wir haben

$$\delta\psi = \sum_{q=1}^{N} \delta\psi_q(x_q)\,\Psi^{(q)}, \tag{24}$$

wo zur Abkürzung

$$\Psi^{(q)} = \frac{\Psi}{\psi_q(x_q)} \tag{25}$$

gesetzt ist. Das Variationsprinzip lautet:

$$\delta J = \int \delta \overline{\Psi} (L - E) \Psi \, d\tau = \sum_{q=1}^{N} \int \delta \overline{\psi}_q (x_q) A_q \, d x_q = 0. \tag{26}$$

Hier ist

$$\left.\begin{aligned} A_q = & \underbrace{\int \cdots \int}_{N=1} \overline{\Psi}^{(q)} \Bigg(\sum_{k=1}^{N} H_k - E \\ & \quad + \sum_{i>k=1}^{N} \frac{1}{2_{ik}} \Bigg) \psi_q (x_q) \psi^{(q)} \, d x_1 \cdots d x_{q-1} \, d x_{q+1} \cdots d x_N \\ = & \, H_q \psi_q (x) + \Bigg[\sum_{i=1}^{N}{}' (G_{ii}(x_q) + H_{ii}) \\ & \quad + \sum_{i>k=1}^{N}{}'' W_{ik} - E \Bigg] \psi_q (x_q) \end{aligned} \right\} \tag{27}$$

mit der Abkürzung

$$W_{ik} = (i k | G | i k) = \iint \frac{|\psi_i(x)|^2 \cdot |\psi_k(x')|^2}{r} d x \, d x'. \tag{28}$$

Der Strich am Summenzeichen soll hier und im folgenden andeuten, daß das Glied mit $i = q$ oder $k = q$ fortzulassen ist.

Im Ausdruck (26) für δJ müssen die Koeffizienten der unabhängigen Variationen $\delta \overline{\psi}_q$ gleich Null gesetzt werden. Falls die Funktion ψ_q in Ψ nur einmal vorkommt, muß $A_q = 0$ sein; wenn deren zwei gleich sind, z. B. $\psi_q = \psi_{q+1}$, so sind, wie eine leichte Überlegung zeigt, auch die Koeffizienten von $\delta \overline{\psi}_q$ und $\delta \overline{\psi}_{q+1}$ einander gleich, d. h. $A_q = A_{q+1}$. In jedem Falle folgt $A_q = 0$.

Wir schreiben diese Gleichung in der Form:

$$H \psi_q(x) + [V(x) - G_{qq}(x)] \psi_q(x) = \lambda_q \psi_q(x). \tag{29}$$

Hier bezeichnet

$$V(x) = \sum_{k=1}^{N} G_{kk}(x) \tag{30}$$

und

$$\lambda_q = E - \sum_{i=1}^{N}{}' H_{ii} - \sum_{i>k=1}^{N}{}'' W_{ik} \tag{31}$$

Die Gleichungen (29) stimmen genau mit den von Hartree abgeleiteten überein.

Für die Energie des Atoms gewinnt man den Ausdruck

$$E = \sum_{i=1}^{N} H_{ii} + \sum_{i>k=1}^{N} W_{ik}. \tag{32}$$

Man bestätigt leicht, daß dieser Ausdruck gleich

$$E = \frac{\int \overline{\psi} L \psi \, d\tau}{\int \overline{\psi} \psi \, d\tau} \tag{33}$$

ist, trotzdem die Gleichung $L\psi = E\psi$ nicht gilt, da Ψ keine exakte Lösung der Schrödingergleichung ist.

Setzt man den Ausdruck (32) in (31) ein, so bekommt man

$$\lambda_q = H_{qq} + \sum_{i=1}^{N}{}' W_{iq}. \tag{34}$$

Summiert man über q, so wird

$$\sum_{q=1}^{N} \lambda_q = 2E - \sum_{q=1}^{N} H_{qq}. \tag{35}$$

Die Gleichungen (29) sind die Eulerschen Gleichungen des folgenden Variationsproblems:

Es soll das Integral

$$W = \sum_{i=1}^{N} \int \overline{\psi}_i H \psi_i dx + \frac{1}{2} \sum_{i,k=1}^{N} (1-\delta_{ik}) \int\int \frac{\overline{\psi}_k(x')\psi_k(x')\overline{\psi}_i(x)\psi_i(x)}{r} dx\,dx' \tag{36}$$

zum Minimum gemacht werden, mit den Nebenbedingungen

$$\int \overline{\psi}_i(x)\, \psi_i(x)\, dx = 1. \tag{37}$$

Der Wert des Integrals W ist gleich der Energie E, wie der Vergleich mit Formel (32) zeigt. Die Größen λ_q sind Lagrangesche Faktoren.

Man kann (29) auch aus einem anderen Variationsprinzip ableiten. Die Koeffizienten $V(x)$ und $G_{qq}(x)$ in (29) hängen von den Funktionen $\psi_i(x)$ ab; man kann aber rein formal diese Koeffizienten als gegeben und die Gleichungen (29) als lineare Differentialgleichungen für $\psi_q(x)$ betrachten. Dann machen die $\psi_q(x)$ das Integral

$$W^* = \sum_{i=1}^{N} \int \overline{\psi}_i(x)\, [H + V(x) - G_{ii}(x)]\, \psi_i(x)\, dx \tag{38}$$

mit den früheren Nebenbedingungen (37) zum Minimum. Dieser Minimalwert ist gleich

$$W^* = 2E - \sum_{q=1}^{N} H_{qq} = \sum_{q=1}^{N} \lambda_q. \tag{39}$$

In unseren Gleichungen bezeichnet x symbolisch alle drei Raumkoordinaten xyz und $\psi_q(x)$ steht statt $\psi_q(x, y, z)$ usw. Geht man zu spezielleren Ansätzen für ψ_q über, so hat man folgendermaßen zu verfahren. Man bilde den Ausdruck

$$\iiint \delta \overline{\psi}_q(x,y,z)\, [H + V(x,y,z) - G_{qq}(x,y,z) - \lambda_q]\, \psi_q(x,y,z)\, dx\, dy\, dz, \tag{40}$$

mache für ψ_q den gewünschten Ansatz und setze den Koeffizienten der noch frei zu variierenden Funktion gleich Null.

Wir wollen hier die Rechnung für

$$\psi_q(x, y, z) = f_{nl}(r) Y_l(\vartheta, \varphi); \quad \int\int |Y_l(\vartheta, \varphi)|^2 \sin\vartheta\, d\vartheta\, d\varphi = 1 \quad (41)$$

(Y_l Kugelfunktion) durchführen. Das frei zu variierende Element ist hier die Funktion $f_{nl}(r)$, während $Y_l(\vartheta, \varphi)$ fest ist. Man hat dann

$$\int\int\int \delta\bar{\psi}_q(x, y, z) \Delta \psi_q(x, y, z)\, dx\, dy\, dz$$
$$= \int \delta\bar{f}_{nl}(r) \left[\frac{\partial}{\partial r}\left(r^2 \frac{\partial f_{nl}}{\partial r}\right) - l(l+1) f_{nl}(r)\right] dr.$$

Ferner ist z. B.

$$\int\int\int \delta\bar{\psi}_q V(xyz) \psi_q\, dx\, dy\, dz = \int \delta\bar{f}_{nl}(r) f_{nl}(r) V^0(r) r^2\, dr,$$

wo

$$V^0(r) = \int\int V(xyz) |Y_l(\vartheta, \varphi)|^2 \sin\vartheta\, d\vartheta\, d\varphi. \quad (42)$$

Analog bildet man aus $G_{qq}(xyz)$ die Funktion $G^0_{qq}(r)$.

Für $f_{nl}(r)$ bekommt man die Gleichung

$$-\frac{1}{2}\left(\frac{d^2 f_{nl}}{d r^2} + \frac{2}{r}\frac{d f_{nl}}{d r} - \frac{l(l+1)}{r^2} f_{nl}\right)$$
$$+ \left(-\frac{N}{r} + V^0(r) - G^0_{qq}(r)\right) f_{nl} = \lambda_q f_{nl}. \quad (43)$$

Wie man sieht, entspricht unsere Gleichung (43) nicht ganz dem von Hartree angegebenen Verfahren; nach Hartree hätte man z. B. die Funktion $V(x, y, z)$ über die Kugelfläche vom Radius r zu mitteln, d. h. den Ausdruck

$$\frac{1}{4\pi}\int\int V(xyz) \sin\vartheta\, d\vartheta\, d\varphi$$

zu nehmen, während bei uns nach (42) die Mittelung mit Hilfe der „Gewichtsfunktion" $|Y_l(\vartheta, \varphi)|^2$ geschieht.

5. Wir betrachten jetzt wieder das N-Elektronenproblem, suchen aber für Ψ einen Ansatz mit der richtigen Symmetrie. Die Eigenschaften der Wellenfunktionen, die verschiedenen Termen entsprechen, wurden bereits eingehend von mehreren Autoren* mit Hilfe der Gruppentheorie untersucht, so daß wir hier fertige Resultate vor uns haben.

Der Sachverhalt ist hier kurz der folgende. Einem bestimmten Term entsprechen im allgemeinen mehrere, sagen wir s Wellenfunktionen

$$\omega_1, \omega_2, \ldots, \omega_s,$$

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* Vgl. z. B. W. Heitler (l. c.) und I. Waller und D. R. Hartree (l. c.)

die von den Koordinaten der N Elektronen abhängen. Bei einer beliebigen Permutation P^a der Elektronen geht ω_j in ω_j' über; diese neue Funktion ω_j' läßt sich als eine lineare Kombination der alten, zum selben Term gehörenden Funktionen $\omega_1, \omega_2, \ldots, \omega_s$ ausdrücken:

$$P^a \omega_j = \omega_j' = \sum_{i=1}^{s} P_{ij}^a \omega_i. \tag{44}$$

Die Koeffizienten P_{ij}^a bilden eine irreduzible Darstellung der Substitutionsgruppe. Die Funktionen $\omega_1, \ldots, \omega_s$ kann man immer so wählen, daß der Ausdruck

$$|\omega_1|^2 + |\omega_2|^2 + \cdots + |\omega_s|^2$$

in allen Elektronen symmetrisch wird, dann sind alle Matrizen P_{ij}^a unitär.

Wir wollen nun folgendes beweisen. Bildet man eine beliebige lineare Kombination der ω_i:

$$\Omega = a_1 \omega_1 + a_2 \omega_2 + \cdots + a_s \omega_s \tag{45}$$

und ist L ein selbstadjungierter, in allen Elektronen symmetrischer Operator, so ist der Ausdruck

$$A = \frac{\int \overline{\Omega} L \Omega \, d\tau}{\int \overline{\Omega} \Omega \, d\tau} \tag{46}$$

unabhängig von der Wahl der Konstanten a_i.

Ist L der Energieoperator, so liefert das Nullsetzen der Variation von A

$$\delta A = 0$$

die Schrödingergleichung für Ω. Unsere Behauptung besagt also, daß man bei der Ableitung der Schrödingergleichung aus dem Variationsprinzip eine beliebige lineare Kombination der Wellenfunktionen $\omega_1, \omega_2, \ldots, \omega_s$ benutzen kann.

Zum Beweis zeigen wir zunächst, daß

$$\left.\begin{aligned} \int \overline{\omega}_j L \omega_i \, d\tau &= 0 \quad (i \neq j), \\ \int \overline{\omega}_1 L \omega_1 \, d\tau = \int \overline{\omega}_2 L_2 \omega_2 \, d\tau &= \cdots = \int \overline{\omega}_s L \omega_s \, d\tau \end{aligned}\right\} \tag{47}$$

gilt, so daß die Matrix

$$L_{ji} = \int \overline{\omega}_j L \omega_i \, d\tau \quad (i, j = 1, 2, \cdots, s) \tag{48}$$

proportional der Einheitsmatrix ist. Die letztere Tatsache ist bekannt*; der Vollständigkeit wegen wollen wir aber hier den Beweis andeuten.

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* Vgl. z. B. E. Wigner, ZS. f. Phys. **43**, 624, 1927, Formel (7a).

Ist L ein symmetrischer Operator, so erleiden die Funktionen

$$\xi_j = L\,\omega_j$$

bei einer Permutation P^a dieselbe Substitution wie die ω_j, nämlich

$$\xi_i' = P^a \xi_i = \sum_{l=1}^{s} P^a_{li}\,\xi_l.$$

Die Größen $\eta_j = \bar{\omega}_j$ erleiden, da die Matrix P^a unitär ist, die Substitution

$$\eta_j' = \sum_{k=1}^{s} P^{(a^{-1})}_{jk}\,\eta_k.$$

Wir bilden das Produkt $\eta_j' \xi_i'$ und berechnen dessen Mittelwert über alle $N!$ Permutationen. Infolge der Gleichung

$$\frac{1}{N!}\sum_a P^{(a^{-1})}_{jk}\,P^{(a)}_{li} = \frac{1}{s}\,\delta_{ij}\,\delta_{kl},$$

die in der Gruppentheorie bewiesen wird*, bekommt man

$$\frac{1}{N!}\sum_a \eta_j'\,\xi_i' = \frac{1}{s}\,\delta_{ij}\sum_{k=1}^{s}\eta_k\,\xi_k.$$

Integriert man diesen Ausdruck über den ganzen Konfigurationsraum und beachtet man die Gleichung

$$\int \eta_j'\,\xi_i'\,d\tau = \int \eta_j\,\xi_i\,d\tau = \int \bar{\omega}_j\,L\,\omega_i\,d\tau,$$

so bekommt man

$$\int \bar{\omega}_j\,L\,\omega_i\,d\tau = \delta_{ij}\,\frac{1}{s}\sum_{k=1}^{s}\int \bar{\omega}_k\,L\,\omega_k\,d\tau, \tag{49}$$

was mit (47) gleichbedeutend ist.

Aus (47) oder (49) folgt aber unmittelbar die Unabhängigkeit des Ausdrucks (46) von den Konstanten a_i; denn setzt man Ω in (46) ein, so treten im Zähler und im Nenner die α_i nur in der Kombination

$$|\,a_1|^2 + |\,a_2|^2 + \cdots + |\,a_s|^2$$

auf, welcher Ausdruck sich bei der Bildung des Quotienten heraushebt.

Unsere Aufgabe ist nun die folgende. Wir müssen aus den Funktionen $\psi_i(x_k)$ der Koordinaten je eines Elektrons einen Ausdruck bilden, der sich (in bezug auf Permutationen) wie eine lineare Kombination der zu einem Term gehörigen Eigenfunktionen $\omega_1, \omega_2, \ldots, \omega_s$ verhält; dieser Ausdruck ist dann in das zu variierende Integral einzusetzen.

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* Vgl. A. Speiser, Theorie der Gruppen von endlicher Ordnung, Satz 144.

In einem wichtigen Spezialfall, wo der betrachtete Term zu einem Termsystem gehört, das vollständig entartet ist, läßt sich bekanntlich der entsprechende Ausdruck in Form eines Produktes zweier Determinanten schreiben.

Wir betrachten als Beispiel den Fall von drei Elektronen (Lithiumatom); dabei sollen zwei unter ihnen auf einer und derselben Bahn sein. Aus den drei einfachen Produktfunktionen

$$\begin{gathered}\psi_1(x_2)\,\psi_1(x_3)\,\psi_2(x_1),\\ \psi_1(x_3)\,\psi_1(x_1)\,\psi_2(x_2),\\ \psi_1(x_1)\,\psi_1(x_2)\,\psi_2(x_3)\end{gathered}$$

bilden wir die folgenden drei linearen Kombinationen:

$$\begin{aligned}\omega &= \psi_1(x_2)\,\psi_1(x_3)\,\psi_2(x_1) + \psi_1(x_3)\,\psi_1(x_1)\,\psi_2(x_2)\\ &\qquad\qquad\qquad\qquad + \psi_1(x_1)\,\psi_1(x_2)\,\psi_2(x_3),\\ \omega_1 &= -\,\psi_1(x_3)\begin{vmatrix}\psi_1(x_1) & \psi_2(x_1)\\ \psi_1(x_2) & \psi_2(x_2)\end{vmatrix},\\ \omega_2 &= \frac{1}{\sqrt{3}}\,\psi_1(x_2)\begin{vmatrix}\psi_1(x_3) & \psi_2(x_3)\\ \psi_1(x_1) & \psi_2(x_1)\end{vmatrix} + \frac{1}{\sqrt{3}}\,\psi_1(x_1)\begin{vmatrix}\psi_1(x_3) & \psi_2(x_3)\\ \psi_1(x_2) & \psi_2(x_2)\end{vmatrix}.\end{aligned}$$

Die Funktion ω ist in allen drei Elektronen symmetrisch; der entsprechende Term ist durch das Pauliprinzip verboten. Die Funktionen ω_1 und ω_2 gehören zu einem Term. Die Substitutionen, die ω_1 und ω_2 bei der Vertauschung der Elektronen erleiden, liefern die folgende irreduzible orthogonal-unitäre Darstellung der Permutationsgruppe

$$P^{(23)} = \left\{\begin{matrix}\frac{1}{2} & \frac{\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & -\frac{1}{2}\end{matrix}\right\}, \quad P^{(31)} = \left\{\begin{matrix}\frac{1}{2} & -\frac{\sqrt{3}}{2}\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2}\end{matrix}\right\}, \quad P^{(12)} = \left\{\begin{matrix}-1 & 0\\ 0 & 1\end{matrix}\right\},$$

$$P^{(123)} = \left\{\begin{matrix}-\frac{1}{2} & \frac{\sqrt{3}}{2}\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2}\end{matrix}\right\}, \quad P^{(213)} = \left\{\begin{matrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & -\frac{1}{2}\end{matrix}\right\}, \quad E = \left\{\begin{matrix}1 & 0\\ 0 & 1\end{matrix}\right\},$$

Aus der allgemeinen Theorie folgt (was hier auch unmittelbar leicht zu bestätigen ist):

$$\int \bar{\omega}_1\, L\, \omega_2\, d\tau = 0; \quad \int \bar{\omega}_1\, L\, \omega_1\, d\tau = \int \bar{\omega}_2\, L\, \omega_2\, d\tau.$$

Aus diesem Beispiel sehen wir also, daß, trotzdem einem Term nicht eine, sondern mehrere (hier zwei) Funktionen angehören, es dennoch genügt, im Variationsprinzip nur eine, und zwar eine beliebige lineare Kombination Ω der ω_i zu benutzen. Als solche können wir in unserem Beispiel einfach das Determinantenprodukt $\Psi = -\omega_1$ wählen:

$$\Psi = \begin{vmatrix} \psi_1(x_1) & \psi_2(x_1) \\ \psi_1(x_2) & \psi_2(x_2) \end{vmatrix} \cdot \psi_1(x_3).$$

6. Wir wollen die Ableitung der Variationsgleichungen für den Fall durchführen, daß die Wellenfunktion durch ein Produkt zweier Determinanten approximiert werden kann.

Wir setzen

$$\Psi = \Psi_1 \Psi_2, \tag{50}$$

$$\Psi_1 = \begin{vmatrix} \psi_1(x_1) & \psi_2(x_1) & \cdots & \psi_q(x_1) \\ \psi_1(x_2) & \psi_2(x_2) & \cdots & \psi_q(x_2) \\ \cdot & \cdot & \cdot & \cdot \\ \psi_1(x_q) & \psi_2(x_q) & \cdots & \psi_q(x_q) \end{vmatrix} \tag{51}$$

$$\Psi_2 = \begin{vmatrix} \psi_1(x_{q+1}) & \psi_2(x_{q+1}) & \cdots & \psi_p(x_{q-1}) \\ \psi_1(x_{q+2}) & \psi_2(x_{q+2}) & \cdots & \psi_p(x_{q+2}) \\ \cdot & \cdot & \cdot & \cdot \\ \psi_1(x_{q+p}) & \psi_2(x_{q+p}) & \cdots & \psi_p(x_{q+p}) \end{vmatrix}. \tag{51 *}$$

Hier ist $q + p = N$ die Anzahl der Elektronen; der Bestimmtheit wegen sei $q > p$ angenommen. Durch die Funktion Ψ wird ein Zustand beschrieben, in welchem q Bahnen vertreten sind, unter denen p doppelt besetzte vorkommen.

Die Funktionen

$$\psi_1(x),\ \psi_2(x),\ \ldots,\ \psi_q(x)$$

können alle orthogonal und normiert vorausgesetzt werden. In der Tat können zunächst die ersten p Funktionen orthogonalisiert werden; denn eine beliebige Substitution unter den ersten p Funktionen bewirkt nur die Multiplikation der Determinanten mit einem konstanten Faktor. Ferner kann man $\psi_{p+1}, \ldots, \psi_q$ durch lineare Kombinationen aller q Funktionen ersetzen, die so gewählt sind, daß $\psi_{p+1}, \ldots, \psi_q$ mit $\psi_1, \ldots, \psi_p$ und miteinander orthogonal werden. Endlich kann man alle q Funktionen normieren. Dadurch werden alle q Funktionen orthogonal und normiert, und es bleibt noch eine unitäre Substitution von $\psi_1, \ldots, \psi_p$ unter sich und von $\psi_{p+1}, \ldots, \psi_q$ unter sich frei wählbar.

Um bequemer mit Determinanten rechnen zu können, führen wir den „vollständig antisymmetrischen Tensor“

$$\varepsilon_{(\alpha)} = \varepsilon_{\alpha_1 \alpha_2 \ldots \alpha_q} \tag{52}$$

ein, indem wir festsetzen:

$\varepsilon_{\alpha_1 \alpha_2 \ldots \alpha_q} = 1$, wenn $\alpha_1, \ldots, \alpha_q$ alle verschieden sind und eine gerade Permutation von $1, 2, \ldots, q$ bilden, $\varepsilon_{\alpha_1 \ldots \alpha_q} = -1$, wenn die Permutation ungerade ist, und $\varepsilon_{\alpha_1 \ldots \alpha_q} = 0$, wenn unter den Zahlen $\alpha_1, \ldots, \alpha_q$ zwei oder mehrere gleiche vorkommen.

Die Determinante ψ_1 läßt sich dann schreiben

$$\Psi_1 = \sum_{(\alpha)} \varepsilon_{\alpha_1 \alpha_2 \ldots \alpha_q} \psi_{\alpha_1}(x_1)\, \psi_{\alpha_2}(x_2) \cdots \psi_{\alpha_q}(x_q). \tag{53}$$

Den Energieoperator L [Formel (3)] des N-Körperproblems zerlegen wir in drei Summanden. Der erste Summand L_1 soll alle Glieder enthalten, die nur von x_1 bis x_q abhängen, der zweite L_2, die nur von x_{q+1} bis x_{q+p} abhängigen, der dritte L_{12} die übrigen Glieder.

In Formeln:

$$L = L_1 + L_2 + L_{12}, \tag{54}$$

$$L_1 = \sum_{k=1}^{q} H_k + \sum_{i>k=1}^{q} \frac{1}{r_{ik}}, \tag{55}$$

$$L_2 = \sum_{k=q+1}^{q+p} H_k + \sum_{i>k=q+1}^{q+p} \frac{1}{r_{ik}}, \tag{56}$$

$$L_{12} = \sum_{i=1}^{q} \sum_{k=q+1}^{q+p} \frac{1}{r_{ik}}. \tag{57}$$

Die Variation des Integrals

$$\delta J = \int \delta \overline{\psi} (L - E)\, \psi\, d\tau$$

läßt sich dann schreiben:

$$\delta J = \iint \delta (\overline{\psi}_1 \overline{\psi}_2)(L_1 + L_2 + L_{12} - E)\, \psi_1 \psi_2\, d\tau_1\, d\tau_2, \tag{58}$$

wo

$$d\tau_1 = dx_1\, dx_2 \ldots dx_q,$$
$$d\tau_2 = dx_{q+1}\, dx_{q+2} \ldots dx_{p+q}$$

gesetzt ist. Wir bezeichnen zur Abkürzung

$$\left.\begin{aligned} A_1 &= \int \overline{\psi}_1 \psi_1\, d\tau_1, & A_2 &= \int \overline{\psi}_2 \psi_2\, d\tau_2, \\ B_1 &= \int \overline{\psi}_1 L_1 \psi_1\, d\tau_1, & B_2 &= \int \overline{\psi}_2 L_2 \psi_2\, d\tau_2, \\ F_1 &= \int \overline{\psi}_1 L_{12} \psi_1\, d\tau_1, & F_2 &= \int \overline{\psi}_2 L_{12} \psi_2\, d\tau_2. \end{aligned}\right\} \tag{59}$$

Die A_i und B_i sind Konstanten, F_i Funktionen der Koordinaten. Mit diesen Abkürzungen bekommt man

$$\begin{aligned} \delta J = & \int \delta \overline{\psi}_1 [A_2(L_1 - E) + B_2 + F_2]\, \psi_1\, d\tau_1 \\ & + \int \delta \overline{\psi}_2 [A_1(L_2 - E) + B_1 + F_1]\, \psi_2\, d\tau_2. \end{aligned} \tag{60}$$

Wir müssen die hier auftretenden Integrale berechnen. Wir berechnen zunächst das folgende Integral:

$$\int \overline{\Psi}_1 \Psi_1 \, d x_3 \, d x_4 \cdots d x_q$$
$$= \sum_{(\alpha)} \sum_{(\alpha')} \varepsilon_{(\alpha)} \varepsilon_{(\alpha')} \overline{\psi}_{\alpha_1}(x_1) \overline{\psi}_{\alpha_2}(x_2) \psi_{\alpha'_1}(x_1) \psi_{\alpha'_2}(x_2) \delta_{\alpha_3 \alpha'_3} \cdots \delta_{\alpha_q \alpha'_q},$$

da die ψ_i orthogonal und normiert sind. Die Summation nach (α') ergibt

$$\int \overline{\psi}_1 \psi_1 \, d x_3 \cdots d x_q = \sum_{(\alpha)} \varepsilon_{(\alpha)} \overline{\psi}_{\alpha_1}(x_1) \overline{\psi}_{\alpha_2}(x_2) \begin{vmatrix} \psi_1(x_1) & \cdots & \psi_q(x_1) \\ \psi_1(x_2) & \cdots & \psi_q(x_2) \\ \delta_{\alpha_3 1} & \cdots & \delta_{\alpha_3 q} \\ \cdot & \cdot\;\cdot\;\cdot & \cdot \\ \delta_{\alpha_q 1} & \cdots & \delta_{\alpha_q q} \end{vmatrix}.$$

Diese Summe enthält $(q-2)!$ gleiche Glieder, da der Ausdruck unter dem Summenzeichen sich nicht ändert, wenn $\alpha_3, \ldots, \alpha_q$ beliebig permutiert werden.

Weiter ist

$$\varepsilon_{(\alpha)} \begin{vmatrix} \psi_1(x_1) & \cdots & \psi_q(x_1) \\ \cdot & \cdot\;\cdot\;\cdot & \cdot \\ \cdot & \cdot\;\cdot\;\cdot & \cdot \\ \delta_{\alpha_q 1} & & \delta_{\alpha_q q} \end{vmatrix} = \left|\begin{array}{ccc} \delta_{11} & \cdots & \delta_{1q} \\ \cdot & \cdot\;\cdot\;\cdot & \cdot \\ \psi_1(x_1) & \cdots & \psi_q(x_1) \\ \cdot & \cdot\;\cdot\;\cdot & \cdot \\ \psi_1(x_2) & \cdots & \psi_q(x_2) \\ \delta_{q1} & \cdots & \delta_{qq} \end{array}\right| \begin{array}{l} \\ \\ \alpha_1 \\ \\ \alpha_2 \\ \\ \end{array}.$$

$\psi_1(x_1) \ldots \psi_q(x_1)$ bildet hier die α_1-te und $\psi_1(x_2) \ldots \psi_q(x_2)$ die α_2-te Zeile. Die Determinante ist gleich

$$\begin{vmatrix} \psi_{\alpha_1}(x_1) & \psi_{\alpha_2}(x_1) \\ \psi_{\alpha_1}(x_2) & \psi_{\alpha_2}(x_2) \end{vmatrix}.$$

Schreiben wir i und k statt α_1 und α_2, so wird das gesuchte Integral gleich

$$\int \overline{\psi}_1 \psi_1 \, d x_3 \cdots d x_q = (q-2)! \sum_{i, k = 1}^{q} \overline{\psi}_i(x_1) \overline{\psi}_k(x_2) \left[\psi_i(x_1) \psi_k(x_2) - \psi_k(x_1) \psi_i(x_2)\right]. \tag{61}$$

Wir setzen

$$\left.\begin{aligned} \varrho_1(x_1, x_2) &= \sum_{i=1}^{q} \overline{\psi}_i(x_1) \psi_i(x_2) = \overline{\varrho_1(x_2, x_1)}, \\ \varrho_1(x) &= \varrho_1(x, x). \end{aligned}\right| \tag{62}$$

Dann wird

$$\int \overline{\psi}_1 \psi_1 \, d x_3 \cdots d x_q = (q-2)! \left[\varrho_1(x_1) \varrho_1(x_2) - |\varrho_1(x_1, x_2)|^2\right]. \tag{63}$$

Diese Formel erlaubt es, die Integrale (59) ohne Mühe zu berechnen. Wir haben

$$\int \varrho_1(x) \, d x = q, \qquad \int |\varrho_1(x_1, x_2)|^2 \, d x_2 = \varrho_1(x_1) \tag{64}$$

und deshalb

$$\int \overline{\psi}_1 \psi_1 \, dx_2 \cdots dx_q = (q-1)! \; \varrho_1(x_1), \tag{65}$$

$$A_1 = \int \overline{\psi}_1 \psi_1 \, dx_1 \cdots dx_q = q! \tag{66}$$

Das Integral B_1 ist gleich

$$B_1 = \int \overline{\psi}_1 L_1 \psi_1 \, d\tau_1 = \sum_{k=1}^{q} \int \overline{\psi}_1 H_k \psi_1 \, d\tau_1 + \sum_{i>k=1}^{q} \int \overline{\psi}_1 \frac{1}{r_{ik}} \psi_1 \, d\tau_1 .$$

Wegen der Symmetrie von $\overline{\psi}_1 \psi_1$ in bezug auf alle Koordinaten $x_1, x_2, \ldots, x_q$ sind alle $\frac{1}{2} q(q-1)$-Glieder der Doppelsumme einander gleich. Ebenso überzeugt man sich, daß alle q Glieder der einfachen Summe einander gleich sind. Wir haben also

$$B_1 = q \int \overline{\psi}_1 H_1 \psi_1 \, d\tau_1 + \tfrac{1}{2} q(q-1) \int \overline{\psi}_1 \frac{1}{r_{12}} \psi_1 \, d\tau_1 .$$

Die Integration nach x_2 bis x_q im ersten und nach x_3 bis x_q im zweiten Integral läßt sich nach dem soeben geschilderten Verfahren ausführen, und man bekommt schließlich

$$B_1 = q! \; E_1, \tag{67}$$

wo

$$E_1 = \sum_{k=1}^{q} H_{kk} + \frac{1}{2} \iint \frac{\varrho_1(x_1)\,\varrho_1(x_2) - |\varrho_1(x_1, x_2)|^2}{r_{12}} \, dx_1 \, dx_2 \tag{68}$$

und

$$H_{ik} = \int \overline{\psi}_i(x) \, H \, \psi_k(x) \, dx \tag{69}$$

gesetzt ist.

Das Integral F_1 ist gleich

$$\left. \begin{aligned} F_1 &= q! \sum_{k=q+1}^{q+p} V^{(1)}(x_k), \\ V^{(1)}(x_k) &= \frac{1}{q!} \sum_{i=1}^{q} \int \overline{\psi}_1 \psi_1 \frac{1}{r_{ik}} \, d\tau_1 . \end{aligned} \right\} \tag{70}$$

Alle Glieder der letzten Summe sind einander gleich, und durch eine Anwendung der Formel (65) bekommt man

$$V^{(1)}(x_k) = \int \frac{\varrho_1(x_1)}{r_{1k}} \, dx_1 = \sum_{i=1}^{q} G_{ii}(x_k), \tag{71}$$

wo

$$G_{ik}(x) = \int \frac{\overline{\psi}_i(x') \, \psi_k(x')}{r} \, dx' \tag{72}$$

gesetzt ist.

Aus den gewonnenen Werten von A_1, B_1, F_1 lassen sich ohne Rechnung die Werte von A_2, B_2, F_2 entnehmen. Wir setzen, analog (62), (68), (71),

$$\left.\begin{aligned} \varrho_2(x_1, x_2) &= \sum_{i=1}^{p} \overline{\psi}_i(x_1)\, \psi_i(x_2) = \overline{\varrho_2(x_2, x_1)}, \\ \varrho_2(x) &= \varrho_2(x, x), \end{aligned}\right\} \tag{62*}$$

$$E_2 = \sum_{k=1}^{p} H_{kk} + \frac{1}{2} \iint \frac{\varrho_2(x_1)\, \varrho_2(x_2) - |\varrho_2(x_1, x_2)|^2}{r_{12}}\, d x_1\, d x_2, \tag{68*}$$

$$V^{(2)}(x_k) = \int \frac{\varrho_2(x_1)}{r_{1k}}\, d x_1 = \sum_{i=1}^{p} G_{ii}(x_k) \tag{71*}$$

und erhalten

$$\left.\begin{aligned} A_2 &= p!,\ B_2 = p!\ E_2, \\ F_2 &= p! \sum_{k=1}^{q} V^{(2)}(x_k). \end{aligned}\right\} \tag{73}$$

Setzt man diese Werte der Integrale (59) in (60) ein, so bekommt man

$$\begin{aligned} \delta J = p! \int \delta \overline{\psi}_1 [L_1 - E + E_2 + \sum_{k=1}^{q} V^{(2)}(x_k)]\, \psi_1\, d\tau_1 \\ + q! \int \delta \overline{\psi}_2 [L_2 - E + E_1 + \sum_{k=p+1}^{q+p} V^{(1)}(x_k)]\, \psi_2\, d\tau_2. \end{aligned} \tag{74}$$

Die Berechnung der Integrale, die in diesem Ausdruck für δJ vorkommen, geschieht, analog den früheren Rechnungen, mit Hilfe der Entwicklung der Determinanten nach der Formel (53); wir wollen hier nur die Resultate angeben.

Wir setzen

$$E_{12} = \iint \frac{\varrho_1(x_1)\, \varrho_2(x_2)}{r_{12}}\, d x_1\, d x_2 \tag{75}$$

und definieren für $s = 1, 2$ die Größen

$$\left.\begin{aligned} V_{ki}^{(s)} &= \int \overline{\psi}_k(x) V^{(s)}(x)\, \psi_i(x)\, d x = \iint \overline{\psi}_k(x_1)\, \psi_i(x_1)\, \frac{\varrho_s(x_2)}{r_{12}}\, d x_1\, d x_2, \\ T_{ki}^{(s)} &= \iint \overline{\psi}_k(x_2)\, \psi_i(x_1)\, \frac{\varrho_s(x_1, x_2)}{r_{12}}\, d x_1\, d x_2, \\ U_{ki}^{(s)} &= V_{ki}^{(s)} - T_{ki}^{(s}. \end{aligned}\right\} \tag{76}$$

Die Größen $V_{ki}^{(s)}$, $T_{ki}^{(s)}$, $U_{ki}^{(s)}$ bilden positiv-definite Hermitesche Matrizen. $V_{ki}^{(s)}$ und $T_{ki}^{(s)}$ lassen sich durch die in § 3, Formel (18) eingeführten Matrixelemente $(ik|G|lm)$ wie folgt ausdrücken:

$$\left.\begin{aligned} V_{ki}^{(1)} &= \sum_{l=1}^{q} (kl\,|\,G\,|\,il), & V_{ki}^{(2)} &= \sum_{l=1}^{p} (kl\,|\,G\,|\,il), \\ T_{ki}^{(1)} &= \sum_{l=1}^{p} (kl\,|\,G\,|\,li), & T_{ki}^{(2)} &= \sum_{l=1}^{p} (kl\,|\,G\,|\,li). \end{aligned}\right\} \tag{77}$$

Die Größen E_1, E_2, E_{12} können ihrerseits wie folgt ausgedrückt werden:

$$\left.\begin{aligned} E_1 &= \sum_{k=1}^{q}\left(H_{kk} + \tfrac{1}{2} U_{kk}^{(1)}\right), \\ E_2 &= \sum_{k=1}^{p}\left(H_{kk} + \tfrac{1}{2} U_{kk}^{(2)}\right), \\ E_{12} &= \sum_{k=1}^{q} V_{kk}^{(2)} = \sum_{k=1}^{p} V_{kk}^{(1)}. \end{aligned}\right\} \tag{78}$$

Mit Hilfe dieser Größen können nun die in (74) vorkommenden Integrale berechnet werden. Man bekommt

$$\int \delta \overline{\psi}_1 \psi_1 \, d\tau_1 = q! \sum_{i=1}^{q} \int \delta \psi_i(x) \psi_i(x) \, dx, \tag{79}$$

$$\begin{aligned} \int \delta \psi_1 \sum_{k=1}^{q}\left(H_k + V^{(2)}(x_k)\right) \psi_1 \, d\tau_1 = q! \sum_{i=1}^{q} \int \delta \overline{\psi}_i(x) \left[H + V^{(2)}(x) + \sum_{k=1}^{q} H_{kk} + E_{12}\right] \psi_i(x) \, dx \\ - q! \sum_{i=1}^{q} \int \delta \overline{\psi}_i(x) \sum_{k=1}^{q}\left(H_{ki} + V_{ki}^{(2)}\right) \psi_k(x) \, dx, \end{aligned} \tag{80}$$

$$\begin{aligned} \sum_{>k=1}^{q} \int \delta \overline{\psi}_1 \frac{1}{r_{ik}} \psi_1 \, d\tau_1 = q! \sum_{i=1}^{q} \int \delta \overline{\psi}_i(x) \left[V^{(1)}(x) + E_1 - \sum_{k=1}^{q} H_{kk}\right] \psi_i(x) \, dx \\ - q! \sum_{i=1}^{q} \int \delta \overline{\psi}_i(x) \sum_{k=1}^{q} \left[G_{ki}(x) + U_{ki}^{(1)}\right] \psi_k(x) \, dx. \end{aligned} \tag{81}$$

Diese Ausdrücke, in δJ eingesetzt, ergeben

$$\begin{aligned} \frac{1}{p!\,q!} \delta J = \sum_{i=1}^{q} \int \delta \overline{\psi}_i(x) \left[H + V^{(1)}(x) + V^{(2)}(x) + E_1 + E_2 + E_{12} - E\right] \psi_i(x) \, dx \\ - \sum_{i=1}^{q} \int \delta \overline{\psi}_i(x) \sum_{k=1}^{q} \left[G_{ki}(x) + H_{ki} + V_{ki}^{(2)} + U_{ki}^{(1)}\right] \psi_k(x) \, dx \\ + \sum_{i=1}^{p} \int \delta \overline{\psi}_i(x) \left[H + V^{(1)}(x) + V^{(2)}(x) + E_1 + E_2 + E_{12} - E\right] \psi_i(x) \, dx \\ - \sum_{i=1}^{p} \int \delta \overline{\psi}_i(x) \sum_{k=1}^{p} \left[G_{ki}(x) + H_{ki} + V_{ki}^{(1)} + U_{ki}^{(2)}\right] \psi_k(x) \, dx. \end{aligned} \tag{82}$$

Hier müssen wir die Koeffizienten der unabhängigen Variationen $\delta \overline{\psi}_i(x)$ gleich Null setzen, wobei zu beachten ist, daß für $i = 1, 2, \ldots, p$ $\delta \overline{\psi}_i(x)$ im Ausdruck für δJ zweimal und für $i = p + 1, \ldots, q$ einmal vorkommt.

Man bekommt für $i = 1, 2, \ldots, p$:

$$2\left[H + V(x) + E_1 + E_2 + E_{12} - E\right] \psi_i(x) - \sum_{k=1}^{p} \left[2\, G_{ki}(x) + 2\, H_{ki} + U_{ki} + V_{ki}\right] \psi_k(x) \\ - \sum_{k=p+1}^{q} \left[G_{ki}(x) + H_{ki} + U_{ki}^{(1)} + V_{ki}^{(2)}\right] \psi_k(x) = 0 \tag{83}$$

und für $i = p + 1, \ldots, q$:

$$\left[H + V(x) + E_1 + E_2 + E_{12} - E\right] \psi_i(x) - \sum_{k=1}^{q} \left[G_{ki}(x) + H_{ki} + U_{ki}^{(1)} + V_{ki}^{(2)}\right] \psi_k(x) = 0, \tag{84}$$

wo zur Abkürzung

$$V(x) = V^{(1)}(x) + V^{(2)}(x), \tag{85}$$

$$\left.\begin{aligned} V_{ki} &= V_{ki}^{(1)} + V_{ki}^{(2)}, \\ U_{ki} &= U_{ki}^{(1)} + U_{ki}^{(2)} \end{aligned}\right\} \tag{86}$$

gesetzt ist.

Multipliziert man (83) mit $\overline{\psi}_l(x)$ $(l = 1, 2, \ldots, p)$ und integriert, so bekommt man, wenn man die Relationen (76), (77) und die Orthogonalität der $\psi_i(x)$ beachtet, für $l \neq i$ eine Identität, für $l = i$ dagegen die Beziehung

$$E = E_1 + E_2 + E_{12}. \tag{87}$$

Dasselbe Resultat bekommt man, wenn man Gleichung (84) mit $\overline{\psi}_l(x)$ $(l = p + 1, \ldots, q)$ multipliziert und integriert.

Multipliziert man dagegen (83) mit einer der Funktionen $\overline{\psi}_{p+1}, \ldots, \overline{\psi}_q$ oder (84) mit $\overline{\psi}_1, \ldots, \overline{\psi}_p$ und integriert, so bekommt man

$$K_{ki} + V_{ki}^{(1)} + U_{ki}^{(2)} = 0 \tag{88}$$

für $k = p + 1, \ldots, q$; $i = 1, \ldots, p$ oder $i = p + 1, \ldots, q$; $k = 1, \ldots, p$. Man bestätigt, daß hier, ebenso wie im Falle der Hartreeschen Gleichungen (29), die Beziehung

$$E = \frac{\int \overline{\psi}\, L\, \psi\, d\tau}{\int \overline{\psi}\, \psi\, d\tau} \tag{89}$$

gilt.

7. Wir wollen nun das gewonnene Gleichungssystem (83) und (84) etwas näher betrachten.

Wir setzen

$$\left.\begin{aligned} \lambda_{ki} &= 2\, H_{ki} + U_{ki} + V_{ki} \quad (i \text{ oder } k = 1, 2, \ldots, p), \\ \lambda_{ki} &= H_{ki} + U_{ki}^{(1)} + V_{ki}^{(2)} \quad (i \text{ oder } k = p + 1, \ldots, q) \end{aligned}\right\} \tag{90}$$

(für $i = 1, \ldots, p$; $k = p + 1, \ldots, q$ fallen wegen (88) die beiden Definitionen von $\lambda_{k\,i}$ zusammen); ferner

$$\left.\begin{aligned} \varepsilon_k &= 2 \qquad (k = 1, \ldots, p), \\ \varepsilon_k &= 1 \qquad (k = p + 1, \ldots, q). \end{aligned}\right\} \tag{91}$$

Die Gleichungen (83) und (84) lassen sich dann schreiben:

$$\left.\begin{aligned} 2\,[H + V(x)]\,\psi_i(x) - \sum_{k=1}^{q} \varepsilon_k G_{k\,i}(x)\,\psi_k(x) &= \sum_{k=1}^{q} \lambda_{k\,i}\,\psi_k(x)\,(i = 1, \ldots, p), \\ [H + V(x)]\,\psi_i(x) - \sum_{k=1}^{q} G_{k\,i}(x)\,\psi_k(x) &= \sum_{k=1}^{q} \lambda_{k\,i}\,\psi_k(x)\,(i = p + 1, \ldots, q). \end{aligned}\right\} \tag{92}$$

Streichen wir hier alle Glieder mit $i \neq k$, so bekommen wir die Gleichungen (29) von Hartree. Die Glieder mit $i \neq k$ repräsentieren den „Austausch“, der in der Hartreeschen Methode außer acht gelassen ist. Diese nicht-diagonalen Glieder sind im allgemeinen klein im Vergleich zu den Diagonalgliedern, so daß sie als eine Störung behandelt werden können.

Der für die Hartreesche Theorie charakteristische Umstand, daß von der vollen potentiellen Energie $V(x)$ die Wirkung $G_{i\,i}(x)$ des Elektrons auf sich selbst abgezogen ist, tritt auch in unseren Gleichungen zutage.

Unsere Gleichungen (92) können, ebenso wie die Hartreeschen Gleichungen (29), aus einem dreidimensionalen Variationsprinzip abgeleitet werden. Das entsprechende Wirkungsintegral ist gleich

$$\begin{aligned} W = \sum_{i=1}^{q} \int \bar{\psi}_i H\,\psi_i\,d\,x + \frac{1}{2} \int\!\!\int \frac{\varrho_1(x)\,\varrho_1(x') - |\,\varrho_1(x, x')\,|^2}{r}\,d\,x\,d\,x' \\ + \sum_{i=1}^{q} \int \psi_i H\,\psi_i\,d\,x + \frac{1}{2} \int\!\!\int \frac{\varrho_2(x)\,\varrho_2(x') - |\,\varrho_2(x, x')\,|^2}{r}\,d\,x\,d\,x' \\ + \int\!\!\int \frac{\varrho_1(x)\,\varrho_2(x')}{r}\,d\,x\,d\,x' \end{aligned} \tag{93}$$

und die Nebenbedingungen lauten

$$\int \bar{\psi}_i(x)\,\psi_k(x)\,d\,x = \delta_{i\,k}. \tag{94}$$

Die Größen $\lambda_{k\,i}$ (die eine Hermitesche Matrix bilden) treten als Lagrangesche Faktoren auf. Der Wert des Wirkungsintegrals ist gleich der Energie des Atoms, denn es ist offenbar

$$W = E_1 + E_2 + E_{12} = E. \tag{95}$$

Ebenso wie früher in § 4 können jetzt die Koeffizienten unserer Gleichungen (92) als gegeben und das Gleichungssystem als ein lineares aufgefaßt werden. Dieses Gleichungssystem kann dann aus der Variation des Integrals

$$W^* = \int \left[\sum_{i=1}^{q} \overline{\psi}_i (H + V)\, \psi_i - \sum_{i,\,k=1}^{q} G_{k\,i}\, \overline{\psi}_i\, \psi_k \right] d\,x$$

$$+ \int \left[\sum_{i=1}^{p} \overline{\psi}_i (H + V)\, \psi_i - \sum_{i,\,k=1}^{p} G_{k\,i}\, \overline{\psi}_i\, \psi_k \right] d\,x \tag{96}$$

unter den Nebenbedingungen (94) abgeleitet werden. Der Wert des Integrals ist gleich

$$W^* = 2\,E - \sum_{i=1}^{p} H_{i\,i} - \sum_{i=1}^{q} H_{i\,i} = \sum_{i=1}^{q} \lambda_{i\,i}. \tag{97}$$

Unsere Formeln, insbesondere der Ausdruck (93) für die Energie, lassen die folgende Deutung zu. Die N Elektronen im Atom zerfallen in zwei „Elektronenschwärme" mit q bzw. mit p Elektronen, deren jeder dem Pauliprinzip im engeren Sinne genügt. Im Ausdruck (93) für die Energie ist das erste Doppelintegral die Wechselwirkungsenergie der Elektronen des einen Schwarms, das zweite Doppelintegral die des zweiten Schwarms; das letzte Doppelintegral ist die gegenseitige potentielle Energie der Elektronen der beiden Schwärme. Charakteristisch ist der Umstand, daß in den beiden ersten Doppelintegralen der Integrand für $x = x'$ verschwindet. Diese Ausdrücke bieten eine auffallende — und gewiß nicht nur formale — Ähnlichkeit mit denjenigen, die von P. Jordan nach der Methode der nochmaligen Quantisierung abgeleitet† sind.

Die numerische Integration der Gleichungen kann etwa in folgender Weise vollzogen werden. In erster Näherung streiche man alle nicht-diagonalen Glieder; man bekommt dann die Gleichungen von Hartree. Nachdem eine Näherungslösung der Hartreeschen Gleichungen gefunden ist, kann man die nicht-diagonalen Glieder als Störungsglieder in Betracht ziehen, indem man die Koeffizienten $G_{k\,i}$ und $\lambda_{k\,i}$ aus der ersten Näherung berechnet. Durch sukzessive Näherungen kann man dann die Funktionen ψ_i ermitteln. Wenn man sich mit dem Ansatz für die sphärische Symmetrie begnügt, so ist zu erwarten, daß die Rechenarbeit nicht wesentlich mühsamer ist als in den bereits von Hartree durchgeführten Rechnungen; die Resultate dürften dagegen beträchtlich genauer als in der Hartreeschen Methode sein.

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† Siehe z. B. den zusammenfassenden Bericht von P. Jordan, Phys. ZS. **30**, 700, 1929.

8. Wenn die Funktionen ψ_i bekannt sind, kann man auch die Frequenzen und Intensitäten der Spektrallinien berechnen. Die Energieniveaus können nach der Formel (93) berechnet werden. Zur Berechnung der Intensitäten hat man das Integral

$$(E\,|\,f\,|\,E') = \frac{1}{p!\,q!}\int \overline{\Psi} \sum_{k=1}^{N} f(x_k)\, \Psi'\, d\tau \tag{98}$$

auszuwerten, wo

$$f(x) = x,\ y,\ z$$

zu setzen ist.

Die Eigenfunktionen $\psi_i(x)$, die zum Energieniveau E gehören, bezeichnen wir ausführlicher mit

$$\psi_i(x, E).$$

Setzt man zur Abkürzung

$$\left.\begin{aligned} a_{ik} &= \int \overline{\psi}_i(x, E)\, \psi_k(x, E')\, dx, \\ f_{ik} &= \int \overline{\psi}_i(x, E)\, f(x)\, \psi_k(x, E')\, dx, \end{aligned}\right\} \tag{99}$$

so ergibt die Rechnung für das Matrixelement $(E|f|E')$ den Ausdruck

$$\begin{aligned} (E\,|\,f\,|\,E') = {} & \begin{vmatrix} a_{11} \cdots a_{1p} \\ a_{21} \cdots a_{2p} \\ \cdots\cdots\cdots \\ a_{p1} \cdots a_{pp} \end{vmatrix} \cdot \sum_{k=1}^{q} \begin{vmatrix} a_{11} \cdots a_{1q} \\ \cdots\cdots\cdots \\ f_{k1} \cdots f_{kq} \\ \cdots\cdots\cdots \\ a_{q1} \cdots a_{qq} \end{vmatrix} \\ & + \begin{vmatrix} a_{11} \cdots a_{1q} \\ a_{21} \cdots a_{2q} \\ \cdots\cdots\cdots \\ a_{q1} \cdots a_{qq} \end{vmatrix} \cdot \sum_{k=1}^{p} \begin{vmatrix} a_{11} \cdots a_{1p} \\ \cdots\cdots\cdots \\ f_{k1} \cdots f_{kp} \\ \cdots\cdots\cdots \\ a_{p1} \cdots a_{pp} \end{vmatrix} \cdot \end{aligned} \tag{100}$$

Die Elemente f_{k1}, f_{k2}, ... bilden die k-te Zeile der Determinanten.

Wir wollen zeigen, daß dieser Ausdruck für $(E|f|E')$ im Falle eines Valenzelektrons mit dem gewöhnlichen Ausdruck näherungsweise übereinstimmt. In diesem Falle ist $q = p + 1$ zu setzen. Die Funktionen $\psi_i(x, E)$ $(i = 1, \ldots, p)$ unterscheiden sich dann nur wenig von $\psi_i(x, E')$, da der Übergang des äußeren Elektrons auf eine andere Bahn die inneren Elektronen verhältnismäßig wenig beeinflußt. Daraus folgt, daß die a_{ik} für $i, k = 1, \ldots, p$ näherungsweise gleich δ_{ik} sind. Die Funktion $\psi_q(x, E)$ ist dagegen nicht nur mit $\psi_i(x, E')$ $(i = 1, \ldots, p)$, sondern auch mit $\psi_q(x, E')$ nahezu orthogonal, denn betrachtet man das Feld der inneren Elektronen als fest, so sind $\psi_q(x, E)$ und $\psi_q(x, E')$ die zu verschiedenen Eigenwerten gehörigen Eigenfunktionen des Valenzelektrons. Folglich sind a_{qq} und $a_{1q}, \ldots, a_{q-1,q}$, sowie $a_{q1}, \ldots, a_{q,q-1}$ als klein anzusehen. Das einzige Glied im Ausdruck für $(E|f|E')$, das nicht kleine Größen als Faktoren enthält, ist nun

$$f_{qq} = \int \overline{\psi}_q(x, E) f(x) \psi_q(x, E') \, dx, \tag{101}$$

d. h. der gewöhnliche Ausdruck für das Matrixelement.

Es dürften aber Fälle vorkommen, wo die durch die Formel (94) gegegebenen Korrektionen nicht zu vernachlässigen sind. Diese Korrektionen können als durch eine Umgruppierung der inneren Elektronen verursacht gedeutet werden.

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30-2

An Approximate Method for Solving the Quantum Many-Body Problem

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1 Introduction

The mathematical formulation of the quantum many-body problem (without relativistic corrections) was given by Schrödinger in one of his pioneer works.[1] Since the wave function sought depends on the great number of variables (namely, there are as many of them as degrees of freedom in the N electron system), the exact solution of this problem encounters the insuperable difficulties and consequently one needs to resort to approximate methods. An extremely ingenious way was proposed by Hartree.[2] However, the derivation of the equations given by Hartree himself was based on the consideration not related to the Schrödinger equation in the configuration space. Another work by Gaunt[3] was devoted to the statement of this link, but the problem was not solved entirely because nothing was mentioned about Hartree's equations being connected with the variational principle. The main point of Hartree's method called by him as that of the "self-consistent field" consists of the following. Hartree preserves the classical notion of the individual electron orbit provided each orbit is described, according to Schrödinger, by the wave function. For each wave function (i.e., for each individual electron) one constructs the Schrödinger equation with the potential energy originating from the interaction first with a nucleus and second with other electrons continuously distributed with the charge density $\varrho = \overline{\psi}\psi$.

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[1] E. Schrödinger, *Quantisiering als Eigenwertproblem*, Ann. Phys. (1926).

[2] D.R. Hartree, *The Wave Mechanics of an Atom with a Non-Coulomb Central Field*, Proc. Cambr. Phil. Soc. **24**, 89, 111, 1928.

[3] J.A. Gount, *A Theory of Hartree's Atomic Fields*, Proc. Cambr. Phil. Soc. **24**, 328, 1928.

Because Hartree uses the notion of orbits, his method is more descriptive. However, one can speak about orbits in the context of quantum mechanics only with a certain approximation. At the same time, one can expect that this approximation is good enough, since the preceding Bohr theory, operating with the electronic orbits, gives a quite satisfactory classification of the atomic spectra. The question is whether the Hartree method is able to give the extreme accuracy, combined with a concept of orbits, i.e., with a description of the atom by means of the individual electron wave functions.

In this paper, we shall show that the most extreme accuracy is not achieved in Hartree's method, but can be attained by means of a certain modification. Physically speaking, this corresponds to the so-called exchange energy to be taken into account. In the mathematical sense, it is realized by using the wave functions of the required symmetry in the variational principle.

Our modification of Hartree's equations, combined with the notion of orbits, is the best in the sense of the variational principle.

We take into account the magnetic properties of electrons (so-called spins) insofar as they are required by the Pauli principle. Their presence influences the wave function symmetry, while the correction terms in the energy operator are omitted. Such an approach is quite rightful because correction due to the "spin" is less than that due to the exchange energy.

2 The Idea of the Method

As is well known, the Schrödinger equation can be obtained from the variational principle

$$\delta \int \overline{\Psi}(L - E)\Psi d\tau = 0\,. \tag{1}$$

Here Ψ is the wave function depending on the coordinates of all the N electrons,

$$\Psi = \Psi(x_1 y_1 z_1, x_2 y_2 z_2, \ldots, x_N y_N z_N)\,,$$

L is the energy operator (its expression will be written later), E is a constant (the atomic energy), and $d\tau$ is an elementary volume of the configuration space,

$$d\tau = dx_1 dy_1 dz_1 \ldots dx_N dy_N dz_N\,.$$

It is possible to show that *in virtu* of the operator L hermiticity, eq. (1) is equivalent to the following:

$$\int \delta\overline{\Psi}(L - E)\Psi d\tau = 0\,.$$

For brevity, we shall denote the three coordinates of a k-th electron by a single letter x_k. Besides, we shall use the so-called atomic system of units, in which for units of length, charge and mass we take correspondingly: $a_H = \frac{h^2}{4\pi^2 me^2} = 0.529 \cdot 10^{-8}$ cm, the radius of the first hydrogen orbit; $e = 4.77 \cdot 10^{-10}$ CGSE, the electron charge; $m = 9.00 \cdot 10^{-28}$ g, the electron mass.

In these units, the Planck constant divided by 2π is equal to one, and the light velocity is equal to 137 (the inverse of Sommerfeld's fine structure constant).

In atomic units, the energy operator for the atom with N electrons assumes the form

$$L = \sum_{k=1}^{N} H_k + \sum_{i,k=1}^{N} \frac{1}{r_{ik}}\,, \tag{2}$$

providing

$$H_k = -\frac{1}{2}\Delta_k - \frac{N}{r_k}\,. \tag{3}$$

Here Δ_k is the Laplace operator applied to the coordinates of the k-th electron, r_k is the distance between the electron and the nucleus, and r_{ik} is the distance between the i-th and k-th electrons.

For the solution of the variational problem (1) we shall use the generalized Ritz method.[4] As it is known, the Ritz method is in the following: one substitutes into the varied functional the expression of the function sought, which depends on some unknown constants; then these constants are determined from the minimum condition of the functional. Generalizing this method, we shall seek Ψ as a sum of a definite number of products of functions $\psi_i(x_k)$, each one depending on the coordinates of a single electron. Thus, we shall have unknown functions instead of unknown coefficients, and this is just our generalization. In the physical sense, the expression of the wave function Ψ by means of a definite number of the one-electron functions $\psi_i(x_k)$ corresponds to the notion of the individual electronic orbits. In fact, we can say that there are definite orbits in the atom that are described by the wave functions $\psi_i(x_k)$ and are occupied by a definite number of electrons.

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[4] See, e.g., Walther Ritz, Gesammelte Werke, Gauthier-Villars, Paris, 1911. (*V. Fock*)

Different assumptions about the form of the wave function Ψ lead to different forms of the system of equations for functions $\psi_i(x_k)$. We shall see that the assumption of

$$\Psi = \psi(x_1)\psi(x_2)\ldots\psi(x_N) \tag{4}$$

leads one to the Hartree equations. However, such a form of function does not possess (save a case of the normal state of the He atom) the symmetry required by the group theory. Therefore, Hartree's equations are only a relatively rough approximation that corresponds, as will be seen later, to the neglect of the exchange energy.

We can obtain a better approximation if we seek Ψ in the form of the required symmetry. Then the terms presenting the quantum exchange will appear in the equations for functions $\psi_i(x_k)$.

Generally, the product of two determinants constructed by functions $\psi_i(x_k)$, or a sum of such products, possesses the correct symmetry. In the simplest and commonly occurring case and, therefore, most important partial one (the so-called Heitler's case of complete degeneration of the term system), it is sufficient to take one product of determinants.[5] In our work, we restrict ourself to the consideration of this partial case and infer for it the system of equations, which permit us to determine the functions $\psi_i(x_k)$.

3 Example: A Helium Atom

To clarify the way of calculations, we start from the simplest example, namely, from a helium atom.

In the two-electron problem, the energy operator is of the form

$$L = H_1 + H_2 + \frac{1}{r_{12}}\,. \tag{5}$$

The variational principle is written in the form

$$\int\!\!\int \delta\overline{\Psi}(L-E)\Psi dx_1 dx_2 = 0\,. \tag{6}$$

Here dx_1 and dx_2 are the elementary volumes; e.g., we write dx_1 instead of $dx_1dy_1dz_1$. For the ground state, we take

$$\Psi = \psi(x_1)\psi(x_2)\,. \tag{7}$$

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[5] W. Heitler, *Störungsenergie und Austausch beim Mehrkörperproblem*, Zs. Phys. **46**, 47, 1927; J. Waller and D.R. Hartree, *On the Intensity of Total Scattering of X Rays*, Proc. Roy. Soc. London **A124**, 119, 1929.

Substituting this function into equation (6), we obtain

$$\iint \left[\delta\overline{\psi}(x_1)\overline{\psi}(x_2) + \overline{\psi}(x_1)\delta\overline{\psi}(x_2)\right] (L - E)\psi(x_1)\psi(x_2)dx_1dx_2 = 0\,.$$

As the consequence of the symmetry of L and Ψ with respect to x_1 and x_2, both terms in square brackets give the same result. Taking this into account and substituting instead of L its expression (5), we shall have

$$\int dx_1\delta\overline{\psi}(x_1)\int\overline{\psi}(x_2)(H_1 + H_2 + \frac{1}{r_{12}})\psi(x_1)\psi(x_2)dx_2 = 0\,. \qquad (8)$$

The integral over x_2 is equal to

$$H_1\psi(x_1) + G(x_1)\psi(x_1) - E_0\psi(x_1),$$

where

$$G(x_1) = \int \frac{|\psi(x_2)|^2}{r_{12}}dx_2; \qquad (9)$$

$$E_0 = E - \int\overline{\psi}(x_2)H_2\psi(x_2)dx_2\,. \qquad (10)$$

Consequently, we have

$$\int dx\delta\overline{\psi}(x)[H + G(x) - E_0]\psi(x) = 0\,. \qquad (11)$$

Therefore, for function ψ one obtains the equation:

$$\Big[H + G(x) - E_0\Big]\psi(x) = 0\,. \qquad (12)$$

This equation coincides exactly with that of Hartree. The characteristic number of the energy operator is connected with the parameter E_0 by relations (10), which by means of equation (12) can be written in the form

$$E = 2E_0 - \int G(x)|\psi(x)|^2dx\,. \qquad (13)$$

The latter relation coincides with that given by Gaunt (l.c.). Hartree's equation (12) as well as Gaunt's (13) are obtained by us from the variational principle in an absolutely natural way.

Now one can make the following assumption: let the function $\psi(x) = \psi(x, y, z)$ depend only on the distance r from the nucleus. Then the function $G(x, y, z)$ will also depend only on r and one should seek the solution of equation (12), which possesses the spherical symmetry.

For the excited state of a helium atom, one should take

$$\Psi = \psi_1(x_1)\psi_2(x_2) + \psi_1(x_2)\psi_2(x_1)\,, \tag{14}$$

and for parahelium,

$$\Psi = \psi_1(x_1)\psi_2(x_2) - \psi_1(x_2)\psi_2(x_1)\,. \tag{15}$$

In the latter case, one can also assume ψ_1 and ψ_2 to be orthogonal and normalized. If we substitute expression (15) into (6), we obtain the system of equations

$$\begin{aligned} H\psi_1(x) + G_{22}(x)\psi_1(x) - G_{21}(x)\psi_2(x) &= (E - H_{22})\psi_1(x) + H_{21}\psi_2(x)\,, \\ H\psi_2(x) + G_{11}(x)\psi_2(x) - G_{12}(x)\psi_1(x) &= H_{12}\psi_1(x) + (E - H_{11})\psi_2(x)\,, \end{aligned} \tag{16}$$

where for brevity we put

$$G_{ik}(x) = \int \frac{\overline{\psi}_i(x')\psi_k(x')}{r}dx', \qquad H_{ik} = \int \overline{\psi}_i(x)H\psi_k(x)\,, \tag{17}$$

and

$$\begin{aligned} \langle ik \mid sG \mid lm\rangle &= \iint \frac{\overline{\psi}_i(x')\overline{\psi}_k(x)\psi_l(x')\psi_m(x)}{r}dxdx' = \\ &= \int \overline{\psi}_i(x)\psi_l(x)G_{km}(x)dx = \int \overline{\psi}_k(x)\psi_m(x)G_{il}(x)dx\,. \end{aligned} \tag{18}$$

In the system (16), the values $G_{12}(x)$ and $G_{21}(x)$ as well as H_{12} and H_{21} (i.e., the coefficients with different subscripts) present the quantum exchange. In general, the values of $G_{12}(x)$ and $G_{21}(x)$ are less[6] than those of $G_{11}(x)$ and $G_{22}(x)$ but not so much to be neglected.

Multiplying the first of eqs. (16) by $\overline{\psi}(x)$ and integrating, we obtain the following expression for the atomic energy:

$$E = H_{11} + H_{22} + \langle 12 \mid G \mid 12\rangle - \langle 12 \mid G \mid 21\rangle\,. \tag{19}$$

This expression can be presented in another form, which permits a simple interpretation. Putting

$$\varrho(x,x') = \overline{\psi}_1(x)\psi_1(x') + \overline{\psi}_2(x)\psi_2(x')\,, \tag{20}$$

$$\varrho(x) = \varrho(x,x)\,, \tag{21}$$

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[6] See Gaunt, the footnote on page 137. (*V. Fock*)

we obtain

$$E = H_{11} + H_{22} + \frac{1}{2}\int\!\!\int \frac{\varrho(x)\varrho(x') - |\varrho(x,x')|^2}{r} dx dx' \,. \qquad (22)$$

Here the first two terms represent the single electron energies, while the integral can be interpreted as the energy of their interaction. It should be noted that in the numerator of the integrand there is not mere $\varrho(x)\varrho(x')$ but $\varrho(x)\varrho(x')$-$|\varrho(x',x)|^2$, the expression which tends to zero when $x = x'$. This situation can be interpreted in the sense that an electron does not interact with itself.

Expression (14) for the wave function of excited parahelium leads to the equations, which are analogous to (16) with a distinction that the terms G_{12}, H_{12} , etc., which characterize the quantum exchange, have a minus, and besides there are some new terms because now the functions ψ_1 and ψ_2 should not be considered to be orthogonal.

4 Hartree's Equations

Turning to the N-electron problem, at first we shall seek Ψ in the form

$$\Psi = \prod_{q=1}^{N} \psi_q(x_q) \,. \qquad (23)$$

We have mentioned already that this expression does not possess the required symmetry. In spite of this, we shall perform the calculation to the end to be sure that this expression does lead to Hartree's equation. Due to the Pauli principle there could not be more than two functions among ψ_q that are the same. We have

$$\delta\Psi = \sum_{q=1}^{N} \delta\psi_q(x_q)\Psi^{(q)}, \qquad (24)$$

where

$$\Psi^{(q)} = \frac{\Psi}{\psi_q(x_q)} \,. \qquad (25)$$

The variational principle has the form

$$\delta I = \int \delta\overline{\Psi}(L - E)\Psi d\tau = \sum_{q=1}^{N} \int \delta\overline{\psi}_q(x_q) A_q dx_q = 0 \,. \qquad (26)$$

Here we assume

$$A_q = \int \cdots \int \overline{\Psi}^{(q)} \left(\sum_{k=1}^{N} H_k - E + \sum_{i,k=1}^{N} \frac{1}{r_{ik}} \right) \psi_q(x_q) \Psi^{(q)} \cdot$$

$$\cdot dx_1 \ldots dx_{q-1} dx_{q+1} \ldots dx_N =$$

$$= H_q \psi_q(x_q) + \left[\sum_{i=1}^{N}{}' (G_{ii}(x_q) + H_{ii}) + \sum_{i>k=1}^{N}{}'' W_{ik} - E \right] \psi_q(x_q) \,, \tag{27}$$

provided that

$$W_{ik} = \langle ik \mid G \mid ik \rangle = \iint \frac{|\psi_i(x)|^2 |\psi_k(x')|^2}{r} dx dx' \,. \tag{28}$$

Here and in the following, the primed sum means that the terms with $i = q$ and $k = q$ should be omitted.

In expression (26) for δI, one should equal the coefficients under the independent variations $\delta\overline{\psi}_q$. If the function ψ_q is encountered in Ψ only once, then it must be $A_q = 0$; if it is encountered twice, e.g., $\psi_q = \psi_{q+1}$, then, as can be easily seen, the coefficients under the variations $\delta\overline{\psi}_q$ and $\delta\overline{\psi}_{q+1}$ are equal to each other, i.e., $A_q = A_{q+1}$. In both cases, $A_q = 0$.

We shall write these equations in the form

$$H\psi_q(x) + [V(x) - G_{qq}(x)]\psi_q(x) = \lambda_q \psi_q(x) \qquad (q = 1, \ldots, N), \tag{29}$$

where

$$V(x) = \sum_{k=1}^{N} G_{kk} \,, \tag{30}$$

$$\lambda_q = E - \sum_{i=1}^{N}{}' H_{ii} - \sum_{i>k=1}^{N}{}'' W_{ik} \,. \tag{31}$$

Equations (29) exactly coincide with those inferred by Hartree.

For the energy of the atom, one obtains the expression

$$E = \sum_{i=1}^{N} H_{ii} + \sum_{i>k=1}^{N} W_{ik} \,. \tag{32}$$

It is easy to verify that this expression is equal to

$$E = \frac{\displaystyle\int \overline{\Psi} L \Psi d\tau}{\displaystyle\int \overline{\Psi}\Psi d\tau}\,, \tag{33}$$

in spite of the fact that the equality $L\Psi = E\Psi$ does not take place because Ψ is not the exact solution of the Schrödinger equation.

Substitution of expression (32) into (31) gives

$$\lambda_q = H_{qq} + {\sum_{i=1}^{N}}' W_{iq}\,. \tag{34}$$

If one takes a sum over q, one obtains

$$\sum_{q=1}^{N} \lambda_q = 2E - \sum_{q=1}^{N} H_{qq}\,. \tag{35}$$

Equations (29) are the variational equations of the problem on the minimum of the integral

$$\begin{aligned} W = {} & \sum_{i=1}^{N} \int \overline{\psi}_1 H \psi_i dx + \\ & + \frac{1}{2} \sum_{i,k=1}^{N} (1 - \delta_{ik}) \int\!\!\int \frac{\overline{\psi}_k(x')\psi_k(x')\overline{\psi}_i(x)\psi_i(x)}{r} dx dx' \end{aligned} \tag{36}$$

under the supplementary conditions

$$\int \overline{\psi}_i(x)\psi_i(x) dx = 1 \qquad (i = 1, \ldots, N)\,. \tag{37}$$

By comparing equations (36) and (32), one can conclude that the value of the integral is equal to energy E. The coefficients λ_q play the roles of Lagrange's constants.

Equations (29) can be also inferred from another variational principle. The coefficients $V(x)$ and G_{qq} in these equations depend, in turn, on the unknown functions $\psi_i(x)$. But we can consider these coefficients as given and equations (29) as a system of linear differential equations for functions $\psi_q(x)$. The solution of these equations turns the following integral to be minimum

$$W^* = \sum_{i=1}^{N} \int \overline{\psi}_i(x)[H + V(x) - G_{ii}(x)]\psi_i(x)dx \tag{38}$$

provided the above supplementary conditions (37) are fulfilled. This minimum is equal to

$$W^* = 2E - \sum_{q=1}^{N} H_{qq} = \sum_{q=1}^{N} \lambda_q \,. \tag{39}$$

In our equations, the symbol x denotes all three coordinates x, y, z, so that $\psi_q(x)$ stands instead of $\psi_q(x, y, z)$ etc. If one would like to make more partial assumptions regarding $\psi_q(x, y, z)$, one should proceed as follows. One should substitute the function ψ_q of required form into the integral

$$\iiint \delta\overline{\psi}_q(x, y, z)[H + V(x, y, z) - G_{qq}(x, y, z) - \lambda_q]\psi_q(x, y, z)dxdydz \tag{40}$$

and then send to zero the coefficients, standing under the independent variations (of functions or constants, which are needed to be determined). Here we shall present the calculations for the case

$$\psi_q(x, y, z) = f_{nl}(r)Y_l(\vartheta, \varphi)\,,$$

where Y_l is the spherical function normalized as follows:

$$\iint |Y_l(\vartheta, \varphi)|^2 \sin\vartheta d\vartheta d\varphi = 1\,. \tag{41*}$$

Here the element to be determined is the function $f_{nl}(r)$, while the spherical function is not varying. In our case

$$\begin{aligned}\iiint \delta\overline{\psi}_q(x, y, z)\Delta\psi_q(x, y, z)dxdydz &= \\ = \int \delta\overline{f}_{nl}(r)\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial f_{nl}}{r}\right) - l(l+1)f_{nl}(r)\right] dr\,.\end{aligned} \tag{37}$$

Further

$$\iiint \delta\overline{\psi}_q V(x, y, z)\psi_q dxdydz = \int \delta\overline{f}_{nl}(r)V^0(r)r^2dr\,,$$

where we put

$$V^0(r) = \iint V(x,y,z)|Y_l(\vartheta,\varphi)|^2 \sin\vartheta d\vartheta d\varphi\,. \tag{42}$$

The function $G^0_{qq}(r)$ can be constructed by functions $G_{qq}(x,y,z)$ in an analogous way. Then for $f_{nl}(r)$ one can obtain the equation

$$-\frac{1}{2}\left(\frac{d^2 f_{nl}}{dr^2} + \frac{2}{r}\frac{df_{nl}}{\partial r^2} - \frac{l(l+1)}{r^2} f_{nl}\right) + \\ + \left(-\frac{N}{r} + V^0(r) - G^0_{qq}(r)\right) f_{nl} = \lambda_q f_{nl}\,. \tag{43}$$

Our equation (43) does not exactly coincide with that obtained by Hartree's method. According to Hartree, one should average the function $V(x,y,z)$ over a sphere of radius r, i.e., write the expression

$$\frac{1}{4\pi}\iint V(x,y,z)\sin\vartheta d\vartheta d\varphi,$$

while we take the average, in accordance with (42), with a "weight function" $|Y_l(\vartheta,\varphi)|^2$.

5 The Symmetry Properties of the Wave Function. Example: A Lithium Atom

We shall consider the n-electron problem anew, but now seek Ψ in the form, which possesses the required symmetry. The symmetry properties of the wave function corresponding to different terms were investigated in detail by various authors[7] with the help of the group theory, so that we can use here the well-known results.

Generally, some (e.g., s) wave functions

$$\omega_1, \omega_2, \ldots, \omega_s,$$

each depending on the coordinates of all N electrons, correspond to a definite term. If one performs any permutations (say, p^a) of the electron coordinates in the function ω_j, it transforms into a new one, ω'_j. This

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[7] See, e.g., Heitler (l.c.), Waller and Hartree (l.c.). (*V. Fock*)

new function can be expressed as a linear combination of the former ones, corresponding to the same term:

$$P^a \omega_j = \omega'_j = \sum_{i=1}^{s} P^a_{ij} \omega_i \,. \tag{44}$$

The set of coefficients gives the irreducible representation of the permutation group. The functions $\omega_1, \omega_2, \ldots, \omega_s$ can be always chosen so that the sum of their square modules

$$|\omega_1|^2 + |\omega_2|^2 + \ldots |\omega_s|^2$$

is symmetric with respect to all the electrons. Then all matrices P^a_{ij} will be unitary.[8]

Now we shall show the following. Let L be a Hermitian operator, which is symmetric with respect to all the electrons. If we construct an arbitrary linear combination Ω of the functions:

$$\Omega = \alpha\omega_1 + \alpha\omega_2 + \ldots + \alpha\omega_s \tag{45}$$

and, by means of it, calculate the expression

$$A = \frac{\displaystyle\int \overline{\Omega} L \Omega d\tau}{\displaystyle\int \overline{\Omega}\Omega d\tau}\,, \tag{46}$$

then the latter does not depend on coefficients $\alpha_1, \ldots, \alpha_s$.

If L is the energy operator, then, equaling the variation of A to zero, one obtains the Schrödinger equation for the function Ω. This statement means that, to infer the Schrödinger equation from the variational principles, one can take any linear combination of functions $\omega_1, \ldots, \omega_s$.

In order to deduce this, we show first the validity of the equalities

$$\int \overline{\omega_j} L \omega_i d\tau = 0 \quad (i \neq j)\,,$$

$$\int \overline{\omega_1} L \omega_1 d\tau = \int \overline{\omega_2} L \omega_2 d\tau = \ldots = \int \overline{\omega_s} L \omega_s d\tau\,, \tag{47}$$

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[8] A matrix is unitary if its inverse is obtained by interchanging rows by columns and complex conjugating all its elements, i.e.,

$$(P^a)^{-1}_{ij} = \overline{P}^a_{ji}.$$

The partial case of a unitary matrix is that of orthogonal transformation with real coefficients. (*V. Fock*) from which it follows that the matrix

$$L_{ji} = \int \overline{\omega_j} L \omega_i d\tau \quad (i, j = 1, 2, \ldots, s) \tag{48}$$

is proportional to the unity matrix.[9]

If L is the symmetric operator, then under permutation P^a the functions

$$\xi_j = L\omega_j$$

expose the same transformation as functions ω_j do themselves, namely,

$$\xi'_i = P^a \xi_i = \sum_{l=1}^{s} P^a_{li} \xi_l \,.$$

If the matrix P^a is unitary, the functions $\eta_j = \overline{\omega}_j$ expose a transformation

$$\eta'_j = \sum_{k=1}^{s} (P^a)^{-1}_{ik} \eta_k \,.$$

Let us construct the product $\eta'_j \xi'_i$ and calculate its average over all $N!$ permutations. In the group theory, it is shown that[10]

$$\frac{1}{N!} \sum_a (P^a)^{-1}_{ik} P^a_{li} = \frac{1}{s} \delta_{ij} \delta_{kl},$$

whence it follows that the average sought is equal to

$$\frac{1}{N!} \sum_\alpha \eta'_j \xi'_i = \frac{1}{s} \delta_{ij} \sum_{k=1}^{s} \eta_k \xi_k \,.$$

Integrating this expression over the configurational space and taking into account that

$$\int \eta'_j \xi'_i d\tau = \int \eta_j \xi_i d\tau = \int \overline{\omega_j} L \omega_i d\tau \,,$$

we obtain

$$\int \overline{\omega_j} L \omega_i d\tau = \frac{1}{s} \delta_{ij} \sum_{k=1}^{s} \int \overline{\omega_k} L \omega_k d\tau, \tag{49}$$

whence equality (47) follows directly.

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[9] See, e.g., E. Wigner, Zs. Phys. **43**, 624, 1927, eq. (3). (*V. Fock*)

[10] See Speiser, Theorie der Gruppen von endlicher Ordung, theorem 144. (*V. Fock*)

Now it is easy to verify the validity of our statement. Indeed, if we substitute the expression of Ω into (46), the constants α_i are encountered in the same combination both in the numerator and in the denominator only,

$$|\alpha_1|^2 + |\alpha_2|^2 + \ldots + |\alpha_s|^2 ,$$

and this expression in the fraction cancels.

Now our challenge consists of the following. We must construct such an expression by the one-electron functions $\psi_i(x_k)$, which ought to have the same symmetric properties with respect to any permutations of electrons as a linear combination of functions $\omega_1, \ldots, \omega_s$, belonging to the same term. Thus, the expression obtained should be substituted into the variational principle.

As it has been shown in the cited papers by Heitler, Waller and Hartree, in one important partial case one can write the corresponding expression as the product of two determinants. By Heitler's terminology, this partial case corresponds to the term, which belongs to "the quite degenerate system of terms" (vollständig ausgeartetes Termsystem).

To clarify the above treatment, let us consider a lithium atom as an example. Suppose that two of three electrons are on the same orbit. Since each orbit is described by the respective function, we shall have two functions $\psi_1(x)$ and $\psi_2(x)$. By means of these functions, one can construct three products

$$\psi_1(x_2)\psi_1(x_3)\psi_2(x_1) ,$$

$$\psi_1(x_3)\psi_1(x_1)\psi_2(x_2) ,$$

$$\psi_1(x_1)\psi_1(x_2)\psi_2(x_3) ;$$

and then construct three linear combinations

$$\omega = \psi_1(x_2)\psi_1(x_3)\psi_2(x_1) + \psi_1(x_3)\psi_1(x_1)\psi_2(x_2) + \psi_1(x_1)\psi_1(x_2)\psi_2(x_3),$$

$$\omega_1 = -\psi_1(x_3) \begin{vmatrix} \psi_1(x_1) & \psi_2(x_1) \\ \psi_1(x_2) & \psi_2(x_2) \end{vmatrix} ,$$

$$\omega_2 = \frac{1}{\sqrt{3}}\psi_1(x_2) \begin{vmatrix} \psi_1(x_3) & \psi_2(x_3) \\ \psi_1(x_1) & \psi_2(x_1) \end{vmatrix} + \frac{1}{\sqrt{3}}\psi_1(x_1) \begin{vmatrix} \psi_1(x_3) & \psi_2(x_3) \\ \psi_1(x_2) & \psi_2(x_2) \end{vmatrix} ;$$

the function ω is symmetric of all three electrons and the corresponding term is forbidden by the Pauli principle; the functions ω_1 and ω_2 belong to just the same term. Their substitutions under permutations of the electrons give the following irreducible orthogonal representation of the permutation group:

$$P^{(23)} = \left\{ \begin{matrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{matrix} \right\}, \quad P^{(31)} = \left\{ \begin{matrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{matrix} \right\}, \quad P^{(12)} = \left\{ \begin{matrix} -1 & 0 \\ 0 & 1 \end{matrix} \right\},$$

$$P^{(123)} = \left\{ \begin{matrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{matrix} \right\}, \quad P^{(213)} = \left\{ \begin{matrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{matrix} \right\}, \quad E = \left\{ \begin{matrix} 1 & 0 \\ 0 & 1 \end{matrix} \right\}.$$

From the general theory, it follows:

$$\int \overline{\omega_1} L \omega_2 d\tau = 0, \qquad \int \overline{\omega_1} L \omega_1 d\tau = \int \overline{\omega_2} L \omega_2 d\tau \,,$$

which can be verified directly in the simple case considered.

As is seen, though several functions (in our case two) correspond to a single term, one can choose a single combination of these functions for the variational principle. For a lithium atom, one can choose the product of determinants, for example, $\Psi = -\omega_1$:

$$\Psi = \psi_1(x_3) \begin{vmatrix} \psi_1(x_1) & \psi_2(x_1) \\ \psi_1(x_2) & \psi_2(x_2) \end{vmatrix}$$

(here $\psi_1(x_3)$ can be treated as the determinant of the first order).

6 The Derivation of Generalized Hartree's Equations

We present here the derivation of equations for the one-electron wave functions that describe individual orbits. We restrict ourselves to the case when a multi-electron function in the configurational space can be expressed in the form of the product of two determinants:

$$\Psi = \Psi_1 \Psi_2 \,, \tag{50}$$

$$\Psi_1 = \begin{vmatrix} \psi_1(x_1) & \psi_2(x_1) & \ldots & \psi_q(x_1) \\ \psi_1(x_2) & \psi_2(x_2) & \ldots & \psi_q(x_2) \\ \ldots & \ldots & \ldots & \ldots \\ \psi_1(x_q) & \psi_2(x_q) & \ldots & \psi_q(x_q) \end{vmatrix}, \tag{51}$$

$$\Psi_2 = \begin{vmatrix} \psi_1(x_{q+1}) & \psi_2(x_{q+1}) & \ldots & \psi_q(x_{q+1}) \\ \psi_1(x_{q+2}) & \psi_2(x_{q+2}) & \ldots & \psi_q(x_{q+2}) \\ \ldots & \ldots & \ldots & \ldots \\ \psi_1(x_{q+p}) & \psi_2(x_{q+p}) & \ldots & \psi_q(x_{q+p}) \end{vmatrix}. \tag{51*}$$

Here $q + p = N$ is the number of electrons. For definiteness, we put $q > p$. The function Ψ describes an atomic state, in which there are q different orbits, each of p being occupied by two electrons.

Without the loss of generality, we can suppose that the functions

$$\psi_1(x), \psi_2(x), \ldots, \psi_q(x)$$

are normalized and orthogonal to each other. Indeed, if one replaces the first p functions by their linear combinations, the determinants will be multiplied by constants only, but we can choose these linear combinations to be normalized and mutually orthogonal. Further leaving these new p functions unchanged, we can replace other functions $\psi_{p+1}, \ldots, \psi_q$ by such linear combinations of all the functions $\psi_1, \ldots, \psi_q$ that are normalized and orthogonal both with each other and with the first p functions $\psi_1, \ldots, \psi_p$. As a result, all the functions will be normalized and orthogonal. This set of functions is determined up to an arbitrary unitary transformation of the first p and the last $q - p$ functions separately.

To facilitate manipulations with determinants, we introduce the coefficients

$$\varepsilon_{(\alpha)} = \varepsilon_{\alpha_1 \alpha_2 \ldots \alpha_q} , \tag{52}$$

which are equal to $+1$, when all the subscripts $\alpha_1 \alpha_2 \ldots \alpha_q$ are different and present an even permutation of numbers $1, 2, \ldots, q$; equal to -1 for an odd permutation; and equal to zero, when among subscripts there are the same ones. Then the determinant Ψ_1 can be written in the form

$$\Psi_1 = \sum_{(\alpha)} \varepsilon_{\alpha_1 \alpha_2 \ldots \alpha_q} \psi_{\alpha_1}(x_1) \psi_{\alpha_2}(x_2) \ldots \psi_{\alpha_q}(x_q) . \tag{53}$$

The energy operator L has been already written down [see (3)]. We split it into three parts. The first one, L_1, contains terms depending on coordinates $x_1, \ldots, x_q$ only; the second one, L_2, depends on $x_{q+1}, \ldots, x_{q+p}$; the last, L_{12}, contains all the other terms. We have

$$L = L_1 + L_2 + L_{12} , \tag{54}$$

$$L_1 = \sum_{k=1}^{q} H_k + \sum_{i>k=1}^{q} \frac{1}{r_{ik}} , \tag{55}$$

$$L_2 = \sum_{k=q+1}^{q+p} H_k + \sum_{i>k=q+1}^{q+p} \frac{1}{r_{ik}} , \tag{56}$$

$$L_{12} = \sum_{k=i}^{q} \sum_{k=q+1}^{q+p} \frac{1}{r_{ik}}\,. \tag{57}$$

The variation of the integral

$$\delta I = \int \delta\overline{\Psi}(L - E)\Psi d\tau$$

will be

$$\delta I = \int\!\!\int \delta(\overline{\Psi}_1\overline{\Psi}_2)(L_1 + L_2 + L_{12} - E)\Psi_1\Psi_2 d\tau_1 d\tau_2, \tag{58}$$

where

$$d\tau_1 = dx_1 dx_2 \dots dx_q\,,$$

$$d\tau_2 = dx_{q+1} dx_{q+2} \dots dx_{q+p}\,.$$

For brevity, we put

$$\begin{aligned} A_1 &= \int \overline{\Psi}_1\Psi_1 d\tau_1, & A_2 &= \int \overline{\Psi}_2\Psi_2 d\tau_2, \\ B_1 &= \int \overline{\Psi}_1 L_1 \Psi_1 d\tau_1, & B_2 &= \int \overline{\Psi}_2 L_2 \Psi_2 d\tau_2, \\ F_1 &= \int \overline{\Psi}_1 L_{12} \Psi_1 d\tau_1, & F_2 &= \int \overline{\Psi}_2 L_{12} \Psi_2 d\tau_2\,. \end{aligned} \tag{59}$$

The values A_i and B_i are constants, while F_i are functions of coordinates. By means of these notations, the variation can be written as

$$\begin{aligned} \delta I = &\int \delta(\overline{\Psi}_1[A_2(L_1 - E) + B_2 + F_2]\Psi_1 d\tau_1 + \\ &+ \int \delta(\overline{\Psi}_2\left[A_1(L_2 - E) + B_1 + F_1\right]\Psi_2 d\tau_2\,. \end{aligned} \tag{60}$$

Now we must calculate the integrals involved. We start with the following integral:

$$\int (\overline{\Psi}_1\Psi_1) dx_3 dx_4 \dots dx_q\,.$$

It will be equal to

$$\begin{aligned} &\int (\overline{\Psi}_1\Psi_1) dx_3 dx_4 \dots dx_q = \\ &= \sum_{(\alpha)} \sum_{\alpha'} \varepsilon_{(\alpha)}\varepsilon_{(\alpha')}\overline{\psi}_{\alpha_1}(x_1)\overline{\psi}_{\alpha_2}(x_2)\psi_{\alpha_1}(x_1)\psi_{\alpha_2}(x_2)\delta_{\alpha_3\alpha'_3}\dots\delta_{\alpha_q\alpha'_q} \end{aligned}$$

because ψ_i are normalized and orthogonal. Summation over α' gives

$$\int (\overline{\Psi}_1 \Psi_1) dx_3 dx_4 \ldots dx_q = \sum_{\alpha} \varepsilon_{(\alpha)} \overline{\psi}_{\alpha_1}(x_1) \psi_{\alpha_2}(x_2) \begin{vmatrix} \psi_1(x_1) & \ldots & \psi_q(x_1) \\ \psi_1(x_2) & \ldots & \psi_q(x_2) \\ \delta_{\alpha_3 1} & \ldots & \delta_{\alpha_3 q} \\ \hdotsfor{3} \\ \delta_{\alpha_q 1} & \ldots & \delta_{\alpha_q q} \end{vmatrix} .$$

The expression under the summation sign is invariant with regard to any permutations of subscripts $\alpha_3, ..., \alpha_q$. Therefore, the summation over these subscripts gives $(q-2)!$ of identical terms. Further,

$$\varepsilon_{(\alpha)} \begin{vmatrix} \psi_1(x_1) & \ldots & \psi_q(x_1) \\ \psi_1(x_2) & \ldots & \psi_q(x_2) \\ \delta_{\alpha_3 1} & \ldots & \delta_{\alpha_3 q} \\ \hdotsfor{3} \\ \delta_{\alpha_q 1} & \ldots & \delta_{\alpha_q q} \end{vmatrix} = \begin{vmatrix} \delta_{11} & \ldots & \delta \\ \hdotsfor{3} \\ \psi_1(x_1) & \ldots & \psi_q(x_1) \\ \hdotsfor{3} \\ \psi_1(x_2) & \ldots & \psi_q(x_2) \\ \delta_{\alpha_3 1} & \ldots & \delta_{\alpha_3 q} \\ \hdotsfor{3} \\ \delta_{q1} & \ldots & \delta_{qq} \end{vmatrix} .$$

Here $\psi_1(x_1) \ldots \psi_q(x_1)$ form a row number α_1 and $\psi_1(x_2) \ldots \psi_q(x_2)$ forms a row number α_2. This determinant is equal to

$$\begin{vmatrix} \psi_{\alpha_1}(x_1) & \psi_{\alpha_2}(x_1) \\ \psi_{\alpha_1}(x_2) & \psi_{\alpha_2}(x_2) \end{vmatrix} .$$

If we denote the summation subscripts by i and k instead of α_1 and α_2, the integral under consideration can be written in the form

$$\int (\overline{\Psi}_1 \Psi_1) dx_3 dx_4 \ldots dx_q = \\ = (q-2)! \textstyle\sum_{i,k=1}^{q} \overline{\psi}_i(x_1) \overline{\psi}_k(x_2) [\psi_i(x_1)\psi_k(x_2) - \psi_k(x_1)\psi_i(x_2)] . \quad (61)$$

We put

$$\varrho_1(x_1, x_2) = \sum_{i=1}^{q} \overline{\psi}_i(x_1) \psi_i(x_2) = \overline{\varrho_1(x_1, x_2)}, \qquad \varrho_1(x) = \varrho_1(x, x) . \quad (62)$$

Then

$$\int (\overline{\Psi}_1 \Psi_1) dx_3 dx_4 \ldots dx_q = (q-2)! [\varrho_1(x_1)\varrho_1(x_2) - |\varrho_1(x_1, x_2)|^2] . \quad (63)$$

Now, integrals (59) can be easily calculated by means of (63). We have

$$\int \varrho_1(x)dx = q, \qquad \int |\varrho_1(x_1, x_2)|^2 dx_2 = \varrho_1(x_1)\,, \tag{64}$$

whence

$$\int (\overline{\Psi}_1 \Psi_1) dx_2 \ldots dx_q = (q-1)!\varrho_1(x_1)\,, \tag{65}$$

$$A_1 = \int \overline{\Psi}_1 \Psi_1 dx_1 \ldots dx_q = q!\ . \tag{66}$$

The integral B_1 is equal to

$$B_1 = \int \overline{\Psi}_1 L_1 \Psi_1 d\tau = \sum_{k=1}^{q} \int \overline{\Psi}_1 H_k \Psi_1 d\tau_1 + \sum_{i>k=1}^{q} \int \overline{\Psi}_1 \frac{1}{r_{ik}} \Psi_1 d\tau_1\,.$$

Since the expression of $\overline{\Psi}_1 \Psi_1$ is symmetric with respect to all coordinates $x_1, x_2, \ldots, x_q$, all $\frac{1}{2}q(q-1)$ terms of the double sum are equal to one another; likewise, all q terms of the ordinary sum are also equal to one another. Thus,

$$B_1 = q \int \overline{\Psi}_1 H_1 \Psi_1 d\tau_1 + \frac{1}{2} q(q-1) \int \overline{\Psi}_1 \frac{1}{r_{12}} \Psi_1 d\tau_1\,.$$

Integration over $x_2 \ldots x_q$ in the first integral and integration over $x_3 \ldots x_q$ in the second integral are performed by means of the above expressions. As a result, we obtain

$$B_1 = q!E_1, \tag{67}$$

where

$$E_1 = \sum_{k=1}^{q} H_{kk} + \frac{1}{2} \int\!\!\int \frac{\varrho_1(x_1)\varrho_1(x_2) - |\varrho_1(x_1, x_2)|^2}{r_{12}} dx_1 dx_2\,; \tag{68}$$

here, in accordance with (17),

$$H_{ik} = \int \overline{\psi}_i(x) H \psi_k(x) dx.$$

The integral F_1 can be written in the form

$$F_1 = q! \sum_{k=q+1}^{q+p} V^{(1)}(x_k)\,, \tag{69}$$

where

$$V^{(1)}(x_k(= \frac{1}{q!}\sum_{i=1}^{q}\int \frac{\overline{\Psi}_1\Psi_1}{r_{ik}}d\tau_1\,. \tag{70}$$

In the latter sum, all terms are equal to one another. Applying relation (65), we obtain

$$V^{(1)}(x_k) = \int \frac{\varrho_1(x_1)}{r_{ik}}dx_1 = \sum_{i=1}^{q} G_{ii}(x_k)\,, \tag{71}$$

where

$$G_{ik}(x) = \int \frac{\overline{\psi}_i(x')\psi_k(x')}{r}dx'\,. \tag{72}$$

The values of A_2, B_2 and F_2 can be obtained from A_1, B_1 and F_1 without calculations. Analogously to (62), (68) and (71), we put

$$\varrho_2(x_1,x_2) = \sum_{i=1}^{p}\overline{\psi}_i(x_1)\psi_i(x_2) = \overline{\varrho_2(x_2,x_1)}\,,$$

$$\varrho_2(x) = \varrho_2(x,x)\,, \tag{62*}$$

$$E_2 = \sum_{k=1}^{p} H_{kk} + \frac{1}{2}\int\int \frac{\varrho_2(x_1)\varrho_2(x_2) - |\varrho_2(x_1,x_2)|^2}{r_{12}}dx_1dx_2\,, \tag{68*}$$

$$V^{(2)}(x_k) = \int \frac{\varrho_2(x_1)}{r_{ik}}dx_1 = \sum_{i=1}^{p} G_{ii}(x_k), \tag{71*}$$

and then obtain

$$A_2 = p!, \qquad B_2 = p!E_2, \qquad F_2 = p!\sum_{k=1}^{q} V^{(2)}(x_k)\,. \tag{73}$$

Substitution of the values of the sought integrals (59) into expression (60) leads to

$$\delta I = p!\int \delta\overline{\psi}_1\left[L_1 - E + E_2 + \sum_{k=1}^{q} V^{(2)}(x_k)\right]\psi_1 d\tau_1 +$$

$$+q!\int \delta\overline{\psi}_2\left[L_2 - E + E_1 + \sum_{k=1}^{q} V^{(1)}(x_k)\right]\psi_2 d\tau_2\,. \tag{74}$$

The calculations of the integrals in this expression for δI can be performed analogously to the above calculations by expanding the determinants in accordance with (53). Here we present only the results. We put

$$E_{12} = \iint \frac{\varrho_1(x_1)\varrho_2(x_2)}{r_{12}} dx_1 dx_2 \tag{75}$$

and introduce the values

$$V_{ki}^{(s)} = \int \overline{\psi}_k(x) V^{(s)}(x) \psi_i(x) dx = \iint \overline{\psi}_k(x_1)\psi_i(x_1) \frac{\varrho_s(x_2)}{r_{12}} dx_1 dx_2,$$

$$T_{ki}^{(s)} = \iint \overline{\psi}_k(x_2)\psi_i(x_1) \frac{\varrho_s(x_1, x_2)}{r_{12}} dx_1 dx_2\,, \tag{76}$$

$$U_{ki}^{(s)} = V_{ki}^{(s)} - T_{ki}^{(s)}, \qquad s = 1, 2\,.$$

The values $V_{ki}^{(s)}$, $T_{ki}^{(s)}$ and $U_{ki}^{(s)}$ are the definite (positive) Hermitian matrices. The values $V_{ki}^{(s)}$ and $T_{ki}^{(s)}$ can be expressed by the matrix elements $(ik|G|lm)$, which have been introduced in Section 3 [see (18)], in the following manner:

$$V_{ki}^{(1)} = \sum_{l=1}^{q} \langle kl \mid G \mid il\rangle, \quad V_{ki}^{(2)} = \sum_{l=1}^{p} \langle kl \mid G \mid il\rangle,$$

$$T_{ki}^{(1)} = \sum_{l=1}^{q} \langle kl \mid G \mid li\rangle, \quad T_{ki}^{(2)} = \sum_{l=1}^{q} \langle kl \mid G \mid li\rangle\,. \tag{77}$$

In turn, the values E_1, E_2 and E_{12} are expressed by $V_{ki}^{(s)}$ and $U_{ki}^{(s)}$:

$$E_1 = \sum_{k=1}^{q} \left(H_{kk} + \frac{1}{2} U_{kk}^{(1)} \right),$$

$$E_2 = \sum_{k=1}^{q} \left(H_{kk} + \frac{1}{2} U_{kk}^{(2)} \right), \tag{78}$$

$$E_{12} = \sum_{k=1}^{q} V_{kk}^{(2)} = \sum_{k=1}^{p} V_{kk}^{(1)}\,.$$

Now the integrals in (74) can be written in the form

$$\int \delta\overline{\Psi}_1 \Psi_1 \partial\tau_1 = q! \sum_{i=1}^{q} \int \delta\overline{\psi}_i(x)\psi_i(x) dx\,, \tag{79}$$

$$\begin{aligned}
&\int \delta\overline{\Psi}_1 \sum_{k=1}^{q} (H_k + V^{(2)}(x_k)\Psi_1 d\tau_1 = \\
&= q! \sum_{i=1}^{q} \int \delta\overline{\psi}_1 \left[H_{kk} + V^{(2)}(x) \sum_{k=1}^{q} H_{kk} + E_{12} \right] \psi_i(x)dx - \\
&\qquad -q! \sum_{i=1}^{q} \int \delta\overline{\psi}_i(x) \sum_{k=1}^{q} (H_{ki} + V_{ki}^{(2)})\psi_k(x)dx \,, \qquad (80)
\end{aligned}$$

$$\begin{aligned}
&\sum_{i>k+1}^{q} \int \delta\overline{\Psi}_1 \frac{1}{r_{ik}} \Psi_1 d\tau_1 = \\
&\quad = q! \sum_{i=1}^{q} \int \delta\overline{\psi}_1 \left[V^{(1)}(x) + E_1 - \sum_{k=1}^{q} H_{kk} \right] \psi_i(x)dx - \\
&\qquad -q! \sum_{i=1}^{q} \int \delta\overline{\psi}_i(x) \sum_{k=1}^{q} \left[G_{ki}(x) + U_{ki}^{(1)} \right] \psi_k(x)dx \,. \qquad (81)
\end{aligned}$$

Substituting these expressions into (74) gives

$$\begin{aligned}
&\frac{1}{p!q!}\delta I = \\
&\quad = \sum_{i=1}^{q} \int \delta\overline{\psi}_i(x) \Big[H + V^{(1)}(x) + V^{(2)}(x) + E_1 + E_2 + E_{12} - E \Big] \psi_i(x)dx \\
&\quad - \sum_{i=1}^{q} \int \delta\overline{\psi}_i(x) \sum_{k=1}^{q} \left[G_{ki}(x) + H_{ki} + V_{ki}^{(2)} + U_{ki}^{(1)} \right] \psi_k(x)dx \\
&\quad + \sum_{i=1}^{p} \int \delta\overline{\psi}_i(x) \Big[H + V^{(1)}(x) + V^{(2)}(x) + E_1 + E_2 + E_{12} - E \Big] \psi_k(x)dx \\
&\quad - \sum_{i=1}^{p} \int \delta\overline{\psi}_i(x) \sum_{k=1}^{p} \left[G_{ki}(x) + H_{ki} + V_{ki}^{(1)} + U_{ki}^{(2)} \right] \psi_k(x)dx \,. \qquad (82)
\end{aligned}$$

Here one needs to put zero the coefficients at independent variations $\delta\overline{\psi}_i(x)$, keeping in mind that in the expression of δI for $i = 1, 2, \ldots, p$ the values of $\delta\overline{\psi}_i(x)$ are encountered twice, while for $i = p+1, \ldots, q$ only once.

For $i = 1, 2, \ldots, p$ we get

$$2[H + V(x) + E_1 + E_2 + E_{12} - E]\psi_i(x) -$$

$$-\sum_{k=1}^{p}[2G_{ik}(x)+2H_{ki}+U_{ki}+V_{ki}]\psi_k(x)-$$

$$-\sum_{k=p+1}^{q}[G_{ik}(x)+H_{ki}+U_{ki}^{(1)}+V_{ki}^{(2)}]\psi_k(x)=0\,, \tag{83}$$

while for $i = p+1, \dots, q$

$$[H+V(x)+E_1+E_2+E_{12}-E]\psi_i(x)-$$

$$-\sum_{k=1}^{q}[G_{ki}(x)+H_{ki}+U_{ki}^{(1)}+V_{ki}^{(2)}]\psi_k(x)=0\,. \tag{84}$$

Here for brevity we assume

$$V(x)=V^{(1)}(x)+V^{(2)}(x)\,, \tag{85}$$

$$V_{ki}=V_{ki}^{(1)}+V_{ki}^{(2)} \qquad U_{ki}=U_{ki}^{(1)}+U_{ki}^{(2)}\,. \tag{86}$$

Let us multiply equality (83) by $\overline{\psi}_l(x)$ and integrate it over x. If we take into account (70) and (77) as well as the orthogonality of functions $\psi_i(x)$, then for $l \neq i$ we obtain an identity, while for $l = i$ we get the relation

$$E=E_1+E_2+E_{12}. \tag{87}$$

We should get the same result if we multiply equality (83) by $\overline{\psi}_l(x)$ $(l = p+1, \dots, q)$ and then integrate it.

However if we multiply (83) by one of the functions $\overline{\psi}_{p+1}(x)$, ..., $\overline{\psi}_q(x)$ or (84) by $\overline{\psi}_1(x)$, ..., $\overline{\psi}_p(x)$, we obtain

$$H_{ki}+V_{ki}^{(1)}+U_{ki}^{(2)}. \tag{88}$$

It can be verified that now as well as for the case of Hartree's equation the relation

$$E=\frac{\displaystyle\int\overline{\Psi}L\Psi d\tau}{\displaystyle\int\overline{\Psi}\Psi d\tau} \tag{89}$$

is fulfilled.

7 Analysis of the Equations and a New Formulation of the Variational Principle

Let us consider the system of equations (83) and (84). We have

$$\begin{aligned} \lambda_{ki} &= 2H_{ki} + U_{ki} + V_{ki} \qquad (i \quad \text{or} \quad k = \quad 1,2,\ldots,p), \\ \lambda_{ki} &= H_{ki} + U_{ki}^{(1)} + V_{ki}^{(2)} \qquad (i \quad \text{or} \quad k = p+1,2,\ldots,q)\,. \end{aligned} \tag{90}$$

$$\begin{aligned} \varepsilon_k &= 2 \qquad (k = 1,2,\ldots,p), \\ \varepsilon_k &= 1 \qquad (k = p+1,\ldots,q)\,. \end{aligned} \tag{91}$$

(For $i = 1,2,\ldots p$ and $k = p+1,\ldots q$, both determinations of λ_{ki} coincide due to relation (88).)

Then equations (83) and (84) can be written in the form

$$\begin{gathered} 2[H + V(x)]\psi_i(x) - \sum_{k=1}^{q} \varepsilon_k G_{ki}(x)\psi_k(x) = \sum_{k+1}^{q} \lambda_{ki}\psi_k(x) \quad i = 1,\ldots,p, \\ [H + V(x)]\,\psi_i(x) - \sum_{k=1}^{q} G_{ki}(x)\psi_k(x) = \sum_{k+1}^{q} \lambda_{ki}\psi_k(x) \quad i = p+1,\ldots,q. \end{gathered} \tag{92}$$

If one omits all terms for which $i \neq k$, then one obtains the Hartree equations (29). Thus the terms with different subscripts represent the quantum exchange, which is not taken into account in the Hartree equations. Generally speaking, these non-diagonal terms ($i \neq k$) are small as compared with the diagonal ones ($i = k$).

The characteristic feature of Hartree's theory, that the effect of an electron on itself $G_{ii}(x)$ is subtracted from the total potential energy $V(x)$, is also reproduced here.

Like (29) our equations (92) can be derived from the three-dimensional variational principle. The varied integral is of the form

$$\begin{aligned} W = \sum_{i=1}^{q} \int \overline{\psi}_i H\psi_i + \frac{1}{2}\iint \frac{\varrho_1(x)\varrho_1(x') - |\varrho_1(x,x')|^2}{r} dx dx' + \\ + \sum_{i=1}^{p} \int \overline{\psi}_i H\psi_i + \frac{1}{2}\iint \frac{\varrho_2(x)\varrho_2(x') - |\varrho_2(x,x')|^2}{r} dx dx' + \\ + \iint \frac{\varrho_1(x)\varrho_2(x')}{r} dx dx'\,. \end{aligned} \tag{93}$$

Let us take a variation of this integral under additional conditions

$$\int \overline{\psi}_i(x)\psi_k(x) = \delta_{ik}\,. \tag{94}$$

The coefficients λ_{ik} forming a Hermitian matrix play the role of the Lagrange arbitrary multipliers. Expression (93) represents the atomic energy because it reads

$$W = E_1 + E_2 + E_{12} = E\,. \tag{95}$$

Just as we have proceeded above in Section 4, we can treat coefficients in equations (92) as given. Then these equations will represent a self-adjoint linear system. This system can be obtained by a variation of the integral

$$W^* = \int \left[\sum_{i=1}^{q} \overline{\psi}_i(H+V)\psi_i - \sum_{i,k=1}^{q} G_{ki}\overline{\psi}_i\psi_k\right] dx +$$

$$+ \int \left[\sum_{i=1}^{p} \overline{\psi}_i(H+V)\psi_i - \sum_{i,k=1}^{p} G_{ki}\overline{\psi}_i\psi_k\right] dx \tag{96}$$

under the previous additional conditions (94).

Now the value of the varied integral is not equal to an energy, but is equal to

$$W^* = 2E - \sum_{i=1}^{p} H_{ii} - \sum_{i=1}^{q} H_{ii} = \sum_{i=1}^{q} \lambda_{ii}\,. \tag{97}$$

Our results, in particular, expression (93) for the energy, can be interpreted as follows. The atomic electrons are divided into two groups, having q and p electrons, correspondingly ($q + p = N$). The electrons of the same group obey the Pauli principle in the narrow sense (i.e., without taking a spin into account). In expression (93) for the energy, the first double integral over volume represents the interaction energy of electrons of the first group; the second integral is that for the second group; the last double integral represents the mutual potential energy of both groups. Note that in the first two integrals the integrands tend to zero when $x = x'$. Our expressions for the energy are much similar to those obtained by Jordan by means of the second quantization method.[11]

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[11] See, e.g., a review by Jordan in Phys. Zs. **30**, 700, (1929). (*V. Fock*)

The numerical solution of our system of equations can be done by the method of successive approximations.

If we assume the spherical symmetry, the equations can be considerably simplified.[12] The solution of our equations for the case of the spherical symmetry is, apparently, not more complicated than that of the corresponding Hartree's equations, but its result has to be much more precise.

8 The Spectral Line Intensities

Having obtained the wave functions ψ_i, one can calculate the frequencies and intensity of the spectral lines. The energy levels can be calculated by means of formula (93). It should be taken into account that this formula gives not the term but the total atomic energy. To obtain the term, one has to calculate the difference between the atomic and ion energy.

To obtain the intensity, one needs to calculate the integral

$$\langle E \mid f \mid E' \rangle = \frac{1}{p!q!} \int \overline{\Psi} \sum_{i=k}^{N} f(x_k) \Psi' d\tau \,, \tag{98}$$

where

$$f(x_k) = f(x_k \;, y_k \;, z_k) \,.$$

We denote the basic functions ψ_i for the level E in more detail as $\psi_i(x,E)$. The total wave function for the entire atom in state E is denoted as before by Ψ and the same function for state E' by Ψ'. If, for brevity, we put

$$\begin{aligned} a_{ik} &= \int \overline{\psi}_i(x,E)\psi_k(x,E')dx, \\ f_{ik} &= \int \overline{\psi}_i(x,E)f(x)\psi_k(x,E')dx \,, \end{aligned} \tag{99}$$

the value of $(E|f|E')$ will be equal to

$$\langle E \mid f \mid E' \rangle = \begin{vmatrix} a_{11} & \dots & a_{1p} \\ a_{21} & \dots & a_{2p} \\ \dots & \dots & \dots \\ a_{p1} & \dots & a_{pp} \end{vmatrix} \cdot \sum_{k=1}^{q} \begin{vmatrix} a_{11} & \dots & a_{1q} \\ \dots & \dots & \dots \\ f_{k1} & \dots & f_{kq} \\ \dots & \dots & \dots \\ a_{q1} & \dots & a_{qq} \end{vmatrix} +$$

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[12] The detailed derivation of the equations with the spherical symmetry for the sodium atom ($N = 11$) will be given in a separate paper. (*V. Fock*) (See [30-3] in this book. (*Editors*))

$$+\begin{vmatrix} a_{11} & \dots & a_{1q} \\ a_{21} & \dots & a_{2q} \\ \dots & \dots & \dots \\ a_{q1} & \dots & a_{qq} \end{vmatrix} \cdot \sum_{k=1}^{p} \begin{vmatrix} a_{11} & \dots & a_{1p} \\ \dots & \dots & \dots \\ f_{k1} & \dots & f_{kp} \\ \dots & \dots & \dots \\ a_{p1} & \dots & a_{pp} \end{vmatrix} . \tag{100}$$

Here the entries $f_{k1}, f_{k2} \dots$ form the k-th row. We shall show that in the case of a single valence electron this expression for the matrix element is approximately equal to an ordinary expression obtained by solution of the one-electron Schrödinger equation.

In this case, one needs to put $q = p + 1$. The functions $\psi_i(x, E)$ for subscripts i equal to $1, 2, \dots, p$ differ only slightly from the corresponding functions $\psi_i(x, E')$ because the transition of the valence electron to another orbit affects the internal electron relatively weakly. Whence it follows that for $i, k = 1, 2, \dots, p$ the coefficients are close to δ_{ik}. The wave function $\psi_q(x, E)$ of the valence electron will be approximately orthogonal not only to $\psi_i(x, E')$ for $i = 1, 2, \dots, p$, but to the function $\psi_q(x, E')$ of the valence electron in state E'. In fact, if one supposes the field to be unchanged by the core electrons, then $\psi_q(x, E)$ and $\psi_q(x, E')$ will be approximately equal to the eigenfunctions of the Schrödinger energy operator for the valence electron with different eigenvalues. Whence it follows that the coefficients a_{qq}, as well as $a_{1q}, \dots, a_{q-1,q}$ and $a_{q,1}, \dots, a_{q,q-1}$, will be small. The single term in the expression for $\langle E \mid f \mid E' \rangle$, not containing small factors, is equal to

$$f_{qq} = \int \overline{\psi}_q(x, E) f(x) \psi_q(x, E') dx\,, \tag{101}$$

i.e., to usual expression for the matrix entry.

In some cases the deviation of $\langle E|f|\,E' \rangle$ from its approximate value (101) can be noticeable enough. This deviation can be attributed to the rearrangement of the core electrons.

Translated by E.D. Trifonov

30-3
Application of the Generalized Hartree Method to the Sodium Atom

V.A. Fock

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TOI **5**, N51, 29, 1931

1 A Form of Wave Functions

The number of electrons in a sodium atom is equal to 11; one of them is a valence electron. Ten inner electrons are distributed in pairs at five orbitals. Thus, we have six orbitals, and, hence, six different wave functions. In the equations of the previous article, it should be taken

$$N = 11,\ p = 5,\ q = 6.$$

Let us denote a wave function of a valence electron by ψ_6, and wave functions of inner electrons by $\psi_1, \ldots, \psi_5$. In the case of spherical symmetry, these functions should have the form

$$\left.\begin{aligned}
\psi_1 &= \frac{1}{r} f_1(r) \frac{1}{\sqrt{4\pi}}, \\
\psi_2 &= \frac{1}{r} f_2(r) \frac{1}{\sqrt{4\pi}}, \\
\psi_3 &= \frac{1}{r} f_3(r) \frac{\sqrt{3}}{\sqrt{4\pi}} \cos\vartheta, \\
\psi_4 &= \frac{1}{r} f_3(r) \frac{\sqrt{3}}{\sqrt{4\pi}} \sin\vartheta \cos\varphi, \\
\psi_5 &= \frac{1}{r} f_3(r) \frac{\sqrt{3}}{\sqrt{4\pi}} \sin\vartheta \sin\varphi, \\
\psi_6 &= \frac{1}{r} f_4(r) \frac{1}{\sqrt{4\pi}} Y_l(\vartheta, \varphi).
\end{aligned}\right\} \tag{1}$$

The spherical function $Y_l(\vartheta, \varphi)$ is normalized by the following condition:

$$\frac{1}{4\pi} \iint \mid Y_l(\vartheta, \varphi) \mid^2 \sin\vartheta \; d\vartheta \; d\varphi = 1\,. \tag{2}$$

The normalized condition for $f_i(r)$ is

$$\int\limits_0^\infty [f_i(r)]^2\,dr = 1 \qquad (i = 1, 2, 3, 4). \tag{3}$$

In order for the functions $\psi_1, \ldots, \psi_5$ to be orthogonal, $f_i(r)$ should obey the following conditions:

$$\left.\begin{aligned} \int\limits_0^\infty f_1(r)f_2(r)dr = 0; \qquad \delta_{l0}\cdot\int\limits_0^\infty f_1(r)f_4(r)dr = 0; \\ \delta_{l0}\cdot\int\limits_0^\infty f_2(r)f_4(r)dr = 0; \qquad \delta_{l1}\cdot\int\limits_0^\infty f_3(r)f_4(r)dr = 0. \end{aligned}\right\} \tag{4}$$

The functions f_1, f_2, f_3, f_4 correspond to different electronic shells. For simplicity we denoted them by one subscript only; more complete notation would be $f_{10}, f_{20}, f_{21}, f_{nl}$, where two subscripts are nothing else but the quantum numbers of the electron shell under consideration.

2 Expressions for the Energy of an Atom

To obtain the equations, we will vary the expression for the energy of an atom derived in the previous article [formula (93)]. In this formula we should carry out integration over the variables ϑ and φ. Let us denote a sum of simple volume integrals by W_1 and a sum of double volume integrals by W_2, so that

$$W = W_1 + W_2. \tag{5}$$

Evaluation of W_1 is quite trivial; as the result, one gets

$$\begin{aligned} W_1 = \int\limits_0^\infty \Bigg[\left(\frac{df_1(r)}{dr}\right)^2 + \left(\frac{df_2(r)}{dr}\right)^2 + 3\left(\frac{df_3(r)}{dr}\right)^2 + \frac{1}{2}\left(\frac{df_4(r)}{dr}\right)^2 + \\ + \frac{6}{r^2}f_3^2 + \frac{l(l+1)}{2r^2}f_4^2\Bigg]dr - \int\limits_0^\infty \left(2f_1^2 + 2f_2^2 + 6f_3^2 + f_4^2\right)\frac{11}{r}dr. \end{aligned} \tag{6}$$

In this expression the first integral represents an average kinetic energy, and the second integral gives the average potential energy of electrons with respect to the nucleus (without the energy of interaction).

Evaluation of the interaction energy W_2 is more complicated; it can be carried out as follows. Let us suppose in formulae (62) and (62*) of the previous article

$$\left.\begin{aligned} \varrho_2(x,x') &= \varrho(\mathbf{r},\mathbf{r}'); \qquad & \varrho_1(x,x') &= \varrho(\mathbf{r},\mathbf{r}') + \sigma(\mathbf{r},\mathbf{r}'), \\ \varrho(\mathbf{r},\mathbf{r}) &= \varrho(\mathbf{r}); \qquad & \sigma(\mathbf{r},\mathbf{r}) &= \sigma(\mathbf{r}), \end{aligned}\right\} \tag{7}$$

where

$$\varrho(\mathbf{r},\mathbf{r}') \text{ and } \sigma(\mathbf{r},\mathbf{r}')$$

have the following values:

$$\left.\begin{aligned} \varrho(\mathbf{r},\mathbf{r}') &= \frac{1}{4\pi r r'}\,(f_1 f_1' + f_2 f_2' + 3 f_3 f_3' \cos\gamma), \\ \sigma(\mathbf{r},\mathbf{r}') &= \frac{1}{4\pi r r'} f_4 f_4'\ \overline{Y_l(\vartheta,\varphi)}\, Y_l(\vartheta',\varphi'). \end{aligned}\right\} \tag{8}$$

Here we assumed for brevity that

$$f_i = f_i(r); \qquad f_i' = f_i(r')$$

and

$$\cos\gamma = \cos\vartheta\cos\vartheta' + \sin\vartheta\sin\vartheta'\cos(\varphi-\varphi'). \tag{9}$$

We also suppose that

$$d\omega = \sin\vartheta\ d\vartheta\ d\varphi; \qquad d\omega' = \sin\vartheta'\ d\vartheta'\ d\varphi'. \tag{10}$$

The interaction energy W_2 will have the form

$$\begin{aligned} W_2 = \iint \big[2\varrho(\mathbf{r})\ \varrho(\mathbf{r}') - \mid \varrho(\mathbf{r},\mathbf{r}') \mid^2 + 2\varrho(\mathbf{r})\ \sigma(\mathbf{r}') - {} \\ - \varrho(\mathbf{r},\mathbf{r}')\ \sigma(\mathbf{r}',\mathbf{r})\big] \frac{r^2\ dr\ d\omega\ r'^2\ dr'\ d\omega'}{\sqrt{r^2 + r'^2 - 2rr'\cos\gamma}}. \end{aligned} \tag{11}$$

On account of

$$\sigma(\mathbf{r})\sigma(\mathbf{r}') - \mid \sigma(\mathbf{r},\mathbf{r}') \mid^2 = 0$$

the integrand does not contain terms quadratic with respect to σ, which greatly simplifies the calculations. Evaluating the integral, we will use the known expansion

$$\frac{1}{\sqrt{r^2 + r'^2 - 2rr'\cos\gamma}} = \sum_{n=0}^{\infty} (2n+1) K_n(r,r') P_n(\cos\gamma)\,, \tag{12}$$

which assumed that

$$\left.\begin{aligned} K_n(r,r') &= \frac{1}{2n+1}\frac{{r'}^n}{r^{n+1}} \qquad \text{for} \ \ r' \le r, \\ K_n(r,r') &= \frac{1}{2n+1}\frac{r^n}{{r'}^{n+1}} \qquad \text{for} \ \ r' \ge r, \end{aligned}\right\} \tag{13}$$

as well as the integral property of the spherical functions

$$\frac{2n{+}1}{4\pi}\int Y_l(\vartheta',\varphi')\ P_n(\cos\gamma)\ d\omega' = \delta_{nl}\ Y_n(\vartheta,\varphi)\,. \tag{14}$$

Here we will write down the evaluation for only one term of expression (11) for W_2, namely, for

$$J = \iint \varrho(\mathbf{r},\mathbf{r}')\sigma(\mathbf{r}',\mathbf{r})\frac{r^2\ dr\ d\omega\ r'^2\ dr'\ d\omega'}{\sqrt{r^2+r'^2-2rr'\cos\gamma}}\,.$$

Let us write this integral in more detail:

$$J = \frac{1}{(4\pi)^2}\iint f_4f_4'\ dr\ dr' \cdot \iint [f_1f_1' + f_2f_2' + 3f_3f_3'\cos\gamma]\cdot$$

$$\cdot\overline{Y_l(\vartheta,\varphi)}\,Y_l(\vartheta',\varphi')\frac{d\omega\ d\omega'}{\sqrt{r^2+r'^2-2rr'\cos\gamma}}\,.$$

Using the known relation between the spherical functions

$$(2n{+}1)\ x\ P_n(x) = (n{+}1)P_{n+1}(x) + n\,P_{n-1}(x)\,,$$

one gets

$$\frac{f_1f_1' + f_2f_2' + 3f_3f_3'\cos\gamma}{\sqrt{r^2+r'^2-2rr'\cos\gamma}} = \sum_{n=0}^{\infty}\Big\{(2n{+}1)(f_1f_1'+f_2f_2')K_n +$$

$$+3f_3f_3'\,[nK_{n-1} + (n{+}1)K_{n+1}]\Big\}\cdot P_n(\cos\gamma)\,.$$

Integration over $d\omega'$ and $d\omega$ gives

$$J = \iint f_4f_4'\Big\{(f_1f_1'+f_2f_2')K_l +$$

$$+3f_3f_3'\left[\frac{l}{2l{+}1}K_{l-1} + \frac{l{+}1}{2l{+}1}K_{l+1}\right]\Big\}dr\ dr'.$$

In order to carry out integration over r', let us suppose

$$F_l^{ik}(r) = \int_0^\infty f_i(r')\; f_k(r')\; K_l(r,r')\; dr'\;; \tag{15}$$

then we will finally get

$$J = \int_0^\infty \left\{ f_1 f_4\, F_l^{14} + f_2 f_4\, F_l^{24} + 3 f_3 f_4 \left[\frac{l}{2l{+}1} F_{l-1}^{34} + \frac{l{+}1}{2l{+}1} F_{l+1}^{34} \right] \right\} dr\;.$$

The other integrals in expression (11) for W_2 can be evaluated in the same manner. As the result, one has

$$\begin{aligned} W_2 = \int_0^\infty \Big\{ &\frac{1}{2}(2f_1^2 + 2f_2^2 + 6f_3^2 + f_4^2)(2F_0^{11} + 2F_0^{22} + 6F_0^{33} + F_0^{44}) - \\ &-f_1^2 F_0^{11} - f_2^2 F_0^{22} - 3f_3^2(F_0^{33} + 2F_2^{33}) - \frac{1}{2} f_4^2 F_0^{44} - \\ &-2f_1 f_2 F_0^{12} - 6 f_1 f_2 F_1^{13} - f_1 f_4 F_l^{14} - 6 f_2 f_3 F_1^{23} - \\ &-f_2 f_4 F_l^{24} - 3 f_3 f_4 \left[\frac{l}{2l{+}1} F_{l-1}^{34} + \frac{l{+}1}{2l{+}1} F_{l+1}^{34} \right] \Big\} dr\;. \end{aligned} \tag{16}$$

In this formula the terms containing products of different functions $f_i(r)$ (the last two lines) represent the energy of quantum exchange.[1]

3 Variational Equations

To derive variational equations, we should vary the energy $W = W_1 + W_2$ under additional conditions (3) and (4) ensued from orthogonalization and normalization of the wave functions. Constructing the variation of W_2, we should take into account that the coefficients $F_l^{ik}(r)$ also depend on the varied functions. We can distinguish between two kinds of W_2 variation: total variation δW_2, when both $f_i(r)$ and $F_l^{ik}(r)$ are varied, and partial variation $\delta^* W_2$, when only $f_i(r)$ is varied. It is not difficult to see that total and partial variations are related as follows:

$$\delta W_2 = \delta^*\, W_2\;. \tag{17}$$

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[1] According to preliminary calculations these terms are about 3% of the total value W_2 for the ground state of sodium. (*V. Fock*)

This remark simplifies constructing of the equations because a partial variation is evaluated easier than the total one.

The variational equations have the form:

$$\begin{aligned} &-\frac{d^2 f_1}{dr^2} + 2\left(-\frac{11}{r} + F_0^{11} + 2F_0^{22} + 6F_0^{33} + F_0^{44}\right) f_1 - \\ &-2F_0^{21} f_2 - 6F_1^{31} f_3 - F_l^{41} f_4 = \lambda_{11} f_1 + \lambda_{21} f_2 + \lambda_{41}\delta_{l0} f_4 \ , \end{aligned} \tag{18}$$

$$\begin{aligned} &-\frac{d^2 f_2}{dr^2} + 2\left(-\frac{11}{r} + 2F_0^{11} + F_0^{22} + 6F_0^{33} + F_0^{44}\right) f_2 - \\ &-2F_0^{12} f_1 - 6F_1^{32} f_3 - F_l^{42} f_4 = \lambda_{12} f_1 + \lambda_{22} f_2 + \lambda_{42}\delta_{l0} f_4 \ , \end{aligned} \tag{19}$$

$$\begin{aligned} &-3\frac{d^2 f_3}{dr^2} + 6\left(\frac{1}{r^2} - \frac{11}{r} + 2F_0^{11} + 2F_0^{22} + 5F_0^{33} - 2F_2^{33} + F_0^{44}\right) f_3 \\ &-6F_1^{13} f_1 - 6F_1^{23} f_2 - 3\left(\frac{l+1}{2l+1} F_{l+1}^{34} + \frac{l}{2l+1} F_{l-1}^{34}\right) f_4 = \\ &= \lambda_{33} f_3 + \lambda_{43}\delta_{l1} f_4 \ , \end{aligned} \tag{20}$$

$$\begin{aligned} &-\frac{1}{2}\frac{d^2 f_4}{dr^2} + \left[\frac{l(l+1)}{2r^2} - \frac{11}{r} + 2F_0^{11} + 2F_0^{22} + 6F_0^{33}\right] f_4 - \\ &-F_l^{14} f_1 - F_l^{24} f_2 - 3\left[\frac{l+1}{2l+1} F_{l+1}^{34} + \frac{l}{2l+1} F_{l-1}^{34}\right] f_3 = \\ &= \lambda_{14}\delta_{l0} f_1 + \lambda_{24}\delta_{l0} f_2 + \lambda_{34}\delta_{l1} f_3 + \lambda_{44} f_4 \ . \end{aligned} \tag{21}$$

The last of these equations is the wave equation for a valence electron, and the first three are the ones for inner electrons. Constants $\lambda_{ik} = \lambda_{ki}$ are nothing else but the Lagrangian factors. Off-diagonal terms (for example, the terms with f_1, f_2, f_3 in the last equation) describe the influence of quantum exchange. Equations (18), (19), (20) are invariant with respect to substitution f_1, f_2, f_3, f_4, keeping the quadratic form $2f_1^2 + 2f_2^2 + 6f_3^2 + f_4^2$ invariant. We can assume this substitution to be chosen so that

$$\lambda_{ik} = \lambda_i \delta_{ik} \ .$$

4 Properties of the Coefficients of the Equations

The coefficients $F_l^{ik}(r)$ of our system of equations defined by formula (15) satisfy the differential equation

$$r^2 \frac{d^2 F_l^{ik}}{dr^2} + 2r \frac{dF_l^{ik}}{dr} - l(l+1) F_l^{ik} = -f_i(r)\ f_k(r)\,. \tag{22}$$

The function $F_l^{ik}(r)$ can be determined as a solution of this equation, which remains finite at $r = 0$ and tends to zero at infinity. The value $K_l(r, r')$ is the Green's function of the self-conjugate differential operator in the left-hand side of (22). Numerical integration of the differential equation (22) by the Adams–Störmer method gives a convenient way for calculating the functions $F_l^{ik}(r)$ when $f_i(r)$ are known.

Let us write down expression (15) for $F_l^{ik}(r)$ in more detail:

$$F_l^{ik}(r) = \frac{1}{2l+1} \left(\frac{1}{r^{l+1}} \int\limits_0^r f_i(r') f_k(r') r'^l\, dr' + r^l \int\limits_r^\infty f_i(r') f_k(r')\, \frac{dr'}{r'^{l+1}} \right). \tag{23}$$

As we treat only those functions $f_i(r)$, which belong to a discrete spectrum and rapidly decrease at infinity, we can transform this expression in the following manner:

$$F_l^{ik}(r) = \frac{C_l^{ik}}{r^{l+1}} - R_l^{ik}(r)\,, \tag{24}$$

where it is supposed that

$$C_l^{ik} = \frac{1}{2l+1} \int\limits_0^\infty f_i(r)\ f_k(r)\ r^l dr \tag{25}$$

and

$$R_l^{ik}(r) = \frac{1}{2l+1} \int\limits_r^\infty \left(\frac{r'^l}{r^{l+1}} - \frac{r^l}{r'^{l+1}} \right) f_i(r') f_k(r') dr'\,. \tag{26}$$

This formula allows one to obtain an approximate expression for $F_l^{ik}(r)$ at large values of r. Let us suppose that for sufficiently large values of r (in any case, larger than the largest root of $f_i(r)$) the function $f_i(r)$ approximately equals[2]

$$f_i(r) = M_i\ r^{\alpha_i}\ e^{-\beta r} \left[1 + O\left(\frac{1}{r}\right) \right], \tag{27}$$

---

[2] On account of the fact that the functions $f_i(r)$ are bound by the system of equations, they have the equal coefficients β in indices. (*V. Fock*)

where the symbol $O\left(\frac{1}{r}\right)$ denotes a value of the order of $\frac{1}{r}$. In this case formula (26) gives the following approximate expression for $R_l^{ik}(r)$:

$$R_l^{ik}(r) = \frac{M_i M_k}{4\beta^2}\ r^{\alpha_i+\alpha_k-2}\ e^{-2\beta r}\left[1+O\left(\frac{1}{r}\right)\right] . \tag{28}$$

We see that this expression is notably small as compared with the first term of formula (24) and does not depend on the subscript l in the approximation considered.

Thus, formula (24) can be treated as the asymptotic expression for $F_l^{ik}(r)$, such that the first term gives an approximate value of the function, and $R_l^{ik}(r)$ does the remainder. When $i = k$ and $l = 0$, the constant value C_0^{kk} is equal to unity due to the normalization of $f_k(r)$, so that the functions $F_0^{kk}(r)$ are asymptotically equal to $\frac{1}{r}$, as should be expected, because they are the potential of a unit charge, the density of which decreases rather quickly with the separation from the origin.

5 Calculation of Terms

Numerical solution of the system of equations (18)–(21) can be carried out by means of consequent approximations. After getting the functions $f_i(r)$, as well as $F_l^{ik}(r)$, the energy of an atom $W = W_1 + W_2$ can be found by means of formulae (6) and (16). Herewith, in order to control the calculations it is possible to use the following relation:

$$W_1 + \frac{1}{2}W_2 = \lambda_{11} + \lambda_{22} + \lambda_{33} + \lambda_{44} . \tag{29}$$

Besides, the calculations can be controlled by means of the virial theorem, according to which the double kinetic energy must be equal to the absolute value of the potential energy (including the energy of the electron interaction). As was shown by the author,[3] this relation takes place not only for the exact solution of the Schrödinger equation, but also for an approximate solution obtained by the method described in the present article.

It is necessary to take into account that the total energy W of an atom does not coincide with the value of the term; the term is equal to the difference between the energies of an atom in the present state and

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[3] V.A. Fock, *Comment on the Virial Relation*, JRPKhO **62**, N4, 379, 1930. (See [30-1] in this book. (*Editors*))

in the ionization state. In order to get the value of the energy in the ionization state, it is necessary to solve a new system of equations that is derived from the present one, if all functions having the symbol 4 are assumed to equal zero. However, the first-hand calculation of the term as the energy difference is disadvantageous in the sense that the term is obtained as a small difference between two large quantities. In view of this, it is more expedient to do as follows. Let us denote the solutions of the equation system for an ionized atom by $f_i^0(r)$ $(i = 1, 2, 3)$ and for an atom in the present state by $f_i(r)$, and construct the differences (for the first three functions)

$$\delta f_i = f_i(r) - f_i^0(r) \qquad (i = 1, 2, 3)\,. \tag{30}$$

For these differences, it is possible to develop a system of equations that allows one to calculate them directly (i.e., without knowing $f_i(r)$). If $f_i(r)$, as well as $f_4(r)$, are known with sufficient accuracy, it is possible to get the value of the energy difference, i.e., the value of a term, also with the same accuracy.

6 Intensities

Finally we need to obtain the formulae for intensities. For the general case, these formulae have been derived in our first article (formulae (99) and (100)).[4] In them we will make the simplifications that follow from the assumption of a spherical symmetry.

Let us calculate a matrix element for the coordinate $z = r\cos\vartheta$. The matrix entries for $x = r\sin\vartheta\cos\varphi$ and for $y = r\sin\vartheta\sin\varphi$ can be written by analogy.

For convenience, we will present formula (100) of the previous article replacing f_{ik} by z_{ik} in it and assuming $p = 5$, $q = 6$:

$$\langle E \mid z \mid E' \rangle = \begin{vmatrix} a_{11} & \dots & a_{15} \\ \multicolumn{3}{c}{\dots\dots\dots\dots} \\ \multicolumn{3}{c}{\dots\dots\dots\dots} \\ a_{51} & \dots & a_{55} \end{vmatrix} \cdot \sum_{k=1}^{6} \begin{vmatrix} a_{11} & \dots & a_{16} \\ \multicolumn{3}{c}{\dots\dots\dots\dots} \\ z_{k1} & \dots & z_{k6} \\ \multicolumn{3}{c}{\dots\dots\dots\dots} \\ a_{61} & \dots & a_{66} \end{vmatrix} +$$

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[4] See [30-2] in this book. (*Editors*)

$$+\begin{vmatrix} a_{11} & \dots & a_{16} \\ \multicolumn{3}{c}{\dots\dots\dots\dots} \\ \multicolumn{3}{c}{\dots\dots\dots\dots} \\ a_{61} & \dots & a_{66} \end{vmatrix} \cdot \sum_{k=1}^{5} \begin{vmatrix} a_{11} & \dots & a_{15} \\ \multicolumn{3}{c}{\dots\dots\dots\dots} \\ z_{k1} & \dots & z_{k5} \\ \multicolumn{3}{c}{\dots\dots\dots\dots} \\ a_{51} & \dots & a_{55} \end{vmatrix} . \qquad (31)$$

The values a_{ik} and $z_{ik} = f_{ik}$ are written in formula (99) of the previous article. They are equal to

$$a_{ik} = \int \overline{\psi_i}(r, E)\, \psi_k(r, E')\, d\tau\,; \qquad z_{ik} = \int \overline{\psi_i}(r, E)\, z\, \psi_k(r, E')\, d\tau\,. \quad (32)$$

Let us make a table of values a_{ik} and z_{ik} for the case of spherical symmetry under consideration. Because of the orthogonality of the spherical functions, many of these values will be equal to zero, and we will get

$$((a_{ik})) = \left\{ \begin{matrix} a_{11} & a_{12} & 0 & 0 & 0 & a_{16} \\ a_{21} & a_{22} & 0 & 0 & 0 & a_{26} \\ 0 & 0 & a_{33} & 0 & 0 & a_{36} \\ 0 & 0 & 0 & a_{44} & 0 & a_{46} \\ 0 & 0 & 0 & 0 & a_{55} & a_{56} \\ a_{61} & a_{62} & a_{63} & a_{64} & a_{65} & a_{66} \end{matrix} \right\},$$

$$((z_{ik})) = \left\{ \begin{matrix} 0 & 0 & z_{13} & 0 & 0 & z_{16} \\ 0 & 0 & z_{23} & 0 & 0 & z_{26} \\ z_{31} & z_{32} & 0 & 0 & 0 & z_{36} \\ 0 & 0 & 0 & 0 & 0 & z_{46} \\ 0 & 0 & 0 & 0 & 0 & z_{56} \\ z_{61} & z_{62} & z_{63} & z_{64} & z_{65} & z_{66} \end{matrix} \right\}. \qquad (33)$$

It is not difficult to see that all determinants in the second sum of formula (31) are equal to zero. In order to calculate the first sum, as well as the factor in front of it, we will introduce the values

$$\beta_{ik} = \int\limits_0^\infty f_i(r, E)\; f_k(r, E')\; dr\,; \qquad \gamma_{ik} = \int\limits_0^\infty f_i(r, E)\; r\; f_k(r, E')\; dr \quad (34)$$

and denote by b_{ik} and c_{ik} the matrix elements

$$((a_{ik})) = \left\{ \begin{matrix} \beta_{11} & \beta_{12} & 0 & \delta_{0l'}\beta_{14} \\ \beta_{21} & \beta_{22} & 0 & \delta_{0l'}\beta_{24} \\ 0 & 0 & \beta_{33} & \delta_{1l'}\beta_{34} \\ \delta_{l0}\beta_{41} & \delta_{l0}\beta_{42} & \delta_{l1}\beta_{43} & \beta_{44} \end{matrix} \right\}, \qquad (35)$$

$$((c_{ik})) = \left\{ \begin{matrix} 0 & 0 & \gamma_{13} & \gamma_{14} \\ 0 & 0 & \gamma_{23} & \gamma_{24} \\ \gamma_{31} & \gamma_{32} & \gamma_{33} & \gamma_{34} \\ \gamma_{41} & \gamma_{42} & \gamma_{43} & \gamma_{44} \end{matrix} \right\}. \tag{36}$$

Then the matrix element $\langle E|z|\, E'\rangle$ corresponding to the transition from the level E to the level E' will be equal to

$$\langle E \mid z \mid E'\rangle = C \cdot \frac{1}{4\pi} \iint \overline{Y_l}\, Y_{l'} \cos\vartheta \ \sin\vartheta \ d\vartheta \ d\varphi\,, \tag{37}$$

where

$$C = (b_{33})^5 \cdot \begin{vmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{vmatrix} \cdot \sum_{k=1}^{4} \begin{vmatrix} b_{11} & \ldots & b_{14} \\ \ldots & \ldots & \ldots \\ c_{k1} & \ldots & c_{k4} \\ \ldots & \ldots & \ldots \\ b_{41} & \ldots & b_{44} \end{vmatrix}. \tag{38}$$

The matrix elements for the coordinates x and y are expressed absolutely analogously. Thus, we will have

$$\left. \begin{aligned} \langle E|x|E'\rangle &= C \cdot \frac{1}{4\pi} \int \overline{Y_l}\, Y_{l'} \ \sin\vartheta \ \cos\varphi \ d\omega, \\ \langle E|y|E'\rangle &= C \cdot \frac{1}{4\pi} \int \overline{Y_l}\, Y_{l'} \ \sin\vartheta \ \sin\varphi \ d\omega, \\ \langle E|z|E'\rangle &= C \cdot \frac{1}{4\pi} \int \overline{Y_l}\, Y_{l'} \ \cos\vartheta \ d\omega. \end{aligned} \right\} \tag{39}$$

These expressions have the same form, as in the usual theory where only a valence electron is treated. The selection rule remains valid without any changes. Here the distinction is only in the factor C, which has a slightly different meaning than in the usual theory, when it is equal to

$$C = c_{44} = \int_0^\infty f_4(r, E) \ r \ f_4(r, E') \ dr\,. \tag{40}$$

In our theory the equality $C = c_{44}$ is only approximate. The exact calculation of the factor C by means of formula (38) has no problems, as many elements in the determinants in this formula are equal to zero.

Translated by A.K. Belyaev

Annexe C

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