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Q. M.

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James Kedo

107 Edgemore Lane

[illegible] New York

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THIS BOOK CONTAINS EYE-EASE PAPER

"Easy on the Eyes"

Q.M.

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5/13/47

Hartree Method of Calculating the energy levels of an atom.

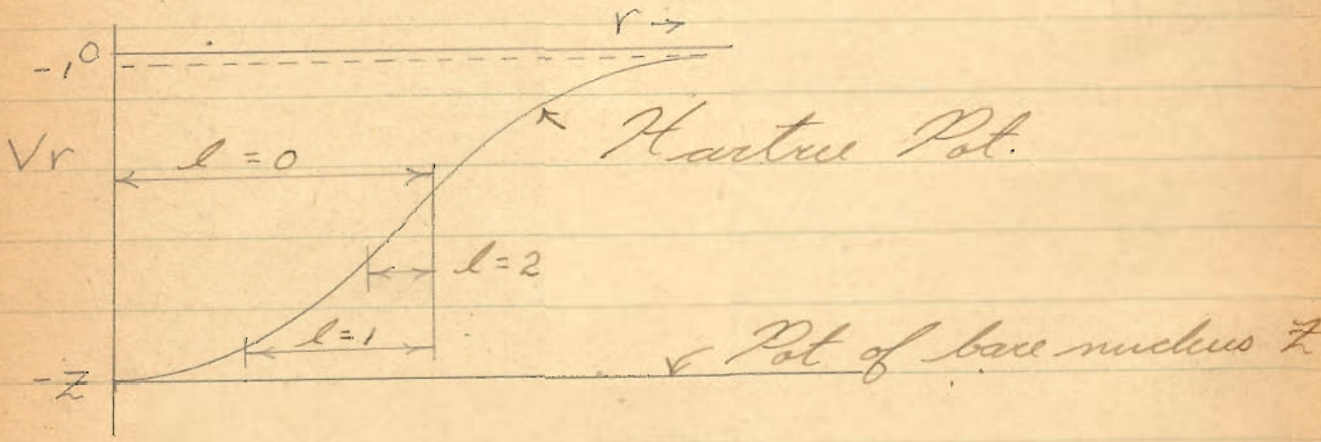
In general the energy levels of an atom depend on n and l. For an H-like atom the energy depends on n alone and is given by the formula

$$E = \frac{Z^2}{n^2} Ry$$

The Hartree method employs the same formula but inserts for Z an effective value which depends on l. The effective value of Z is obtained from the Hartree potential. Actually the energy values of the atom are found first

and then the value of Z_{eff} determined.

The Hartree potential looks as pictured below. Also indicated on the plot are the regions in which electrons of various angular momentum, l, move. It is seen that higher values of l mean the electron moves in a weaker average potential and hence is more loosely bound.



A comparison of the binding energies of the various electrons

in Hg as computed from the Hartree potential and the H-like formula shows the effect of shielding by the inner electrons. Notice that even for the innermost 1s state the binding has been reduced by the presence of the outer electrons. The effect is known as outer screening.

For Hg $Z = 80$

		S $l=0$	P 1	D 2	F 3
	Hartree E Ry.	H-like E			$\frac{Z^2}{n^2}$ Ry
1s	5553	6400			
2s	925	1600			
2p	892	"			
3s	217	711			
3p	201	"			
3d	170	"			
4s	46	400			
4	39	"			
4	26	"			
4f	8.4	"			

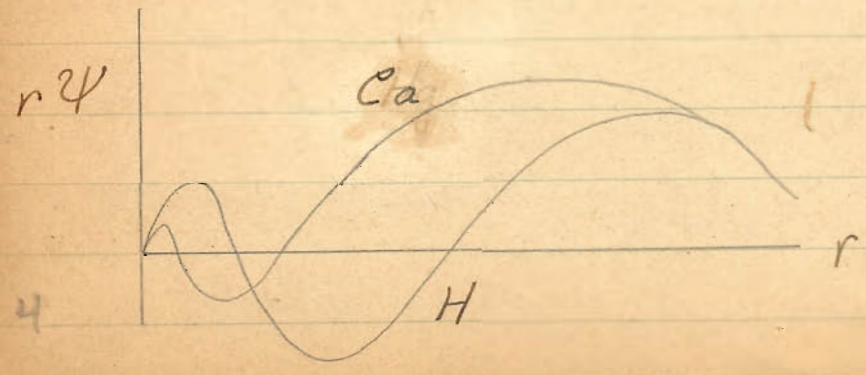
5 s	6.9	256
5 p	4.6	"
5 d	.92	"
6 s	.47	180

$$E = \frac{Z_{eff}^2}{n^2}$$

$$Z_{eff} = n\sqrt{E}$$

For the 5s electron $Z_{eff} \sim 13$
Note that the 6s electron is more strongly bound than the 5s which does not appear.

The value of Z_{eff} enables us to get an idea of the radial scale of the wave function since this is proportional to $1/Z$.



The wave function is very small near the origin.

Comparison of zeros of various wave functions.

4s electron

	r_2/r_1	r_3/r_1
H	3.7	8.3
Ca.	4.5	15.4
Hg	3.78	9.8

The 4s electron in Hg is so far inside the atom that it moves in an essentially H-like field, hence its zeros are not much ~~of~~ from those of Hydrogen. This is in general true for inner electrons

Problem: Read Article on calculating Zeff in PR 36 (1938) Use the method outlined there to calculate the B.E. of a

2s electron in Ca. Compare with Hartree value of 30.7 Ry.

II Periodic Table.

The Pauli principle implies that no two electrons can be in the same quantum state. An electron is characterized by four numbers

$$n,\ l,\ m,\ s.$$

$$0 \le l \le n-1\ ;\ -l \le m \le l\ ;\ s = \pm \tfrac{1}{2}$$

For a given n there are $2n^2$ states. For a given n and l there are $2(2l+1)$ states.

State	#el	Chem	Z complete shell
1s	2	H, He	2
2s	2	Li, Be	4
2p	6	B C N O F Ne	10
3s	2	Na Mg	12
3p	6	A	18
4s	2	K Ca	20

21 ... $4s^2\ 4p$

22 ... $4s^2\ 4p\ 3d$

23

... ...

28 ... $4s^2\ 3d^8$

29 ... $4s^2\ 3d^{10}$

30 ... $4s\ 3d^{10}$

3d	10		30
4p	6	Kr	36
5s	2		38
5p	6	Xe	54
4d	10		
6s	2		
6p	1		
4f	14	Rare earths	

5d	10		
6p	5	Rn	86
7s	2		
7p	1		
6d	3	U	92
5f	2		94

94 ... $7s^2\ 7p\ 6d^3\ 5f^2$

95 ... $7s^2\ 7p\ 5f^6$ Am

96 ... $7s^2\ 7p\ 5f^7$ Curium

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Periodic Table

Follows the following scheme

$n+l$ = 1	1s				
= 2	2s				
3	2p	3s			
4	3p	4s			
5	3d	4p	5s		
6	4d	5p	6s		
7	4f	5d	6p	7s	
8	5f				

The above has no physical meaning. It is just a convenient scheme for numbering the order in which shells are filled

4f Rare earths (14)
3d Sc Ferromag
4d Y - Ru Rh Pd
5d Hf - Os Ir Pt

The rare gases occur for filled p shells.

Chemical Activity of the Elements

Consider:

a) Sodium. The valence electron in sodium is a 2s electron moving outside of a closed p shell. It is very weakly bound and therefore is easily given up.

b) Neon. The element just preceding Na is Ne. Its valence electron is a 2p electron. The wave function of this electron

is similar to that of the 5 other 2p electrons in Ne. On the average, an 2p electron is 1/2 the time inside and 1/2 the time outside the other 2p electrons. The shielding is therefore relatively small and the electron is strongly bound.

The table below gives the ionization potential of a few elements

	volts Ion. pot	Rz
H	13.6	1
He		1.83
Li		.4
Be		.7
Na		1.7
Na		.3

As we go to the higher alkali elements the ionization energy becomis smaller since the chemical activity increases.

The Halogens lack one electron for a complete shell. They have a strong affinity for an extra electron. This affinity decreases as the atomic weight of the halogen increases. There is less shielding for the light nuclei. The light halogens are the most active.

The above discussion applies to ionic compounds.

Pauli Principle

states: The atomic wave function must be antisymmetric to the interchange of any to electrons.

Let us investigate the implications of the Pauli Principle

We assume a Hartree Wave function

$$\Psi(\underline{r}_1, \underline{r}_2) = \phi_1(n_1)\phi_2(n_2)\ldots$$

where the n_i are numbers labeling the electrons.

For two electrons the antisymmetric combination is

$$\Psi = \phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)$$

For n electrons

$$\Psi = \text{Det } C \begin{vmatrix} \phi_1(r_1, u_1) & \phi_1(r_2, u_2) \cdots & \phi_1(r_n, u_n) \\ \phi_2(r_1, u_1) & & \\ & & \\ \phi_n(r_1, u_1) & & \phi_n(r_n, u_n) \end{vmatrix}$$

C is the normalization

It will be convenient to write the determinant in the following form.

$$\Psi = C \sum_p \epsilon_p \prod_{j=1}^{n} \phi_j(P_j)$$

where p designates some permutation of the electrons in the wave function.

The sum is taken over all permutations.

$\epsilon_P = +1$ for an even permutation.

$= -1$ for an odd permutation.

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The total Hartree wave function for an atom may be written

$$\Psi = C \sum_P \epsilon_P \prod_j \phi_j(P_j)$$

$$= C \sum_P \epsilon_P \prod_j \phi_{P_j}(j)$$

where C is the normalization

$\phi = \phi(r, u)$

$\epsilon = 1$ even permutation

$\epsilon = -1$ odd permutation

$$\int \phi_{P_j}(j)\, \phi_{Q_j}(j)\, d\tau = \delta_{P_j Q_j}$$

$$\int |\psi|^2 d\tau_1 \ldots d\tau_n$$

$$= |C|^2 \int \sum_P \sum_Q \epsilon_P \epsilon_Q \prod_j \phi_{P_j}(j) \phi^*_{Q_j}(j) d\tau_j$$

$$= |C|^2 \sum_P \epsilon_P^2 \cdot \left\{ \prod_j \int \phi_{P_j}(j) \phi^*_{P_j}(j) d\tau_j \right\}$$

The number of permutations of n states is $n!$. Also $\epsilon_P^2 = 1$

$$1 = |C|^2 N!$$

$$C = 1/\sqrt{N!}$$

Let us investigate the <u>Energy</u>

$$\int \psi H \psi \, d\tau$$

where:

$$H = -\frac{\hbar}{2m} \sum_j \nabla_j^2 - \sum_j \frac{Ze^2}{r_j} + \sum_{j<k} \frac{e^2}{r_{jk}}$$

Consider a typical term in the second sum. Ze^2/r_k

$$-\frac{Ze^2}{N!} \sum_P \sum_Q \epsilon_P \epsilon_Q \int \phi^*_{Q_k}(k) \phi_{P_k}(k) \frac{1}{r_k} d\tau_k \prod_{j \neq k} \int \phi_{Q_j}(j) \phi^*_{P_j}(j) d\tau_j$$

$P_j = Q_j$ for $j \neq k$, hence $P = Q$

$$= -\frac{Ze^2}{N!} \sum_P \epsilon_P^2 \int |\psi_{P_k}|^2 \frac{1}{r_k} d\tau_k$$

There are $(N-1)!$ permutations for which $P_k = m$

$$= -\frac{Ze^2}{N} \sum_m \int |\psi_m(r_k)|^2 \frac{1}{r_k} d\tau_k$$

To get the total contribution of the second sum we simply add N of the typical terms above.

$$= -Ze^2 \sum_m \int |\psi_m(r)|^2 \frac{1}{r} d\tau$$

This is the coulomb interaction energy due to the interaction of nucleus and electrons.

The first term in the energy, the K.E., may be treated in the same way to give:

$$K.E. = -\frac{\hbar^2}{2m}\sum_m \int \phi_m^*(r)\,\nabla^2\phi_m(r)\,d\tau$$

We now consider the last sum. A typical term is e^2/r_{jk}

$$\frac{e^2}{N!}\sum_P\sum_Q \epsilon_P\epsilon_Q \int d\tau_k\,d\tau_l\; \phi_{Qk}^*(k)\,\phi_{Ql}^*(l)\,\frac{1}{r_{kl}}\,\phi_{Pk}(k)\,\phi_{Pl}(l)$$

$$\cdot\left\{\prod_{j\neq k,l}\int d\tau_j\,\phi_{Qj}^*\,\phi_{Pj}\right.$$

$P_j = Q_j$ for all $j \neq k, l$. We must consider two cases:

1) $P = Q$ $\quad \epsilon_P^2 = 1$

2) $Q = P$ [k & l transposed] $\quad \epsilon_P\epsilon_{Q\text{ transposed}} = -1$

$$= \frac{e^2}{N!}\sum_P \int d\tau_k\,d\tau_l\; \phi_{Pk}^*(k)\,\phi_{Pl}^*(l)\,\frac{1}{r_{kl}}\,\phi_{Pk}(k)\,\phi_{Pl}(l)$$

$$-\frac{e^2}{N!}\sum_P \int d\tau_k\,d\tau_l\; \phi_{Pl}^*(k)\,\phi_{Pk}^*(l)\,\frac{1}{r_{kl}}\,\phi_{Pk}(k)\,\phi_{Pl}(l)$$

There are $(N-2)!$ permutations for which $Pk = m$ and $Pl = n$.

$$= \frac{e^2(N-2)!}{N!}\sum_m\sum_n\left\{\int d\tau_k\,d\tau_l\;\frac{1}{r_{kl}}\,|\phi_m(k)|^2\,|\phi_n(l)|^2\right.$$

$$- \int d\tau_k d\tau_l \, \psi_m^*(k) \psi_m(k) \psi_m^*(l) \psi_m(l) \frac{1}{r_{kl}} \Big\}$$

For $m = n$ the terms in the sum disappear. We can replace the double sum by twice the sum over all $m < n$.

To get the total energy we sum over all pairs of electrons

$$\sum_{k<l} \sum_{m<n} 2 \frac{e^2}{N(N-1)} \Big\{ \int d\tau_k d\tau_l \, \frac{1}{r_{kl}} |\psi_m(k)|^2 |\psi_n(l)|^2$$

$$- \int d\tau_k d\tau_l \, \frac{1}{r_{kl}} \psi_m^*(k) \psi_m(k) \psi_m^*(l) \psi_n(l) \Big\}.$$

Summing over the $k < l$ yields $N(N-1)/2$ terms.

$$= e^2 \sum_{m<n} (C_{mn} - X_{mn})$$

where:

$$C_{mn} = \int d\tau_1 d\tau_2 \, \frac{1}{r_{12}} |\psi_m(1)|^2 |\psi_n(2)|^2$$

$$X_{mn} = \int d\tau_1 d\tau_2 \, \frac{1}{r_{12}} \psi_m \psi_n(1) \psi_n \psi_m^*(2)$$

C = Coulomb interaction

X = Exchange integral

We have already encountered these integrals in studying the Helium Atom.

The exchange integral arises from the interchange of electrons in different states. The frequency of this interchange is given by the exchange energy divided by h.

The total energy

$$W = \sum_m \langle T_m \rangle - 2e^2 \sum_m \left\langle \frac{1}{r} \right\rangle_m + e^2 \sum_{m<n} (C_{mn} - X_{mn})$$

C_{mn} is positive. We can show by application of the Schwarz inequality that X is also positive

We see that introduction of the Pauli principle leads to a lower energy, and hence to

a stronger binding of the atom.

We consider now the effect of the spin on the exchange integral

$$X_{mn} = \int d\tau_1 \int d\tau_2 \sum_{\mu_1} \sum_{\mu_2} \frac{1}{r_{12}}$$

$$\cdot \{ \psi_m \psi_n^*(1) \chi_m \chi_n^*(1) \psi_m^* \psi_n(2) \chi_m^* \chi_n(2) \}$$

If we take the spin parallel to the Z axis we have the spin functions α and β. There are two possible cases

$$\chi_m = \chi_n \qquad \sum_{\mu} \chi_m \chi_n = 1$$

$$\chi_m \neq \chi_n \qquad \sum_{\mu} \alpha(\mu)\beta(\mu) = 0$$

Hence $X_{mn} = 0$ if spins of states m and n are opposite

$X_{mn} = \int$ [space coordinates] if spins are in same direction.

Ref: Slater PR 36 1930

Method of calculating screening factors and binding energies of electrons in atoms.

If we assume the nodes of the wave function are unimportant we can write

$$\psi \sim r^{n^*-1} e^{(Z-s)/n^* r}$$

where:

n^* is an effective q. n.

s is the shielding const.

n^* is given in the table below

n	1	2	3	4	5	6
n^*	1	2	3	3.7	4	4.2

To get s for a given electron we procede as follows:

a. The electrons are arranged in shells according to the pattern 1s; 2(s,p); 3(s,p); 3d; 4(s,p); 4d; 4f; etc.

b. s is the sum of the following contributions:

20.

1. Nothing from electrons outside the shell considered.
2. .35 from each other electron in group considered. In the 1s group only .30.
3. If an (s, p) shell .85 from each electron with n less by 1 and 1.00 for all electrons farther inside.

If a d or f shell 1.00 from every electron inside.

To compute the energy of an atom or ion one sums over the energies of the individual electrons.

$$E = \sum_e \left(\frac{Z - S_e}{n_e^*}\right)^2$$

This energy does not take into account the outer screening. However in computing the

binding energy of an electron, we take the difference in the energy of atom and ion, and the outer screening is compensated for by a change in the screening constants which lowers the energy of the ion by just the right factor to account for screening.

Example: Consider a C atom $Z = 6$

		$Z - S$
2	$1s$ $(6 - .30)$	5.7
4	$2(s,p)$ $(6 - 3 \cdot .35 - 2 \cdot .85)$	3.25

Energy of Atom

$$2\left(\frac{5.7}{1}\right)^2 + 4\left(\frac{3.25}{2}\right)^2 = 75.6 \text{ Ry}$$

5/20/97

Last lecture we derived an expression for the energy of an atom assuming a Hartree wave function:

$$E = \sum_j V_j + \sum_j T_j + \sum_{m<n} \left(C_{mn} - \delta_{\mu_m \mu_n} X_{mn} \right)$$

where: C_{mn} is the coulomb integral

X_{mn} is the exchange integral

and μ_m and μ_n are the components of the electron spin for electrons m and n in the z direction.

In deriving this expression, we assumed each electron was in a definite state. Let us now consider what happens in an atom containing an unfilled shell. Carbon is an example of such an atom.

Its electron configuration is:

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

The 2p electrons can be in any of 6 possible states esp to $m = 1\ 0\ -1$; $\mu = \pm 1/2$. The number of different states for the two electrons will be $6 \cdot 5 / 2 = 15$. The Coulomb and Exchange interaction will be different for different electron eigenfunctions. We have the possibility of a single electron configuration esp to different atomic energy levels. If there were no degeneracy, we would expect 15 diff. levels for Carbon in the above configuration. In general, however there is multiple degeneracy, so the number of energy levels is reduced to a few.

Let us consider the case of He in the first excited state

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

Let m denote the component of the spin and m the component of the orbital angular momentum in the z direction. Capitol letters will be used to denote states of the atom.

The total angular momentum is $L = 1$

The total spin of the atom is $S = 1, 0$. The component of S in the z direction may be $S_z = m_{atom} = 1\ 0 - 1$. This follows from:

$m_s = \frac{1}{2}\ -\frac{1}{2}\ \frac{1}{2}\ -\frac{1}{2}$

$m_p = \frac{1}{2}\ \frac{1}{2}\ -\frac{1}{2}\ -\frac{1}{2}$

$m_{atom} = 1\ \ 0\ \ 0\ \ -1$

We shall denote opuators by underscoreing them. We have the following relations

$$\underline{S}_{atom} = \sum_n \underline{S}_n$$

$$\underline{S}^2 \chi = S(S+1)\chi$$
$$\underline{S}_z \chi = \mu_{atom} \chi$$

$$\mu_{atom} = -S, -S+1, \ldots S$$

$$[\underline{S}^2, \underline{S}_z] = 0$$

We must have four spin wave functions esp to the four spin states of our atom.
For $\mu_a = 1$ we have $\alpha(s)\alpha(p)$
$\mu_a = -1$ we have $\beta(s)\beta(p)$
We can find one of the spin wave functions for $\mu_a = 0$ by letting $\underline{S}_x$ operate on $\chi_1 = \alpha(s)\alpha(p)$. $\underline{S}_x$ has the matrix elements $\langle \mu | \underline{S}_x | \mu \pm 1 \rangle$.
In our case:

$$\underline{S}_x \chi_1 = \chi_0$$

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$$\underline{S}_x = \underline{S}_{sx} + \underline{S}_{px}$$

Neglecting normalization

$$\underline{S}_x\, \alpha(s)\alpha(p) \doteq \alpha(s)\beta(p) + \beta(s)\alpha(p)$$

The remaining spin function must be orthogonal to this and hence is:

$$\alpha(s)\beta(p) - \beta(s)\alpha(p)$$

We could have gotten the same result by symmetry in this case but this method is not as general as the one above. We have for the coarse functions

$$\Psi = \alpha\alpha\,[\,\psi_1(s)\psi_2(p) - \psi_2(s)\psi_1(p)\,] \quad S=1 \quad \mu=1$$
$$\Psi = \alpha\beta + \beta\alpha\,[\quad " \quad] \quad " \quad \mu=0$$
$$\Psi = \beta\beta\,[\quad " \quad] \quad " \quad \mu=-1$$

Since $[\,\underline{S}^2 H\,] = 0$, all these states have the same energy, $C - X$.

The remaining wave function is

$$\Psi = \alpha\beta - \beta\alpha \left[\psi_1(s)\psi_2(p) + \psi_2(s)\psi_1(p) \right] \quad S=0$$

In this case the energy is different, C + X. The + sign arises from the fact that there is no definite assignment of spin to a given wave function and hence we have a mixture of states. The energy in the $S=1$ state is lower than the energy in the $S=0$ state by 2X.

For the configuration $1s^2\,2s\,2p$ we have 2 energy levels each of which is degenerate:

			# states
$S=0$	$M=1,0,-1$	$M_a=0$	3
$S=1$	$M=1,0,-1$	$M_a=1,0,-1$	9
		Total	12

28 This should equal the number of

independent products of electron wave functions

2s	2	states
2p	6	"

products = 12

The total orbital ang. mom $\underline{L}$ and its components $\underline{M}$ must commute with the Hamiltonian

$$\underline{M} = \sum_j \underline{m}_j$$

$\underline{M}$ commutes with the K.E. $\nabla_j^2 \equiv \underline{p}_j^2$

$$[\underline{M}\ \underline{p}_j] = 0$$

$\underline{M}$ commutes with the nuclear potential

$$[\tfrac{1}{r_j}\ \underline{m}_j] = 0$$

$\underline{M}$ commutes with $\frac{1}{r_{jk}}$

$$r_{jk}^2 = (x_j - x_k)^2 + (y_j - y_k)^2 + (z_j - z_k)^2$$

$$[r_{jk}^2\ m_{z_j}] = 2(x_j - x_k)(-i\hbar y_j) + 2(y_j - y_k)(i\hbar x_j)$$

$$= 2i\hbar(x_k y_j - y_k x_j)$$

$$[\, r_{jk}^2 \, m_{zk} \,] = -2i\hbar (x_k y_j - y_k x_j)$$

Hence $[\, r_{jk}^2 (m_{zj} + m_{zk}) \,] = 0$

The individual m_j are not quantized but their sum is.

$$[\, H \, \underline{M} \,] = 0$$

5/22/47

We saw last lecture that the total angular momentum of an atom was quantized while the angular moments of the individual electrons was not. This is somewhat analogous to the classical case of a body having internal degrees of freedom. In the absence of external forces, the angular momentum of the system as a whole is a constant of

the motion, but the angular momenta of the individual components are not.

$$\underline{M}^2 \Psi = L(L+1)\Psi$$
$$\underline{M}_z \Psi = M \Psi$$

L = total orbital ang. momentum of atom

M = mag. quantum number of atom.

Each energy level of the atom has an L and an $M = -L \ldots +L$

$$[m_j, H] \neq 0$$

There is degeneracy between states of different m_j. There is no degeneracy between states of different l_j, hence in first approx. the l_j will not get mixed. This is true

if the interaction between electrons << difference in energy levels of a single electron in a Hartree field.

Let us consider an atom having a definite electron configuration and a definite L and S. We wish to investigate the possible states for two electrons l_1 and l_2 outside of a closed shell. We shall assume that the electrons are not in the same shell so that we do not have to take the Pauli principle into consideration.

	electron 1	electron 2	atom
	m_1	m_2	M
a	l_1	l_2	$l_1 + l_2$
b	$l_1 - 1$	l_2	$l_1 + l_2 - 1$
c	l_1	$l_2 - 1$	"
d	$l_1 - 2$	l_2	$l_1 + l_2 - 2$
e	$l_1 - 1$	$l_2 - 1$	"
f	l_1	$l_2 - 2$	"

The spatial wave functions asp to these states are:

a') $\psi_{l_1}(1)\,\phi_{l_2}(2) \pm \phi_{l_2}(1)\,\psi_{l_1}(2)$ spin $\pm$ ~ 0, ~ 1

This is the only state giving $M = l_1 + l_2$

b') $\psi_{l_1}(1)\,\phi_{l_2-1}(2) \pm$

c') $\psi_{l_1-1}(1)\,\phi_{l_2}(2) \pm$

States b and c both give $M = l_1 + l_2 - 1$. There are two linear combinations of b' and c' which are wavefunctions for the atom. We can obtain one of these wave functions by applying the operator M_x to a'.

$$M_x \psi_a(L = l_1 + l_2,\ M = l_1 + l_2)$$

$$= C\,\psi(L = l_1 + l_2,\ M = l_1 + l_2 - 1)$$

$$= C\{c_1 \psi_{b'} + c_2 \psi_{c'}\}$$

The wave function orthogonal to $c_1 \psi_{b'} + c_2 \psi_{c'}$ also represents a state of the system

$$c_2 \psi_{b'} - c_1 \psi_{c'} = \psi(L = l_1 + l_2 - 1,\ M = l_1 + l_2 - 1)$$

By operating this function by M_x we can find a wave function corr to $L = l_1 + l_2 - 1$, $M = l_1 + l_2 - 2$. The orthogonality conditions may be used to determine the functions for $M = l_1 + l_2 - 2$; $L = l_1 + l_2$, $L = l_1 + l_2 - 2$. We can continue in this way to obtain all the wave functions for the atom.

L can take on the values $l_1 + l_2 \ldots |l_1 - l_2|$. For each value of L there are $2L + 1$ mag. substates. The total number of states for the two electrons will be:

$$\sum_{L = |l_1 - l_2|}^{l_1 + l_2} (2L + 1) = (2l_1 + 1)(2l_2 + 1)$$

This is just the number of product wave functions we can obtain from our original table which is as it should be. Since the total spin may be 1 or 0 we have double the number of states.

Energy

If it were possible to assign a definite m to each of the two electrons the energy would be given by:

$$C_{m_1, m_2} \pm X_{m_1, m_2} \qquad \begin{matrix} + \sim S=0 \\ - \sim S=1 \end{matrix}$$

This can be done for the state $L = M = l_1 + l_2$

$m_1 = l_1$, $m_2 = l_2$

We know the wave functions for this state and can compute E_1. We can make

use of the fact that the spur of a matrix is invariant to a similarity transformation to find the rest of the energy levels.

Consider the 2×2 matrix of states esp to $M = l_1 + l_2 - 1$. We can compute the diagonal elements of this matrix and hence get the spur. But the spur equals the sum of the two eigenvalues and one of these is already known, namely that for $L = l_1 + l_2$, (the energy does not depend on the value of M). Hence we can find the second energy level. We can proceed in this way to get all the energy levels.

5/24/47

Last lecture we outlined a procedure by means of which we could find the energy levels for two electrons outside a closed shell and not in the same shell. This method depended on the fact that spur of a matrix is an invariant. We found we could compute the first eigenvalue in the m_j representation, and then a knowledge of the spur of the energy matrix in the L representation gave us the rest of the values.

In the m_j representation the energy is given in terms of integrals of the following type:

$$\int \psi^{a*}(1)\, \psi^{b*}(2)\, \frac{1}{r_{12}}\, \psi^{c}(1)\, \psi^{d}(2)\, d\tau$$

For: $a = c$, $b = d$ we have the Coulomb interaction

$b = c$, $a = d$ we have the Exchange interaction

[The following analysis of the electrostatic energy of an atom with 2 electrons appears in London and Shortley. Read!]

Let $r_1 > r_2$, we can expand $\frac{1}{r_{12}}$ as follows:

$$\frac{1}{r_{12}} = \sum_0^\infty \frac{r_2^k}{r_1^{k+1}} P_k(\cos\omega) \qquad \omega = \measuredangle \vec{r}_1, \vec{r}_2$$

We adopt the following notation for ψ^a

$$= R(r, n_a l_a) \Theta(\theta, l_a m_a) \Phi(\phi, m_a) \chi(\mu, \sigma_a)$$

We shall break up our integral into four parts, 1) sum over spins, 2) integral over ϕ, 3) int. over θ,

ϕ int over r. We consider each part separately.

1) $\chi(\mu, \sigma_a) = \delta_{\mu \sigma_a}$

$$\sum_{\mu_1} \sum_{\mu_2} \delta_{\mu_1 \sigma_a} \delta_{\mu_1 \sigma_c} \delta_{\mu_2 \sigma_b} \delta_{\mu_2 \sigma_d} = \delta_{\sigma_a \sigma_c} \delta_{\sigma_b \sigma_d}$$

2) We can express ω in terms of the coordinates of our system by use of the addition theorem for Legendre polynomials.

$$P_k(\cos\omega) = \frac{4\pi}{2k+1} \sum_{m=-k}^{k} \Theta(\theta, km)\, \Phi(\phi, m) \cdot \Theta(\theta_2, km)\, \Phi(\phi_2, -m)$$

Integral over ϕ_1

$$\int_0^{2\pi} d\phi_1\, \bar{\Phi}^*(\phi_1, m_a)\, \bar{\Phi}(\phi, m_c)\, \bar{\Phi}(\phi_1, m)$$

$$= \int_0^{2\pi} d\phi_1\, \frac{1}{2\pi^{\frac{3}{2}}}\, e^{i(m_c + m - m_a)\phi_1}$$

$$= \delta_{m_a, m_c + m}\, \frac{1}{\sqrt{2\pi}}$$

Int over ϕ_2

$$= \delta_{m_b, m_d - m}\, \frac{1}{\sqrt{2\pi}}$$

This gives us the condition

$$m_a + m_b = m_c + m_d$$

$$m = m_a - m_c = m_d - m_b$$

3) Θ integrals. Condon & Shortley gives a table of the Θ integrals.

$$\int_0^\pi \sin\theta_1 \, d\theta_1 \; \Theta(\theta_1, l_a, m_a)\, \Theta(\theta_1, l_c, m_c)\, \Theta(\theta_1, k, m_a - m_c)$$

notation

$$= C^k(l_a m_a, l_c m_c) \quad 1^{st} \text{ electron}$$

$$= C^k(l_b m_b, l_d m_d) \quad 2^{nd} \quad "$$

4) r, radial integral. The radial integrals can not be calculated in general since they depend on the particular atom considered. They have the form.

$$F_k = \int_0^\infty \int_0^\infty r_1^2 dr_1 \, r_2^2 dr_2 \; R(r_1, n_a l_a) R(r_1, n_c l_c) \frac{r_2^k}{r_1^{k+1}} \cdot R(r_2, n_b l_b) R(r_2, n_d l_d)$$

$$= \int_0^\infty r_1^2 dr_1 \left\{ \int_0^{r_1} r_2^2 dr_2 \, \frac{r_2^k}{r_1^{k+1}} \cdots + \int_{r_1}^\infty r_2^2 dr_2 \, \frac{r_1^k}{r_2^{k+1}} \cdots \right\}$$

The general theory of Legendre polynomials enables us to make certain observations about the Θ integral.

The integral will be different from 0 only if

$$l_a + l_c + k \text{ is even.}$$

If we assume $m_a = m_c = 0$ the orthogonality relations give

$$k \geq |l_a - l_c|$$

$$k \geq |m_a - m_c|$$

$$k \leq l_a + l_c$$

Problem: Using the method developed above, calculate the three energy levels for a $p^1 d^1$ configuration. Express answer in terms of the radial integral.

Case of 3 valence electrons in different shells: The total orbital momentum for three electrons will be the vector sum of the orbital momentum of the first two electrons and the orbital momentum of the third.

$L(2)$	L
l_1+l_2	$l_1+l_2+l_3, l_1+l_2+l_3-1 \ldots \lvert l_1+l_2-l_3\rvert$
l_1+l_2-1	$l_1+l_2+l_3-1 \ldots \lvert l_1+l_2-l_3-1\rvert$

In the case of 3 electrons we have the possibility of several states of the same orbital momentum. The method of finding the energy levels given last time breaks down. We can only get the sum of the energy levels for a given L. In order to get the energy levels for a given L we must construct the

matrix and solve it bodily. We must know the wave functions since the energy depends on the potential in this case.

Case of 2 electrons in the same shell

m_1	m_2	μ_1	μ_2	M	S_z	L	S
l	l	+	−	$2l$	0	$2l$	0
l	$l-1$	+	+	$2l-1$	1	$2l-1$	1
l	$l-1$	+	−	$2l-1$	0	a	
l	$l-1$	−	+	$2l-1$	0	b	
l	$l-2$	+	+	$2l-2$	1	$(2l-1)$	1
l	$l-2$	+	−	$2l-2$	0	$2l-2$	0
$l-1$	$l-1$	+	−	"	0	c	
l	$l-2$	−	+	"	0	d	

Slater a & b combine to give the two wave functions

1) $\Psi(L = 2l, M = 2l-1)$ $S = 0$

2) $\Psi(L = 2l-1, M = 2l-1)$ $S = 1$

Slater c & d combine to give

the wave functions

1) $\Psi(L = 2l, M = 2l-2)$ $S = 0$

2) $\Psi(L = 2l-1, M = 2l-2)$ $S = 1$

Our choice of S and L is dictated by the Pauli principle. We must have:

$S = 0$; $L = 2l, 2l-2, 2l-4, \ldots 0$

$S = 1$; $L = 2l-1, 2l-3, \ldots 1$

For each value of L, there is only one state with S either 0 or 1 but not both. We can construct all the wave functions uniquely.

Consider p^2

$S = 0$ $L = 2, 0$ ^1D ^1S

$S = 1$ $L = 1$ ^3P

The superscript gives the multiplicity of the state. It is equal to $2S+1$. We will discuss this later.

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Equivalent Electrons (same n, l)

Energy of the system.

Consider all states having opposite spins, $m_1 = +\frac{1}{2}$, $m = -\frac{1}{2}$. The electrons are no longer equivalent and in addition the exchange integral is zero. The energy may be calculated by the scheme previously outlined without regard for the Pauli principle.

$N = 2l$ 1 state

$N = 2l-1$ 2 "

... ...

For parallel spins we must use only wave functions allowed by the Pauli principle.

States of two p electrons

p^2 ^3P ^1D ^1S

States of three p electrons, p^3

			S_z	M_L		L	State
a) spins	+	+ +	$3/2$	0		0	^4S
m's	1	0 −1					
b) spins	+	+ −					
	1	0 1	$1/2$	2		2	^2D
	1	0 0	"	1	}	{ 2	
	1	−1 1	"	1	}	{ 1	^2P
	1	0 −1	"	0	}	{ 2	
	1	−1 0	"	0	}	{ 1	
	0	−1 1	"	0	}	{ 0	

Number of states ^4S 4

^2D $2 \cdot 5 = 10$

^2P $2 \cdot 3 = 6$

Number of product Ψs $6 \cdot 5 \cdot 4 / 1 \cdot 2 \cdot 3 = 20$

For a given n states of the highest spin have the lowest energy. Among states of a given n, and S, states of the highest L have the lowest energy. The energy levels for

the second period are:

Li	$2s$	^2S
Be	$2s^2$	^1S
B	$2s^2 2p$	^2P
C	$2s^2 2p^2$	^3P ^1D ^1S
N	$2s^2 2p^3$	^4S ^2D ^2P
O	$2s^2 2p^4$	^3P ^1D ^1S
F	$2s^2 2p^5$	^2P
Ne	$2s^2 2p^6$	^1S

We can get the states for Ne, F, and O by considering the states of the electrons needed to complete the p shell.

When we go to the d shell the number of wave functions greatly increases. We can always get the wave function for the lowest energy state, however, for if all spins are positive, all we have to do is write down

the determinant of the spatial wave functions.

Lowest d states

$d^2 (d^8)$	$S = 1$	$L = 3\ m = 2\ 1$	^3F
$d^3 (d^7)$	$S = 3/2$	$L = 3\ m = 2\ 1\ 0$	^4F
$d^4 (d^6)$	$S = 2$	$L = 2\ m = 2\ 1\ 0\ -1$	^5D
d^5	$S = 5/2$	$L = 0\ m = 2\ 1\ 0\ -1\ -2$	^6S

Spin-Orbit Interaction

So far, our energies do not depend on the electron spin. However, we have neglected the small interaction between the magnetic moment associated with the electron spin and the magnetic field produced do to the motion of the electron in the electric field of the nucleus (Lorentz field). The energy due to this interaction is:

$$E = \underline{H} \cdot \underline{\mu}$$

$$\underline{\mu} = \frac{e\hbar}{2mc}\underline{\sigma}$$

The Lorentz transformation gives

$$\underline{H} = -\frac{\underline{V}}{c} \times \underline{E}$$

$$\underline{E} = -\frac{\underline{r}}{r}\frac{d\phi}{dr}$$

$$\underline{H} = \frac{1}{cr}\frac{d\phi}{dr}(\underline{r} \times \underline{v})$$

$$m(\underline{r} \times \underline{v}) = \underline{M}\hbar$$

$$\Delta E = -\frac{e\hbar}{2mc}\frac{\hbar}{mc}\frac{1}{r}\frac{d\phi}{dr}\underline{M}\cdot\underline{\sigma}$$

$$e\phi = -V$$

$$\Delta E = \frac{1}{2}\left(\frac{\hbar}{mc}\right)^2\frac{1}{r}\frac{dV}{dr}\underline{M}\cdot\underline{\sigma}$$

Thomas discovered that an additional factor $\frac{1}{2}$ should be introduced on relativistic grounds. The final result is:

$$\Delta E = \left(\frac{\hbar}{2mc}\right)^2 \left\langle \frac{1}{r}\frac{dV}{dr} \right\rangle_{av} \underline{M}\cdot\underline{\sigma}$$

The factor c^{-2} appearing in this expression makes the interaction energy very small. For a complete atom, the spin-orbit interaction is:

$$\Delta E_T = \left(\frac{\hbar}{2mc}\right)^2 \sum_k \int \frac{1}{r}\frac{dV}{dr} \psi_k^2(r)\, d\tau \; \underline{M}_k \cdot \underline{\sigma}_k$$

The total angular momentum, $\underline{j}$ Show:

$$[\underline{M}\cdot\underline{\sigma},\ M_z] \neq 0$$
$$[\underline{M}\cdot\underline{\sigma},\ S_z] \neq 0$$
$$[\underline{M}\cdot\underline{\sigma},\ M_z + S_z] = 0$$
$$[\underline{M}\cdot\underline{\sigma},\ \underline{M}^2] = 0$$
$$[\underline{M}\cdot\underline{\sigma},\ \underline{S}^2] = 0$$

The total angular momentum, $\underline{j} = \underline{M} + \underline{S}$, commutes with the Hamiltonian including the spin-orbit interaction.

$$\underline{j}^2 = \underline{M}^2 + 2\underline{M}\cdot\underline{S} + \underline{S}^2$$

$$j(j+1) = l(l+1) + 2\underline{M}\cdot\underline{S} + S(S+1)$$

This relation gives $\underline{M}\cdot\underline{S}$ from which we get the energy values. The possible values of j are:

$$j = l+S \ \ldots \ |l-S|$$

There is one state for each value of j. For $S = \frac{1}{2}$, we have $j = l \mp \frac{1}{2}$, hence the energy level is split in two. In general, for a given $l \geq s$, the energy will be split into $2S+1$ values. This is just the multiplicity.

The splitting due to spin orbit interaction is called <u>Fine structure</u>

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The energy shift due to the spin-orbit interaction is:

$$\Delta E = \left(\frac{h}{mc}\right)^2 \sum_k \left\langle \frac{1}{r}\frac{dV}{dr} \right\rangle_k \underline{M}_k \cdot \underline{S}_k$$

We now proceed to calculate $\underline{M}_k \cdot \underline{S}_k$.

$$\underline{M}^2 = \left(\sum_k \underline{M}_k\right)^2 = L(L+1)$$

$\underline{M}_k$ does not commute with $\underline{M}^2$ and hence its matrix will have elements between states of different L and S. We are interested in the submatrix for $L, S = L', S'$. The matrix is $(LS|\underline{M}_k|LS)$ and has $(2L+1)(2S+1)$ rows and columns.

Consider the commutator relations

$$[\underline{M}_{kx}, \underline{M}_z] = -i M_{ky}$$

$$[\underline{M}_x, \underline{M}_z] = -i M_y$$

Similar relations hold for the other components, and from this we can deduce that the matrix $(LS|\underline{M}_k|LS)$ is proportional to $(LS|\underline{M}|LS)$. A similar relation

holds for the spin matrices.

$$\underline{M}_k = a_k \underline{M}$$

$$\underline{S}_k = b_k \underline{S}$$

For two equivalent electrons we have

$$M = 2l$$
$$M_1 = M_2 = l$$
$$\underline{M}_1 = \tfrac{1}{2} \underline{M}$$

Here $a_1 = a_2 = \tfrac{1}{2}$.

We can rewrite our energy as follows

$$\Delta E = \left(\frac{\hbar}{mc}\right)^2 \sum_k \left[\left(\frac{1}{r} \frac{dV}{dr} \right)_k a_k b_k \right] \underline{M} \cdot \underline{S}$$

$\underline{M} \cdot \underline{S}$ does not commute with the components of $\underline{M}$ and $\underline{S}$ but it does commute with

$$\underline{M}^2 = L(L+1)$$
$$\underline{S}^2 = S(S+1)$$
$$\underline{J} = \underline{M} + \underline{S}$$

Our atom is characterized by

$$J_z \; ; \; \underline{J}^2 = J(J+1)$$

It is easily shown

$$2\,\underline{M}\cdot\underline{S} = J(J+1) - L(L+1) - S(S+1)$$

For a given L and S we have a multiplett energy level of

$2S+1$ components $\quad L \geq S$

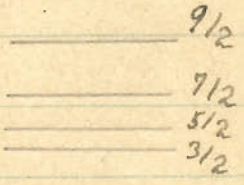
$2L+1$ " $\quad L < S$

$$\Delta E_J \sim J(J+1) + \dots$$

$$\Delta E_J - \Delta E_{J+1} \sim 2J$$

This tells us that the spacing of the levels in the multiplett is proportional to the J of the higher level.

$^4F \qquad S = \frac{3}{2}, \; L = 3$



From the no. of components, we can get S. From the spacing, we can get J. $J - S$ gives L. This is the way in which spectra are analyzed.

We shall now take up the following topics on Spectra.

1. Selection rules
2. Effect of Magnetic Field
3. Orders of Magnetude
4. Effect of Nuclear Spin.

1) Selection Rules.

By application of the commutation rules it can be shown

$$(M_z \mid x \mid M_z') = 0 \text{ unless } M_z - M_z' = \pm 1$$

$$(L \mid x \mid L') = 0 \text{ unless } L - L' = \pm 1, 0$$

Parity Rule

A state has even parity if it remains unchanged on $r \to -r$, and odd parity if it changes sign under the transformation. It can be shown that even L esp to even parity and odd L to odd parity.

For an atom we have

$\sum_k l_k$ even $\Rightarrow$ even parity.

$\sum_k l_k$ odd $\Rightarrow$ odd parity.

Laporte Rule: We can have transitions only between states of different parity. For more than one electron, L is independent of $\sum_k l_k$ and so the parity rule is independent of the ΔL rule. For one electron $\Delta L = \Delta l$ and the parity rule forbides the transition $\Delta l = 0$. This is true for Hydrogen.

Our selection & polarization rules for <u>dipole</u> radiation are:

A. $\Delta L = \pm 1, 0$

B. $\Delta J = \pm 1, 0$

C. $\Delta S = 0$ since $[x, S] = 0$

Z polarization esp $\Delta J = 0$

X, Y " " $\Delta J = \pm 1$

The ΔJ rule is good as long as there is no preferred direction in space.

The ΔL rule is good as long as L is a good quantum number, and similarly for the ΔS rule. This implies that the L S coupling is small.

In Helium, these selection rules are strictly obeyed which led earlier spectroscopists to postulate two types of Helium

Ortho $S = 1$

Para $S = 0$

3) The magnitudes of the various interaction energies are given in the following table.

	Light Atoms	Heavy Atoms	
		outer electrons	L electrons
	I	II	III
B.E.	2 - 10 ev.	2 - 10 ev	20 Kev
Electrostatic	1 ev	1 ev	100 ev
Spin Orbit	10^{-4} - 10^{-3} ev	.1 - 1 ev	3000 ev

I L S coupling

II Intermediate coupling - must consider electrostatic and spin orbit interaction simultaneously.

III j j coupling - must consider spin orbit coupling first then electro static interaction.

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2) Effect of a Magnetic Field on atomic spectra.

For an electron with no spin:

$$\Delta E = \underline{H} \cdot \underline{\mu}$$

where $\underline{\mu} = (e\hbar/2mc)\underline{M}$

For an electron having spin,

$$\underline{\mu} = \left(\frac{e\hbar}{2mc}\right)\left(\underline{M} + 2\underline{S}\right)$$

Historically, this was the first property of spin observed. Later Dirac derived the spin from the relativistic wave equation.

Since Laboratory fields are small on a nuclear scale, we can treat the problem as a perturbation problem.

For given j

$$\underline{M} = \alpha \underline{J}$$

$$\underline{M} \cdot \underline{J} = \alpha J^2 = \alpha J(J+1)$$

$$\underline{S}^2 = (\underline{J} - \underline{M})^2 = [(1-\alpha)\underline{J}]^2$$

$$S(S+1) = J(J+1) + L(L+1) - 2\underline{J}\cdot\underline{M}$$

$$[S(S+1) - L(L+1)] = J(J+1)[1 - 2\alpha]$$

$$[1 - 2\alpha] \equiv b = [S(S+1) - L(L+1)] / J(J+1)$$

$$\underline{M} + 2\underline{S} = \frac{3}{2}(\underline{M} + \underline{S}) + \frac{1}{2}(\underline{S} - \underline{M})$$
$$= \frac{3}{2}\underline{J} + \frac{1}{2}\underline{J}(1 - 2\alpha)$$

$$\underline{M} + 2\underline{S} = \left(\frac{3}{2} + \frac{1}{2}b\right)\underline{J}$$

Landé "g" factor $= \left(\frac{3}{2} + \frac{1}{2}b\right)$

$$\Delta E = g\left(\frac{e\hbar}{2mc}\right)(\underline{H} \cdot \underline{J})$$

In a magnetic field, the energy levels are split into $2J+1$ components equally spaced. The spacing is determined by the g factor. This is called the anomalous Zeeman effect. It is difficult to measure because the energy differences are so small, $\Delta E \sim 1\ cm^{-1}$

4) Magnetic Moment of the Nucleus.

The magnetic moments of nucleus and electrons interact

to cause a further splitting of the energy levels known as Hyperfine Structure.

$$\Delta E \sim \frac{\mu_{nuc} \cdot \mu_d}{r^3} \sim .1\ cm^{-1}$$

Ref: Molecular Spectra
Herzberg
Chemical Bonds
Pauling
Theory of Solids
Seitz
Mott & Jones.

Advanced Q. M.

H. A. Bethe — Fall 1947

Sept 29

Topics Relativistic Q. M.
Radiation Theory
Self Energy

Ref: RMP Apr 1938 Hill & Landshoff
Handbuch der Physik 24 I Pauli
Wentzel Theory of wave fields

Q. M.

In classical expression for energy,

$$H = \frac{p^2}{2m} + V,$$

insert

$$p = -i\hbar\nabla$$
$$H = i\hbar\frac{\partial}{\partial t}$$

to get Schrodinger Equation

Relativistic Q.M.

To get the relativistic Wave Eq., we proceed in a manner analogous to that by which we derived the Schroedinger Eq.

$$\frac{(E-V)^2}{c^2} = m^2c^2 + (\underline{p} - \tfrac{e}{c}\underline{A})^2$$

V = scalar potential $\underline{A}$ = vector potential

Replace E by $i\hbar\frac{\partial}{\partial t}$

" $\underline{p}$ " $-i\hbar\nabla$

$$(i\hbar\frac{\partial}{\partial t} - V)^2\psi = m^2c^4\psi + (-i\hbar c\nabla - e\underline{A})^2\psi$$

$$-\hbar^2\frac{\partial^2\psi}{\partial t^2} - 2i\hbar V\frac{\partial\psi}{\partial t} - \underline{i\hbar\frac{\partial V}{\partial t}\psi} + V^2\psi - m^2c^4\psi + \hbar^2c^2\nabla^2\psi - 2i\hbar c e\underline{A}\nabla\psi - \underline{i\hbar c e\nabla\cdot A\,\psi} - e^2\underline{A}^2\psi = 0$$

The Gage Eq., $\frac{1}{c}\frac{\partial\phi}{\partial t} + \nabla\cdot A = 0$: $V = e\phi$, permits us to cancel two of the terms in the above equation. This yields the Klein Gordon Eq. for particles of spin zero.

Continuity Eq

We now investigate the K G equation to see if it leads to a sensible continuity equation. [In the nonrelativistic case we found

$$\nabla \cdot j + \frac{\partial \rho}{\partial t} = 0$$

where

$$\rho = |\psi|^2$$

$$j = -\frac{ih}{2m}(\psi^* \nabla \psi - \psi \nabla \psi^*)$$]

We proceed as in the nonrel case to write down the K G eq and its conjugate, multiply the first eq by ψ^* and the second by $-\psi$ and add. We obtain

$$-h^2\left(\psi^* \frac{\partial^2 \psi}{\partial t} - \psi \frac{\partial^2 \psi^*}{\partial t}\right) - 2ihV\left(\psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t}\right)$$
$$+h^2c^2(\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^*) - 2ihce\underline{A}(\psi^* \nabla \psi + \psi \nabla \psi^*)$$
$$= 0$$

$$\nabla \cdot j + \frac{\partial \rho}{\partial t} = 0$$

If

$$\rho = a\left(\psi^* \frac{\partial \psi}{\partial t} - \psi \frac{\partial \psi^*}{\partial t} - \frac{2iV}{\hbar}\psi^*\psi\right)$$

$$j = -ac^2\left(\psi^* \nabla\psi - \psi \nabla\psi^* + \frac{2ieA}{\hbar c}\psi^*\psi\right)$$

The rel expression for j is the same as the nonrel expression (with vector potential). From this we can get $a = i\hbar/2mc^2$

Let $V \ll mc^2$

$$\psi \sim e^{-\frac{iEt}{\hbar}} = e^{-\frac{imc^2 t}{\hbar}}$$

$$\frac{\partial \psi}{\partial t} = -\frac{imc^2}{\hbar}\psi$$

ρ reduces to $\psi^*\psi$. Hence our equations are correct in the ~~non-rel~~ limit. In nonrel case ρ is pos def. This is what we want. Our relativistic expression, however, may be either + or −, since it contains

both V, and $\frac{\partial V}{\partial t}$ which may be chosen arbitrarily. To get around this Pauli & Weisskopf interpreted ρ as a charge rather than particle density.

The Klein Gordon Equation admits pos and neg energies.

Solutions of K G Eq. are not orthogonal.

The eq as it stands does not include spin (1926)

In 1927 Pauli included the spin

Oct 1

Dirac Equations.

Dirac did not like the dodges employed to get around the shortcoming of the K G equation. He postulated a positive def ρ and required relativistic invariance. Relativistic invariance means that the equations must be of the same order in derivatives with respect to x y z and t. A positive def. ρ make it attractive to have an equation in first order derivatives with respect to t. But since E^2 appears in relativistic expression for the energy, the eq must be 2nd order in t derivatives. Dirac took his cue from Maxwell's equations. They are first order equations in x y z and t, and they imply a second order

wave equation similar in form to our Q'm wave equation.

Divide Ψ into component wave functions, Ψ_k, related by first order equations esp to Maxwells equations and such that each component satisfies the 2nd order wave equation.

The most general expression is:

$$\frac{1}{c}\frac{\partial \Psi_k}{\partial t} = \sum_l \left(a_{kl}\frac{\partial \Psi_l}{\partial x} + b_{kl}\frac{\partial \Psi_l}{\partial y} + c_{kl}\frac{\partial \Psi_l}{\partial z} + d_{kl} K \Psi_l \right)$$

Introduce the matrix notation

$$\alpha = (a_{kl})$$

$$\Psi = \begin{pmatrix} \Psi_1 \\ \vdots \\ \Psi_n \end{pmatrix}$$

$$-\frac{1}{c}\frac{\partial \psi}{\partial t} = \alpha_x \frac{\partial \psi}{\partial x} + \alpha_y \frac{\partial \psi}{\partial y} + \alpha_z \frac{\partial \psi}{\partial z} + i\beta\kappa\psi$$

$$= \underline{\alpha} \cdot \nabla \psi + i\beta\kappa\psi$$

$$\underline{\alpha} = (\underline{i}\alpha_x + \underline{j}\alpha_y + \underline{k}\alpha_z)$$

$$\begin{cases} \frac{1}{c}\frac{\partial \underline{E}}{\partial t} = \nabla \times \underline{H} \\ \frac{1}{c^2}\frac{\partial^2 f}{\partial t} = \nabla^2 f \end{cases}$$

$$\frac{1}{c^2}\frac{\partial^2 \psi}{\partial t^2} = (\underline{\alpha} \cdot \nabla + i\beta\kappa)^2 \psi$$

$$= \alpha_x^2 \frac{\partial^2 \psi}{\partial x^2} + \ldots + (\alpha_x \alpha_y + \alpha_y \alpha_x)\frac{\partial^2 \psi}{\partial x \partial y} + \ldots$$

$$-\beta^2\kappa^2\psi + i\kappa(\alpha_x\beta + \beta\alpha_x)\frac{\partial \psi}{\partial x} + \ldots$$

$$= \nabla^2\psi - \left(\frac{mc}{\hbar}\right)^2 \psi$$

This eq must hold for each component.

$\therefore \alpha_x^2 = \alpha_y^2 = \alpha_z^2 = 1$

$(\alpha_x\alpha_y + \alpha_y\alpha_x) = \ldots = \ldots = 0$

$\beta^2 = 1$ then $\kappa = mc/\hbar = 1/\text{compton } \lambda$

$(\alpha_x\beta + \beta\alpha_x) = \ldots = \ldots = 0$

The Pauli spin matrices almost satisfy these relations. We need a fourth matrix which will anticommute with them. There is none. We must have at least 4 × 4 matrices in order to get 4 which anti commute. Try:

$$\underline{\alpha} = \begin{pmatrix} 0 & \underline{\sigma} \\ \underline{\sigma} & 0 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} u & 0 \\ 0 & -u \end{pmatrix}$$

where $\underline{\sigma} = i\sigma_x + j\sigma_y + k\sigma_z$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$u = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\underline{\alpha}\beta = \begin{pmatrix} 0 & -\underline{\sigma} \\ \underline{\sigma} & 0 \end{pmatrix}$$

$$\beta\underline{\alpha} = \begin{pmatrix} 0 & \underline{\sigma} \\ -\underline{\sigma} & 0 \end{pmatrix}$$

$(\underline{\alpha}\beta + \beta\underline{\alpha}) = 0$ as required.

β is not the only anticommuting matrix.

Expression for Charge

$$-\psi^* \| \frac{1}{c}\frac{\partial \psi_k}{\partial t} = \sum_l \underline{\alpha}_{kl} \cdot \nabla \psi_l + i\beta_{kl}\frac{mc}{\hbar}\psi_l$$

$$-\psi \| \frac{1}{c}\frac{\partial \psi_k^*}{\partial t} = \sum_l \underline{\alpha}_{kl}^* \cdot \nabla \psi_l^* - i\beta_{kl}^*\frac{mc}{\hbar}\psi_l^*$$

Add

$$-\frac{1}{c}\frac{\partial}{\partial t}\psi_k^*\psi_k = \sum_l \psi_k^* \underline{\alpha}_{kl} \cdot \nabla \psi_l + \nabla \psi_l^* \cdot \underline{\alpha}_{kl}\psi_k + i\frac{mc}{\hbar}(\psi_k^*\beta_{kl}\psi_l - \psi_l^*\beta_{kl}\psi_k)$$

Sum both sides over k. For a continuity equation we want only derivatives. This is the case if $\beta_{lk}^* = \beta_{kl}$ i.e. β Hermitian. Also postulate α Hermitian

$$-\frac{1}{c}\frac{\partial}{\partial t}\sum_k \psi_k^*\psi_k = \sum_{kl} \psi_k^* \underline{\alpha}_{kl} \cdot \nabla \psi_l + \nabla \psi_k^* \cdot \underline{\alpha}_{kl}\psi_l$$

$$= \sum_{kl} \nabla(\psi_k^*\psi_l) \cdot \underline{\alpha}_{kl}$$

$$= \sum_{kl} \nabla \cdot (\psi_k^* \underline{\alpha}_{kl} \psi_l)$$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot j = 0$$

If $\rho = \sum_k |\psi_k|^2$

$$j = +c \sum_{kl} \psi_k^+ \underline{\alpha}_{kl} \psi_l$$

Oct 3,

The Dirac equation also implies the relation

$$\frac{\partial W}{\partial t} + \nabla \cdot \underline{P} = 0$$

where

$$W = c \sum_k \left(\psi_k^+ \frac{\partial \psi_k}{\partial t} - \psi_k \frac{\partial \psi_k^+}{\partial t} \right)$$

$$\underline{P} = c\, c^2 \sum_k \left(\psi_k^+ \nabla \psi_k - \psi_k \nabla \psi_k^+ \right)$$

If we analyze ψ into its Fourier components, $\psi_k \sim e^{-iEt/\hbar}$, we find that

W = energy density $\sum_k \psi_k^* \psi_k E$

$\underline{P}$ = momentum density

Suppose we define

$$\psi = \begin{pmatrix} \psi_1 \\ \vdots \\ \psi_b \end{pmatrix} \qquad \psi^* = \overline{\psi_1^* \cdots \psi_k^*}$$

Then $\rho = \psi^* \psi$

$$j = c\, \psi^* \underline{\alpha}\, \psi$$

Exercise: Show that $\underline{\alpha}$ and β are Hermitian.

Dirac Eq $\quad \frac{1}{c}\frac{\partial \psi}{\partial t} + \underline{\alpha} \cdot \nabla \psi + \frac{imc}{\hbar} \beta \psi = 0$

Conjugate $\quad \frac{1}{c}\frac{\partial \psi^*}{\partial t} + \sum_l \underline{\alpha}^*_{kl} \cdot \nabla \psi^*_l - \frac{imc}{\hbar} \sum_l \beta^*_{kl} \psi^*_l$

$$\frac{1}{c}\frac{\partial \psi}{\partial t} + \nabla \psi^* \cdot \underline{\alpha} - \frac{imc}{\hbar} \psi^* \beta$$

Free particle

$$\psi = u\, e^{-\frac{iEt}{\hbar}}\, e^{\frac{i\underline{p}\cdot\underline{r}}{\hbar}}$$

u = four component constant independent of $\underline{r}$ and t

$$\frac{E^2}{c^2} = p^2 + mc^2$$

Note that a given p corresponds to two solutions for the energy E, one $+$ and one $-$. From the Dirac Eq.

$$-\frac{iE}{\hbar c}\psi + \frac{i\underline{p}}{\hbar}\cdot\underline{\alpha}\,\psi + \frac{imc}{\hbar}\beta\psi = 0$$

[redacted]

$$Eu = (c\underline{p}\cdot\underline{\alpha} + mc^2\beta)u$$

Apply the operation again

$$E^2 u = c^2(\underline{p}\cdot\underline{\alpha} + mc^2\beta)^2 u$$

We can expand this to get the

classical equation.

$$1)\left(-\frac{E}{c}+mc\right)u_1 + p_x u_4 - i p_y u_4 + p_z u_3 = 0$$
$$2)\left(-\frac{E}{c}+mc\right)u_2 + p_x u_3 + i p_y u_3 + p_z u_4 = 0$$
$$3)\left(-\frac{E}{c}+mc\right)u_3 + p_x u_2 - i p_y u_2 + p_z u_1 = 0$$
$$4)\left(-\frac{E}{c}+mc\right)u_4' + p_x u_1 + i p_y u_1 - p_z u_2 = 0$$

For solutions the determinant of the coefficients of the u's must vanish. This gives:

$$E^2/c^2 = p^2 + m^2c^2$$

We look for a solution for which

$$u_2 = 0$$

$$u_3 = \left(\frac{c p_z}{E + mc^2}\right) u_1$$

$$u_4 = \left(\frac{c(p_x + i p_y)}{E + mc^2}\right) u_1$$

Substituting these solutions for u_3 and u_4 in equation 1 and 2 we find that there are two solutions each for u_3 and u_4 esp to $\pm E$.

Normalization

$$\int \rho \, d\tau = 1$$

Free particle $\rho = \sum_k \psi_k^* \psi_k = \sum_k u_k^* u_k$

$= 1$

$$1 = u_1^+ u_1 \left(1 + \frac{c^2 p^2}{(E+mc^2)^2}\right)$$

$$= |u_1|^2 \left[1 + (E^2 - m^2c^4)/(E+mc^2)^2\right]$$

$$= |u_1|^2 \; 2E/(E+mc^2)$$

$$|u_1|^2 = \frac{E+mc^2}{2E}$$

$$\psi = \frac{1}{\sqrt{2E(E+mc^2)}} \begin{pmatrix} E+mc^2 \\ 0 \\ cp_z \\ c(p_x + ip_y) \end{pmatrix}$$

Orthogonality

$$\int \sum_k \psi_k'^* \psi_k \, d\tau = 0$$

Consider states of same p but different energy

$$\sum u_k'^* u_k = 0$$

$$(E+mc^2)(-E+mc^2) + 0 + c^2p^2 = 0$$

The orthogonality of the components can be proved in general from the Dirac Eq.

Another solution for ψ is:

$$\psi = \frac{1}{\sqrt{2E(E+mc^2)}} \begin{pmatrix} 0 \\ E+mc^2 \\ c(p_x - i p_y) \\ -cp_z \end{pmatrix}$$

Hence there are 4 mutually orthogonal solutions for the same value of p. These solutions make up the general wave packet.

In the classical limit $E \sim mc^2$

$W \rightarrow$ charge density

$\underline{P} \rightarrow$ current density (velocity)

Oct 8

We have, $\frac{1}{c}\frac{\partial \psi}{\partial t} + \underline{\alpha} \cdot \nabla \psi + \frac{imc}{\hbar} \beta \psi = 0$

In classical limit

$$E \sim mc^2$$

$$\frac{\partial \psi}{\partial t} \sim -\frac{imc^2}{\hbar}\psi$$

$$\underline{\alpha} \cdot \nabla \psi + \frac{imc}{\hbar}(-1+\beta)\psi = 0$$

$$(-1+\beta) = \begin{pmatrix} 0 & & & \\ & 0 & & \\ & & -2 & \\ & & & -2 \end{pmatrix}$$

Hence ψ_3 and ψ_4 will be small in the classical limit.

Let:

$$\psi = \begin{pmatrix} \chi \\ \phi \end{pmatrix}$$

where

$$\chi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}, \quad \phi = \begin{pmatrix} \psi_3 \\ \psi_4 \end{pmatrix}$$

1) $\frac{1}{c}\frac{\partial \chi}{\partial t} + \frac{imc}{\hbar}\chi + \underline{\sigma} \cdot \nabla \phi = 0$

2) $\frac{1}{c}\frac{\partial \phi}{\partial t} - \frac{imc}{\hbar}\phi + \underline{\sigma} \cdot \nabla \chi = 0$

From 2') and $\phi \sim e^{\frac{imc^2 t}{\hbar}}$

$$-\frac{2imc}{\hbar}\phi + \underline{\sigma}\cdot\nabla\chi = 0$$

$$\phi = \frac{\hbar}{2imc}\underline{\sigma}\cdot\nabla\chi$$

In the nonrel. limit, a knowledge of ϕ follows from a knowledge of χ alone. (This can be extended to include a force field)

Let us write

$$\chi = \chi' e^{-\frac{imc^2}{\hbar}t}$$

Then χ' has only a small time dependence in the nonrel. limit.

$$\frac{1}{c}\frac{\partial\chi'}{\partial t} + \underline{\sigma}\cdot\nabla\phi' = 0$$

$$\frac{\partial\chi'}{\partial t} + \frac{\hbar}{2im}(\underline{\sigma}\cdot\nabla)(\underline{\sigma}\cdot\nabla)\chi' = 0$$

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[Lemma $(\underline{\sigma}\cdot\underline{A})^2 = A^2$]

$$\therefore \quad i\hbar \frac{\partial \chi}{\partial t} + \frac{\hbar^2}{2m} \nabla^2 \chi = 0$$

This is the Schroedinger eq (without V). The 2 components of χ correspond to the 2 possible spins.

Current

$$\psi^* \underline{\alpha} \psi = \phi^* \underline{\sigma} \chi + \chi^* \underline{\sigma} \phi$$

$$\frac{\iota}{c} = \frac{\hbar}{2imc} \left(\chi^* \underline{\sigma} (\underline{\sigma} \cdot \nabla \chi) - (\nabla \chi^* \cdot \underline{\sigma}) \underline{\sigma} \chi \right)$$

(σ Hermitian)

$$j_x = \frac{\hbar}{2im} \Big(\chi^* \sigma_x \left(\sigma_x \frac{\partial \chi}{\partial x} + \sigma_y \frac{\partial \chi}{\partial y} + \sigma_z \frac{\partial \chi}{\partial z} \right)$$

$$- \left(\frac{\partial \chi^*}{\partial x} \sigma_x^2 \chi + \frac{\partial \chi^*}{\partial y} \sigma_y \sigma_x \chi + \frac{\partial \chi^*}{\partial z} \sigma_z \sigma_x \chi \right) \Big)$$

Since $\sigma_x \sigma_y = +i\sigma_z$, $\sigma_z \sigma_x = +i\sigma_y$, etc.

$$j_x = \frac{\hbar}{2mi} \Big[\left(\chi^* \frac{\partial \chi}{\partial x} - \frac{\partial \chi^*}{\partial x} \chi \right)$$

$$+ i\sigma_z \left(\chi^* \frac{\partial \chi}{\partial y} + \frac{\partial \chi^*}{\partial y} \chi \right) + i\sigma_y \left(\chi^* \frac{\partial \chi}{\partial z} + \frac{\partial \chi^*}{\partial z} \chi \right) \Big]$$

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$$j = \frac{\hbar}{2im}\left(\chi^*\nabla\chi - \chi\nabla\chi^* + i\nabla\rho\times\underline{\sigma}\right)$$

If we integrate over the wave packet the 2nd term vanishes since

$$\int d\tau\, \nabla\rho = 0$$

and the first term becomes the Schrodinger current.

Angular Momentum

$$H = c\,\underline{\alpha}\cdot\underline{p} + \beta mc^2 + V$$

If $V = V(r)$, let us investigate $\underline{M} = \underline{r}\times\underline{p}$ to see if this quantity is conserved.

For conservation $\underline{L}[\underline{M}H] = 0$

Consider the x component

$$M_x' = \frac{iM_x}{\hbar} = y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}$$

βmc^2 commutes

$y\frac{\partial V}{\partial z} - z\frac{\partial V}{\partial y} = 0$ if $V = V(r)$

$y\frac{\partial}{\partial z}\alpha\cdot\nabla = \alpha\cdot\nabla\, y\frac{\partial}{\partial z} - \alpha_y\frac{\partial}{\partial z}$

$[M_x' H] = (\alpha_z\frac{\partial}{\partial y} - \alpha_y\frac{\partial}{\partial z})(-ihc)$

$[M' H] = ihc\,\underline{\alpha}\times\nabla$

Hence $\underline{M} = \underline{r}\times\underline{p}$ is not a constant of the motion.

Assume $\underline{N}$ a constant matrix containing $\underline{\alpha}$ matrices such that

$$[\underline{N} H] = -[\underline{M}' H] = -ihc\,\underline{\alpha}\times\nabla$$

Consider the x component. The following relations must be satisfied:

$[N_x H] = -ihc(\alpha_y\frac{\partial}{\partial z} - \alpha_z\frac{\partial}{\partial y})$

$[N_x V] = 0$

$[N_x \beta] = 0$

$[N_x \alpha_x] = 0$

$[N_x \alpha_y] = -\alpha_z$

$[N_x \alpha_z] = \alpha_y$

Assume $N_x \equiv k \alpha_y \alpha_z$

$[k \alpha_y \alpha_z, \alpha_y] = k(-\alpha_z - \alpha_z) = -2k\alpha_z$

$= -\alpha_z$

$\therefore \quad k = \frac{1}{2}$

If we define $\underline{G}_x = M_x + \frac{1}{2i} \alpha_y \alpha_x$, then G_x is a constant of the motion.

$$\underline{G} = \underline{M} + \tfrac{1}{2} \hbar \underline{\sigma}_D$$

where $\underline{\sigma}_D = \begin{pmatrix} \underline{\sigma}_p & 0 \\ 0 & \underline{\sigma}_p \end{pmatrix}$

Oct 10

$\underline{M}$ is analogous to the classical angular momentum. The term involving $\underline{\sigma}_D$, the Dirac spin matrix, is associated with the

electron spin. The prediction of the electron spin was the first triumph of the Dirac Theory.

The $\underline{\sigma}_D$ obeys the same rules as the $\underline{\sigma}_P$

$$\sigma_x \sigma_y + \sigma_y \sigma_x = 0$$
$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1$$
$$\sigma_x \sigma_y = i \sigma_z$$
etc.

The eigenvalues of the $\underline{\sigma}_D$ matrix are ± 1. $(1, 1, -1)$ Since $\underline{M} \sim \hbar$

$$G_z = \tfrac{1}{2} \text{ integer times } \hbar$$
$$G^2 = \hbar^2 j(j+1) \qquad j = \tfrac{1}{2} \text{ integer}$$

While the prediction of the electron spin was a great triumph for the Dirac Theory, the prediction of negative energy states leads to some trouble. It is the feeling at present, that the Klein-Gordon Theory is almost

as good as the Dirac Theory.

Problem: (Due Oct 17) Assume the wave function for a free particle.

$$u^* u = 1 \qquad u = \sum \psi_k$$

Calc. 1) For same energy $u_+^* \underline{\alpha} u_+$, $u_+^* \beta u_+$, $u_+^* \underline{\sigma} u_+$

2) For same momentum

$$u_\pm^* \beta u_\pm$$

3) $u_\pm^*(\underline{p}') \alpha_2 u_\pm(\underline{p})$

Consider

$$u^* \sigma_z u = |u_1|^2 + |u_3|^2 - |u_2|^2 - |u_4|^2$$

In the normal limit only u_1 & u_2 are large and these two wave functions cop to the 2 spins of the electron in the z direction. i.e + & −.

Let us calc $\langle \sigma_z \rangle$ using one of our rel solutions for u

$$u = \frac{1}{\sqrt{2E(E+mc^2)}} \begin{pmatrix} E+mc^2 \\ 0 \\ cp_z \\ c(p_x + ip_y) \end{pmatrix}$$

$$\langle \sigma_z \rangle = \left[(E+mc^2)^2 + c^2 p_z^2 + c^2 (p_x^2 + p_y^2) \right] / 2E(E+mc^2)$$

$$= \left[(E+mc^2)^2 + c^2 p^2 - 2c^2 (p_x^2 + p_y^2) \right] / 2E(E+mc^2)$$

$$= 1 - \frac{c^2 p^2 \sin^2\theta}{E(E+mc^2)}$$

$$= 1 - \frac{E - mc^2}{E} \sin^2\theta$$

In the nonrel limit $E \sim mc^2$

$\langle \sigma_z \rangle = +1$

In the rel case, the spins are not diagonal with respect to u_1 u_2 u_3 u_4 for a given E & p. Only in the non rel limit can we say E, p and σ simultaneously and associate a particular spin with a particular u_k

Force Field

$$p_- = p_{-f} - \frac{e}{c}\underline{A}$$

$$H_f = e\phi + \underbrace{\frac{(p_f - \frac{e}{c}\underline{A})^2}{2m} + \sqrt{(p_f - \frac{e}{c}\underline{A})^2 c^2 + m^2 c^4}}_{H}$$

In the Dirac equation replace H by $H_f - e\phi$ and p by $p_f - \frac{e}{c}\underline{A}$

$$(H_f - e\phi)\psi = \alpha \cdot (cp_{-f} - e\underline{A})\psi + \beta mc^2 \psi$$

$$\left(\frac{1}{c}\frac{\partial}{\partial t} + \frac{ie}{\hbar c}\phi + \underline{\alpha} \cdot (\nabla - \frac{ie}{\hbar c}\underline{A}) + \frac{imc}{\hbar}\beta\right)\psi = 0$$

This equation gives the correct E's for hydrogen

Ref. Hill & Landshoff.
Handbuch

Define an operator:

$$B = \left[\frac{1}{c}\frac{\partial}{\partial t} + \frac{ie}{\hbar c}\phi - \alpha \cdot (\nabla - \frac{ie}{\hbar c}\underline{A}) - \frac{imc}{\hbar}\beta\right]$$

Apply B to the Dirac equation $D\psi = 0$

$$B D\psi = 0$$

$$\left(\frac{1}{c}\frac{\partial}{\partial t} + \frac{ie}{\hbar c}\phi\right)^2 - \left(\nabla - \frac{ie}{\hbar c}\underline{A}\right)^2 + \left(\frac{mc}{\hbar}\right)^2$$

$$+ \frac{ie}{\hbar c}\,\underline{\alpha}\cdot\left(-\frac{1}{c}\frac{\partial \underline{A}}{\partial t} - \nabla\phi\right) + \frac{ie}{\hbar c}\,\alpha_x\alpha_y\left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right)$$

$$+ \ldots + \ldots$$

The first 3 terms are the K G operator. The 4 term involves the electric field $E = \frac{1}{c}\frac{\partial A}{\partial t} + \nabla\phi$. The last three terms involve the magnetic field

$$\left[(K G) - \frac{e}{\hbar c}(\underline{\sigma}\cdot\underline{H} - i\underline{\alpha}\cdot\underline{E})\right]\psi = 0$$

This equation gives 1 B.M., $\left(\frac{e\hbar}{2mc}\right)$, as the magnetic moment of the electron. This is twice the value the classical theory gives and is the correct value. This was the second great triumph of the Dirac Theory.

(The $\underline{\alpha}\cdot\underline{E}$ term arises because

the electric center and mass center do not coincide.)

Oct 13

See Hill & Landshoff on non-relativistic limit of above equations.

Relativistic Invariance

Relativistic invariance requires that the wave equation must have the same form in all Lorentz coordinate systems. We constructed our equations with this in mind, and we shall now show that they are really invariant.

It will be convenient to use a new notation in showing invariance. This is introduced below.

$$\frac{1}{c}\frac{\partial \psi}{\partial t} + \underline{\alpha}\cdot\nabla\psi + \frac{imc}{\hbar}\beta\psi = 0$$

The components of our 4 vector are $x_1\ x_2\ x_3$ and $x_4 = ict$

$$(-i\beta)\frac{i\partial\psi}{\partial x_4} + (-i\beta)\underline{\alpha}\cdot\nabla\psi + \frac{mc}{\hbar}\psi = 0$$

$$\underline{\gamma}_{1,2,3} \equiv -i\beta\underline{\alpha} \qquad \gamma_4 \equiv \beta$$

$$\sum_{\mu=1}^{4}\gamma_\mu\frac{\partial\psi}{\partial x_\mu} + \frac{mc}{\hbar}\psi = 0$$

Conjugate equation

$$\frac{1}{c}\frac{\partial\psi^*}{\partial t} + \nabla\psi^*\cdot\underline{\alpha} - \frac{imc}{\hbar}\psi^*\beta = 0$$

$$\frac{\partial\psi}{\partial x_4} - \nabla\psi^*\cdot\underline{\alpha}\,i - \frac{mc}{\hbar}\psi^*\beta = 0$$

Let $\psi^+ \equiv i\psi^*\beta$

$$\frac{\partial\psi^+\beta}{\partial x_4} - \nabla\psi^+\beta\cdot\alpha\,i - \frac{mc}{\hbar}\psi^+ = 0$$

$$\sum_{\mu=1}^{4}\frac{\partial\psi^+}{\partial x_\mu}\gamma_\mu - \frac{mc}{\hbar}\psi^+ = 0$$

Consider also

$$\underline{S} = \mathcal{J}/c \qquad S_4 = iP$$

$$\frac{\mathcal{J}}{c} = \underline{S} = \psi^* \underline{\alpha} \psi$$

$$S_k = i \psi^* \beta \gamma_k \psi = \psi^+ \gamma_k \psi$$

(We use the convention that Greek letters are summed 1 to 4 and Latin letter 1 to 3)

$$S_4 = iP = i \psi^* \psi = \psi^+ \gamma_4 \psi$$

The introduction of the γ's gives us a nice symmetric form for our equations.

The γ's anticommute.

$$\gamma_4 \gamma_1 = -i \beta^2 \alpha_x = -i \alpha_x$$

$$\gamma_1 \gamma_4 = -i \beta \alpha_x \beta = +i \alpha_x$$

$$\gamma_1 \gamma_2 = (-i)^2 \beta \alpha_x \beta \alpha_y = \alpha_x \alpha_y$$

$$\gamma_2 \gamma_1 = -\beta \alpha_y \beta \alpha_x = \alpha_y \alpha_x$$

Normalization $\gamma_4^2 = \beta^2 = 1$

$$\gamma_1^2 = (-i)^2 \beta\alpha_x \beta\alpha_x = \beta^2 \alpha_x^2 = 1$$

The γ's are Hermitian

$$\gamma^k_{mn} = -i \sum_l \beta_{ml} \alpha^k_{ln}$$

$$(\gamma^k_{mn})^* = +i \sum_l \beta^*_{ml} \alpha^*_{li}$$

$$= i \sum_l \beta_{lm} \alpha_{nl} = i(\alpha\beta)_{nm}$$

$$= (-i\beta\alpha)_{nm} = \gamma_{nm}$$

<u>Lorentz Transformation</u>

$$x'_\mu = \sum_\nu a_{\mu\nu} x_\nu$$

$a_{\mu\nu}$ (1,2,3) real
$a_{\mu\nu}$ imaginary if <u>one</u> index = 4

$$x_\nu = \sum_\mu a_{\mu\nu} x'_\mu$$

$$\sum_u a_{uv}\, a_{up} = \delta_{vp}$$

This is the condition for an orthonormal transformation.

Oct. 15, 1947

We developed a new notation last time which we now use to prove the Lorentz invariance of our Ψ

Primes refer to the moving system.

$$\Psi'_a = \sum_b S_{ab}\, \Psi_b \quad ; \quad x'_u = \sum_v a_{uv}\, x_v$$

$$\Psi' = S\Psi$$

S = transformation matrix

$$\sum_u \gamma_u \frac{\partial \Psi'}{\partial x'_u} + \frac{mc}{\hbar}\Psi' = 0$$

If the equations of motion are to be the same in our

transformed system, the γ's must be the same.

$$\sum_\mu \gamma_\mu S \sum_\nu \frac{\partial \psi}{\partial x_\nu} a_{\mu\nu} + \frac{mc}{\hbar} S\psi = 0$$

$$\sum_\nu \sum_\mu S^{-1} \gamma_\mu S a_{\mu\nu} \frac{\partial \psi}{\partial x_\nu} + \frac{mc}{\hbar} \psi = 0$$

$$\sum_\mu S^{-1} \gamma_\mu S a_{\mu\nu} = \gamma_\nu$$

$$\sum_\nu a_{\lambda\nu} \sum_\mu a_{\mu\nu} S^{-1} \gamma_\mu S = \sum_\nu a_{\lambda\nu} \gamma_\nu$$

$$\sum_\nu a_{\lambda\nu} a_{\mu\nu} = \delta_{\lambda\mu}$$

$$\boxed{S^{-1} \gamma_\mu S = \sum_\nu a_{\mu\nu} \gamma_\nu}$$

This is the defining equation for the transformation matrix S.

We now wish to find S. Assume an infinitessimal Lorentz transformation

$$a_{\mu\nu} = \delta_{\mu\nu} + \epsilon_{\mu\nu}$$

where $\epsilon_{\mu\nu} \ll 1$

$$\sum_\mu a_{\mu\nu} a_{\mu\rho} = \sum_\mu (\delta_{\mu\nu} + \epsilon_{\mu\nu})(\delta_{\mu\rho} + \epsilon_{\mu\rho}) = \delta_{\sigma\rho}$$

$\therefore$ for $\nu \neq \rho$ $\quad \epsilon_{\nu\rho} + \epsilon_{\rho\nu} = 0$

Hence ϵ antisym

for $\nu = \rho$ $\quad (1 + \epsilon_{\nu\nu})^2 = 1$

Hence $\epsilon_{\nu\nu} = 0$

$$\epsilon_{\mu\nu} = -\epsilon_{\nu\mu}$$

Let $S = I + \frac{1}{2} \sum_{\mu<\nu} \epsilon_{\mu\nu} T_{\mu\nu}$

where I = identity matrix. $T_{\mu\nu}$ are 6 four by four matrices.

Zero order trans $I \gamma_\mu I = \gamma_\mu$. O.K.

First order trans.

$$-\frac{1}{2} \sum_{\lambda<\nu} \epsilon_{\lambda\nu} T_{\lambda\nu} \gamma_\mu I + I \gamma_\mu \frac{1}{2} \sum_{\lambda<\nu} \epsilon_{\lambda\nu} T_{\lambda\nu}$$

$$= \sum_\nu \epsilon_{\mu\nu} \gamma_\nu$$

This equation must be satisfied for arbitrary ϵ

Case I $\lambda = \mu$ Equate Coefficients of $\epsilon_{\lambda\nu}$

$$-\tfrac{1}{2} T_{\mu\nu}\gamma_\mu + \tfrac{1}{2}\gamma_\mu T_{\mu\nu} - \gamma_\nu = 0$$

Try $T_{\mu\nu} = \gamma_\mu\gamma_\nu$

$$-\tfrac{1}{2}\gamma_\mu\gamma_\nu\gamma_\mu + \tfrac{1}{2}\gamma_\mu^2\gamma_\nu = \gamma_\nu \quad \text{O.K.}$$

Case II $\lambda \neq \mu$ Coefficient of $\epsilon_{\lambda\nu}$ on right $= 0$

$$\gamma_\mu T_{\lambda\nu} - T_{\lambda\nu}\gamma_\mu = 0$$

$$\gamma_\mu\gamma_\lambda\gamma_\nu - \gamma_\lambda\gamma_\nu\gamma_\mu = 0 \quad \text{O.K.}$$

Special Case of a Rotation

$\epsilon_{4k} = 0 \qquad \epsilon_{kl} \neq 0$

$$T_{kl} = \gamma_k\gamma_l = -\beta\alpha_k\,\beta\alpha_l = \alpha_k\alpha_l = i\sigma_m$$

$$S = I + \frac{1}{2} \sum_m i \overset{\theta_m}{\epsilon_{kl}} \sigma_m$$

ϵ_{kl} = m component of a rotation

$$S = I + \frac{1}{2} i \underline{\theta} \cdot \underline{\sigma}$$

This tells how the wave function transforms if the coordinate system is given a small rotation.

Lorentz Trans.

$$\epsilon_{4k} \neq 0 \qquad \epsilon_{kl} = 0$$

$$T_{4k} = \gamma_4 \gamma_k = -i\beta^2 \alpha_k = -i\alpha_k$$

$$S = I - \frac{1}{2} i \sum_k \epsilon_{4k} \alpha_k$$

$$= I - \frac{v}{c} \cdot \underline{\alpha}$$

Conjugate wave function ψ^+

$$\psi'^+ = \psi^+ S^{-1}$$

$$\psi^+ = i\psi^* \gamma_4$$

$$\psi'^* = (S\psi^*)^* = \psi^* \tilde{S}$$

$$\tilde{S}_{mn} = S^*_{nm}$$

$$\psi'^+ = i\psi^* \gamma_4 S^{-1} = i\psi^* \tilde{S} \gamma_4 = i\psi'^* \gamma_4$$

$$\gamma_4 S^{-1} = \tilde{S} \gamma_4$$

To show this:

$$S^{-1} = I - \frac{1}{2} \sum \epsilon_{\mu\nu} \gamma_\mu \gamma_\nu$$
$$= I + \frac{1}{2} \sum \epsilon_{\mu\nu} \gamma_\nu \gamma_\mu$$

$$S^* = I + \frac{1}{2} \sum \epsilon^*_{\mu\nu} \gamma^*_\mu \gamma^*_\nu$$

$$\tilde{S} = I + \frac{1}{2} \sum \epsilon^*_{\mu\nu} \tilde{\gamma}_\nu \tilde{\gamma}_\mu$$
$$= I + \frac{1}{2} \sum \epsilon^*_{\mu\nu} \gamma_\nu \gamma_\mu$$

ϵ_{kl} real

$\gamma_4 \gamma_k \gamma_l = \gamma_k \gamma_l \gamma_4$ O.K.

ϵ_{4k} imaginary $= -\epsilon^*_{4k}$

$\gamma_4 \gamma_4 \gamma_k = -\gamma_4 \gamma_k \gamma_4$ O.K.

Oct 17, 1947

Finite Lorentz Trans.

A Rotation about z axis

For an infinitesimal rotation

$$S = I + \tfrac{1}{2} i \theta \sigma_2$$

2 rotations

$$S^2 = f(\theta) I + i g(\theta) \sigma_2$$

We choose this as the general form.

$$S = f(\theta) I + i g(\theta) \sigma_2$$

$$S' = I + \tfrac{1}{2} i \delta \sigma_2$$

$$S'S = S(\theta+\delta) = f(\theta+\delta) I + i g(\theta+\delta) \sigma_2$$

$$= \left[f(\theta) - \tfrac{1}{2} g(\theta) \delta \right] I + i \sigma_2 \left[g(\theta) + \tfrac{1}{2} f(\theta) \delta \right]$$

Equate coef of I and $i\sigma_2$

$$\frac{df}{d\theta} = -\tfrac{1}{2} g \qquad \frac{dg}{d\theta} = \tfrac{1}{2} f$$

$$\left.\begin{aligned} f &= 1 \\ g &= 0 \end{aligned}\right\} \theta = 0$$

$$f = \cos \tfrac{1}{2}\theta$$
$$g = \sin \tfrac{1}{2}\theta$$

$$S = \cos \tfrac{1}{2}\theta + i \sin \tfrac{1}{2}\theta \, \sigma_2$$

This is similar to the way in which the ψ function for a particle of angular momentum m behaves under a rotation about the z axis

$$\psi \rightarrow \psi' e^{im\theta}$$

$$e^{im\theta} = \cos m\theta + i \sin m\theta$$

The $\tfrac{1}{2}$ is associated with the electron spin.

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix}$$

The first two components transform among themselves, and the last two likewise.

$$S\psi = \begin{pmatrix} \psi_1 e^{i\frac{1}{2}\theta} \\ \psi_2 e^{-i\frac{1}{2}\theta} \\ \psi_3 e^{i\frac{1}{2}\theta} \\ \psi_4 e^{-i\frac{1}{2}\theta} \end{pmatrix}$$

Rotation thru $2\pi \rightarrow S = -1$

The wave function is double valued for each point in space.

$-S$ or S are equally good.

B Lorentz Trans

$$x_1' = x_1 + i\chi x_4$$
$$x_4' = x_4 - i\chi x_1$$

Let $x_4 = i x_0$

$$x_1' = x_1 - \chi x_0$$
$$x_0' = x_0 - \chi x_1$$

For a finite transformation

$$x_1' = f(\chi) x_1 - g(\chi) x_0$$
$$x_0' = g(\chi) x_0 - f(\chi) x_1$$

$$f(\chi) = \cosh \chi$$
$$g(\chi) = \sinh \chi$$

$$\tanh \chi = \frac{v}{c}$$

For an infinitesimal trans

$$S = I + \tfrac{1}{2} \epsilon_{41} \gamma_4 \gamma_1$$
$$I + \tfrac{1}{2}(-i\chi)\beta(-i\beta\alpha_x)$$
$$= I - \tfrac{1}{2}\chi\alpha_x$$

Hence for a finite trans.

$$S = \cosh \tfrac{1}{2}\chi \, I - \sinh \tfrac{1}{2}\chi \, \alpha_x$$

c <u>Current Transformation</u>

$$S_\mu = \psi^+ \gamma_\mu \psi$$
$$S_k = j_k / c$$
$$S_4 = i\rho$$

$$S'_\mu = \psi^+ S^{-1} \gamma_\mu S \psi$$

$$S^{-1} \gamma S = \sum_\mu a_{\mu\nu} \gamma_\nu$$

$$S'_\mu = \sum_\nu a_{\mu\nu} S_\nu$$

S transforms like a four vector.

D Charge

$$\psi'^{+}\psi' = \psi^{+}S^{-1}S\psi = \psi^{+}\psi$$

E $$\psi'^{+}\gamma_\mu\gamma_\nu\psi' = \psi^{+}S^{-1}\gamma_\mu S S^{-1}\gamma_\nu S\psi$$

$$S^{-1}\gamma_\mu S = \sum_\rho a_{\mu\rho}\gamma_\rho$$
$$S^{-1}\gamma_\nu S = \sum_\sigma a_{\nu\sigma}\gamma_\sigma$$

$$\psi'^{+}\gamma_\mu\gamma_\nu\psi' = M'_{\mu\nu} = \sum_{\rho\sigma} a_{\mu\rho}a_{\nu\sigma}M_{\rho\sigma}$$

$M_{\mu\nu}$ transforms like a second order tensor.

$$x'_\mu x'_\nu = \sum_{\rho\sigma} a_{\mu\rho}a_{\nu\sigma}x_\rho x_\sigma$$

Antisymmetrical. Can make diagonal elements zero by redefining $M_{\mu\nu} = \frac{1}{2}\psi^{+}(\gamma_\mu\gamma_\nu - \gamma_\nu\gamma_\mu)\psi$

Scalar product of 2 4-vectors is an invariant.

Scalar product of 2 antisym tensor is an invariant.

In Electro Dynamics we have the antisym tensor

$$\underline{H}\,\underline{E} = F$$

Hence

$$\sum_{\mu\nu} F_{\mu\nu} M_{\mu\nu} = \text{invariant}$$

Let $\psi = i\phi^{\text{scalar pot}}$ $\psi_k = A_k^{\text{vector pot}}$

$$\frac{ie}{\hbar c} \sum_\mu \gamma_\mu \psi_\mu \psi \quad \text{an invariant}$$

$$\kappa \sum_{\mu<\nu} \gamma_\mu \gamma_\nu F_{\mu\nu} \quad \text{an invariant}$$

equivalent to $\underline{H}\cdot\underline{\sigma} + \underline{E}\cdot i\underline{\alpha}$
In non rel limit $\alpha \to 0$. Since we can add any invariant to the wave equation, we could add the above expression involving a magnetic moment. Since the add moment is arbitrary, this makes the Dirac equation good for the proton and neutron.

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The following quantities of the form $\psi^+ A \psi$ transform in a simple way.

$A = 1$	Invariant	1
$A = \gamma_\mu$	4-vector	4
$A = i\gamma_\mu\gamma_\nu$	Antisym Tensor	6
$A = i\gamma_\mu\gamma_\rho\gamma_\sigma$		4
$A = \gamma_1\gamma_2\gamma_3\gamma_4$		1

We have already investigated the transformation properties of all but the last two of these expressions.

$$\psi^{+\prime}\gamma_1\gamma_2\gamma_3\gamma_4\psi' = \psi^+ S^{-1}\gamma_1 S S^{-1}\gamma_2 S S^{-1}\gamma_3 S S^{-1}\gamma_4 S S \psi$$

$$= \psi^+ \sum_{\mu\nu\rho\sigma} a_{1\mu}\gamma_\mu a_{2\nu}\gamma_\nu a_{3\rho}\gamma_\rho a_{4\sigma}\gamma_\sigma \psi$$

If any two indices over which the sums are taken are alike then the sum is zero.

i.e. Suppose $\mu = \sigma$

then $\sum_{\mu} a_{1\mu} a_{4\mu} = 0$.

The net result can be expressed in the form

$$\psi^{+'} \gamma_1 \gamma_2 \gamma_3 \gamma_4 \psi' = \psi^{+} \gamma_1 \gamma_2 \gamma_3 \gamma_4 \psi \begin{vmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & & & \\ a_{31} & & & \\ a_{41} & & & a_{44} \end{vmatrix}$$

For a proper Lorentz Trans this Det = 1.

If no transformation

$$Det = \begin{vmatrix} 1 & & & \\ & 1 & & \\ & & 1 & \\ & & & 1 \end{vmatrix} = 1$$

If time alone is reversed

$$Det = \begin{vmatrix} 1 & & & \\ & 1 & & \\ & & 1 & \\ & & & -1 \end{vmatrix} = -1$$

The quantity $\psi^{+} \gamma_1 \gamma_2 \gamma_3 \gamma_4 \psi$ behaves like a scalar except that it changes sign as $t \to -t$. It is called a <u>pseudo scalar</u>.

We now investigate $\psi^+ A_\lambda \psi$

$$\psi \quad A_\lambda = \gamma_\mu \gamma_\nu \gamma_\rho$$

$$A'_\lambda = \sum_\mu b_{\lambda\mu} A_\mu$$

It can be shown that $b_{\lambda\mu}$ is the $\lambda\mu$ minor of the determinant of the a's.

$$D = \sum_\mu a_{\lambda\mu} b_{\lambda\mu} = \pm 1$$

$$\sum_\mu a_{\lambda\mu} b_{\nu\mu} = 0$$

We can identify the above sums with the orthogonality relations for the b's

If $b_{\lambda\mu} = +a_{\lambda\mu}$ the trans is proper

If $b_{\lambda\mu} = -a_{\lambda\alpha}$ the trans is improper

$\psi^+ \gamma_\mu \gamma_\nu \gamma_\rho \psi$ is a pseudovector.

Not all the quantities we have discussed have any physical meaning. However, if there were fields which transformed the way they do we could incorporate them into the Dirac Eq. by multiplying them by the appropriate γ products to make an invariant.

A fifth anti commuting matrix

$$\gamma_5 = \gamma_1 \gamma_2 \gamma_3 \gamma_4$$

$$\gamma_\mu \gamma_5 + \gamma_5 \gamma_\mu = 0$$

Oct 22.

Spicial Problems

1) Potential depending on one coord. $V = V(z)$

$\frac{\partial}{\partial t}, \frac{\partial}{\partial x}, \frac{\partial}{\partial y}$

$E \quad p_x \quad p_y$ = constants of motion. It is convenint to

transform the Dirac eq to a system in which $p_x' = p_y' = 0$. We have:

$$E\psi = c\,\underline{\alpha}\cdot\underline{p}\,\psi + V\psi + \beta mc^2\psi$$

$$E\psi = -i\hbar c\,\alpha_2 \frac{\partial\psi}{\partial z} + V\psi + \beta mc^2\psi$$

$$\alpha_2 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} \qquad \beta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

$$(E - mc^2)\psi_1 = V\psi_1 \overset{\oplus}{-} i\hbar c \frac{\partial\psi_3}{\partial z}$$

$$(E + mc^2)\psi_3 = V\psi_3 \overset{\oplus}{-} i\hbar c \frac{\partial\psi_1}{\partial z}$$

The equations connecting ψ_2 & ψ_4 are identical with the above except for the circled + signs.

Substituting from the second eq into the first:

$$(E - mc^2 - V)\psi_1 = -\hbar^2 c^2 \frac{\partial}{\partial z}\left(\frac{1}{E + mc^2 - V}\frac{\partial\psi_1}{\partial z}\right)$$

This second order equation is the same for the ψ_2 component. It is independent of spin direction.

Current: $\psi^* \alpha \psi = \psi_1^* \psi_3 + \psi_3^* \psi_1$

$$\psi^* \psi = \psi_1^* \psi_1 + \psi_3^* \psi_3$$

2) Const. Magnetic Field B_z

$$A_y = Bx \quad , \quad A_x = A_y = 0$$

The eq will contain terms:

$$\frac{\partial}{\partial t}, \frac{\partial}{\partial z}, \frac{\partial}{\partial y}, \frac{\partial}{\partial x} + x \alpha_y$$

We may transform $p_z \to 0$ but must carry p_y as a parameter due to the presence of α_y.

Problem: Solve the above system. Find eigenfunctions and eigenvalues.

3) Central Field

Ref Hill & Landshoff; PRS 118; Bethe, Handbuch; Dirac 2nd paper.

$$V = V(r)$$

$$\frac{i}{\hbar c}(E - mc^2 - V)\psi_1 + \frac{\partial \psi_3}{\partial z} + \frac{\partial \psi_4}{\partial x} - i\frac{\partial \psi_4}{\partial y} = 0$$

To solve this problem use the non rel Pauli Eq. to get large components. Then get small components in terms of large. The solution is:

$$u_1 = g(r)\sqrt{\frac{l+m+\frac{1}{2}}{2l+1}}\; Y_{l\, m-\frac{1}{2}}(\theta,\phi)$$

$$u_2 = -g(r)\sqrt{\frac{l-m+\frac{1}{2}}{2l+1}}\; Y_{l\, m+\frac{1}{2}}$$

$$u_3 = i f(r)\sqrt{A}\; Y_{l+1\, m-\frac{1}{2}}$$

$$u_4 = i f(r)\sqrt{B}\; Y_{l+1\, m+\frac{1}{2}}$$

Where A & B constants and

$$\frac{1}{\hbar c}(E - V + mc^2) f = \frac{dg}{dr} - l\frac{g}{r}$$

$$\frac{1}{\hbar c}(E - V - mc^2) g = -\frac{df}{dr} - (l+2)\frac{f}{r}$$

Mag Q.N. $\equiv$ angular momentum about $z = m$

Total angular momentum $= j(j+1)$

where $j = l + \frac{1}{2}$

The max. value of m is $l + \frac{1}{2}$.

otherwise $Y_{l\, m-\frac{1}{2}}$ is not defined

For the coulomb potential $V = -Z\frac{e^2}{r}$ an analytic solution is possible.

$$E = mc^2 \Big/ \sqrt{1 + \left(\frac{\alpha Z}{n - k + \sqrt{k^2 - \alpha^2 Z^2}}\right)^2}$$

$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}$ = fine structure const.

$k = j + 1/2$

This is Sommerfeld fine structure formula. It is valid

for H, He or X-ray spectra.
It is correct even in higher relativistic approximations.
If Z is small, we can expand in powers of αZ

$$E = mc^2 - Ry\frac{Z^2}{n^2} - Ry\frac{\alpha^2 Z^4}{n^3}\left(\frac{1}{k} - \frac{3}{4n}\right)$$

$$+ O\, Ry\, \alpha^4 Z^6 \ldots$$

There is also a solution for $j = l - \frac{1}{2}$. This leads to a different equation, but gives the same result for E. E depends only on j and not on l in a coulomb field. This gives rise to the accidental degeneracy

$$2p \text{ ——— } j = 3/2$$

$$\longrightarrow \quad 2p\ 2s \text{ ——— } j = 1/2$$

$$2s \text{ ——— } j = -1/2$$

Lamb & Rutherford have shown that the 2p and 2s lines are distinct. This cannot be explained by the Dirac Theory. Bethe has a theory which explains this on the basis of the electrons interaction with its electric field.

Oct 24,

The energy of an electron in a coulomb field is:

$$E = mc^2 / \sqrt{1 + \left(\frac{\alpha Z}{n - k + \sqrt{k^2 - \alpha^2 Z^2}}\right)^2}$$

where $k = j + 1/2$. If $j = 1/2$ the term

$\sqrt{k^2 - \alpha^2 Z^2}$ is real only if $\alpha Z < 1$. This is tied in with the fact that if an electron has an energy less than $-mc^2$ it can leak out into the neg.

energy continuum and since the time dependent term in ψ contains a decay part esp to a complex E.

Historically, it was thought that this αZ restriction placed an upper limit of 137 on Z.

Near the origin

$$\psi \sim r^{\sqrt{k^2 - \alpha^2 Z^2} - 1}$$

for $k = 1$

$$\psi \sim r^{-E} \qquad E > 0$$

For $Z = 1$, there is a weak infinity at the origin.

$$\psi \sim \left(\frac{r}{a}\right)^{-\frac{1}{2}\alpha^2} \qquad a = \text{Bohr radius}$$

$$r = \frac{e^2}{mc^2} \quad ! \quad \frac{r}{a} = \alpha^2$$

$$\psi \sim \alpha^{-\alpha^2} = 137^{\frac{1}{137^2}} = e^{\frac{1}{4000}}$$

All we really need require of V is that $\int |V|^2 d\tau$ be finite.

Relativity correction for the Pauli Theory.

The Pauli Eq. may be obtained from the Dirac equation by expanding in powers of c^{-1} and neglecting powers greater than 2. The result is:

$$\left(W - V - \frac{\hbar^2}{2m}\nabla^2 - \frac{1}{2mc^2}(W-V)^2 + \left(\frac{\hbar}{2mc}\right)^2 \frac{dV}{dr}\frac{d}{dr} - \frac{1}{r}\underline{M}\cdot\underline{\sigma}\right)\chi = 0$$

Ref Bethe, Handbuch.

Oct 27

Relativistic Scattering

There is no rel equation parallel to the Schrodinger equation for the many electron atom. In rel a value of the time must be associated with each electron. It is not clear what this means.

We can ask for the prob of $\bar{r}_1, t_1$ and $\bar{r}_2 t_2$ if no light signal can get from $\bar{r}_1$ to $\bar{r}_2$ in the time $|t_2 - t_1|$. i.e. $\psi(\bar{r}_1 t_1, \bar{r}_2 t_2)$ is defined if $|\bar{r}_1 - \bar{r}_2| > c|t_1 - t_2|$ If this is not the case an interaction between the electron is possible. There is no solution to this difficulty. Approximations are made:

1) We can start with the Schrodinger approximation and

add terms of order $\frac{v^2}{c^2}$. For two electron the interaction will be of the form $V = \frac{1}{r} + \frac{v_1 \cdot v_2}{rc^2} + \frac{v_1 \cdot r \; v_2 \cdot r}{r^3 c^2}$. This can be extended to many electrons by considering the interaction between pairs. This approx. holds as long as $\underline{v^2 < c^2}$.

Breit has solved the Helium atom in this way. The spectrum of Helium differs from that of other atoms because the electronic interaction is as important as the nuclear interaction.

2) We can start with the free particle equation and consider a <u>small interaction</u>. This leads to the Born approximation.

For $V = V(r)$

$$E\psi = c\underline{\alpha}\cdot\underline{p}\psi + \beta mc^2\psi + V\psi$$

Let $\psi = \psi_0 + \psi_1$ and neglect $\psi_1 V$.

$$(E - c\underline{\alpha}\cdot\underline{p} - \beta mc^2)\psi_1 = V\psi_0$$

Multiply by $(E + c\underline{\alpha}\cdot\underline{p} + \beta mc^2)$

$$(E^2 - c^2p^2 - m^2c^4)\psi_1 = (E + c\underline{\alpha}\cdot\underline{p} + \beta mc^2)V\psi_0 = F(r)$$

Solved by Evans Method

$$\psi_1(\underline{r}) = \int F(r')\frac{e^{ik|\underline{r}-\underline{r}'|}}{|\underline{r}-\underline{r}'|}\,d\tau'$$

where $k = \sqrt{E^2 - m^2c^4}/\hbar c = p_0/\hbar$

<u>Scatter of an electron by a potential</u>

This problem can be solved by separating the Dirac eq in spherical coordinates then combining the solutions in the form of an incident plane

wave plus out going spherical harmonics. This procedure gives the scattering function $|f(\theta)|^2$. The problem has been treated by Mott for a coulomb field. The scattering function for a given angle depends on the spin direction. One should therefore be able to detect polarization by two 90° scatterings. At 100 KV the polarization should be about 10%. No one has yet succeeded in observing any polarization. The reason is not understood.

A second way of treating scattering is to start with the general formula

$$d\sigma = \frac{2\pi}{\hbar} |P_E| V_{P.P}|^2 d\omega$$

where in relativity (ovvi)

$$V_{P_0P} = \int V(r)\, e^{\frac{i}{\hbar}(P_0 - P)\cdot r} \left(u_P^* u_{P_0}\right) d\tau$$

The integral breaks up into the Schroedinger V_{P_0P} times a sum over the spins of the initial and final states of $u_P^* u_{P_0}$

Oct 29

$$(V_{P_0P})_{Rel} = (V_{P_0P})_{Echo} \sum_{spin} u_P^* u_{P_0}$$

In summing over the spins we want to consider only positive energy states, we want to average over the spins of the initial state and sum over the spins of the final state. We write

$$\frac{1}{2} \sum_{spin\, P_0} \sum_{spin\, P} \left| u_{Ps}^* u_{P_0 s_0} \right|^2$$

For each p there are 4 solutions, 2 pos E and 2 neg E

$$s = \underbrace{1\ 2}_{+E} \quad \underbrace{3\ 4}_{-E}$$

These solutions form a complete

orthonormal set. We can expand our initial wave function in terms of them.

$$\omega_p = \sum_{s=1}^{4} a_s u_{ps}$$

$$\sum_{s=1}^{4} |u_{ps}^* \omega_p|^2 = \sum_{s=1}^{4} (\omega^* u_{ps})(u_{ps}^* \omega) = \omega_p^* \omega_p$$

We want to sum only over pos energy $s = 1, 2$. To do this we introduce an operator O_s due to Casimir. O_s is the <u>projection operator</u>

$$O_s^+ u_{ps} = u_{ps} \quad s = 1\,2$$
$$O_s^+ u_{ps} = 0 \quad s = 3\,4$$

We find O_s^+ as follows. For pos energy

$$E = + \sqrt{p^2c^2 + m^2c^4}$$

$$E u_{ps} = (c\underline{\alpha} \cdot \underline{p} + \beta m c^2) u_{ps} \quad s = 12$$
$$-E u_{ps} = (c\underline{\alpha} \cdot \underline{p} + \beta m c^2) u_{ps} \quad s = 34$$

For this it is obvious that if we take

$$O^+ = (E + \underline{\alpha}\cdot p c + \beta m c^2)/2E$$

then

$$O^+ u_{ps} = u_{ps} \qquad s = 1\,2$$
$$O^+ u_{ps} = 0 \qquad s = 3\,4$$

We can also define an O^- which singles out the neg energy states

$$O^- = 1 - O^+$$
$$= (E - \underline{\alpha}\cdot p c - \beta m c^2)/2E$$

For an arbitrary ω we can find the positive and neg energy components by applying O^+ or O^-. The momentum must be specified.

In terms of O we may write

$$\sum_{s=1}^{2} |u_{ps}^* \omega|^2 = \sum_{s=1}^{4} (\omega^* O^+ u_{ps})(u_{ps}^* \omega)$$

$$= \omega^* O_p^+ \omega = u^*_{p_0 s_0} O^+ u_{p_0 s_0}$$

The average over spins of the initial wave function yields

$$\frac{1}{2} \sum_{s_0=1}^{2} \left(u^*_{p_0 s_0} O_p^+ u_{p_0 s_0} \right)$$

In this average $E \to E$

$$\alpha \to v_0/c$$

$$\beta \to mc^2/E$$

In terms of O

$$\text{Av over } s_0 = \frac{1}{2} \sum_{s_0=1}^{4} \left(u^*_{p_0 s_0} O_p^+ O_{p_0}^+ u_{p_0 s_0} \right)$$

The operator $O_p^+ O_{p_0}^+$ can be expanded in terms of the 16 O products

$$O_p^+ O_{p_0}^+ = a + b_\mu \alpha_\mu + c_{\mu\nu} \alpha_\mu \alpha_\nu + \dots$$

In the sum only the constant term (unit matrix times a) will give a result different from

zero. This can be seen as follows: The spur of a matrix A is invariant to the transformation SAS^{-1}. By choosing S properly, we can transform the ψ_{ps} into a set of four one column matrices in each of which only one element is different from zero. If this is done our sum over the spins reduces to a sum over the diagonal elements. Since the unit matrix is the only one having a spur diff. from zero, it will be the only one which gives anything.

Our sum over the initial spins will be four times the constant term in $O_p^+ O_{p_0}^+$, one from each value of the spin.

$$\text{Low energy } S = \frac{1}{2}\,4\,\frac{(E_0 E + c^2 \vec{p}\cdot\vec{p}_0 + m^2c^4)}{4E_0E} +$$

(terms in α & β = 0)

The projection operator is the same as the operator we used to get the energy equation in our first treatment of the scattering problem.

Problem: Calc explicitly the scattering of an electron by a potential for.

a) Stationary Born Approx.

b) Non " " "

Then specify $V = -\frac{Ze^2}{r}$

2. Do a & b for the K G equation (neglect V^2 terms)

Find $d\sigma$ as a function of θ and E. Discuss diff between K G and

Dirac Eq.

Scattering of one electron by another

We shall use the scalar and vector potential produced by one electron, and determine its effect on the other.

Oct 31, 1997

Electron 1 produces the field

" 2 is scattered by the field.

$$\psi_1 \rightarrow \psi_1'$$

$$\rho = \psi_1'^* \psi_1 \qquad j = c\,\psi_1'^* \alpha \psi_1$$

Assume ψ_1 a plane wave

$$\psi_1 = u_1 e^{\frac{i}{\hbar}(p_1 \cdot r_1 - E_1 t)}$$

$$\rho = e\, u_1'^* u_1 e^{\frac{i}{\hbar}\left[(p_1 - p_1')\cdot r_1 - (E_1 - E_1')\frac{t}{c}\right]}$$

$$j = e\, c\,(u_1'^* \alpha u_1) \quad "$$

The field equations are

$$\Box \phi = -4\pi\rho$$

$$\Box \underline{A} = -4\pi \underline{j}/c$$

For plane wave dependence we can integrate these equations. Try

$$\phi(r) = \frac{4\pi\rho(r)\,k^2}{(\underline{p}_i - \underline{p}_i')^2 - (E_i - E_i')^2/c^2}$$

$$\nabla^2\phi(r) = -\phi\,\frac{(\underline{p}_i - \underline{p}_i')^2}{k^2}$$

$$-\frac{1}{c^2}\frac{\partial\phi}{\partial t^2} = +\frac{1}{c^2}\phi\,\frac{(E_i - E_i')^2}{k^2}$$

$$\Box\phi = -\phi\left[(\underline{p}_i - \underline{p}_i')^2 - (E_i - E_i')^2\right]/k^2 = -4\pi\rho$$

O.K.

$$\underline{A}(r) = 4\pi\,\underline{j}\,\frac{k^2}{(\underline{p}_i - \underline{p}_i')^2 - (E_i - E_i')^2/c^2}$$

The Hamiltonian for the system is:

$$H = H(\text{no field}) + \left[e\phi - e\underline{\alpha}\cdot\underline{A}\right]$$

In treating the problem we consider the bracketed term as

a perturbation.

$$\#\text{ of processes per sec} = \frac{2\pi}{\hbar}\left|\int \psi_2^{*} V \psi_2\right|^2 \rho_E$$

This must be independent of the time.

$$\psi_2^{*}\psi_2 \sim e^{-\frac{i}{\hbar}(E_2 - E_2')t}$$
$$V \sim e^{-\frac{i}{\hbar}(E_1 - E_1')t}$$

Hence $E_2 - E_2' = -(E_1 - E_1')$

$$E_2 + E_1 = E_2' + E_1'$$

Also if the integral is not to be zero, the integrand must be independent of r or the integration over space will be zero.

$$V(r_2) \sim e^{\frac{i}{\hbar}(\vec{p}_1 - \vec{p}_1')\cdot r_2}$$
$$\psi_2'^{*}\psi_2 \sim e^{\frac{i}{\hbar}(\vec{p}_2 - \vec{p}_2')\cdot r_2}$$

Hence $\vec{p}_1 - \vec{p}_1' = -(\vec{p}_2 - \vec{p}_2')$

$$\vec{p}_1 + \vec{p}_2 = \vec{p}_1' + \vec{p}_2'$$

The integration over space just

gives the volume. The integrand is now of the form

$$u_2'^{*} u_2 \, \rho - (u_2'^{*} \underline{\alpha} u_2) \cdot \underline{A}$$

$$\rho \sim u_1'^{*} u_1 \qquad A \sim (u_1'^{*} \underline{\alpha} u_1)$$

Heitler gives for the # of process per sec.

$$\frac{2\pi}{\hbar} H^2 \rho_E$$

where ρ_E refers to a unit volume.

and

$$H = \frac{4\pi \hbar^2 c^2 c^2}{(P_1 - P_1')^2 - (E_1 - E_1')^2} \left[(u_1'^{*} u_1)(u_2'^{*} u_2) - (u_1'^{*} \underline{\alpha} u_1) \cdot (u_2'^{*} \underline{\alpha} u_2) \right]$$

This is symmetric in 1 & 2 as it should be.

The first factor is a relativistic invariant (square of momentum change 4 vector)

The second factor would be a scalar invariant except for the way in which we have normalized. Instead of $u_1^{+} u_1 = 1$ we have $u_1^{*} u_1 = 1$ because

we want charge to be conserved. What we have is a (relativistic invariant) $\sqrt{E_1 E_1' E_2 E_2'}$
(Consider $u_1'' \beta u_1$. Show this equals rel invar $/ \sqrt{E_1 E_1'}$

Scatter x-section

equals # of process per sec divided by the current. For unit density $j = v$.

The scattering x-section will be contracted in an system moving $\pm$ to the direction of motion of the incident particle. Therefore we consider only transformations in the direction of motion. In c m system.

$v_{1z} \rightarrow \quad \leftarrow v_{2z}$

$$\text{x-sec.} = \frac{2\pi}{\hbar(v_{1z} - v_{2z})} |H|^2 \frac{1}{(2\pi\hbar)^3} \frac{d p_{1x}' d p_{1y}' d p_{1z}'}{d(E_1' + E_2')}$$

where $\frac{1}{(2\pi\hbar)^3}$ is the no. of states

per unit volume in momentum space for a unit cube and $dp_{1x}' dp_{1y}' dp_{1z}' / d(E_1' + E_2')$ is the volume in momentum space per unit energy of the final state.

$$dp_{1x}' dp_{1y}' dp_{1z} / d(E_1' + E_2') = dp_{1x}' dp_{1y}' / \left(\frac{\partial E_1'}{\partial p_{1z}'} + \frac{\partial E_2'}{\partial p_{1z}'} \right)$$

Let us investigate the transformation of $\frac{\partial E_1'}{\partial p_{1z}'} + \frac{\partial E_2'}{\partial p_{1z}'}$.

We have $dp_{1z}' = -dp_{2z}'$ Let $c = 1$

$$\frac{\partial E_1'}{\partial p_{1z}'} - \frac{\partial E_2'}{\partial p_{2z}'} = \frac{p_{1z}'}{E_1'} - \frac{p_{2z}'}{E_2'}$$

$$= E_2' p_{1z}' - E_1' p_{2z}' / E_1' E_2'$$

Lorentz Trans in z direction

$$\tilde{E}_1 = \gamma E_1 + \gamma \beta p_{1z} \qquad \gamma = \frac{1}{\sqrt{1-\beta^2}}$$

$$\tilde{p}_{2z} = \gamma p_{2z} + \gamma \beta E_2$$

$$\tilde{E}_1 \tilde{p}_{2z} = \gamma^2 E_1 p_{2z} + \gamma^2\beta(E_1 E_2 + p_{1z}p_{2z}) + \gamma^2\beta^2 E_2 p_{1z}$$

$$\tilde{E}_1 \tilde{p}_{2z} - \tilde{E}_2 \tilde{p}_{1z} = \gamma^2(1-\beta^2)E_1 p_{2z} - \gamma(1-\beta^2)E_2 p_{1z}$$

$$= E_1 p_{2z} - E_2 p_{1z}$$

$$\frac{\partial E_1'}{\partial p_{1z}} + \frac{\partial E_2'}{\partial p_{2z}} = \text{rel invariant} / E_1' E_2'$$

$$(V_{1z} - V_{2z}) = \frac{\partial E_{1z}}{\partial p_{1z}} - \frac{\partial E_{2z}}{\partial p_{2z}} = \text{rel invariant} / E_1 E_2$$

Combining the two above expression with H^2 in the X section formula, we find that the X-section is invariant to transformations in the direction of motion. This justifies our treating such problems in the center of mass system.

$$2\pi\sigma(\theta)\sin\theta\,d\theta = 4\pi\left(\frac{e^2}{mv^2}\right)^2 \frac{\gamma+1}{\gamma^2}\,dx\,f(x)$$

where: $\gamma = \dfrac{E}{mc^2}$ E in c m sys.

$x = \cos\theta^*$.

θ^* = scattering $\angle$ in c m sys.

$$f(x) = \left[\frac{4}{(1-x^2)^2} - \frac{3}{(1-x^2)} + \left(\frac{\gamma-1}{2\gamma}\right)\left(1 + \frac{4}{1-x^2}\right)\right]$$

In lab system

$$\cos\theta^* = (2-(\gamma+3)\sin^2\theta)/(2+(\gamma-1)\sin^2\theta)$$

The first 2 terms in $f(x)$ give the classical result including exchange. The last term includes the effect of spin. For small $\angle$'s, the first term is most important. To observe the effect of spin one must go to large $\angle$ scattering. For 90° scattering the terms have the magnitudes given below

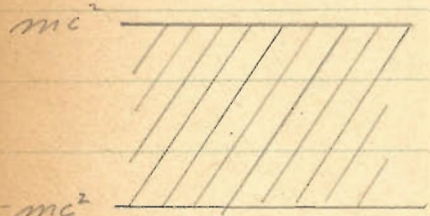
$$4 - 3 + \underset{\text{spin}}{\tfrac{5}{1/4}}$$

If positrons are scattered only the exchange, 2nd term is different.

Nov 3

Neg Energy Solutions of Dirac Eq

$E > mc^2$



$E < -mc^2$

$$\bar{V} = \frac{dE}{dp}\frac{\bar{p}}{p}$$

$$E = -\sqrt{p^2+m^2} \qquad c = 1$$

$$\bar{V} = \frac{dE}{dp}\frac{\bar{p}}{p} = -\frac{\bar{p}}{\sqrt{p^2+m^2}}$$

V is opposite in direction to $\bar{p}$

$$F_x = \frac{dp_x}{dt} \approx -\frac{dV}{dt} = -a$$

Hence a force in one direction causes an increase in velocity in the opposite direction. These negative energy electrons are called Donkey electrons by Gamow. In a collision a donkey electron

is accelerated. This rapidly leads to infinite velocities.

In classical mechanics the negative energy continuum does not worry us because we can postulate that all electrons are in positive energy states and there is then no possibility of a transition to the negative energy states.

In Q.M., the electrons can make transitions from the positive to the negative energy states. Such a transition will occur in the order of 10^{-10} sec. This means that it would be difficult to have any electrons in positive energy states unless the negative energy states were all filled. Since the # of neg energy states is infinite this

leads to difficulties: inf. charge, mass, energy; polarizability of the vacuum.

Positron

A negative E. electron can be induced to make a transition to the positive energy state by absorption of a γ ray. (Pair production) Oppinheimer has shown that the "hole" left in the negative energy state has all the properties of a positive electron, positron. The difficulty of infinite charge can be remedied by making a symmitric theory in which electrons are "holes" in a positive charge distribution.

Radiation Theory Heitler

Classical Theory in Hamiltonian Form.

$$\nabla^2 \underline{A} - \frac{1}{c^2}\ddot{\underline{A}} = 0$$

$$\nabla^2 \phi - \frac{1}{c^2}\ddot{\phi} = 0$$

$$\nabla \cdot \underline{A} = 0$$

Suppose $\underline{A}$ is periodic in a box $L \times L \times L$. We can expand in normal modes

$$\underline{A} = \sum_\lambda q_\lambda(t)\, \underline{A}_\lambda$$

$$\underline{A}_\lambda = \sqrt{\frac{8\pi}{\omega_\lambda}}\, c\, \underline{e}_\lambda \cos \underline{k}_\lambda \cdot \underline{r}$$

where $k_{\lambda x} = \frac{2\pi n_x}{L}$, etc.

and $\underline{e}_\lambda$ is a unit vector $\perp \underline{k}_\lambda$

now 5

The energy of the field is:

$$U = \frac{1}{8\pi}\int (E^2 + H^2)\, d\tau$$

$$\underline{E} = -\frac{1}{c}\dot{\underline{A}} = -\frac{1}{c}\sum_\lambda \dot{q}_\lambda \underline{A}_\lambda$$

$$\underline{H} = \operatorname{curl} \underline{A} = \sum_\lambda \dot{q}_\lambda \operatorname{curl} \underline{A}_\lambda$$

(These equations hold for a pure radiation field where there is no scalar potential)

$$\frac{1}{8\pi} \int \underline{E}^2 d\tau = \frac{1}{8\pi} \frac{1}{c^2} \sum_\lambda \sum_\mu \dot{q}_\lambda \dot{q}_\mu \int \underline{A}_\lambda \cdot \underline{A}_\mu \, d\tau$$

$$= \frac{1}{8\pi c^2} \sum_\lambda \sum_\mu \dot{q}_\lambda \dot{q}_\mu \frac{8\pi c^2}{\omega_\lambda} \frac{1}{2} \omega_\lambda \delta_{\lambda\mu}$$

$$= \frac{1}{2} \sum_\lambda \dot{q}_\lambda^2$$

$$\frac{1}{8\pi} \int H^2 d\tau = \frac{1}{8\pi} \sum_\lambda \sum_\mu q_\lambda q_\mu \int \operatorname{curl} \underline{A}_\lambda \cdot \operatorname{curl} \underline{A}_\mu \, d\tau$$

$$\int \operatorname{curl} A_\lambda \cdot \operatorname{curl} A_\mu \, d\tau$$

$$= \int \nabla \cdot (A_\mu \times \nabla \times A_\lambda) \, d\tau + \int \underline{A}_\mu \cdot \operatorname{curl} \operatorname{curl} \underline{A}_\lambda \, d\tau$$

$$= \underbrace{\int (\underline{A}_\mu \times \nabla \times \underline{A}_\lambda) \cdot d\underline{\sigma}}_{0} + \underbrace{\int \nabla (\nabla \cdot \underline{A}_\lambda) \cdot \underline{A}_\mu \, d\tau}_{0 \text{ since } \nabla \cdot \underline{A}_\lambda = 0}$$

$$- \int \underline{A}_\mu \cdot \nabla^2 \underline{A}_\lambda \, d\tau$$

We have: $\nabla^2 \underline{A}_\lambda + k_\lambda^2 A_\lambda = 0$

$$\frac{1}{8\pi} \int H^2 d\tau = \frac{1}{8\pi} \sum_\lambda \sum_\mu q_\lambda q_\mu \int \underline{A}_\mu \cdot k_\lambda^2 A_\lambda \, d\tau$$

$$\frac{1}{8\pi}\int H^2 d\tau = \frac{1}{2}\sum_\lambda c^2 k_\lambda^2 q_\lambda^2$$

$$= \frac{1}{2}\sum_\lambda v_\lambda^2 q_\lambda^2$$

$$U = \frac{1}{2}\sum_\lambda \left[\dot{q}_\lambda^2 + v_\lambda^2 q_\lambda^2\right]$$

This is the classical expression for the energy of an assembly of oscillators.

$$p_\lambda = \partial T/\partial \dot{q}_\lambda = \frac{\partial}{\partial \dot{q}_\lambda}\frac{1}{2}\sum \dot{q}_\lambda^2$$

$$= \dot{q}$$

$$H(pq) = \frac{1}{2}\sum_\lambda \left[p_\lambda^2 + v_\lambda^2 q_\lambda^2\right]$$

$$\dot{p}_\lambda = -\frac{\partial H}{\partial q_\lambda} = -v_\lambda^2 q_\lambda$$

$$\dot{p}_\lambda = \ddot{q}_\lambda$$

$$\ddot{q}_\lambda + v_\lambda^2 q_\lambda = 0$$

—— o ——

We can also expand $\underline{A}$ in terms of running waves

$$\underline{A}_\lambda = \frac{\sqrt{4\pi}}{\sqrt{HN}} c\, \underline{e}_\lambda\, e^{i\underline{k}_\lambda \cdot \underline{r}}$$

$$\int \underline{A}_\lambda \cdot \underline{A}_\mu^* \, d\tau = 4\pi c^2 \delta_{\lambda\mu}$$

$$\underline{A} = \sum_\lambda \left[q_\lambda(t) \underline{A}_\lambda + q^*(t) \underline{A}_\lambda^* \right]$$

In order to put the equations into Hamiltonian form we define

$$Q_\lambda = q_\lambda + q_\lambda^*$$
$$P_\lambda = \dot{q}_\lambda - \dot{q}_\lambda^*$$

No of oscillators per unit frequency

$$= \left(\frac{L}{2\pi}\right)^3 dk_x \, dk_y \, dk_z \sum_{\text{dir pol}}$$

$$= \frac{4V}{(2\pi)^3} k^2 \, dk \, d\omega \sum_{\text{dir pol}}$$

Field Equations with charges and current

$$\text{I} \qquad \nabla^2 \underline{A} - \frac{1}{c} \ddot{\underline{A}} = -4\pi \frac{\underline{j}}{c} = 4\pi \rho \underline{v}$$

$$\text{II} \qquad \nabla^2 \phi - \frac{1}{c} \ddot{\phi} = 4\pi \rho$$

III $\quad \nabla \cdot \underline{A} + \frac{1}{c} \dot{\phi} = 0$

Expand in normal modes

$$\underline{A} = \sum_\sigma q_\sigma \underline{A}_\sigma + \sum_\lambda q_\lambda \underline{A}_\lambda$$

$$\phi = \sum_\sigma a_\sigma \phi_\sigma$$

σ refers to the component in the direction of propagation. The conditions:

$$v_\sigma q_\sigma = \dot{a}_\sigma$$

and $\quad \underline{A}_\sigma = \frac{1}{k_\sigma} \nabla \phi_\sigma$

are equivalent to the Gauge equation, III

$$= \sum_\sigma \left[q_\sigma \nabla \cdot \underline{A}_\sigma + \frac{1}{c} \dot{a}_\sigma \phi_\sigma \right]$$

$$= \sum_\sigma \left[q_\sigma \nabla \cdot \underline{A}_\sigma + q_\sigma k_\sigma \phi_\sigma \right]$$

$$\nabla \cdot \underline{A}_\sigma = \frac{1}{k_\sigma} \nabla^2 \phi_\sigma = -k_\sigma \phi_\sigma$$

$$= \sum_\sigma \left[q_\sigma (-k_\sigma \phi_\sigma) + q_\sigma k_\sigma \phi_\sigma \right] = 0$$

Expanding $\underline{I}$ in terms of $\underline{A}_0$ and $\underline{A}_2$, multiply by $-A_2/4\pi$, and integrating over all space yields

A) $$\ddot{q}_2 + \nu_2^2 q_2 = \frac{1}{c}\int \rho \underline{v} \cdot \underline{A}_2(\bar{r})\, d\tau$$

$$= \frac{1}{c}\sum_k e_k \underline{v}_k \cdot \underline{A}_2(k)$$

where e_k and $\underline{v}_k$ are the charge and velocity of the k^{th} particle. (e is the magnitude of the electronic charge. The sign was taken care of in I)

Similarly:

B) $$\ddot{q}_0 + \nu_0^2 q_0 = \frac{1}{c}\sum_k e_k \underline{v}_k \cdot \underline{A}_0(k)$$

C) $$\ddot{a}_0 + \nu_0 a_0 = \sum_k e_k \phi_0(k)$$

Is the condition $\nu_0 q_0 = \dot{a}_0$ (all t) compatible with our equations? Differentiate C) with respect to time:

$$\ddot{a}_\sigma + v_\sigma^2 \dot{a}_\sigma = \sum_k c_k \dot{\rho}_\sigma = \sum_k c_k \nabla \dot{q}_\sigma \cdot \underline{v}_k$$

$$= \sum_k c_k k_\sigma \underline{A}_\sigma \cdot \underline{v}_k$$

$$\dddot{a}_\sigma + v_\sigma^2 \dot{a}_\sigma = v_\sigma (\ddot{q}_\sigma + v_\sigma^2 q_\sigma)$$

$$(D^2 + v_\sigma^2)(\dot{a}_\sigma - v_\sigma q_\sigma) = 0$$

If initially $(\dot{a}_\sigma - v_\sigma q_\sigma) = 0$ and $\frac{d}{dt}(\dot{a}_\sigma - v_\sigma q_\sigma) = 0$, then $\dot{a}_\sigma - v_\sigma q_\sigma$ will be identically zero for all time.

Prob. 7.

The Hamiltonian for a particle in an E.M. field is:

$$H_k = \beta m c^2 + e\phi(k) + \underline{\alpha}_k \cdot (c\underline{p}_k - e\underline{A})$$

or

$$H_k = e\phi(k) + \sqrt{m^2 c^4 + (c\underline{p}_k - e\underline{A}(k))^2}$$

If we add to this expression the Hamiltonian for the

unperturbed radiation oscillators we get the correct radiation.

Hamiltonian of the Radiation field

$$H_\lambda = \frac{1}{2}(p_\lambda^2 + \nu_\lambda^2 q_\lambda^2)$$

$$\dot{q}_\lambda = \frac{\partial H}{\partial p_\lambda} = p_\lambda \qquad \frac{\partial H}{\partial q_\lambda} = -\frac{\partial (H_\lambda + \sum H_k)}{\partial q_\lambda}$$

$$\ddot{q}_\lambda = \dot{p}_\lambda = -\nu^2 q_\lambda + \sum_k e_k \underline{a}_k \cdot \underline{A}_\lambda(k)$$

$$H_\sigma = \frac{1}{2}(p_\sigma^2 + \nu_\sigma^2 q_\sigma^2) - \frac{1}{2}(b_\sigma^2 + \nu_\sigma^2 a_\sigma^2)$$

The minus sign is necessary for relativistic invariance. It comes in in the same way as the minus sign in the expression $H = A^2 - \phi^2$. It gives the possibility of a neg energy catastrophy. This is taken care of by the initial conditions which make it impossible to have a scalar

potential without a longitudinal vector potential.

$$\dot{a}_\sigma = \frac{\partial H}{\partial b_\sigma} = -b_\sigma$$

$$\ddot{a} = -\dot{b}_\sigma = \frac{\partial H}{\partial a_\sigma} = -v_\sigma^2 a_\sigma + \sum_k e_k \ell_\sigma(k)$$

The above equations obtained using the Hamiltonian $H = (H_2 + \sum_k H_k)$ give the same result as we obtained last time.

The part of the Hamiltonian depending on a_σ is:

$$H_{s\sigma} = \tfrac{1}{2}(p_\sigma^2 + v_\sigma^2 q_\sigma^2) - \tfrac{1}{2}(b_\sigma^2 + v_\sigma^2 a_\sigma^2) + \sum_k e_k \ell_\sigma(k) a_\sigma$$

but $\begin{cases} -b_\sigma = \dot{a}_\sigma = v_\sigma q_\sigma \\ \dot{q}_\sigma = \frac{\partial H_\sigma}{\partial p_\sigma} = p_\sigma = \ddot{a}/v_\sigma \end{cases}$

$$H_{s\sigma} = \tfrac{1}{2}(p_\sigma^2 - v_\sigma^2 a_\sigma^2) + e\sum e_k \ell_\sigma(k) a_\sigma$$

$$p_\sigma = \frac{\ddot{a}_\sigma}{v_\sigma} = -v_\sigma a_\sigma + \frac{1}{v_\sigma} \sum c_k \phi_\sigma(k)$$

$$p_\sigma^2 = v_\sigma^2 a_\sigma^2 - 2 \sum_k c_k a_\sigma \phi_\sigma(k) + \frac{1}{v_\sigma^2} \left(\sum c_k \phi_\sigma(k) \right)^2$$

$$H_{S\sigma} = \frac{1}{2} v_\sigma^2 \sum_{ik} c_i c_k \phi_\sigma(i) \phi_\sigma(k)$$

$$H_S = \sum_\sigma H_{S\sigma} = \frac{1}{2} \sum_{ik} c_i c_k H_{ik}$$

where $H_{ik} = \sum_\sigma \frac{1}{v_\sigma^2} \phi_\sigma(r_i) \phi(r_k)$

$$\nabla_i^2 H_{ik} = \sum_\sigma \frac{1}{v_\sigma^2} \nabla_i^2 \phi(r_i) \phi(r_k)$$

$$\nabla_i^2 \phi_\sigma(r_i) + \frac{v_\sigma^2}{c^2} \phi_\sigma = 0$$

$$\nabla_i^2 H_{ik} = -\frac{1}{c^2} \sum_\sigma \phi_\sigma(i) \phi_\sigma(k)$$

$$\nabla_i^2 H_{ik} = -4\pi \delta(\underline{r}_i - \underline{r}_k)$$

Green function solution

$$H_{ik} = \int \frac{\delta(\underline{r}' - \underline{r}_k)}{|\underline{r}_i - \underline{r}'|} d\tau'$$

$$= \frac{1}{r_{ik}}$$

$$H_S = \frac{1}{2} \sum_{ik} \frac{c_i c_k}{r_{ik}}$$

Hence the longitudinal waves are equivalent to a coulomb potential. The retardation comes in with the transverse waves.

See Heitler!!

The above equations also serve to eliminate the longitudinal component of $\underline{A}$ in H_k.
We may write the complete Hamiltonian as:

$$H = \sum_k H_k(\text{transverse}) + \sum_\lambda H_\lambda + H_S$$

This gives the correct equations of motion.

Note that H_S contains the interaction of an electron with itself which is infinite. This is one difficulty. There are other infinities connected with the emission and reabsorption of virtual quanta.

It is not evident that H is relativistically invariant.

We can show that this Hamiltonian gives the correct emission of light by an oscillator.

$$H = -\frac{e}{c}(\underline{V}_0 \cos \nu_0 t)\cdot\left(\sum_\lambda q_\lambda \underline{A}_\lambda\right)$$

$$+\frac{1}{2}\sum_\lambda (p_\lambda^2 + \nu_\lambda^2 q_\lambda^2)$$

$$\dot{q}_\lambda = \frac{\partial H}{\partial p_\lambda} = p_\lambda$$

$$\dot{p}_\lambda = -\frac{\partial H}{\partial q_\lambda} = \frac{e}{c} V_0 |A_\lambda| \cos \nu_0 t \cos\Theta - \nu_\lambda^2 q_\lambda$$

$$\ddot{q} + \nu_\lambda^2 q_\lambda = \frac{e}{c} b_\lambda \cos \nu_0 t$$

where $\Theta = \underset{\text{polarization}}{\measuredangle}\ \underline{A}$ and $\underline{V}$

$$b_\lambda = \frac{e}{c} V_0 |A_\lambda(k)| \cos\Theta$$

$$q_\lambda = \frac{b_\lambda}{\nu_\lambda^2 - \nu_0^2}(\cos \nu_0 t - \cos \nu_\lambda t)$$

Calc the work done by the exciting force.

$$W = \int B_2 \cos \nu_0 t \, \dot{q}_2 \, dt$$

$$= \frac{B_2^2}{\nu_2^2 - \nu_0^2} \frac{\nu_2}{2} \left\{ \frac{1 - \cos(\nu_2 - \nu_0)t}{\nu_2 - \nu_0} + \frac{1 - \cos(\nu_2 + \nu_0)t}{\nu_2 + \nu_0} \right\}$$

$$S = \frac{dW}{dt} = \frac{e^2 \nu_0^2}{8\pi c^3} V_0^2 \sin^2 \Theta \, d\Omega$$

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