Q. M. Sp 1947 I

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THIS BOOK CONTAINS EYE-EASE PAPER

"Easy on the Eyes"

Applications of Q. M.

Bethe Spring Term 1947

Lecture I Feb. 18, 1947

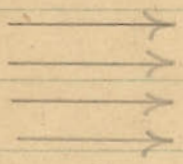
References

1 Collision Theory - Mott & Massey
Atomic Collisions (too detailed
2 Radiation Theory - Heitler
(not enough detail)
3 Transformation Theory and
Matrix Mechanics - Dirac
4 Theory of Atomic Spectra
Condon and Shortley
5 Molecules & Solids - Kemberg;
Mott & Jones; Seitz.

General Text - Kemble,
Quantum Mechanics.

I Collision Theory

Suppose we have a beam of particles incident on a scatterer.



We wish to compute the number of particles per sec. deflected into a solid angle $d\omega$, if the incident beam has unit intensity (1 part / cm^2 - sec). The ratio of scattered particles to incident beam intensity has the dimensions of an area. This ratio is called the scattering X-section. For a rigid classical scatterer: total scattered particles / incident beam intensity = the geometrical X-section of the scatterer perpendicular to the beam.

In general:

$$\frac{\text{total scattered}}{\text{incident beam int}} = \text{total } \times\text{-section}$$

and

$$\frac{\text{scattered in } d\omega}{\text{incident beam int}} = \text{differential } \times\text{-sec.}$$

Types of scattering

1. Elastic scattering – no change in the internal state of the scatterer or incident particle.

2. Inelastic scattering – a change in the internal state of the particle takes place.

Let us assume that the stationary states of the scatterer are known. Therefore the electrostatic potential of the scatterer is known, and the potential energy of interaction

between scatterer and incident particle is known.

$$V + T = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(\underline{r}_1 - \underline{r}_2) = H$$

Introducing the transformation

$$\underline{r} = \underline{r}_1 - \underline{r}_2$$
$$\underline{R} = (m_1 \underline{r}_1 + m_2 \underline{r}_2)/(m_1 + m_2)$$
$$\underline{p}_1 = \underline{p} \frac{m_1}{m_1 + m_2} + \underline{p}$$
$$\underline{p}_2 = \underline{p} \frac{m_2}{m_1 + m_2} - \underline{p}$$

we obtain:

$$H = \frac{\underline{p}^2}{2M} + \frac{\underline{p}^2}{2m} + V(\underline{r}) \qquad M = m_1 + m_2 \quad m = m_1 m_2 / m_1 + m_2$$

In Q.M. $\underline{p} \rightarrow \frac{\hbar}{i} \nabla_R$

$$\underline{p} \rightarrow \frac{\hbar}{i} \nabla_r$$

$$H = -\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2m} \nabla_r^2 + V(\underline{r})$$

$$H\psi = E\psi$$

$$\frac{\hbar^2}{2M}\nabla_R^2\psi + \frac{\hbar^2}{2m}\nabla_r^2\psi + (E - V(\underline{r}))\psi = 0$$

Let $\psi(\underline{R}\,\underline{r}) = \chi(R)\phi(\underline{r})$

$$\frac{\hbar^2}{2M}\nabla^2\chi + E_1\chi = 0$$

This is the equation for the center of mass motion.

$$\frac{\hbar^2}{2m}\nabla^2\phi + (E_2 - V(\underline{r}))\phi = 0$$

Equation for the relative motion of the two particles.

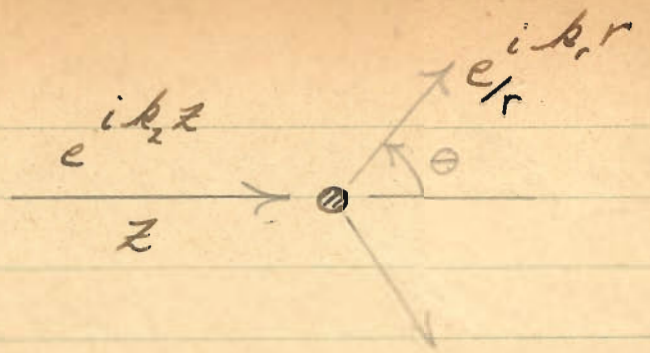
$$E_T = E_1 + E_2$$

Lecture II Feb. 20, 1947

Assume a plane wave

$$e^{ikz} \qquad k = \frac{p}{\hbar}$$

incident on a scatterer.



At large distances from the scatterer the wave function will be

$$\psi = e^{ikz} + e^{ik\cdot r}/r \, f(\theta)$$

where the term $e^{ikr}/r \, f(\theta)$ applies to the scattered particles.
As usual

$$\Psi(\underline{r}t) = \psi e^{-\frac{iEt}{\hbar}}$$

The number of particles going into the solid angle, $d\omega$, per sec will be

$$|\psi_0|^2 v \overbrace{r^2 d\omega}^{dA} = |f(\theta)|^2 \frac{v}{r^2} r^2 d\omega$$

$$= |f(\theta)|^2 v \, d\omega$$

We see from this that $f(\theta)$ must have the dimensions of a length. We have neglected the e^{ikz} part of ψ, since, in practice, a finite beam is incident on the scatterer and the measurements are made well outside this beam. In Q.M. such a beam may be represented by a wave packet

$$e^{ikz} \; e^{-\frac{x^2+y^2}{a^2}}.$$

If the width of the beam, a, $\gg$ than the cross-section, $f(\theta)$ will be approx the same as for an incident plane wave. At large distances outside the beam only the ψ_r function for the scattered particles will

be appreciable.

If the incident current density $|\psi_z|^2 v = V$, the differential scattering x-section will be

$$\sigma_s = |f(\theta)|^2 d\omega$$

The wave equation for a free particle is:

$$\nabla^2 \psi + \underline{k}^2 \psi = 0 \qquad \underline{k} = \frac{\underline{p}}{\hbar}$$

The solution is $\psi = e^{i \underline{k} \cdot \underline{r}}$

In polar coordinates the solution may be written

$$\psi = P_\ell^m(\theta)\, e^{im\phi}\, \frac{U(r)}{kr}$$

This leads to the following diff. equation for $U(r)$

$$\frac{d^2 u}{dr^2} + \left(k^2 - \frac{\ell(\ell+1)}{r^2}\right) u = 0$$

The solution is:

$$u(r) = \sqrt{\frac{\pi kr}{2}}\, J_{n+\frac{1}{2}}(kr)$$

At large distances (large kr)

$$u(r) \approx \sin(kr - \alpha_l)$$

To determine the phase, we may start at the origin and work outward — or we may expand $e^{i\vec{k}\cdot\vec{z}}$ in terms of the polar coordinate solutions. To do this, we choose the polar axis in the z direction. Since $e^{i\vec{k}\cdot\vec{z}}$ independent of ϕ, the expansion in spherical functions will contain only terms with $m = 0$

$$e^{ikz} = e^{ikr\cos\theta} = \sum_{l'} A_{l'} \frac{u_{l'}(r)}{kr} P_{l'}(\theta)$$

To determine the coefficients $A_\ell \frac{U_\ell(r)}{kr}$, multiply by $P_\ell(\theta)\sin\theta$ and integrate over all θ.

$$\int_0^\pi P_\ell(\theta) e^{ikr\cos\theta} \sin\theta \, d\theta$$

$$= \sum_{\ell'} A_{\ell'} \frac{U_{\ell'}(r)}{kr} \int_0^\pi P_\ell(\theta) P_{\ell'}(\theta) \sin\theta \, d\theta$$

$$= \frac{2}{2\ell+1} A_\ell \frac{U(r)}{kr}$$

Since the LHS of the equation is a function of kr, $U(r)$ must also be a function of kr. Make the substitutions $x = kr$; $u = \cos\theta$ in the LHS of the above equation:

$$\int_{-1}^{+1} e^{ixu} P_\ell(u) \, du = \frac{e^{ixu}}{ix} P_\ell(u) \Big|_{-1}^{+1}$$

$$- \int_{-1}^{+1} \frac{e^{ixu}}{ix} P_\ell'(u) \, du$$

Since $P_\ell(u)$ is a polynomial of

order l, it is obvious that if we integrate by parts l times we obtain a polynomial in $\frac{1}{x}$ of $l+1$ terms. For large x we can neglect all but the leading term. We obtain:

$$\int_{-1}^{+1} e^{ixu} P_l(u)\,du \approx \frac{1}{ix}\left[e^{ix} - e^{-ix}(-1)^l\right]$$

$$= \frac{1}{ix} e^{+\frac{\pi i}{2} l}\left[e^{i(x-\frac{\pi l}{2})} - e^{-i(x-\frac{\pi l}{2})}\right]$$

$$= \frac{i^l}{x}\, 2\sin\left(x - \frac{\pi l}{2}\right)$$

$$\frac{2}{2l+1} A_l \frac{U(r)}{kr} \approx \frac{i^l}{kr}\, 2\sin\left(kr - \frac{\pi l}{2}\right)$$

$$\frac{A_l}{2l+1} = i^l \qquad A_l = (2l+1)\, i^l$$

$$U(r) \approx \sin\left(kr - \frac{\pi l}{2}\right)$$

Comparing this expression for $U(r)$ with that obtained from

the differential equation, we find:

$$\alpha_\ell = \frac{\pi \ell}{2}$$

Hence:

$$e^{ikz} = \sum_\ell \frac{(2\ell+1) i^\ell}{kr} u_\ell(kr) P_\ell(\theta)$$

$u_\ell(kr) \equiv U_\ell(r)$ is a solution of the radial wave equation which is zero at the origin.

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We are looking for a solution of the wave equation

$$\frac{\hbar}{2m} \nabla^2 \psi + (E - V(r)) \psi = 0$$

which at large r goes over into a solution of the equation:

$$\nabla^2 \psi + k^2 \psi = 0$$

and which has the form

$$\psi_{as} = e^{ikz} e^{-\frac{x^2+y^2}{a^2}} + \frac{e}{r} f(\theta).$$

Our aim is to compute the function, $f(\theta)$. If a is much larger than the dimensions of the scatter the value of $f(\theta)$ will not be effect if we let $a \to \infty$.

$$\psi_{as} = e^{ikz} + \frac{e}{r} f(\theta)$$

We found last time a formula due to Lord Rayleigh by means of which a plane wave could be expanded in spherical coordinates

$$e^{ikz} = \sum_{\ell} (2\ell+1) i^{\ell} \frac{u_{\ell}(kr)}{kr} P_{\ell}(\theta)$$

where $\frac{d^2 u_{\ell}}{dr^2} + \left(k^2 - \frac{\ell(\ell+1)}{r^2}\right) u_{\ell} = 0$

The phase of U_ℓ is defined by the fact $U_\ell = 0$ at $r = 0$.
Asymtotically as

$$r \to \infty \quad U_\ell \to \sin\left(kr - \frac{\pi \ell}{2}\right)$$

$$\left(\ell = 0 \quad U_0 = \sin kr \right.$$
$$\left. \ell = 1 \quad U_1 = -\cos kr + \frac{\sin kr}{kr} \right)$$

The equation

$$\nabla^2 \psi + \frac{2m}{\hbar^2}(E - V(r))\psi = 0$$

$$U(r) \equiv \frac{2m}{\hbar^2} V(r)$$

$$\nabla^2 \psi + (k^2 - U(r))\psi = 0$$

Has solutions independent of ℓ of the following form

$$\psi = P_\ell(\theta) \frac{V_\ell(r)}{kr}$$

where

$$\frac{d^2 V_\ell}{dr^2} + \left(k^2 - \frac{\ell(\ell+1)}{kr^2} - U(r)\right) V_\ell = 0$$

The equation can be solved

numerically by starting with the conditions $V_\ell = 0$ at $r = 0$.

If at large r

$$k^2 \gg U(r)$$

$$k^2 \gg \ell(\ell+1)/r^2,$$

then

$$V_\ell \to \sin(kr - \alpha_\ell)$$
$$= \sin(kr - \frac{\pi\ell}{2} + \delta_\ell)$$

$\delta_\ell \equiv$ phase for V_ℓ, and must be determined by integration.

Assume the δ_ℓ known. Let

$$\psi = \sum_\ell B_\ell \frac{V_\ell}{kr} P_\ell(\theta)$$

For large r this solution must approach

$$\psi_\infty = e^{ikz} + \frac{e^{ikr}}{r} f(\theta)$$

$$= \sum_\ell \frac{(2\ell+1)}{kr} \frac{i^\ell}{2i} \left[e^{i(kr - \frac{\pi\ell}{2})} - e^{-i(kr - \frac{\pi\ell}{2})} \right] P_\ell(\theta)$$
$$+ \frac{e^{ikr}}{r} f(\theta)$$

For $r \to \infty$

$$\Psi \to \sum_l B_l \frac{1}{kr 2i}\left[e^{i(kr-\frac{\pi l}{2}+\delta_l)} - e^{-i(kr-\frac{\pi l}{2}+\delta_l)}\right] P_l(\theta)$$

$\Psi \to \Psi_{as}$ Comparing the coefficients of $e^{-i(kr-\frac{\pi l}{2})}$ in the expressions for Ψ and Ψ_{as} we find:

$$B_l e^{-i\delta_l} = (2l+1) i^l$$

Solving the equation $\Psi = \Psi_{as}$ for $f(\theta)$ we obtain

$$f(\theta) = \frac{1}{2ik}\sum_l (2l+1) i^l e^{-\frac{i\pi l}{2}}\left[e^{2i\delta_l} - 1\right] P_l(\theta)$$

$$= \frac{1}{2ik}\sum_l (2l+1)(e^{2i\delta_l} - 1) P_l(\theta)$$

This is the Rayleigh scattering formula. It was first derived in Q.M. by Faxin and Holtsmark. It is important that no incident spherical wave be included in the solution. The problem is not defined in this case.

The solution selected must agree with the experimental conditions of the problem.

The dimensions of $f(\theta)$ are those of:

$$\frac{1}{k} = \lambda - \text{cm.}$$

δ_ℓ gives the phase shift due to the potential. If there is no potential $\delta_\ell = 0$ and hence $f(\theta) = 0$. This corresp to no scatterer.

The differential x-section is:

$$d\sigma = |f(\theta)|^2 d\omega$$

The total x-section is:

$$\sigma_T = \frac{2\pi}{(2k)^2} \int \sin\theta d\theta$$

$$\cdot \sum_{\ell\ell'} (2\ell+1)(2\ell'+1)(e^{2i\delta_\ell} - 1)(e^{-2i\delta_{\ell'}} - 1) P_\ell P_{\ell'}$$

We note $\int_0^\pi P_\ell P_{\ell'} \sin\theta d\theta = \frac{2\delta_{\ell\ell'}}{2\ell+1}$

$$|e^{2i\delta_\ell} - 1|^2 = 4\sin^2\delta_\ell$$

$$\sigma_T = 4\pi\lambda^2 \sum_\ell (2\ell+1)\sin^2\delta_\ell$$

The maximum contribution for a given ℓ is:

$$4\pi\lambda^2(2\ell+1)$$

and occurs when $\delta_\ell = \frac{2n-1}{2}\pi$

$\ell \equiv$ angular momentum of the particle in units of $\hbar$. To show that there is some basis for this definition let us study the angular momentum operator L

$$L_z = xp_y - yp_x$$

$$= \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

For a central field the

angular wave function is $P_l^m(\Theta) e^{im\Phi} = Y$, hence

$$L_z Y = \hbar m Y$$

In our case $m = 0$ hence $L_z = M_z = 0$. Let us find the total angular momentum (rather its square)

$$M^2 = M_x^2 + M_y^2 + M_z^2$$
$$L^2 = L_x^2 + L_y^2 + L_z^2$$

(L is an operator; M is a number)

$$L = (-\hbar^2)[(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})^2 + \ldots + \ldots]$$

In polar coordinates the operator contains only angular derivatives and is indeed equal to the angular part of the Laplacian:

$$L = -\hbar^2 \Delta_\Omega$$

where

$$\Lambda_\Omega = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

$$\Lambda_\Omega (P_\ell^m e^{im\phi}) = -\ell(\ell+1)(P_\ell^m e^{im\phi})$$

$$L^2\psi_\ell = -\hbar^2\Lambda_\Omega\psi_\ell = \hbar^2\ell(\ell+1)\psi_\ell$$

The total angular momentum $M^2 = \hbar^2\ell(\ell+1)$ for large ℓ, $M \approx \hbar\ell$. ℓ is the angular momentum Q.N. and gives the a.m. in units of $\hbar$.

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Consider the classical two body problem. The radial momentum is:

$$p_r^2 = m^2\dot{r}^2 = 2m(E-V) - \frac{M^2}{r^2}$$

where M is the classical angular momentum. This equation is

to be compared with the Q. M. equation:

$$\hbar^2 \frac{d^2 V_l}{dr^2} + 2m(E-V)V_l - \frac{\hbar^2 l(l+1)}{r^2} V_l = 0$$

$$-\hbar^2 \frac{d^2 V_l}{dr^2} = \left[2m(E-V) - \frac{\hbar^2 l(l+1)}{r^2} \right] V_l$$

In classical mechanics the distance of closest approach is defined by the equation $\dot{r} = 0$ which gives an equation for r_0

$$2m(E-V) = \frac{\hbar^2 l(l+1)}{r_0^2}$$

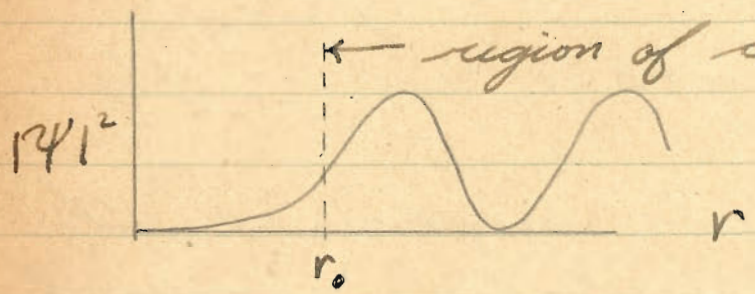
Carrying this definition over into Q. M. we see that if:

$r < r_0$ V_l is a decaying exponential.

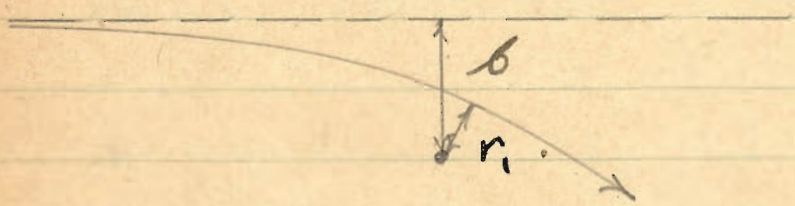
$r > r_0$ V_l has an oscillatory character.

$r << r_1$ $V_l \sim r^{l+1}$ and we

that in particular for large l there is a very small probability of penetration close to the origin.



In classical mechanics, the impact parameter, b, is defined as the distance from the scatterer to the asymptote to the path of the scattered particle.



$$\underbrace{M = pb}_{\text{classical}} \rightarrow \underbrace{\hbar\sqrt{l(l+1)}}_{\text{Q.M.}}$$

$$b \rightarrow \hbar\sqrt{l(l+1)} \sim \hbar l$$

for large l.

Consider a finite scatterer of radius, a, i.e.

$$|V(r)| \ll E \quad \text{for } r > a$$

If $|V(r_0)| \ll E$, then

$$r_0^2 = (\hbar^2/2mE)\,l(l+1)$$
$$= \lambda^2 l(l+1)$$
$$= b^2$$
$$r_0 = b > a$$

In this case the particle "misses" the nucleus. Since the perturbation of $u_l(r)$ depends on $V(r)$ and $V(r)$ is very small, we would expect the δ_l in the asymptotic formula for $V_l(r)$ to be very small. We shall now prove that this is the case:

$$v \left\| \quad \frac{d^2u}{dr^2} + \frac{2m}{\hbar^2}Eu - \frac{l(l+1)}{r^2}u = 0 \right.$$

$$u \left\| \quad \frac{d^2v}{dr^2} + \frac{2m}{\hbar^2}(E-V)v - \frac{l(l+1)}{r^2}v = 0 \right.$$

Multiplying these equations by V & u, as indicated, and subtracting

$$u\frac{d^2V}{dr^2} - V\frac{d^2u}{dr^2} - \frac{2m}{\hbar^2}V\,uV = 0$$

Integrate from 0 to R

$$\left[u\frac{dV}{dr} - V\cdot\frac{du}{dr}\right]_0^R - \frac{2m}{\hbar^2}\int_0^R V\,uv\,dr = 0$$

For $R > a$, $V(R) << V(a) \sim E$, and the above integral may be approximated by an integral from 0 to a which is independent of R. The lower limit in the first term gives 0 since V and $u = 0$ for $r = 0$. In evaluating the expression at the upper limit assume R large and use the asymptotic expressions for u and V.

Large r

$$u = \sin\left(kr - \frac{\pi l}{2}\right)$$

$$V = \sin\left(kr - \frac{\pi l}{2} + \delta_l\right)$$

$$\sin\left(kr - \frac{\pi l}{2}\right)\cos\left(kr - \frac{\pi l}{2} + \delta_l\right)(k)$$

$$- \sin\left(kr - \frac{\pi l}{2} + \delta_l\right)\cos\left(kr - \frac{\pi l}{2}\right)(k)$$

$$\sin\delta_l = -\frac{2m}{k\hbar^2}\int_0^a V u v\, dr$$

Suppose l is large i.e.

$$\lambda \ll \lambda l \sim b$$

If in addition $a \ll b$, then $b \sim r_0$. Under these conditions ($r_0 \sim b \sim \lambda l \gg \max[\lambda, a]$) the

$$\int_0^a V u v\, dr$$ is very small since it is an integral over a region which is highly forbidden ($r \ll r_0$) and hence the u and v are very small.

$\therefore \quad a << r_0 \sim b \sim \lambda l >> \lambda$

$\sin \delta_l \to 0 \; ; \; \delta_l \to 0$

The scattering function

$$f(\theta) = \frac{1}{2ik} \sum (2l+1)(e^{2i\delta_l} - 1) P_l(\theta)$$

Large l (as defined above) will not contribute much to the scattering so only small l need be considered in computing $f(\theta)$

Let us examine under what conditions the integral

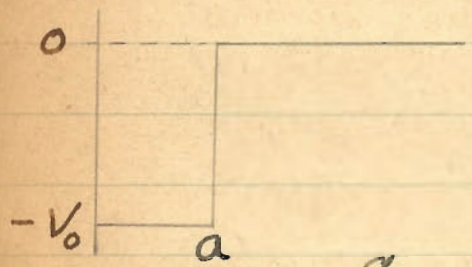
$\int_a^R V u v' dr$ really converges for large R.

$$\int_a^R V u v \, dr \sim \int_a^R V u^2 dr \sim \int_a^R V \sin^2(kr - \tfrac{\pi l}{2}) dr$$

$$\sim \frac{1}{2} \int_a^R V dr \quad \text{which converges}$$

if V decrease faster than $\frac{A}{r}$.
For a coulomb potential the integral does not converge but in this case the problem is soluble exactly.

I Scattering by a square potential well.



All $l < \frac{a}{\lambda} = ka$ will contribute to scattering.

$l > \frac{a}{\lambda} = ka$ will not contribute appreciable to scattering.

For $l = 0$

$$V = A \sin(k_1 r + \delta_0) \quad r > a$$

$$k_1 = p'/\hbar = 1/\lambda.$$

$$V = B \sin(kr \quad r < a$$

$$k = \frac{1}{\hbar}\sqrt{2m(E+V_0)}$$

From the continuity of V and $\frac{dV}{dr}$ at $r = a$ (use continuity of

logarithmic derivative $\frac{d \ln V}{dr}$.)
we find:

$$k \cot(ka + \delta) = k_1 \cot k_1 a$$

This equation may be solved for the phase shift δ.

Problem: Calculate δ for a square well, arbitrary ka, and

1. V_0 small negative
2. V_0 small positive

What must V_0 be small compared to.

For a nucleus $a = 10^{-12}$, a neutron of energy $E = 10^5$ ev repelled with a potential $V = 10^7$ ev for $r < a$, calculate the differential X-section for any angle to 5% (total X-section?) assume μ = mass of the neutron.

Hint: $l = 1$ $u = -\cos kr + \frac{\sin kr}{kr}$

$V = -\cos(kr + \delta_1) + \frac{\sin(kr + \delta_1)}{kr}$

no phase ↑ here

Scattering (cont.)

If $V(r) = 0$ for $r > a$ then

$$f(\theta) = \frac{1}{2ik} \sum (2l+1)(e^{2i\delta_l} - 1) P_l(\theta)$$

converges. If the solution of the radial wave equation is $V_l(r)$ for $r < a$, our problem is to fit $V_l(r)$ to a solution of the free particle equation for $r > a$ at the boundary $r = a$. The general solution of the equation

$$\frac{d^2 w_l}{dr^2} + \left(k^2 - \frac{l(l+1)}{r^2}\right) w_l = 0$$

<u>without</u> boundary conditions is

$$w_l = A\left[\sin(kr + \delta) P_l'(\overline{kr}) + \cos(kr + \delta) P_l''(\overline{kr})\right]$$

where A and δ are arbitrary constants and P_ℓ' and P_ℓ'' are polynomials in $1/kr$ depending on the value of ℓ. W_ℓ and V_ℓ may be fitted together at $r = a$ by a proper choice of the constants A and δ, so that $d \ln \Psi / dr$ is continuous at that point.

To obtain V_ℓ, we must solve the equation:

$$\frac{d^2 V_\ell}{dr^2} + \left(k^2 - U(r) - \frac{\ell(\ell+1)}{r^2}\right) V_\ell = 0$$

where: $k^2 = \frac{2mE}{\hbar^2}$

$U(r) = \frac{2mV(r)}{\hbar^2}$

Let

$$\bar{\Phi}(x) \equiv \left(k^2 - U(r) - \frac{\ell(\ell+1)}{r^2}\right)$$

Our equation becomes:

$$\frac{d^2 V_\ell}{dr^2} = -\bar{\Phi}(x) V_\ell$$

If Φ a constant the solution would be:

$$V_\ell = a \sin kr$$

(The method of solution we are going to apply is known as the WKB method)

Suppose $\Phi(r)$ varies slowly. Assume a solution:

$$V_\ell = a(r) \sin\left(\int^r \sqrt{\Phi}\, dr' + \alpha\right) \quad : \Phi > 0$$

$\Phi(r)$ ~ radial kinetic energy

The solution has a wavelength defined as $\lambda = 2\pi/\sqrt{\Phi(r)}$

Substituting this solution into our differential equation we obtain:

$$(a'' - a\Phi)\sin\int + \left(a'\sqrt{\Phi}\cdot 2 + \frac{a}{2}\frac{\Phi'}{\sqrt{\Phi}}\right)\cos\int$$

$$= -\Phi a \sin\int$$

$$a''\sin\int + \left(2a'\sqrt{\Phi} + \frac{a}{2}\frac{\Phi'}{\sqrt{\Phi}}\right)\cos\int = 0$$

We arrived at the last equation by assuming $a'' << a\bar{\Phi}$. This lead to the following condition on $\bar{\Phi}$

$$\frac{5}{16}\left(\frac{\bar{\Phi}'}{\bar{\Phi}}\right)^2\frac{1}{\bar{\Phi}} - \frac{1}{4}\frac{\bar{\Phi}''}{\bar{\Phi}^2} << 1$$

By setting the coefficient of the cosine term equal to zero

$$\frac{a'}{a} = -\frac{1}{4}\frac{\bar{\Phi}'}{\bar{\Phi}}$$

$$a = A\bar{\Phi}^{-\frac{1}{4}}$$

Hence we have arrived at an approximate solution which when the underlined condition above holds.

$$V_\ell \approx A\bar{\Phi}^{-\frac{1}{4}}\sin\left[\int^r\sqrt{\bar{\Phi}}\,dr' + \alpha\right] : \bar{\Phi} > 0$$

This may also be written

$$V_\ell \approx A\bar{\Phi}^{-\frac{1}{4}}\exp i\int^r\sqrt{\bar{\Phi}}\,dr'$$

In this form v_x represents particles going to positive r.

The total current flowing radially outward is $|\psi|^2 v_p$ where v_p is the radial velocity ~ radial K.E. ~ $\sqrt{E}$. But $|\psi|^2 \sim E^{-\frac{1}{2}}$, hence $|\psi|^2 v_p$ is a constant independent of r. From this, we see that the WKB solution does not take account of the reflection of particles. For this reason there is no point in pushing the approximation further.

For $E < 0$ the WKB solution is:

$$v_x = A |E(r)|^{-\frac{1}{4}} \exp \pm \int^r \sqrt{|E|}\, dr'$$

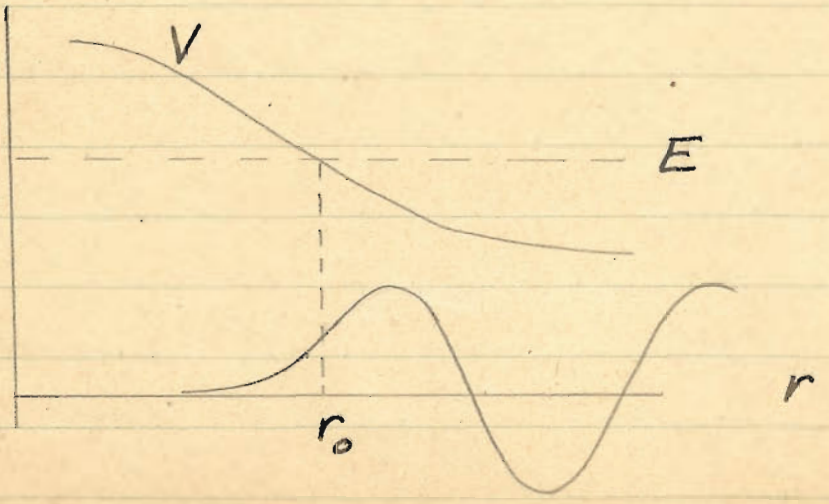
The WKB approximate wave functions are useful for calculating the penetration of

of a potential barrier. In this problem we are faced with the problem of fitting the solutions for $\Phi > 0$ and $\Phi < 0$. The approximate solution is not valid in the region near $\Phi = 0$. The problem is treated by in Z. f. Physik 38

$$\Phi(r) > 0 \quad \text{for} \quad r > r_0$$
$$\Phi(r) < 0 \quad \text{for} \quad r < r_0$$

$$\psi(r) = A\,\Phi(r)^{-\frac{1}{4}} \sin\left[\int_{r_0}^{r} \sqrt{\Phi}\, dr' + \frac{\pi}{4}\right] \qquad r > r_0$$

$$\psi(r) = \frac{A}{2} |\Phi(r)|^{-\frac{1}{4}} \exp -\int_{r}^{r_0} \sqrt{\Phi}\, dr' \qquad r < r_0$$



3/1/47

I The Bessel function satisfies the equation

$$J_n'' + \frac{1}{x} J_n' + \left(1 - \frac{n^2}{x^2}\right) J_n = 0$$

In general, if we have an equation

$$y'' + f(x)y' + g(x)y = 0,$$

the first order term may be eliminated by the substitution

$$y = X e^{-\frac{1}{2}\int f(x)\,dx}$$

The equation reduces to

$$X'' + \left(g(x) - \tfrac{1}{2}f' - \tfrac{1}{4}f^2\right)X = 0$$

In our case $f(x) = \frac{1}{x}$, $f' = -\frac{1}{x^2}$

$$X'' + \left(1 - \frac{n^2 + \frac{1}{4}}{x^2}\right)X = 0$$

This equation may be solved by the WKB method.

$$L(x) = \left(1 - \frac{n^2 + \frac{1}{4}}{x^2}\right)X \qquad \text{drop the } \tfrac{1}{4}$$

$$\varphi(x) = \int_{x_0}^{x} \sqrt{1 - \frac{n^2}{x^2}}\,dx$$

$$\varphi(x) = \sqrt{x^2 - n^2} - n \cos^{-1}\frac{n}{x} + \frac{\pi}{4}$$

For $n \ll x$

$$\varphi(x) = x - (n - \tfrac{1}{2})\frac{\pi}{2}$$

$$\chi = \sin\left[x - (n - \tfrac{1}{2})\frac{\pi}{2}\right]$$

$$J_n = A x^{-\frac{1}{2}} \sin\left[x - (n - \tfrac{1}{2})\frac{\pi}{2}\right]$$

$$\sqrt{kr}\, J_{l+\frac{1}{2}} = \sin\left(x - \frac{l\pi}{2}\right)$$

This is the asymptotic result we obtained before.

Application of WKB method to determining phase shift δ_l

$$\mathcal{I} = k^2 - U(r) - \frac{l(l+1)}{r^2}$$

Experience has shown that replacing $l(l+1)$ by $(l+\tfrac{1}{2})^2$ does not hurt and in fact improves the results.

For large r the phase of ν_ℓ is

$$\left\{ \int_{r_0}^{r} \sqrt{k^2 - U - \frac{(\ell+\frac{1}{2})^2}{r^2}}\, dr + \frac{\pi}{4} \right\}$$

The phase of the Bessel function is:

$$\left\{ kr - \frac{\ell\pi}{2} \right\}$$

δ_ℓ will be the difference of these two quantities

$$\delta_\ell = \int_{r_0}^{r} \sqrt{\quad}\, dr - kr + (\ell+\tfrac{1}{2})\tfrac{\pi}{2}$$

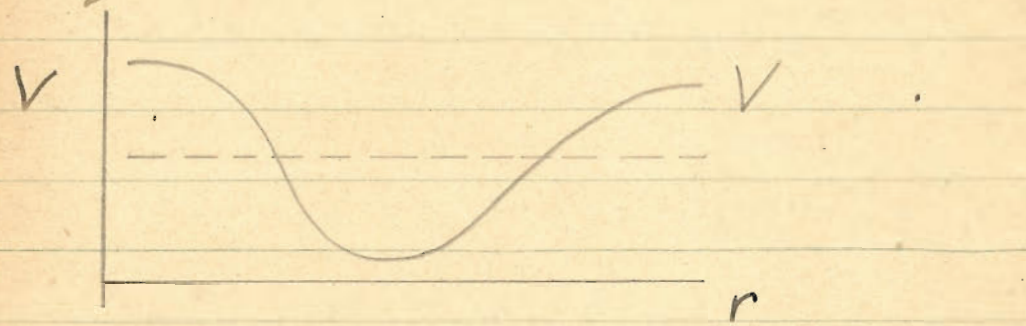
It would be convenient to extend the integral to ∞ but it diverges in this form. We can fix it by adding and subtracting $k(r-r_0)$.

$$\delta_\ell = \int_{r_0}^{\infty} \left[\sqrt{k^2 - U - \frac{(\ell+\frac{1}{2})^2}{r^2}} - k \right] dr$$

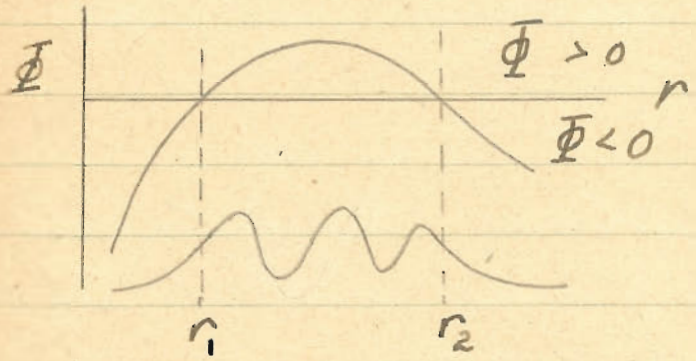
$$- kr_0 + (\ell+\tfrac{1}{2})\tfrac{\pi}{2}$$

Treatment of Stationary States

Suppose we have the situation diagramed below:



There will be a region in which Φ looks as below



Phase $\left\{\frac{\pi}{4}\right\}$ $\left\{n\pi - \frac{\pi}{4}\right\}$

$$\phi(r_2) = \int_{r_1}^{r_2} \sqrt{\Phi}\, dr + \frac{\pi}{4} = n\pi - \frac{\pi}{4}$$

$$\int_{r_1}^{r_2} \sqrt{\Phi}\, dr = \left(n - \tfrac{1}{2}\right)\pi$$

For $l = 0$ $\frac{1}{\hbar}\int_{r_1}^{r_2} \sqrt{2m(E-V)}\,dr = \frac{1}{\hbar}\int_{r_1}^{r_2} p\,dr$

If we go from $r_1 \to r_2 \to r_1$

$$\oint p\,dr = 2\pi\hbar(n-\tfrac{1}{2}) = h(n-\tfrac{1}{2})$$

This is the old quantum condition.

Problem: Consider the H-atom $V = -e^2/r$, $E = -Ry/n'^2$ where n' is not necessarily an integer.

1. Find the stationary states from the phase condition ($\hbar^2/me^2 = a$, Use explicate Ry)
2. Discuss wave function for large n. (amplitude)
3. Normalization of wave function

Scattering of fast electrons (>100 V) by heavy nuclei.

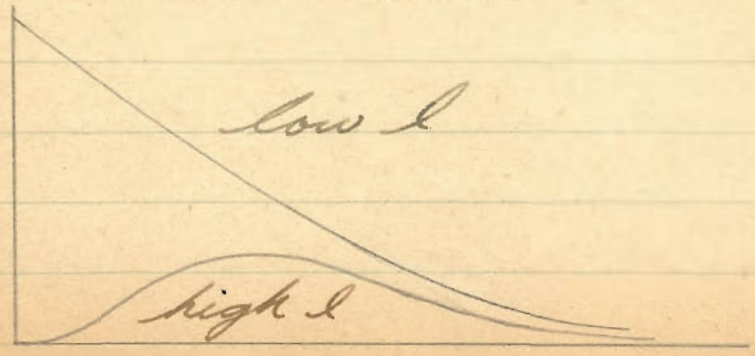
The best method of determining

the charge distribution for heavy nuclii is by the Hartree method of self consistant fields. The results do not scale, however. The Fermi Thomas model of the atoms gives less accurate results but the results scale. The radial scale goes as $Z^{-\frac{1}{3}}$. This means that the radius of the sphere containing $\frac{1}{2}$ the electrons gets smaller for larger nuclei.

1 Hennebrg

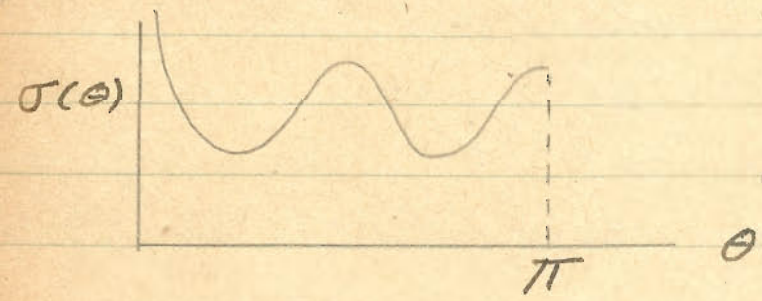
2 Massey & Mohor
Ref. Z. f. Physik 83 555

The phase shift for this problem is shown below:



This behavior is reasonable: Small l means a close approach to the nucleus, hence a large phase shift. For large l, the phase shift will not begin to become appreciable until $l < \frac{a}{\lambda} \sim pr/\hbar$

The scattering X-section as a function of θ



As the energy increases more waves appear. (shorter wavelength)

3/4/47

WKB cont.

Classical Limit of Scattering

$$f(\theta) = \frac{1}{2ik} \sum_l (2l+1)(e^{2i\delta_l} - 1) P_l(\cos\theta)$$

We approach the classical limit for $\lambda \ll R$. In this case a great many l's influence $f(\theta)$. The Legendre equation is:

$$\frac{d^2 P_l(\cos\theta)}{d\theta^2} + \cot\theta \frac{dP_l}{d\theta} + l(l+1) P_l = 0$$

For large θ we may use the WKB solution of this equation as an approximation to $P_l(\cos\theta)$

$$P_l(\theta) \doteq A_l \sqrt{\frac{2}{\pi \sin\theta}} \sin\left[(l+\tfrac{1}{2})\theta + \frac{\pi}{4}\right]$$

we shall also need:

$$\int_0^\pi P_l^2(\theta) \sin\theta \, d\theta = \frac{2}{2l+1}$$

For $l > 1$, the normalization gives

$$A_l \doteq \sqrt{\frac{2}{2l+1}}$$

Hence:

$$f(\theta) \doteq \frac{1}{2ik}\frac{2}{\sqrt{\pi}\sin\theta}\frac{1}{2i}\sum\sqrt{2l+1}\,(e^{2i\delta_l}-1)\cdot\left(e^{i(l+\frac{1}{2})\theta+i\frac{\pi}{4}} - e^{-i(l+\frac{1}{2})\theta-i\frac{\pi}{4}}\right)$$

Regrouping the exponential factors

$$f(\theta) = \ldots\Big\{e^{i[2\delta_l+(l+\frac{1}{2})\theta]+i\frac{\pi}{4}} - e^{i[2\delta_l-(l+\frac{1}{2})\theta]-i\frac{\pi}{4}} - e^{i(l+\frac{1}{2})\theta+i\frac{\pi}{4}} + e^{-i(l+\frac{1}{2})\theta-i\frac{\pi}{4}}\Big\}$$

For large θ these terms oscillate as l is varied in such a way as to contribute nothing to the sum, unless one of the exponents is constant for a range of l in a certain region i.e. has stationary phase. This will be the case where:

$$\frac{d}{dl}\left[2\delta_l \pm (l+\tfrac{1}{2})\theta\right] = 0 = 2\frac{d\delta_l}{dl} \pm \theta$$

The equation $\frac{d\delta_\ell}{d\ell} = \pm\frac{1}{2}\theta$ defines an $\ell_0(\theta)$ for which there a maximum contribution to the sum. Expanding the exponent in a Taylor series about ℓ_0 we obtain:

$$f(\theta) = \left[\frac{1}{2k\sqrt{\pi}\sin\theta}\right]\sqrt{2\ell_0+1}\; e^{i(2\delta_{\ell_0} + (\ell+\frac{1}{2})\theta + \frac{\pi}{4})} \cdot \sum e^{i\frac{d^2\delta}{d\ell^2}\Big|_{\ell_0}(\ell-\ell_0)^2}$$

ℓ_0 is assumed large and only those ℓ's in the neighborhood of ℓ_0 will contribute to the sum. We can replace the sum by an integral from $-\infty$ to $+\infty$

$$\int_{-\infty}^{\infty} e^{i\frac{d^2\delta}{d\ell^2}\Big|_{\ell_0}(\ell-\ell_0)^2} d\ell$$

$$= \sqrt{\pi}\Big/\sqrt{2\frac{d\delta}{d\ell}\Big|_{\ell_0}}\,(1+i)$$

Incorporating this in our expression $f(\theta)$ and taking the absolute value of $f(\theta)$ we obtain

$$|f(\theta)| = \sqrt{2l_0+1}/2k\sqrt{\sin\theta \left.\frac{d^2\delta}{dl}\right|_{l_0}}$$

$$|f(\theta)|^2 2\pi \sin\theta d\theta = \frac{\pi}{2}(2l_0+1)\lambda^2 d\theta \Big/ \left.\frac{d^2\delta}{dl^2}\right|_{l_0}$$

$$= \sigma(\theta)d\theta$$

Let us now look at our WKB solution for δ_l

$$\delta_l = \frac{1}{\hbar}\int_{r_0}^{r}\left[\sqrt{2m}\sqrt{E-V-\frac{\hbar^2(l+\frac{1}{2})^2}{2mr^2}} - k\hbar\right]dr$$

$$- kr_0 + (l+\tfrac{1}{2})\frac{\pi}{2}$$

$$\frac{d\delta_l}{dl} = -\frac{\sqrt{2m}}{\hbar}\int_{r_0}^{r}\hbar^2(l+\tfrac{1}{2})\frac{1}{2mr^2}\Big/\sqrt{\quad} + \frac{\pi}{2}$$

$$\hbar(l+\tfrac{1}{2}) \sim M$$

$$\frac{d\delta_l}{dl} = -\int \frac{M}{r^2}\left(2m(E-V) - \frac{M^2}{r^2}\right)^{-\frac{1}{2}}dr + \frac{\pi}{2}$$

Classically this expression is equal to $+\frac{\theta}{2}$ if $V > 0$ and $-\theta/2$ if $V < 0$ where θ is the angle thru which a particle having angular momentum M is scattered. It was for $\frac{d\delta}{dl} = \pm \theta/2$ that our Q.M. expression for $f(\theta)$ had its maximum.

$$\frac{d^2\delta}{dl^2} = \pm \frac{1}{2}\frac{d\theta}{dl}$$

Substituting in our expression for $\sigma(\theta)d\theta$

$$\sigma(\theta)d\theta \doteq \frac{2\pi l_0 \lambda^2 d\theta}{d\theta/dl}$$

$$= 2\pi \lambda_0^2 dl \qquad \text{Q.M.}$$

In classical mechanics

$$\sigma(\theta)d\theta = 2\pi b\, db$$

$$b = \lambda l$$

$$\sigma(\theta)\,d\theta = 2\pi\lambda^2 l_0\,dl \qquad C.M.$$

We see that in the limit $\lambda \ll R$ the Q.M. and C.M. results agree.

Ref Chap 7 Sect 3 Mott & Massey

Let us now find the scattering X-section for θ near 0. For small θ $\cot\theta \sim 1/\theta$

$$\frac{d^2P}{d\theta^2} + \frac{1}{\theta}\frac{dP}{d\theta} + (l+\tfrac{1}{2})^2 P = 0$$

$$P_l \sim J_0[(l+\tfrac{1}{2})\theta]$$

Putting this approximation into our exact expression for $f(\theta)$ and dropping the oscillating $e^{2i\delta_l}$ term we obtain:

$$|f(\theta)| \doteq \frac{1}{2k}\sum_l (2l+1)\,J_0\left(\frac{2l+1}{2}\theta\right)$$

Replacing the sum by an integral

$$|f(\theta)| = \frac{1}{k}\frac{1}{\theta^2}\int x J_0(x)\,dx$$

$$= \frac{1}{k\theta^2}\, x J_1(x)\Big|_0^{\frac{R\theta}{\lambda}}$$

The upper limit is determined on the basis of the fact that only those l's up to $\sim R/\lambda$ will contribute to the scattering.

$$|f(\theta)| = \frac{R}{\theta} J_1\left(\frac{R\theta}{\lambda}\right)$$

For small $\theta \to 0$ this expression approaches a finite limit. It is possible to have particles scattered thru zero angle. For neutrons there is a very strong forward scattering. This is known as the "Shadow effect". The phenomena is due to diffraction and is observed in optics in the case of small scatterer.

The shadow will be fuzzy in an angular region $\theta \sim \lambda/R$.

3/6/47

Classical Limit of Scattering (cont.)

Suppose δ_ℓ large for $\ell < \ell_0$
δ_ℓ small for $\ell > \ell_0$

The total Q.M. x-section is:

$$\sigma_T = 4\pi\lambda^2 \sum (2\ell+1) \sin^2 \delta_\ell$$

If many ℓ's contribute δ_ℓ will vary randomly in such away that $\sin^2 \delta_\ell$ will average to $1/2$.

$$\sigma_T \simeq 4\pi\lambda^2 \sum_0^{\ell_0} (2\ell+1)\frac{1}{2}$$

$$= 2\pi\lambda^2 \ell_0^2$$

$$b \simeq \lambda \ell_0 = R \text{ classical radius}$$

Hence $\sigma = 2\pi R^2$

The geometrical x-section of the classical scatterer is πR^2. The explanation of the factor 2 which appears above is that the "shadow scattering" at small angles contributes a πR^2 to the total cross-section. The "shadow scattering" is a wave phenomena and does not appear in the classical solution of the problem. If we imagine the scatterer to be perfectly absorbing, we can see that if there is to be a shadow behind the scatterer there must be destructive interference between the waves which just miss the edge of the scatterer. This increases the effective area

of the scatterer by a factor 2.

Convenient Approximate Expressions for δ_ℓ and $f(\theta)$.

From lecture 2/25

$$\sin\delta_\ell = -\frac{2m}{\hbar^2 k}\int_0^\infty V(r)\, u_\ell\, v_\ell\, dr$$

If $V(r)$ small, $u_\ell \approx v_\ell$. Also, if $V(r)$ small, δ_ℓ small and $\sin\delta_\ell \approx \delta_\ell$

$$\delta_\ell \approx -\frac{m\pi}{\hbar^2}\int_0^\infty V(r)\, J^2_{\ell+\frac{1}{2}}(kr)\, r\, dr$$

For small δ_ℓ, $(e^{2i\delta_\ell} - 1) \approx 2i\delta_\ell$ and $f(\theta)$ is linear in $V(r)$. This is a condition for the:

<u>Born Approximation</u> for $f(\theta)$

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0$$

Let $\psi = \psi^{(0)} + \psi^{(1)}$

where $\psi' \ll \psi^0$ and $V \ll E$.
Substituting in the wave equation and neglecting the term $V\psi'$ we obtain:

$$\nabla^2\psi^0 + \frac{2mE}{\hbar^2}\psi^0 = 0 \qquad O(0)$$

$$\nabla^2\psi' + \frac{2mE}{\hbar^2}\psi' = \frac{2mV}{\hbar^2}\psi^0 \qquad O(1)$$

The solution of the zero order equation is

$$\psi^0 = e^{i\underline{k}_0 \cdot \underline{r}}$$

where $|\underline{k}_0| = \sqrt{2mE}/\hbar$ and $\underline{k}_0$ has the direction of the incident beam.
The first order equation can be written:

$$\nabla^2\psi' + k^2\psi' = X(\underline{r})$$

where $X(r) = \frac{2mV}{\hbar^2} e^{i\underline{k}_0 \cdot \underline{r}}$. This equation is the wave equation with source and may be solved by application of Green's Theorem. The solution is:

$$\psi'(\underline{r}) = -\frac{1}{4\pi}\int d\underline{r}' \frac{\chi(\underline{r}')}{|\underline{r}-\underline{r}'|} e^{i\underline{k}\cdot|\underline{r}-\underline{r}'|}$$

If $r >> r'$ for all r' for which $\chi(r')$ appreciable.

$$|\underline{r}-\underline{r}'| \to r$$

$$\underline{k}\cdot|\underline{r}-\underline{r}'| \to kr - \underline{k}\cdot\underline{r}'$$

where $|\underline{k}| = \sqrt{\frac{2mE}{\hbar}}$ and $\underline{k}$ has the direction $\underline{r}$ ($\underline{r}$ gives the position of the observer.) Substituting the above expression in our equation for $\psi'(\underline{r})$:

$$\psi'(\underline{r}) = \frac{e^{ikr}}{r}\left[-\frac{1}{4\pi}\int d\underline{r}' \chi(r') e^{-i\underline{k}\cdot\underline{r}'}\right]$$

The complete solution for ψ is:

$$\psi = e^{i\underline{k}_0\cdot\underline{r}} + \frac{e^{ikr}}{r}\left[-\frac{1}{4\pi}\int d\underline{r}' \chi(r') e^{-\underline{k}\cdot\underline{r}'}\right]$$

Comparing this with the equation

$$\psi = e^{ikz} + \frac{e^{ikr}}{r} f(\theta)$$

we see that

$$f(\theta) = -\frac{1}{4\pi}\int d\tau' \chi(r') e^{-i\underline{k}\cdot\underline{r}'}$$

$$\underline{f(\theta) = -\frac{m}{2\pi\hbar^2}\int d\tau' V(r') e^{i(\underline{k}_0 - \underline{k})\cdot\underline{r}'}}$$

If $V = V(r)$ then $f(\theta)$ is a function only of $|\underline{k}_0 - \underline{k}|$ $= |\underline{p}_0 - \underline{p}|/\hbar$. The scattering depends only on the change of momentum. For elastic scattering $|\underline{p}_0| = |\underline{p}|$ and $|\underline{p}_0 - \underline{p}| = 2p \sin\frac{\theta}{2}$.

For the same V and the same $\underline{k}_0 - \underline{k}$, $f(\theta) \sim$ mass of the scattered particle, and $\sigma(\theta) \sim m^2$. The reduced mass for a neutron scattered by a free proton is $M/2$ and by a bound proton is M. Hence the scattering cross-section for a bound proton is 4 times

as large as for a free proton.

3/18/47

Using the Born approximation let us attempt to calculate the scattering of a particle of charge ez by an atom having atomic charge Z. The potential for the process is

$$V(r) = ez\phi(r)$$

Where ϕ is the atomic potential and obeys the Poisson equation

$$\nabla^2\phi = -4\pi\rho$$

The Born approx. is:

$$f(\theta) = -\frac{1}{4\pi}\frac{2m}{\hbar^2}\int d\tau\, V(r)\, e^{i(\underline{k}_0-\underline{k})\cdot\underline{r}}$$

$$= \frac{1}{4\pi}\frac{2mez}{\hbar^2}\underbrace{\int d\tau\,\phi(r)\, e^{i\underline{q}\cdot\underline{r}}}_{I}$$

where $\underline{q} \equiv \underline{k}_0 - \underline{k}$

We define a quantity χ such that:

$$e^{i\underline{q}\cdot\underline{r}} = -\nabla^2\chi$$

$$\therefore \quad \chi = e^{i\underline{q}\cdot\underline{r}}/q^2$$

$$I = -\int d\tau\, \rho(r)\nabla^2\chi$$

$$= -\int d\tau\, \nabla^2\rho\, \chi$$

Here we have applied Greens Theorem and thrown away the surface integral, $\int(\rho\frac{\partial\chi}{\partial n} - \chi\frac{\partial\rho}{\partial n})d\sigma$, at infinity.

$$I = 4\pi\int d\tau\, \chi\rho = \frac{4\pi}{q^2}\int d\tau\, \rho(r)e^{i\underline{q}\cdot\underline{r}}$$

$$\int d\tau\rho e^{i\underline{q}\cdot\underline{r}} = Ze - e\int d\tau\, n(r)e^{i\underline{q}\cdot\underline{r}}$$

$n(r)$ is the electron density around the nucleus. The integral is called the form factor and is simply the fourier transform

of the electron density. This integral was studied before Q.M. in connection with λ-ray scattering. Hartree developed his method of getting the electron distribution in order to compute this integral.

$$F(q) \equiv \int d\tau\, n(r)\, e^{i\vec{q}\cdot\vec{r}}$$

In terms of our new notation

$$f(\theta) = -2\left(\frac{me^2}{h^2}\right) Z\left[Z - F(q)\right] / q^2$$

$\frac{h^2}{me^2} = a$, the Bohr radius for the scattered particle.

$$f(\theta) = -\frac{2Z}{a q^2}\left[Z - F(q)\right]$$

$$\sigma(\theta) = |f(\theta)|^2$$

Let us now neglect the $F(q)$.

and calculate the scattering due to the nucleus alone.

$$f(\theta) = -\frac{2zZ}{aq^2} = -\frac{2mc^2 zZ}{\hbar^2 4k^2 \sin^2\frac{\theta}{2}}$$

where we have substituted $q = 2k\sin\frac{\theta}{2}$

$$= -\frac{e^2 zZ}{2mv^2 \sin^2\frac{\theta}{2}}$$

$$\sigma(\theta) = \left(\frac{e^2 zZ}{mv^2}\right)^2 / 4\sin^4\frac{\theta}{2}$$

This is exactly the classical Rutherford scattering formula for a coulomb potential. This is the only case in which Q.M. and C.M. agree exactly.

Let us now examine the condition under which $F(q)$ can be neglected.

a. If q very small:

$$F(q) \to \int d\tau\, n(r) = Z$$

b. If $q r_{atom} \gg 1$, the exponential oscillates and $F(q) \ll Z$. Under these conditions the Rutherford formula applies.

$$r_{atom} \sim a_0 Z^{-\frac{1}{3}} \qquad a_0 = \frac{\hbar^2}{m_e c^2}$$

For large atoms $a_0 Z^{-\frac{1}{3}} \sim 10^{-9}$ cm
For 5 Mev alphas $k_\alpha = \frac{1}{\lambda_\alpha} \sim 10^{13}$ cm^{-1}

$$q r_{atom} = 2k \sin\frac{\theta}{2} r_{atom} \sim 10^4 \theta$$

For α's the formula is good even at small angles. It is also good for large angle scattering of fast electrons.

Small angles:

If we examine our original integral for I, we see that for small q I converges

if $\rho(r)$ goes down faster than $1/r^3$. In this case, $f(\theta)$ remains finite for $\theta = 0$.

X-ray scattering $\sim |F(q)|^2$

electron scattering $\sim |Z - F|^2$

Let us now examine our WKB expression for δ_ℓ for $V \sim \frac{1}{r}$.

$$\delta_\ell = \int \left(k^2 - \frac{2m}{\hbar^2} \frac{zZe^2}{r'} - \frac{\ell(\ell+1)}{r'^2} \right)^{\frac{1}{2}} - k \Big] dr'$$

$$- \dots$$

For large r

$$= \int \left(k + \frac{mzZe^2}{\hbar^2 k r} - O\left(\frac{1}{r^2}\right) - k \right) dr + \dots$$

$$\doteq - \frac{mzZe^2}{\hbar^2 k} \ln r \doteq - \alpha \ln r$$

where: $\alpha = \dfrac{zZe^2}{\hbar v}$, $\hbar k = mv$

The phase shift is not defined in the case of a coulomb potential. δ_ℓ is an infinite.

Since the Born approx is only good if δ_l is small, it can not be applied to this problem. The coulomb scattering must be calculated directly.

3/11/47
Feynman

I Scattering by a Coulomb Field.

Ref: Mott & Massey p. 34

$$\nabla^2\psi + \left(k^2 - \frac{\beta}{r}\right)\psi = 0$$

where $\beta = \frac{2mZZ'e^2}{\hbar^2}$. The following substitutions are equivalent to separating the equation in parabolic coordinates:

Let $\psi = e^{ikz} F(xyz)$

$$\nabla^2 F + 2ik\frac{\partial F}{\partial z} - \frac{\beta F}{r} = 0$$

$$F = F(r - z)$$

The Laplacian becomes:

$$\nabla^2 F = 2\left(1 - \frac{z}{r}\right)F'' + \frac{2}{r}F'$$

The equation becomes

$$r \parallel \; 2\left(1 - \frac{z}{r}\right)F'' + \frac{2}{r}F' - 2ik\left(1 - \frac{z}{r}\right)F' - \frac{\beta}{r}F = 0$$

$$2\xi F'' + 2(1 - ik\xi)F' - \beta F = 0$$

This is the hypergeometric equation and has solutions designated as follows:

$$F = {}_1F_1(-i\alpha;\ 1;\ ik\xi) \qquad : \alpha \equiv \frac{i\beta}{2k}$$

The complete solution for Ψ is:

$$\Psi = e^{-\frac{1}{2}\pi\alpha}\Gamma(1 + i\alpha)e^{ikz}\,{}_1F_1(-i\alpha;\ 1;\ ik\xi)$$

where we have normalized the incident amplitude to one by inserting the factor $e^{-\frac{1}{2}\pi\alpha}\Gamma(1+i\alpha)$ So we have run the asymptotic

expression for ψ has the form

$$\psi_{as} \sim I + S f(\theta)$$

where

$$I = \left[1 - \frac{\alpha^2}{ik(r-z)}\right] e^{ikz + i\alpha \ln k(r-z)}$$

$$S = \frac{1}{r} e^{ikr - i\alpha \ln kr}$$

$$f(\theta) = \frac{zz'e^2}{2mv^2} \csc^2\tfrac{1}{2}\theta \, e^{-i\alpha \ln(1-\cos\theta) + i\pi + 2i\eta_0}$$

$$e^{2i\eta_0} = \Gamma(1+i\alpha)/\Gamma(1-i\alpha)$$

$$r - z = r(1-\cos\theta)$$

Hence:

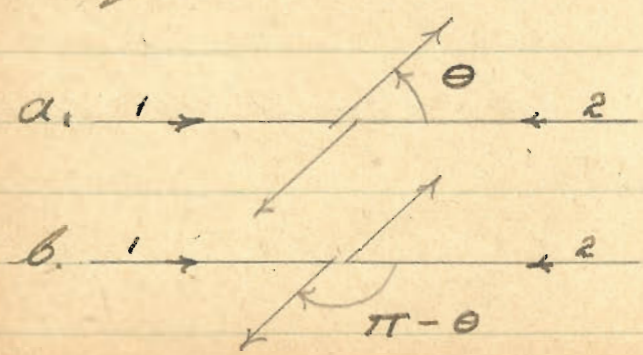
$$|f(\theta)|^2 = \left(\frac{zz'e^2}{2mv^2}\right)^2 \frac{1}{\sin^4\frac{\theta}{2}}$$

Knowing that $S = \frac{1}{r} e^{ikr - i\alpha \ln kr}$ and that asymtotically $e^{ikz} F(r-z) = f(\theta) S$ it is possible to guess the form of $f(\theta)$ without doing any mathematics.

II Collisions

Consider a collision between two unlike particles. One of the two particles plays the roll of scatterer. There is no ambiguity involved and the cross section of the particle is given by the formula we have derived.

Now consider a collision between two exactly identical particles. After the collision has taken place it is impossible to tell the scattered particle from the recoil particle. Classically the situation is as pictured below:



In center of gravity system.

Classically the intensity at an angle θ would simply be the sum of the intensities for the two processes indicated in the diagram:

$$I_T = I(\theta) + I(\pi - \theta)$$

where $I(\theta)$ is the classical analoge of $|f(\theta)|^2$. Q.M. tells us however that we are dealing with a wave phenomena and therefore there may be interference so that the intensities are not simply additive. The Q.M. expression for the intensity at θ is:

$$I_T = |f(\theta) + f(\pi - \theta)|^2$$

$$= |f(\theta)|^2 + |f(\pi-\theta)|^2 + f^*(\theta) f(\pi-\theta) + f(\theta) f^*(\pi-\theta)$$

This applies if the two particles are exactly identical, and obey Bose statistics, and have no spin.

Let us now consider a collision between two electrons. Electrons have spin and obey Fermi statistics (antisymmetric wave function). For electrons with spin up or down it is possible to distinguish two types of scattering, symmetric and antisymmetric:

$$P_S = |f_1(\theta) + f_2(\pi - \theta)|^2$$
$$P_A = |f_1(\theta) - f_2(\pi - \theta)|^2$$

Since the total wave function must be antisymmetric on interchange of all coordinates (spin and space) we can have:

P_S × antisym. spin function
P_A × symm. spin function

The possible spin functions are:

Symmetric $\alpha(\xi_1)\alpha(\xi_2)$

$\frac{1}{\sqrt{2}}[\alpha(\xi_1)\beta(\xi_2) + \alpha(\xi_2)\beta(\xi_1)]$

$\beta(\xi_1)\beta(\xi_2)$

Antisymmetric $\frac{1}{\sqrt{2}}[\alpha(\xi_1)\beta(\xi_2) - \alpha(\xi_2)\beta(\xi_1)]$

For a particle of random spin the scattered intensity should be given by

$$I(\theta) = \frac{3}{4} P_A + \frac{1}{4} P_S$$

Suppose we know that the scatterer has spin up. If the incident particle has:

a. spin up, space P_A

b. spin down, space $\frac{1}{2}(P_A + P_S)$

The spin wave function for spin in the $\theta'\phi'$ direction is

$$\cos\frac{\theta'}{2} e^{i\phi'}\alpha + \sin\frac{\theta'}{2}\beta$$

If the incident particle has spin in an arbitrary direction

the prob. that it is up is $\cos^2\frac{\theta'}{2}$; down $\sin^2\frac{\theta'}{2}$. The scattered intensity will be:

$$I(\theta) = \frac{1}{4}(1-\cos\theta')P_S + \frac{1}{4}(3+\cos\theta')P_A.$$

Averaging over θ' we obtain $I(\theta) = \frac{1}{4}P_S + \frac{3}{4}P_A$ which is the same result we got when we assumed both incident particle and scatterer spins arbitrary. This is as it should be since it is only the relative spins of the two particles that is important.

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Feynman

I Collision of like Particles

For particles of random spin the scattered intensity in the θ direction is given by:

$$I(\theta) = \frac{1}{4}(P_S + 3P_A)$$

where

$$P_S = |f(\theta) + f(\pi-\theta)|^2$$
$$P_A = |f(\theta) - f(\pi-\theta)|^2$$

and

$$f(\theta) = \frac{Z^2 e^2}{2m^* v^2} \csc^2\frac{\theta}{2}\, e^{-i\alpha \ln(1-\cos\theta) + i\pi + 2i\eta_0}$$

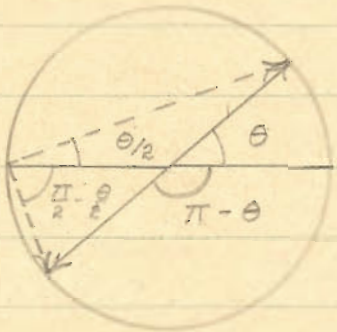
$$m^* = \tfrac{1}{2} m_e$$
$$Z = -1$$

$$|f(\theta) \pm f(\pi-\theta)|^2 = \left(\frac{e^2}{mv^2}\right)^2 \Big| \csc^2\frac{\theta}{2}\, e^{-i\alpha \ln(1-\cos\theta)} \pm \sec^2\frac{\theta}{2}\, e^{-i\alpha \ln(1+\cos\theta)} \Big|^2$$

$$\frac{P_A}{S} = \left(\frac{e^2}{mv^2}\right)^2 \left[\csc^4\frac{\theta}{2} + \sec^4\frac{\theta}{2} \pm 2\csc^2\frac{\theta}{2}\sec^2\frac{\theta}{2}\,\Phi \right]$$

$$\Phi = \cos\left(2\alpha \ln \tan\frac{\theta}{2}\right)$$
$$\alpha = e^2/\hbar v$$

The above expressions enable us to calculate the scattered intensity in the C.G. system. To convert to the laboratory system in which one of the particles is initially at rest, we must subtract off its velocity.



—— C.G. system
- - - - Lab system

It is clear from the above geometry the angles in the lab system are only 1/2 as large as angles in the C.G. system. Also the solid angle in the lab system will be different. The conversion to the laboratory system is accomplished as follows:

$$I_L(\theta_L) = [I_{CG}(2\theta_L)]/(4\cos\theta_L)$$

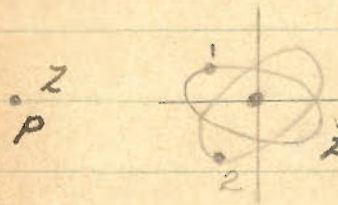
$I_2(\theta_2)$ will have a maximum at $\theta_2 = 45°$.

II Inelastic Scattering

We shall now consider collisions in which the scattering atom may be left in an excited state after a collision.

Let Ψ = wave function for the system, atom plus particle. The Hamiltonian for the system may be written

$$H = H_A + T_P + V_{in}(PA)$$



$$V_{in} = -\frac{Ze^2}{R_p - R_1} - \frac{Ze^2}{R_p - R_2} + \frac{ZZe^2}{R_p}$$

We assume that the states of the atom are already known:

$$H_A \chi_n(A) = W_n \chi_n(A)$$

We can express Ψ in terms of these solutions

$$\Psi(AP) = \sum \varphi_n(P)\chi_n(A)$$

Asymptotically $\varphi_0(P) \sim e^{ik_0 z} + f_0(\theta)\frac{e^{ikr}}{r}$

Since we are assuming the atom to be in the ground state before scattering $\varphi_n(P)$ $(n \neq 0)$ must have the asymptotic form $f_n(\theta)\frac{1}{r}e^{ik_n r}$ in which the incident wave is absent.

The total energy of the system must be conserved:

$$E = \frac{\hbar^2}{2m}k_0^2 + W_0 = \frac{\hbar^2}{2m}k_n^2 + W_n$$

$$E\sum \varphi_n \chi_n = \sum H_A \varphi_n \chi_n$$

$$+ \sum' T_p \varphi_n \chi_n + \sum V \varphi_n \chi_n$$

Multiply thru by χ_m^* and integrate

over the atomic coordinates

$$(E - W_m)\psi_m(P) = -\frac{\hbar^2}{2m}\nabla_P^2\psi(P) + \int \chi_m^* V \Psi \, d\tau_A$$

$$\nabla^2\psi_m + k_m^2\psi_m = \frac{2m}{\hbar^2}\int \chi_m^* V \Psi \, d\tau_A$$

Born Approx. Assume that the interaction has only a small effect on the wave function so the we can substitute the unscattered wave function, $\Psi_0 = e^{ik_0 z}\chi_0(A)$, into the integral:

$$\nabla^2\psi_m + k_m^2\psi_m = \frac{2m}{\hbar^2} e^{i\underline{k}\cdot\underline{r}} \int \chi_m^* V \chi_0 \, d\tau_A$$

where $\underline{k}$ has the z direction

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$$\nabla^2 \psi_n + k_n \psi_n = \frac{2m}{\hbar^2} e^{i\underline{k}\cdot\underline{r}} \int \chi_m^* V \chi_0 \, d\tau_A = F(\underline{r})$$

The solution is:

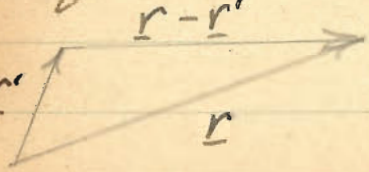
$$\psi = -\int \frac{F(\underline{r}')}{4\pi} e^{ik_n|\underline{r}-\underline{r}'|} \frac{d\tau'}{|\underline{r}-\underline{r}'|}$$

To match the boundary conditions

$$\psi_n = e^{ik_0 z} \delta_{no} - \int \frac{F_n(\underline{r}')}{4\pi} e^{ik_n|\underline{r}-\underline{r}'|} \frac{d\tau'}{|\underline{r}-\underline{r}'|}$$

We are interested only in the asymptotic form, when $|\underline{r}| >> |\underline{r}'|$ for all values of $|\underline{r}'|$ for which $F(r')$ is appreciable.

Define $\underline{k}_n$ as a vector with magnitude k_n and direction θ. Let r be the distance from the origin to the point of observation.



$$k_n|\underline{r}-\underline{r}'| = k_n r - \underline{k}_n \cdot \underline{r}'$$

$$\psi_n = \delta_{no} e^{ik_0 z} - \frac{e^{ik_n r}}{4\pi r} C_n(q)$$

where $C_n(q) = \frac{2m}{\hbar^2} \int e^{i(\underline{k}_0 - \underline{k}_n)\cdot \underline{r}'} V \chi_n^* \chi_0 \, d\tau_A \, d\underline{r}'$

$$= \frac{2m}{\hbar^2} \int e^{i\underline{q}\cdot\underline{r}'} V_{no}(\underline{r}') \, d\underline{r}'$$

and

$$V_{no}(\underline{r}') = \int \chi_n^*(A) \, V(\underline{r}' A) \, \chi_0(A) \, d\tau_A$$

Then $f(\theta) = -\frac{1}{4\pi} C_n(q)$ and $\hbar q$ is the momentum lost by the particle in the collision process. The current per unit solid angle is $I(\theta) = k_n / k_0 \, |f(\theta)|^2$. The ratio of the k's enters because the current is proportional to the velocity times the density.

At this point we must insert the particular properties of the atom. Consider first a one electron atom. Then $\underline{A}$ stands for the three coordinates of the electron.

$$V(\underline{A}\,\underline{r}) = \frac{-e^2 Z}{|\underline{r}-\underline{A}|} + \frac{Z Z' e^2}{|\underline{r}|}$$

$$C_n(\underline{q}) = \frac{2m}{\hbar^2}\int e^{i\underline{q}\cdot\underline{r}}\left[\frac{-e^2 Z}{|\underline{r}-\underline{A}|} + \frac{Z Z' e^2}{|\underline{r}|}\right] \chi_n^* \chi_0 \, d\tau_{\underline{A}}\, d\tau_{\underline{r}}$$

$$\int \frac{e^{i\underline{q}\cdot\underline{r}}}{|\underline{r}-\underline{A}|}\, d\tau_r = \frac{4\pi}{q^2} e^{i\underline{q}\cdot\underline{A}}$$

Therefore: $C_n(\underline{q}) = \frac{2m}{\hbar^2}\frac{4\pi e^2 Z}{q^2}\left[\epsilon_{no}(\underline{q}) - Z'\delta_{no}\right]$

where $\epsilon_{no}(\underline{q}) = \int \chi_n^*(\underline{A})\, e^{i\underline{q}\cdot\underline{A}}\, \chi_0(\underline{A})\, d\tau_{\underline{A}}$

This shows that the scattering by the nucleus Z' enters only in the elastic terms, which is sensible since we regard the nucleus as having no structure.

In case there are many electrons $\underline{A}$ stands for all the position vectors and we get

$$\epsilon_{no} = \int \chi_n^*(\underline{A}) \sum_s e^{i\underline{q}\cdot\underline{A}_s} \chi_0(\underline{A})\, d\tau_{A_1}\, d\tau_{A_2} \ldots$$

Putting everything together, we obtain:

$$2\pi I_{no}(\theta)\sin\theta d\theta = \frac{k_n}{k_o}\left|\frac{2me^2Z}{q^2\hbar^2}(\epsilon_{no} - Z'\delta_{no})\right|^2 2\pi\sin\theta d\theta$$

and $q^2 = k_o^2 + k_n^2 - 2k_o k_n \cos\theta$

$$k_n^2 = k_o^2 - \frac{2m}{\hbar^2}(W_n - W_o)$$

The probability of a given momentum transfer is:

$$N_{no}(q)dq = \frac{k_n}{k_o}\frac{4m^2e^4Z^2}{\hbar^4 q^4}\left|\epsilon_{no}(q) - Z'\delta_{no}\right|^2 2\pi\sin\theta d\theta$$

$$2q\,dq = 2k_n k_o \sin\theta d\theta$$

Therefore $N_{no}(q)dq = \frac{8\pi m^2 e^4 Z^2}{k_o^2 \hbar^4 q^3}dq\left|\epsilon_{no}(q) - Z'\delta_{no}\right|^2$

And the total x-section for a given energy loss is:

$$\sigma_{no} = \int_0^{\pi} I_{no}(\theta) 2\pi\sin\theta d\theta = \int_{q_{min}}^{q_{max}} N_{no}(q)\,dq$$

$$= \int_{k_o - k_n}^{k_o + k_n} N_{no}(q)\,dq$$

In fast collisions the energy loss

is usually very small:

$$q_{max} = 2k_0 me/m$$

$$q_{min} = m\Delta W/k_0\hbar^2$$

The dependence on ΔW is a nuisance

The fact that there is no inelastic scattering from the nucleus is a result of the Born approx. which prevents double scattering. We can check the elastic component against our earlier calculations

$$N_{00}(q)dq = \frac{8\pi m^2 e^4 Z^2}{k^2\hbar^4 q^3}\, dq\, |Z - \epsilon_{00}(q)|^2$$

$\epsilon_{00}(q) = \int \chi_0^* e^{i(q\cdot A)} \chi_0\, d\tau_A$ which is exactly the form factor.

The total inelastic scattering X-section as a function of momentum transfer

$$I(q)dq = \sum_n I_{n0}(q)dq$$

$$= \frac{8\pi m^2 e^4 Z^2}{\hbar^4 k^2}\, \frac{dq}{q^3} \sum |\epsilon_{n0}(q)|^2$$

The relation between momentum transfer and θ depends on the energy.

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I In treating inelastic scattering it is difficult to do better than the Born Approximation. Mott & Massey treats special problems.

Consider the collision in which the incident particle is scattered thru an angle θ and the scatterer is excited from E_0 to E_n. The x-section for this reaction is:

$$\sigma(\theta)d\omega = \frac{k_n}{k_0}\frac{4m^2c^4}{\hbar^4 q^4}|\epsilon_{on}(q)|^2 2\pi \sin\theta d\theta$$

where $\epsilon_{on} = \int \chi_0(\underline{r}) e^{i\underline{q}\cdot\underline{r}} \chi_n^*(\underline{r}) d\tau$

In an experiment what is usually

measured is the total χ-section for scattering thru a given angle, or the total probability of exciting an atom to a given state. Therefore it is of interest to integrate over the various parameters to obtain χ-sections for these processes.

A. Integral Cross-section for excitation of a state E_n.

The probability of exciting a transition will be largest for small q. We expand the exponential

$$e^{i\underline{q}\cdot\underline{r}} = 1 + i\underline{q}\cdot\underline{r} + \dots$$

$$\epsilon_{on} = \int \chi_o \chi_n^* d\tau + i\underline{q}\cdot\int \chi_o \underline{r}\, \chi_n^* d\tau$$

$$\epsilon_{on} = i\underline{q}\cdot\underline{r}_{on}$$

r_{on} is the dipole moment for the transition $o \to n$. $\epsilon_{on} \sim r_{on}$.

The integral x-section is roughly proportional to $|r_{on}|^2$, the square of the dipole moment esp to $0 \to n$. i.e. the optical transition probability.

In second approx. a transition to any state is possible.

B. Integral x-section for a given momentum transfer (scattering thru θ) For reasons which we shall see later we investigate $\sum_n \sigma_{on}(q)$ instead of $\sum \sigma(\theta)$.

$$\sum_n \sigma_{on}(q)\,dq = \frac{8\pi m^2 e^4}{\hbar^4 k^2}\,\frac{dq}{q^3} \sum_{n=1}^{\infty} |\epsilon_{on}(q)|^2$$

where we have been careful to leave out the elastic scattering. We note

$$\sum_1^\infty |\epsilon_{on}|^2 = \sum_0^\infty |\epsilon_{on}|^2 - |\epsilon_{oo}(q)|^2$$

$$\sum_0^\infty |\epsilon_{on}|^2 = \sum_0^\infty \langle e^{iq\cdot r}\rangle_{on} \langle e^{-iq\cdot r}\rangle_{no}$$

$$= \sum_0^\infty \int \chi_o e^{iq\cdot r} \chi_n^*\, d\tau \int \chi_o^* e^{-iq\cdot r} \chi_n\, d\tau$$

The following theorem is true

$$\sum_n A_{on} B_{no} = (AB)_{oo}$$

In our case $e^{i\vec{q}\cdot\vec{r}} \cdot e^{-i\vec{q}\cdot\vec{r}} = 1$

$$\int \chi_o^* \, 1 \, \chi_o \, d\tau = \langle 1 \rangle_{oo} = 1 \text{ normalization}$$

Hence $\sum |\epsilon_{on}(\vec{q})|^2 = 1 - |\epsilon_{oo}(\vec{q})|^2$

$$= 1 - F^2(\vec{q})$$

where $F(\vec{q})$ is the atom form factor.

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I Proof of Theorem on Matrix multiplication and last time.

$$\sum A_{kl} B_{lm}$$

$$A_{kl} = \int \chi_k^* A \chi_l \, d\tau$$

$$B\chi_m = \sum_l B_{lm} \chi_l$$

$$\sum_l A_{kl} B_{lm} = \int X_k^* A \sum_l B_{lm} X_l \, d\tau$$

$$= \int X_k^* A (B X_m) d\tau$$

$$= \int X_k^* A B X_m \, d\tau$$

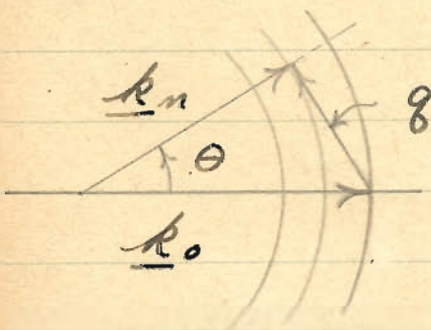
$$= (AB)_{km}$$

In our case $A = e^{i\underline{q}\cdot\underline{r}}$ $B = e^{-i\underline{q}\cdot\underline{r}}$

$k = m = 0$

$$\sum_n |\epsilon_{on}|^2 = 1_{oo} = 1$$

II Relation between q and θ



The vectors $\underline{k}_n$ describe spheres in k space, one for each n.

$$q_{n\,min} = \frac{m}{\hbar^2 k} (E_n - E_o)$$

For $q_n >> q_{n\,min}$ then q_n for a

given θ is practically independent of n.

$$q \approx 2k_0 \sin \theta/2$$

The transition probabilities are $\sim |r_{on}|^2$, the dipole moment, which is large only if $E_n - E_0$ is not too great. Therefore scattering thru a given angle corresponds to a given momentum change.

$$\sigma_{in}(q)dq = \frac{8\pi m^2 e^4}{\hbar^4 k_0^2} \frac{dq}{q^3}\left[1 - |F(q)|^2\right]$$

$$= \frac{2\pi m^2 e^4}{\hbar^4 k_0^4} \frac{\cos\theta' d\theta'}{\sin^3\theta'}\left[1 - |F(q)|^2\right]$$

$$\theta' = \theta/2$$

For small angle scattering

$$F(q) \sim 1 - Aq^2$$
$$|F(q)|^2 \sim 1 - 2Aq^2$$

$$\left.\begin{aligned} \sigma_{in} &\sim \frac{dq}{q} \quad \text{small } q \\ \sigma_{in} &\sim \frac{d\theta}{\theta} \quad \text{small } \theta \end{aligned}\right\} q \gg q_{min}$$

Compare with σ elastic

$$\sigma_{el} \sim \frac{dq}{q^3}(1-F)^2 \sim q\,dq \text{ for small } q$$

For a neutral atom $\sigma_{in} >> \sigma_{el}$ at small angles.

For hydrogen $F(q) = 1/(1+\frac{1}{4}q^2a^2)^2$

For large angle scattering interference becomes important. $F(q) = \int \chi_0^2 e^{i\vec{q}\cdot\vec{r}}\,d\tau$

$$F(q) << 1 \quad : \quad qa >> 1$$

where a = effective atomic radius

$$k_0 a\,\theta >> 1$$

$$\theta >> \lambda/a$$

This problem treated in elastic scattering.

Large angles

$$\sigma_{in} = \frac{2\pi m^2 c^4}{h^4 k_0^2}\,\frac{dq}{q^3}\cdot 1$$

At large angles the particles are scattered as tho by free electrons.

The elastic scattering is the same as the scattering from the nucleus at large angles.

$$\epsilon_{on} = \int \chi_o e^{i\vec{q}\cdot\vec{r}} \chi_n^* \, d\tau$$

For large q, the exponential varies rapidly. χ_o varies slowly. ϵ_{on} will be small unless $\chi_n^* \sim e^{-i\vec{q}\cdot\vec{r}}$ This means that after the scattering the electron wave function $\chi_n \sim e^{i\vec{q}\cdot\vec{r}}$. The electron is moving away from the nucleus with a momentum $\hbar q$. The wave function is approx. a plane wave and is little perturbed by

the potential. The nucleus does not much affect the collision and momentum is approx. conserved between scattered particle and electron.

The treatment is not exact. χ_0 does vary and χ_n is perturbed by the potential. The momentum distribution of the ejected electrons enables one to determine the momentum distribution in the atom.

If there are several electrons in an atom the potential acting on the scattered particle is

$$V = \frac{Ze^2}{r} - e^2 \sum_i \frac{1}{|\underline{r} - \underline{r}_i|}$$

$$\epsilon_{on} = \int \chi_0 \left(Z - \sum_j e^{i\underline{q}\cdot\underline{r}_j} \right) \chi_n^* \, d\tau$$

$$\sum |\epsilon_{on}|^2 = \int |\chi_0|^2 \left| \sum_{j=1}^{Z} e^{i\underline{q}\cdot\underline{r}_j} \right|^2 \doteq Z$$

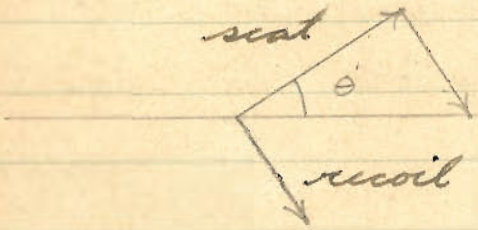
for large q

$\sigma_{in} \sim Z$ for large q.
$\sigma_{el} \sim Z^2$ for large q

For heavy scattered particles

$$q = 2k_0 \sin \theta/2$$

For electrons scattered thru large angles $q \approx k_0 \sin\theta$



Problem: Calculate the scattering (elastic & inelastic) from a spherically symmetric oscillator.

Separate in Cartesian coordinates.

Find probability for inelastic scattering as a function of θ

Integrals in RMP 9 124 452 - 453 6

$M_{osc} << M_{part} << M_{cg} \sim \infty$

Assume Coulomb interaction, Born approx., scatterer initially in ground state.

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I The total x-section for inelastic scattering is

$$\sigma_T \sim \int_{q_{min}}^{q_{max}} \frac{dq}{q^3} b_3 (1 - |F(q)|^2)$$

$$q_{min} \approx \frac{m}{\hbar^2 k} (E_n - E_0)$$

If we average over all n

$$q_{min\,av} \approx -\frac{m}{\hbar^2 k} E_0$$

$$q_{max} \approx 2k m_0/m$$

This is the classical expression for q_{max} and holds if $m \gg m_e$

II Stopping Power

Consider a particle of mass m traversing material having N atoms / cm². The energy loss

in a given collision is $E_n - E_0$. We can calculate the rate of energy loss.

$$\sum_n \int_{q_{min\,av}}^{q_{max}} (E_n - E_0)\,\sigma_{on}(q)\,dq$$

$$= \int_{q_{min\,av}}^{q_{max}} \sum_n \sigma_{on}(E_n - E_0)\,dq$$

$$= \int \frac{8\pi e^4 m^2}{\hbar^4 k^2} \frac{dq}{q^3} \sum_n |\epsilon_{on}|^2 (E_n - E_0)$$

$$E_n \chi_n = H \chi_n$$
$$E_0 \chi_0^* = H \chi_0^*$$

$$\epsilon_{on}(E_n - E_0) = \int \chi_0^* e^{i\mathbf{q}\cdot\mathbf{r}} H \chi_n \, d\tau$$

$$- \int H \chi_0^* e^{i\mathbf{q}\cdot\mathbf{r}} \chi_n \, d\tau$$

$$E_n \epsilon_{on} \epsilon_{on}^* = \langle e^{i\mathbf{q}\cdot\mathbf{r}} H \rangle_{on} \langle e^{-i\mathbf{q}\cdot\mathbf{r}} \rangle_{no}$$
$$E_0 \epsilon_{on} \epsilon_{on}^* = \langle H e^{i\mathbf{q}\cdot\mathbf{r}} \rangle_{on} \langle e^{-i\mathbf{q}\cdot\mathbf{r}} \rangle_{no}$$

$$\sum_n (E_n - E_0) |\epsilon_{on}|^2$$

$$= \sum_n \langle e^{i\mathbf{q}\cdot\mathbf{r}} H - H e^{i\mathbf{q}\cdot\mathbf{r}} \rangle_{on} \langle e^{-i\mathbf{q}\cdot\mathbf{r}} \rangle_{no}$$

$$= \int \chi_0^* (e^{iq\cdot r} H e^{-iq\cdot r} - H) \chi_0 \, d\tau$$

$$H = V(r) - \frac{\hbar^2}{2m_e}\nabla^2$$

$$\nabla^2 e^{-iq\cdot r} = -q^2 e^{-iq\cdot r}$$

$$= \frac{\hbar^2}{2m_e} q^2 \int \chi_0^* \chi_0 \, d\tau = \frac{\hbar^2 q^2}{2 m_e}$$

$$E_{loss/atom} = \frac{4\pi e^4 m^2}{\hbar^2 k^2 m_e} \ln\left(\frac{q_{max}}{q_{min\,av}}\right)$$

$$= \frac{4\pi e^4}{m_e v^2} \ln \frac{2\hbar^2 k^2 m_e}{m^2 E_0}$$

$$= \frac{4\pi e^4}{m_e v^2} \ln \frac{2 m_e v^2}{I} \qquad I = E_0 = \text{ionization potential}$$

Since our beam has unit intensity, the energy loss per particle per cm. will be:

$$E_{tom} = \frac{4\pi e^4}{m_e v^2} N Z \ln \frac{2 m_e v^2}{I}$$

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I Application of Time Dependent perturbation theory to inelastic scattering. Ref.: Lecture 41 1/30/47

$$\Psi(\underline{r}t) = \sum_n a_n(t)\, \Psi_n(\underline{r})\, e^{-iE_n t/\hbar}$$

The perturbing potential is a function of $\underline{r}$ and t, $V(\underline{r}t)$. The coefficients are given by the equations

$$i\hbar \frac{da_n}{dt} = \sum_m V_{nm}(t)\, a_m(t)\, e^{i(E_n - E_m)t/\hbar}$$

where $$V_{nm}(t) = \int \Psi_n^* V(\underline{r}t)\, \Psi_m \, d\tau$$

At $t = 0$ the system is in the ground state $a_0 = 1$ and all other a's $= 0$. Assume

$$V(\underline{r}t) = U(\underline{r})\, e^{-i\omega t}$$

then

$$V_{no}(t) = U_{no}\, e^{-i\omega t}$$

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and

$$a_n = -U_{no}\left(e^{i(E_n - E_o - \hbar\omega)t/\hbar} - 1\right)/(E_n - E_o - \hbar\omega)$$

The probability of a transition from the ground state to the continuum of energies ($E > 0$) near an energy E_n in a unit time is:

$$\frac{d}{dt}\sum_{n-\delta}^{n+\delta} |a_n|^2 = \frac{2\pi}{\hbar}|U_{no}|^2 \frac{dN}{dE}$$

where $\frac{dN}{dE}$ is the density of energy states in the neighborhood of E_n.

Before we can compute U_{no} we must investigate the normalization of the wave function in the continuum.

Assume a box of sides $L_1 L_2 L_3$ We shall normalize ψ inside this box with the boundary condition the ψ equals 0 at the surface of the box. The wave function

for a free particle in the box will be:

$$\Psi = A \sin k_x x \sin k_y y \sin k_z z$$

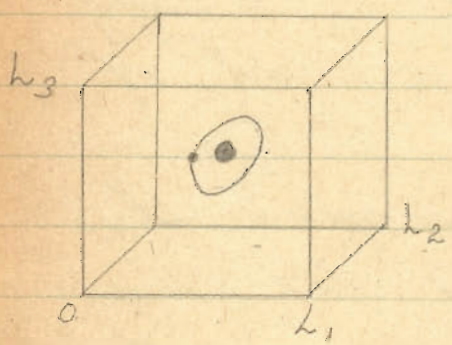
$$k_x = 2\pi n_1 / L_1$$

We want

$$\int \Psi^2 dx\,dy\,dz = 1$$

$$\tfrac{1}{2} L_1 \, \tfrac{1}{2} L_2 \, \tfrac{1}{2} L_3 \, A^2 = 1$$

$$A = \sqrt{\frac{8}{V}} \quad \text{where } V = L_1 L_2 L_3$$



Let $x = X + \xi$
where X = coordinate of atom in the box and ξ = coordinate of electron relative to atom.

$$\sin k_x x = \sin(k_x X + k_x \xi)$$

$$= \sin k_x X \cos k_x \xi + \ldots$$

$\sin k_x X$ changes rapidly with k_x

$\cos k_x z$ changes slowly with k_x

$$U_{n0} = \sqrt{\frac{8}{\mathcal{V}}} \sin k_x X \sin k_y Y \sin k_z Z \, W_{n0} + \dots$$

Where W_{n0} is slowly variable with $\underline{k}$.

$$\sum |a_n|^2 = \sum_{\underline{k}} \frac{A_{n0}}{\mathcal{V}} \sin^2 k_x X \dots \left| \frac{e^{i(\;)} - 1}{E_n - E_0 - \hbar\omega} \right|^2 + \dots$$

By making X large enough we can make $\sin^2 k_x X$ vary arbitrarily fast over the range of E for which the resonance denominator is small. Hence we can replace it by $\frac{1}{2}$. If we consider the rest of the terms we get something $\sim \mathcal{V}$ and hence the transition probability is independent of the volume we have chosen for normalization. This is as it should be physically.

A more satisfactory way of normalizing than the one we have just discussed is to normalize in a box with the boundary condition that the wave function repeat itself in the adjacent boxes.

$$\psi(xyz) = \psi(x+l_1, y, z) = \psi(x y+l_2 z) = \psi(xyz+l_3)$$

$$\psi = e^{i(k_x x + k_y y + k_z z)}$$

The boundary condition is satisfied if $k_x = 2\pi n_1 / l_1$. Hence we have the same number of states as in the previous case. This method has the advantage that we can have running waves and the $|\psi|^2$ is a constant in the box and does not depend on the position of the atom in the box. Let $\underline{R}$ refer to the position of the nucleus and $\underline{r}$ to the position

of the electron relative to the nucleus, then

$$\psi = e^{i\underline{k}\cdot\underline{R}}\, e^{i\underline{k}\cdot\underline{\rho}}$$

$$U_{no} = e^{-i\underline{k}_n\cdot\underline{R}} \int e^{-i\underline{k}_n\cdot\underline{\rho}} U(r)\psi_0 \, d\tau$$

Normalization $\int |\psi_n|^2 d\tau = 1$ n large

$$\psi = \frac{1}{\sqrt{\Omega}}\, e^{i\underline{k}_n\cdot\underline{r}}$$

Hence:

$$U_{no} \sim \frac{1}{\sqrt{\Omega}}$$

$$|U_{no}|^2 \sim \frac{1}{\Omega}$$

The number of states in the interval dk_x $\quad dn_1 = L_1\, dk_x / 2\pi$

$$dN = \frac{\Omega}{(2\pi)^3}\, d\underline{k} = \frac{\Omega}{(2\pi\hbar)^3}\, d\underline{\rho}$$

$$d\underline{\rho} = p^2\, dp\, d\omega$$

$$\frac{dN}{dE} = \frac{\Omega}{(2\pi\hbar)^3}\, p^2 \frac{dp}{dE}\, d\omega$$

In general $\dfrac{dE}{dp} = v$

Non relativistic $p = mv$

$$\frac{dN}{dE} = \frac{dN}{(2\pi\hbar)^3 m^2 v \, d\omega}$$

Since our transition probability is going to be independent of volume we can normalize to unit density.

$$\frac{d}{dt}\sum_{n-\delta}^{n+\delta} |a_n|^2 = \frac{2\pi}{\hbar} |U_{no}|^2 (2\pi\hbar)^3 \frac{1}{V} \frac{p^2}{V} \, d\omega$$

where: $U_{no} = \int e^{-i\underline{k}_n \cdot \underline{r}} V \psi_0 \, d\tau$

This expression gives the transition probability per unit time. In the derivation we have assume the final state of the electron to be a plane wave. This is true if the electron is far from the atom. We normalize ψ_n so that asymptotically it behaves like a plane wave of unit density.

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Let $\psi_m(\underline{R})$ and E_m refer to the wave function and energy of the incident particle; Let $\chi_n(\underline{r})$ and W_n refer to the same quantities of the atom.

We turn on a perturbing potential $V(\underline{r}\,\underline{R})$ which is then held constant in time. We wish to calculate the prob. of a transition from state $\psi_0 \chi_0 \rightarrow \psi_m \chi_n$. Energy must be conserved:

$$E_{nm} = W_0 + E_0 = W_n + E_m$$

$$E_m = E_0 - (W_n - W_0)$$

$$i\hbar \dot{a}_n = \int \psi_0 \chi_0 V(\underline{r}\,\underline{R}) \psi_n^* \chi_n c^{i(E_0 - E_n)t/\hbar} d\underline{r}\, d\underline{R}$$

The probability of a transition to the continuum near E_n per unit time is:

$$\frac{2\pi}{\hbar} |V_{on}|^2 \frac{dN}{dE}$$

Asymptotically $\psi \sim e^{i\underline{k}\cdot\underline{R}}$ hence

$$\frac{dN}{dE} = \frac{\rho^2}{V(2\pi\hbar)^3} d\omega$$

$$\rho^2/V = M^2 V_n$$

$$\text{Prob/sec} = \frac{M^2 V_n}{(2\pi)^2 \hbar^4} |V_{on}|^2 d\omega$$

We normalize to unit density at infinity. The incident current per $cm^2 = V_0$

$$\text{Prob/part.} = d\sigma_n = \frac{V_n}{V_0} d\omega \Big/ \frac{2M}{4\pi\hbar^2 V_{on}}^2$$

This is the result obtained 3/15/49

II. Normalization of the Wave Function in the Continuum.

Suppose we wish to expand a function in terms of the wave function. The expansion will be:

$$f = \int a_k \psi_k \, dk + \sum_n a_n \psi_n$$

The Σ is taken over the discrete spectrum. The integral is taken over the continuum. We wish the coefficients a_k to be:

$$a_k = \int f \psi_k^* \, dx$$

The question is: how must we normalize ψ_k

$$\int f \psi_k^* \, dx = \int dx \, \psi_k^* \int a_{k'} \psi_{k'} \, dk$$

If $a_{k'}$ slowly variable break up the integral as follows

$$\sum_n a_{k_n'} \int dx \, \psi_k^* \int_{k_n'}^{k_{n+1}'} \psi_{k''} \, dk''$$

From this we obtain the orthogonality and normalization conditions in the continuous spectrum. If the

interval k_n' to k_{n+1}' does not contain k the integral is zero. If the interval does contain k the integral is 1. This condition may be written

$$\int dx\, \psi_k^*(x) \int_{k_1-\epsilon}^{k_1+\epsilon} dk'\, \psi_{k'}(x) = 0 \begin{cases} k < k_1 - \epsilon \\ k > k_1 + \epsilon \end{cases}$$

$$= 1 \left\{ k_1 - \epsilon < k < k_1 + \epsilon \right.$$

Illustrative example: $\psi = A e^{ikx}$

$$A \int_{k_1-\epsilon}^{k_1+\epsilon} e^{ik'x}\, dk' = \frac{1}{ix}\left[e^{i(k_1+\epsilon)x} - e^{i(k_1-\epsilon)x} \right]$$

$$A^2 \int_{-\infty}^{\infty} dx \left[e^{i(k_1+\epsilon-k)x} - e^{i(k_1-\epsilon-k)x} \right] / ix$$

By contour integration of each integral (below pole since whole integral has no singularities)

$$\int \frac{e^{i\alpha x}}{ix} = 2\pi \quad \alpha > 0$$

$$= 0 \quad \alpha < 0$$

The original integral

$$= 0 \quad \begin{cases} k_1 + \epsilon < k \\ k_1 - \epsilon > k \end{cases}$$

$$= 2\pi A^2 \{ k_1 - \epsilon < k < k_1 + \epsilon \}$$

$$A = 1/\sqrt{2\pi}$$

We can also normalize with respect to the Energy

$$f(x) = \int a(E)\, \psi_E \, dE$$

$$a(E) = \int f(x)\, \psi_E^* \, dx$$

$$= \int dx\, \psi_E^* \int_{E_1-\epsilon}^{E_1+\epsilon} dE'\, \psi_{E'} \quad = 0 \begin{cases} E_1 + \epsilon < E \\ E_1 - \epsilon > E \end{cases}$$

$$= 1 \{ E_1 - \epsilon < E < E_1 + \epsilon \}$$

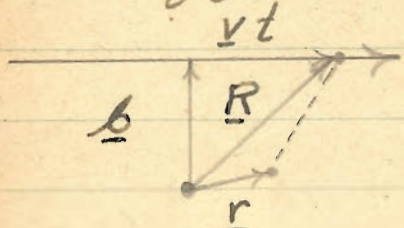
$\psi_E = \psi_k$ except for normalization.

From above:

$$\psi_E = \psi_k \sqrt{\frac{dk}{dE}}$$

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Consider a heavy particle which passes by an atom at a large distance. This particle will give rise to a time dependent perturbing potential. We wish to calculate the effect:



$$\underline{R} = \underline{v}t + \underline{b}$$

$$V(|\underline{R} - \underline{r}|)$$

Applying our time dependent perturbation theory

$$i\hbar \dot{a}_n = \int \chi_n^*(\underline{r}) \chi_0(\underline{r}) V(\underline{R} - \underline{r}) d\tau \, e^{i(E_n - E_0)t/\hbar}$$

$$V(|\underline{R} - \underline{r}|) = V(|\underline{R}|) - \underline{r} \cdot \nabla V|_{\underline{R}}$$

$$i\hbar \dot{a}_n = -\underline{r}_{on} \cdot (\nabla V)_{\underline{R}} \, e^{i(E_n - E_0)t/\hbar}$$

$$\nabla V = \frac{R}{R}\frac{dV}{dR} = (\underline{b} + \underline{v}t)\left(\frac{1}{R}\frac{dV}{dR}\right)$$

$$i\hbar \dot{a}_n = -\left[(\underline{r}_{on}\cdot\underline{b}) + (\underline{r}_{on}\cdot\underline{v})t\right]\left(\frac{1}{r}\frac{dV}{dr}\right)_{\sqrt{b^2+v^2t^2}} \cdot e^{\frac{i}{\hbar}(E_n - E_0)t}$$

Let us considered a fast collision $(E_n - E_0) \cdot$ time of collision $<< \hbar$. The $(\underline{r}\cdot\underline{v})t$ term contributes nothing.

$$a_n = \frac{Zb}{i\hbar}\int_{-\infty}^{\infty}\left(\frac{1}{R}\frac{dV}{dR}\right)_{\sqrt{b^2+v^2t^2}} dt$$

For a coulomb field $V = -\frac{e^2}{r}$

$$\frac{1}{r}\frac{dV}{dr} = \frac{e^2}{r^3}$$

$$\int_{-\infty}^{\infty}\frac{e^2 dt}{(b^2+v^2t)^{\frac{3}{2}}} = \frac{2e^2}{vb^2}$$

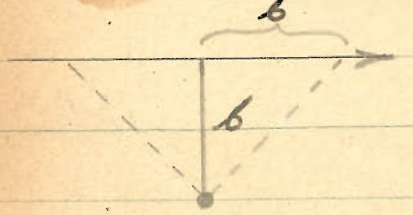
$$a_m = \frac{2Z_{on}e^2}{i\,v\,b\,\hbar}$$

The cross section for a collision having impact parameter b to $b + db$ is:

$$\sigma(b)\,db = 2\pi b\,db\,|a_n|^2$$

$$= \frac{8\pi e^4}{\hbar^2 v^2}\,|Z_{on}|^2\,\frac{db}{b}$$

This relation holds $(E_n - E_o)\tau \ll \hbar$



$$(E_n - E_o)\frac{b}{v} \ll \hbar$$

$$b < v/\omega$$

$$b_{max} \sim v/\omega$$

Momentum transfer = Force × time

$$\hbar q \approx \frac{e^2}{b^2}\,\frac{2b}{v} = \frac{2e^2}{bv}$$

Q. M. the collisions take place over a range of b.

$$q_{min} = \frac{m}{\hbar k^2}\Delta E \doteq \frac{\omega}{v}$$

$$p_{min} b_{max} = \hbar q_{min} b_{max} \approx \hbar$$

Energy Transfer $= \frac{1}{2} m_e (p')^2$.

$$= \frac{1}{2m}\left(\frac{e^2}{b^2}\frac{2b}{v}\right)^2$$

The stopping power per atom is the energy lost per second per atom. Current $\equiv v$

$$S = \int \frac{1}{2m}\left(\frac{e^2}{b^2}\frac{2b}{v}\right)^2 2\pi b\, db$$

$$= \frac{4\pi e^4}{mv^2} \ln\left(\frac{b_{max}}{b_{min}}\right)$$

$b_{max} \approx v/\omega = \hbar v/W$

Classical $b_{min} = e^2/$ where $=$ energy of incident particle.

Q.M. b_{min} = approx. width of wave packet $\approx \hbar/Mv$

Classical formula valid $\frac{e^2}{\hbar v} \gg 1$

$$S = \frac{4\pi e^4}{mv^2} \ln\left(\frac{v\hbar}{e^2}\frac{M}{W}\right)$$

Q.M. formula valid $\frac{e^2}{\hbar v} \ll 1$

This is essentially the condition

that the Born approx hold.

$$S = \frac{4\pi e^2}{m v^2} \ln\left(\frac{E_{in}}{W}\right)$$

II Absorption of Energy

$$\alpha = \frac{2\pi}{\hbar}(eF)^2 \left| \int z \psi_0 \psi_E^d \, d\tau \right|^2 \frac{dN}{dE}$$

α = number of transition to energy E per second. ψ_E^d is normalized to unit density at infinity.

For a wave propagating in the x direction

$$E = F\{e^{i(kx-\omega t)} + e^{-i(kx-\omega t)}\}$$
$$E = 2F \cos k(x - vt)$$
$$V = eFz$$

The energy density is

$$\frac{1}{8\pi}\langle E^2 + B^2\rangle_{av}$$

$$= \frac{1}{8\pi}\, 4F^2 = \frac{F^2}{2\pi}$$

Quanta per cm^3 $= F^2/2\pi h\nu$

Absorption prob. per quanta per cm^3 per sec if there are N_0 atoms per cm^3 is:

$$4\pi^2 e^2 \nu N_0 / Z_{0E}\Big|^2_{\text{energy}}$$

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$$Z_{0E} = \int \psi_0\, z\, \psi_E^{\text{energy}}\, d\tau$$

I Oscillatory Strength

Definition

$$f_{on} = \frac{2i}{h}(p_x')_{on}\, x_{no}$$

$$(p_x')_{on} = m\frac{dx'_{on}}{dt}$$

Where the ' indicates the matrix element including the time

dependence.

$$\psi_n(\underline{r},t) = \psi_n(\underline{r}) e^{-iE_n t/\hbar}$$

$$x'_{on} = \int \psi_n x \psi_o^* \, d\tau$$

$$= x_{on} e^{-i(E_n - E_o)t/\hbar}$$

$$(p_x')_{on} = -\frac{i(E_n - E_o)}{\hbar} e^{-i(E_n - E_o)t/\hbar} m x_{on}$$

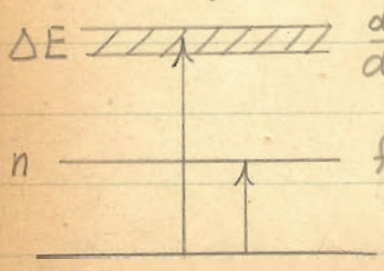
$$(p_x')_{on} = -i m \nu_{no} x_{on}$$

We shall use $\nu = 2\pi f$

$$f_{on} = \frac{2m}{\hbar} \nu_{no} |x_{on}|^2 .$$

In the continuous spectrum

$$\frac{d}{dE}(f_{oE}) = \frac{2m}{\hbar} \nu_{E0} |x^E_{oE}|^2 .$$



f_{on} is a dimensionless constant associated with a transition.

Sum over the f_{on}

$$\sum_n f_{on} + \int \frac{df_{oE}}{dE} dE$$

$$= \frac{2i}{\hbar}\left(\sum_n + \int\right)(p_x)_{on} x_{no}$$

$$(p_x)_{no} = im\nu_{no} x_{no}$$

$$x_{on}(p_x)_{no} = im\nu_{no}|x_{on}|^2$$
$$= -x_{no}(p_x)_{on}$$

$$= \frac{i}{\hbar}\left(\sum_n + \int\right)\left[(p_x)_{on} x_{no} - x_{on}(p_x)_{no}\right]$$

Our theorem on matrix multiplication enables us to write:

$$= \frac{i}{\hbar}\left[p_x x - x p_x\right]_{oo}$$

$$= \frac{i}{\hbar}\int \psi_o^* \frac{\hbar}{i}\left(\frac{\partial}{\partial x} x - x\frac{\partial}{\partial x}\right)\psi_o \, d\tau = 1$$

The subscript o may refer to any state.

In general

$$\sum_n f_{mn} = 1 \quad \text{for any } m.$$

Heisenberg developed his matrix mechanics by working backward from this relation.

Consider

$$g_{on} = (E_n - E_o)\,|(e^{iqx})_{on}|^2$$

$$\sum_1^\infty g_{on} = \frac{\hbar^2}{2m} q^2$$

$$(e^{iqx})_{on} = \int \psi_o^* e^{iqx} \psi_n \, d\tau$$

$$= (1 + iqx - \tfrac{1}{2} q^2 x^2 + O(q^3))_{on}$$

$$|(e^{iqx})_{on}|^2 = q^2 |x_{on}|^2 + O(q^3)$$

$$\sum g_{on} = q^2 \sum (E_n - E_o)\,|x_{on}|^2 + O(q^3) = \frac{\hbar^2 q^2}{2m}$$

$$\sum f_{on} = \frac{2m}{\hbar^2} \sum (E_n - E_o)\,|x_{on}|^2 = 1$$

Comparing these two expressions we see that the higher order terms in the expansion of $e^{i\beta x}$ must sum identically to zero.

The probability / sec of absorption of one quantum:

$$A = 2\pi^2 \frac{e^2 k}{m} N \frac{db}{dE}$$

Suppose we have a continuous spectrum incident on the particle

$Q(\nu)\, d(h\nu)$ = no. of quanta / cm^3 in the energy interval $d(h\nu)$ at ν

$Q(\nu)\, d(h\nu)\, A$ = no. of quanta absorbed / cm^3 / sec. in the interval $d(h\nu)$ at ν =

The no. of absorption processes leaving the electron in an energy interval ΔE at $E_0 + h\nu$

$$= Q(\nu) 2\pi^2 \frac{e^2 h}{m} N \frac{df_{0k\nu}}{dE} \Delta E$$

The no. of processes leaving the atom in a state "n" is:

$$Q(\nu) 2\pi^2 \frac{e^2 h}{m} N f_{on}$$

Continuous Spectrum

$$E = 2 \sum_k F_k \cos k(x - ct)$$

Assume F_k incoherent i.e.

$$\langle F_k F_{k'} \rangle_{av} = 0 \text{ unless } k = k'$$

The number of quanta per cm^3 in mode k.

$$= \frac{\langle F_k^2 \rangle}{2\pi h\nu} \therefore Q(\nu) = \frac{\langle F_k^2 \rangle}{2\pi h\nu} \cdot \frac{dN}{d(h\nu)}$$

The no. of transitions esp to k per sec per unit energy

$$a = \frac{2\pi}{h} e^2 F^2 |Z_{on}|^2 \cdot \frac{dN}{d(h\nu)}$$

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Absorption of radiation

I Recapitulation

Excitation of discrete states in material having N atoms / cm^3 by radiation containing $Q(\nu)$ quanta / cm^3 / unit $h\nu$

Process per second

$$= Q(\nu) N A$$

$$= Q(\nu) N 2\pi^2 \frac{e^2 \hbar}{m} f_{on}$$

$$f_{on} = \frac{2m}{\hbar} \nu |X_{on}|^2$$

$$= Q(\nu) N 4\pi^2 e^2 \nu |X_{on}|^2$$

II Incident field polarized in z direction

$$E = F\{e^{i\nu t} + e^{-i\nu t}\}$$

In absorption process the $e^{-i\nu t}$ combines with the $e^{-iE_0 t/\hbar}$ to give an energy $e^{-i(E_0 + h\nu)t/\hbar}$

$$E = 2F \cos \nu t \qquad : \nu = 2\pi f$$

$$Q(\nu) = \frac{\langle F_k^2 \rangle_{av}}{2\pi \hbar \nu} \cdot \#\text{ of modes } k \text{ / unit } h\nu$$

Transitions per sec for one atom

$$\frac{2\pi}{\hbar} c^2 F_k^2 / Z_{on} /^2 \cdot \#\text{ modes } K / \text{unit } \hbar\nu$$

Transition prob. / sec $= 4\pi^2 \nu c^2 / Z_{on} /^2 Q(\nu)$
(For one atom)

II Emission of Radiation

Statistical considerations (Einstein)

Consider a box containing N atoms + radiation at high temperature. Assume equilibrium

(A.) N_0 atoms in ground state × no. of quanta, ν, × probability of absorb / sec.
= no. atoms excited × prob. of emission / sec.

Boltzman distribution:

No. of atoms in grand state
$N e^{-E_0/kT}$

No. of atoms in state n.
$N e^{-E_n/kT}$

$$Q(\nu) = e^{-\frac{h\nu}{kT}} \times \text{no. of quanta states per unit } h\nu$$

In the box
$$F = e^{i(k_x x + k_z z + k_y y)}$$

Boundary conditions yield
$$k_x = \frac{2\pi n_x}{L_x}$$

The number of states in the interval dk_x
$$dn_x = \left(\frac{L_x}{2\pi}\right) dk_x$$

Total no. of states in the interval dk
$$dn = \sum_k \frac{V}{(2\pi)^3} dk_x dk_y dk_z$$

$V \equiv 1$
$$= \frac{4\pi k^2 dk}{(2\pi)^3} \cdot 2 \text{ (directions of polar.)}$$

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

= No. of modes per cm^3 regardless of polarization.

The no. of modes per polarization is
$$dn_p = \frac{8\pi}{3} \frac{1}{(2\pi)^3} \frac{\nu^2 d\nu}{c^2}$$

We shall justify the factors 2 and $\frac{1}{3}$ later.

$$Q(\nu) = \frac{8\pi}{3}\frac{1}{(2\pi)^3}\frac{\nu^2}{hc^3}e^{-\frac{h\nu}{kT}}$$

From equation (A)

Prob of spontaneous emission per sec. $= \frac{Ne^{-E_0/kT}}{Ne^{-E_n/kT}} \cdot Q(\nu) \cdot 2\pi^2 \frac{e^2 h}{m} f_{on}$

$$= 2\pi^2 \frac{8\pi}{3}\frac{1}{(2\pi)^3}\frac{\nu^2 e^2}{mc^3} f_{on}$$

$$P_{E/sec} = \frac{2}{3}\frac{\nu^2 e^2}{mc^3} f_{on}$$

$$= \frac{4}{3}\frac{e^2\nu^3}{hc^3}|X_{on}|^2$$

$$\text{Energy}_{E/sec} = \frac{4}{3}\frac{e^2\nu^4}{c^3}|X_{on}|^2$$

Classically

$$\text{Energy}_{E/sec} = \frac{2}{3}\frac{e^2\nu^4}{c^3}\langle X^2\rangle_{av}$$

For heavy atoms the energy radiated is proportional to Z^2, hence

$$\nu \sim Z^2$$

and

$$P_{\text{E/su}} \sim Z^4$$

Discussion of initial statistical equation.

In setting up our statistical equation we considered only the absorption of quanta of frequency ν. Q.M. however the $e^{+i\delta t}$ may combine with $e^{-E_n t/\hbar}$ to give $e^{-(E_n - h\nu)t/\hbar}$. In other words, the atom may be induced to emit radiation of frequency ν by having light of frequency ν fall upon it. Planks radiation formula takes care of this. In the limit of small $h\nu$, our formula is correct.

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We found that the emission of light by an atom in an excited state is: $A = \frac{4}{3}(e^2\nu^3/hc^3)|x_{on}|^2$. We neglected induced emission. The absorption probability is:

$$f(\nu)\, e^{-E_o/kT}$$

where $f(\nu)$ gives the probability of a collision. Then the emission probabability is:

$$e^{-E_n/kT}(1 + f(\nu))$$

The "1" esp to spontaneous emission. The "$f(\nu)$" esp to induced emission and is the same as the absorption function.

$$f(\nu)/(1 + f(\nu)) = e^{-(E_n - E_o)/kT}$$

$$f(\nu) = 1/[e^{-h\nu/kT} - 1]$$

To be correct, we should use Fermi statistics for the atoms but we won't.

We now consider the question of polarization and direction of propagation. For a given direction of polarization, integrate over all propagation directions.

$$\int \sin^2\theta \, d\omega = \frac{8\pi}{3}$$

(Use only the field component in the direction of polarization)

Consider the H-atom in the $\ell = 1$ state. We consider transitions to the ground state $\ell = m = 0$. If the excited state also has $m = 0$, the matrix element exists only for the z-coordinate polarization. If it is one of the other mag. substates, the matrix element will exist for the x and y directions. The total transition probability irrespective of polarization is the

sum of the three. [Angular factors is der Handbuch, or Condon & Shortley]

The factor 2 between the classical and Q.M. results is related to the use of the complex exponential in Q.M. and its real part in classical mechanics.

There is a simpler more direct method of deriving the emission probabilities.

$$\text{Emission Prob.} = \frac{2\pi}{\hbar} e^2 F_k^2 |x_{on}|^2$$

$$\times \text{ no. states per unit energy}$$

$$= \frac{2\pi}{\hbar} F^2 e^2 |x_{on}|^2 \frac{8\pi}{3} \frac{(h\nu)^2}{(2\pi\hbar)^3 c^3}$$

$$= \frac{2}{3} \frac{e^2 F^2 \nu^2}{\pi \hbar^2 c^3} |x_{on}|^2$$

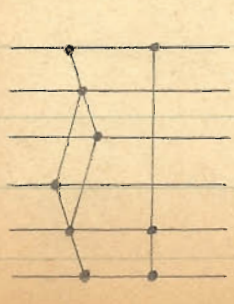
where F is the field due to one

quantum in a box.

Energy / cm^2 = $F^2/2\pi = kv$,
This gives the result directly.

One of the important applications of the theory of radiation is the calculation of the intensity of spectral lines. A line will exist between two states only when there is a matrix element. We shall ignore the direction of polarization and consider only the matrix element of $\underline{r}_{nn'}$. For some transitions, it vanishes and then there is no line.

In a central field $\underline{r}_{nn'}$ vanishes unless $l' = l \pm 1$. Consider the sodium atom. The lowest state is $n = 3$, $l = 0$.



n	l
4	2
4	1
4	0
3	2
3	1
3	0

Unfortunately, it is not possible experimentally to excite just one state. However, we can still calculate the intensity ratios for the lines starting from the same excited state. It is actually a little better to use the intensities of absorption lines. Measurements are best made by using dispersion near the absorption lines. In the case of Hydrogen, the degeneracies spoil all this but an excellent check on the theory can be gotten by considering fine structure and the Stark effect and Zeeman effect. [Ref. London & Shortley]

Another important application is the calculation of lifetimes of excited states. These are determined by the total decay

probability in all modes.
$1/\tau_n = \sum_{n'} A_{nn'}$. These have been tabulated extensively by Bethe (Ref Handbuch 24, 1)

We can get a very rough estimate of the lifetimes

$$\frac{2}{3}\frac{e^2v^2}{mc^3} f_{on} = \frac{2}{3} v \frac{e^2}{mc^2}\frac{v}{c} f_{on}$$

$$= 2.8 \times 10^{-13} \nu \lambda^{-1} \frac{2}{3} f_{on}$$

$$\approx 10^{-7} \nu f_{on}$$

f_{on} is usually of the order of 1, and $\nu \approx 2 \times 10^{16}$, so τ is of the order of 10^{-9} sec.

The true values are apt to be a little longer, since f_{on} is usually a little less than 1.

Excited States of H τ (calc.)

2 S	∞
2 P	1.6×10^{-9} sec
3 S	1.6×10^{-8}
3 P	.5
3 D	1.5
6 S	60
6 P	4
6 D	12
6 H	60

The shortest lives generally come from P states, and the transition is directly to the ground state, which means ν is larger and $A \sim \nu^2$ for a given oscillator strength. The lifetimes tend to increase with n, since the oscillator strength falls off because in a highly excited state the wave function is no longer very similar to that of the ground state. The reason for

the very long lives of the s states is that a given transition in which n and l go in opposite directions is very unlikely. [2] This can be understood thru Fourier analysis and the esp. principle or by the means of the sum rules.]

It is possible that the 2s state is metastable when away from all electric fields (for Hydrogen). Measurements are being made.

The oscillator strengths from the 1s states are

2p	.42
3p	.08
4p	.03
8p	.003
Continuum	.44

Ref. Handbuch der Physik

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I Probability of Emission

(Life time of state n)$^{-1}$ = Σ transition probabilities from n to all lower states. The probability of decay per unit time is proportional to the number of atoms in the state n, hence the probability will decay exponentially in time.

$$\psi_n = u_n(\underline{r})\, e^{-iE_n t/\hbar}\, e^{-\frac{t}{2\tau_n}}$$

where τ_n is the mean life of state n and the factor 2 enters to take care of the fact that the probability is $\propto$ to $|\psi|^2$.

Ref: Wigner + Vaskopf: Zeits f phys. 1929
Heitler

The matrix element of x between the states m n will be:

$$x_{mn} = \int \psi_m^* x \psi_n \, d\tau$$

$$= \int x u_m^* u_n e^{-i(E_n - E_m)t/\hbar} e^{-\frac{t}{2}\left(\frac{1}{\tau_m} + \frac{1}{\tau_n}\right)}$$

we shall denote $\frac{1}{\tau_m} + \frac{1}{\tau_n} \equiv \gamma$

and $(E_n - E_m)/h \equiv \nu_{nm}$

Emission of light of frequency ν

The interaction energy is

$$eFx\left(e^{i\nu t} + \dots\right)$$

Suppose $a_n(t=0) = 1$. Time dependent perturbation theory gives

$$i\hbar \frac{da_m}{dt} = eFx_{mn} e^{-i(\nu_{nm} - \nu)t - \frac{t}{2}\gamma}$$

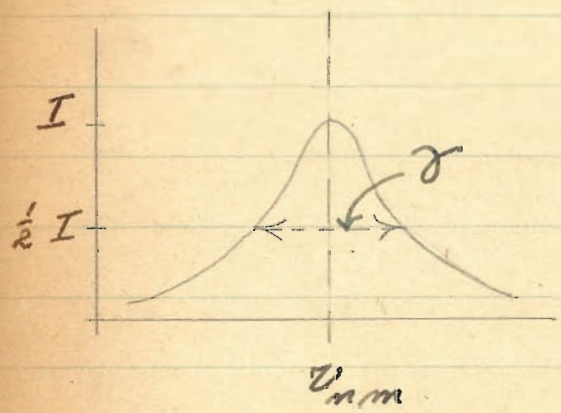
This is the equation for decay of the state n to state m with the emission of a quantum ν. Integrating

$$a_m = \frac{eFx_{mn}}{i\hbar} \frac{\left[e^{-i(\nu_{nm} - \nu)t - \frac{\gamma}{2}t} - 1\right]}{\left[i(\nu - \nu_{nm}) - \frac{\gamma}{2}\right]}$$

We want the asymptotic value of the probability

$$|a_{m_v}(t=\infty)|^2 = \cdots \quad \frac{1}{\frac{\gamma^2}{4} + (\nu - \nu_{nm})^2}$$

This is the formula for the natural line shape. γ is the width of the line at half its maximum value.

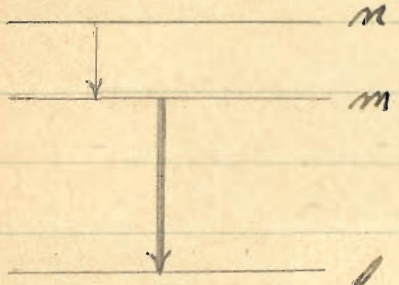


The same formula was known in classical mechanics but with a different γ. The classical and Q. M. results agree in the case of the harmonic oscillator. The classical decay with time was introduced to account for radiation loss.

$$\gamma = \frac{4}{3}\omega^2 \frac{e^2}{mc^3} \quad \text{classical}$$

$$\gamma = \frac{1}{\tau_m} + \frac{1}{\tau_n} \quad \text{Q. M.}$$

The main result of the Q.M. treatment is that δ involves both initial and final states. To check the theory observe a weak spectral line (τ_n large) from n to m and a strong spectral line m to l. (τ_m small). Also let $\nu_{nm} << \nu_{ml}$



Classically the width of the line n, m should be small. Q.M. it should be large. The Q.M. result is the one that checks.
Ref. Heitler

II Photo Electric Effect.

Probability of emission

$$a = \frac{2\pi e^2 N k}{mc} \frac{dt}{dE}$$

Consider large Z and the K

electrons. We can use the Hydrogen wave functions with the following modifications

$$v = Z^2 v_H$$

$$\frac{df}{dE}(vZ) = \frac{df}{dE}(v_H 1)\frac{1}{Z^2}$$

Hence:

$$\mu = \frac{N}{Z^2}\phi\left(\frac{v}{Z^2}\right)$$

(Formula for the absorption of X-rays)

Roughly df/dE for H goes as

$$\left(\frac{df}{dE}\right)_H \approx \frac{8}{R_y}\left(\frac{R_y}{hv_H}\right)^3 \quad \text{(Heitler)}$$

$$\therefore \quad \mu \sim \frac{N}{Z^2}\left(\frac{Z^2}{v}\right)^3 \sim \frac{NZ^4}{v^3}$$

This formula is not really based on physics but it is convenient for rough calculations.

In our treatment, we have not quantized the radiation field. For absorption it is not necessary to do so. In the case of emission it is usually only necessary when the details of the process are of interest. One nice feature of the detailed theory is that it reconciles the wave and particle nature of light.

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Problem: Assume a Hydrogen Atom. Consider the transition $2P_{3/2} \xrightarrow{\nu_0} 2S_{1/2}$. $\int \underline{r}\, \psi_{3/2}\, \psi_{1/2}\, d\tau = 3a$ (Bohr radius = a)

Calculate:

1) Oscillator strength.
2) Transition probability for spontaneous emission.
3) Width of spectral line. (assuming no other transitions)

4) Calculate the dimensions of a cubical cavity having as its lowest mode ν_0. The cavity is excited with the field parallel to its sides. The maximum difference in potential between its top and bottom is 100,000 V. The Q of the cavity is 10,000. Calculate the <u>energy density</u> and the number of <u>quanta per cm^2</u>.

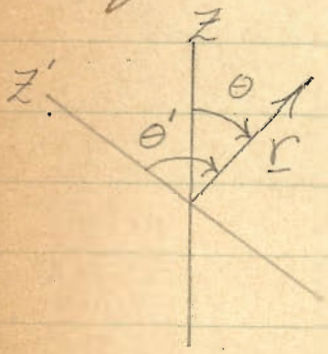
5) Calculate probability of absorption or induced emission. Compare prob. of induced emission with spontaneous emission.

I Transformation Theory

For an electron in a central field $E = E(n, l)$. The wave function is

$$\psi_{nl}(r)\, P_l^m(\theta)\, e^{im\phi}$$

m = magnetic quantum number. Our Z axis was arbitrarily chosen. Any other choice of the Z axis would have done just as well since the system is spherically symmetric.



The wave function for the primed Z axis is:

$$\psi_{nl}(r)\, P_l^{m'}(\theta')\, e^{im'\phi'}$$

where $-l \leq \left(\begin{smallmatrix} m \\ m' \end{smallmatrix}\right) \leq l$. For any choice of axis there will be $2l+1$ solutions corresponding to the different values of m'.

m gives the angular momentum about the z axis.

$$G_z \equiv x p_y - y p_x = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$
$$= \frac{\hbar}{i}\frac{\partial}{\partial \phi}$$

$$G_z \psi_m = \hbar m \psi_m$$

This implies quantization of the angular momentum. The primed wave function can be expressed as a linear combination of the complete set of unprimed solutions.

$$\psi_{m'} = \sum_{m=-l}^{l} c_{m m'} \psi_m$$

$$c_{m m'} = \int \psi_m^* \psi_{m'} \, d\tau$$

ψ_m is the eigenfunction belonging to G_z
$\psi_{m'}$ " " " " " " $G_{z'}$

The eigenvalues in both cases are the same.

G_z - representation = the set of eigenfunctions ψ_m for which G_z is quantized.

The transformation from G_z-rep. to $G_{z'}$-rep. is given by:

$$\psi_{m'} = \sum_m c_{m m'} \psi_m$$

$c_{m m'}$ are the transformation coefficients. (Rotation $c_{m m'}$ = $(m \mid m')$)

Let us now consider the general problem of transformation. A and B are any two observable (Hermitian) operators.

$$A \psi_a = a \psi_a$$
$$B \psi_b = b \psi_b$$

The eigenvalues a & b are simple numbers and are called "c-numbers".

$$\psi_b = \sum_a (a|b)\,\psi_a$$
$$\psi_a = \sum_b (b|a)\,\psi_b$$

$$(a|b) \equiv \int \psi_a^* \psi_b \, d\tau \equiv (\psi_a, \psi_b)$$

Obviously $(a|b) = (b|a)^*$

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Expansion of arbitrary ψ

$$\psi = \sum_a (a|)\,\psi_a = \sum_b (b|)\,\psi_b$$

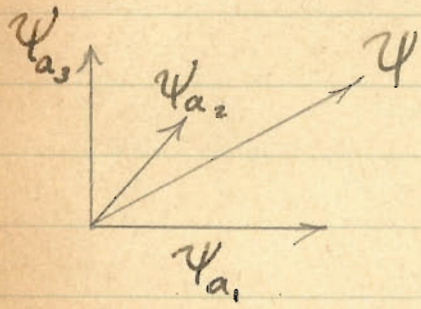
Relations between coefficient

$$\psi = \sum_a \sum_b (b|a)(a|)\,\psi_b$$

$$(b|) = \sum_a (b|a)(a|)$$

Hilbert Space

In Hilbert space the unit vectors are the ψ_a's.



Expansion in the ψ_b esp to a rotation of axes. The transformation $\psi_a \to \psi_b$ is an orthogonal transformation

$$\int \psi_a \psi_{a'} d\tau = \delta_{aa'}$$
$$\int \psi_b \psi_{b'} d\tau = \delta_{bb'}$$

Express ψ_a in terms of ψ_b

$$\int \psi_a^* \psi_{a'} = \sum_{bb'} (b|a)^* (b'|a') \int \psi_b^* \psi_{b'}$$

$$\delta_{aa'} = \sum_b (b|a)^* (b|a')$$

$$\delta_{aa'} = (1) = \sum_b (a|b)(b|a') = (a|a')$$

This is the orthogonality relation for the $\psi_a, \psi_{a'}$. A matrix $(a|b)$ has the above property is called a unitary matrix

The length of a vector is an invariant

$$|\psi|^2 = \sum_b |(b|)|^2 = \sum_b \sum_a \sum_{a'} (b|a)^*(b|a')(a|)(a'|)$$

$$= \sum_{a a'} \left[\sum_b (a|b)(b|a')\right](a|)^*(a'|)$$

$$= \sum_a |(a|)|^2$$

Each representation of operators $A, B, \ldots$ esp to a choice of orthogonal axes in Hilbert space.

$$A_{bb'} \equiv \int \psi_b^* A \psi_{b'} \, d\tau \equiv (b|A|b')$$

$\equiv$ A in the b representation.

$A\psi_a = a\psi_a$

$$\psi_{b'} = \sum_a (a|b')\psi_a$$

$$A\psi_{b'} = \sum_a (a|b')A\psi_a = \sum_a (a|b')a\psi_a$$

$$\int \psi_b A \psi_{b'} = \sum_a (a|b')a \int \psi_b \psi_a = \sum_a (a|b')a(b|a)$$

$$(b|A|b') = \sum_a (b|a)a(a|b')$$

Using this formula, we can calculate the matrix of any operator if we know the eigenvalues, a, of ψ_a and the transformation coefficients.

Let us calculate A in its own representation.

$$\int \psi_a^* A \psi_{a'} = \int \psi_a^* a' \psi_{a'} = a'\delta_{aa'}$$

This is a diagonal matrix i.e. one which has elements on its major diagonal only.

$$(b|A|a') = \sum_a (b|a)a(a|a') = (b|a')a'$$

Rotation

$$(b|a) = S_{ba}$$
$$(a|b') = S^{-1}_{ab'}$$

$$(S S^{-1})_{b'} = \sum_a S_{ba} S^{-1}_{ab'}$$

$$= \sum_a (b|a)(a|b') = \delta_{bb'} = (1)_{bb'}$$

S is a unitary matrix and S^{-1} is its inverse.

$^{B}(A) \equiv A$ in the $B_i(b)$, representation

$$^{B}(A) = S\, ^{A}(A)\, S^{-1}$$
$$S^{-1}\, ^{B}(A)\, S = ^{A}(A)$$

This is called a <u>similarity transformation</u>.

If we know $^{B}(A)$ then $^{C}(A)$

$$= (c|A|c') = \sum_{bb'} (c|b)(b|A|b')(b'|c')$$

$$= \sum_{bb'} (c|b) \int \psi_b^* A \psi_{b'} d\tau\, (b'|c')$$

$$= \int \psi_c^* A \psi_{c'} d\tau$$

Matrices representing observables are Hermitian

$$(b|A|b') = \sum_a (b|a)\, a\, (a|b')$$

$$= \sum_a (a|b)^* a (b'|a)^*$$

The results of an observation (i.e the eigenvalues, a,) must be real since $a = a^*$ and

$$(b|A|b') = (b'|A|b)^*$$

<u>Postulate</u>: All matrices representing observables must be Hermitian.

Consider the diagonal matrix

$$(b|A|b) = (b|A|b)^* \equiv \text{real}$$

∴ In Hermitian matrices, all diagonal elements are real.

$$(a|A|a) = (a|A|a)^* = a \equiv \text{real}$$

Theorems:

a) The eigenvalues of Hermitian matrices are real.

b) If the eigenvalues of an observable are real then the matrix is Hermitian in any representation.

Transformation matrices are not necessarily Hermitian.

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I <u>Continuous Eigenvalues</u> $A\psi_a = \lambda\psi_a$

$$\psi = \int da\,(a|)\,\psi_a$$

where:

$$(a|) = \int \psi_a^* \psi\, dx$$

$$= \int dx\, \psi_a^* \int da'\,(a'|)\,\psi_{a'}$$

$$(a|) = \int \left\{ \int \psi_a^* \psi_{a'}\, dx \right\} (a'|)\, da'$$

$$\therefore \quad \delta(a'-a) = \int \psi_a^* \psi_{a'}\, dx$$

Let $A \sim x$ the position

$$A\psi_a = x\psi_a = a\psi_a$$

By Fourier transforming and solving we find the eigen functions $\psi_a(x) = A\delta(a-x)$ To find the coefficient A we note:

$$(a|a') = A^2 \int \delta(a-x)\delta(x-a')\,dx$$
$$= A^2 \delta(a-a')$$

But

$$\psi_{a'} = \int (a|a')\,\psi_a\,da = A^2 \int \psi_a \delta(a-a')da$$

Hence $A^2 = 1$

We can expand in terms of the ψ_a. The transformation coefficients are:

$$\psi_b = \int (a|b)\,\psi_a\,da$$

where

$$(a|b) = \int \psi_a^* \psi_b\,dx = \int \delta(a-x)\,\psi_b(x)\,dx$$

$$(a|b) = \psi_b(a)$$

The momentum also has a

continuous eigenvalue spectrum

$$(x|p) = (2\pi\hbar)^{-\frac{1}{2}} e^{ipx/\hbar}$$

$\int (p'|x)(x|p)\,dx = \delta(p'-p)$ This corresponds to normalization per unit momentum.

We can find the transformation functions as follows.

$$B\psi_b = b\psi_b$$

$$\psi_b = \sum_a (a|b)\psi_a$$

$$\sum_a B(a|b)\psi_a = b\sum_a (a|b)\psi_a$$

$\therefore$

$$B(a|b) = b(a|b)$$

II Schroedinger Method.

Assumes B can be expressed as a differential operator with respect to "a" operating on $(a|b)$

$$B(a|b) = b(a|b)$$

is therefore a differential

equation in the variable a

Suppose a = coordinate. Then the momentum operator

$$B = p = -ik\frac{\partial}{\partial a}$$

$$-ik\frac{\partial}{\partial a}(a|b) = b(a|b)$$

$$(a|b) = Ce^{-iab/k}$$

A result already known to us.

It should be apparent that the transformation functions $(a|)$ are just the ordinary Schroedinger wave functions where a is the coordinate. These functions obey all the rules developed for transformation coefficients. A knowledge of the transformation coefficients enables us to compute the matrix of an operator in any representation. Knowing

the matrix of the operator we can find its eigenvalues. If the operators are Hermitian the eigenvalues will be real, and represent observables.

Consider $(xp + px)$. What are the eigenvalues and transf. functions in terms of x?

Answer:

$$ihx\frac{\partial \psi}{\partial x} + ih\frac{\partial}{\partial x}(x\psi) = -b\psi$$

Solve this equation

The x-representation is convenient because we are accustomed to think in terms of coordinate space. The simplicity of K.E. $p^2/2m$, is what makes the solution of the Schroedinger equation so easy in terms of x

The 'E representation is convenient because it gives the time dependence in a simple form.

$$H\psi = ih\frac{\partial \psi}{\partial t}$$

It is convenient to express the wave function as the sum of terms having a simple time dependence.

Suppose we wish to find $(a|b)$ and B is not expressible as a differential operator in a. Choose C so that A & B expressed as differential operators in c. We can then find

$$(c|a) \text{ and } (c|b)$$

Then

$$(a|b) = \sum_c (a|c)(c|b)$$

An example of this would be $A \equiv$ momentum, $B \equiv$ Energy $C \equiv$ coordinate.

III Heisenberg Matrix Method

Assume the eigenvalues, a, of the equation $A\psi_a = a\psi_a$ and the matrix of B in the "a" representation are known.

$$B\psi_a = \sum_{a'} (a'|B|a)\psi_{a'}$$
$$B\psi_b = b\psi_b$$
$$\sum_{a'}\sum_{a} (a'|B|a)(a|b)\psi_{a'} = b\sum_{a'}(a'|b)\psi_{a'}$$

Equating coef of $\psi_{a'}$

$$\sum_{a} (a'|B|a)(a|b) = b(a'|b)$$

This gives us a set of equations which may be used to find the unknown $(a|b)$. Suppose there are a finite number of "a"s ~ N. We get N linear homogenious equations. This equations will be suluble if and only if

$$|(a'|B|a) - b\,\delta_{aa'}| = 0$$

This leads to an algebraic equation of the n^{th} order for the "b"s. Once the values of b are determined, the equations for

the $(a|b)$ can be solved.

The matrix $(a|B|a')$ can be transformed by a similarity transformation to a diagonal matrix

$$\sum_{aa'} (b'|a)(a|B|a')(a'|b)$$

$$= \sum_{a} (b'|a) b (a|b)$$

$$= b\,\delta_{bb'}$$

This esp to a transformation to principal axes.

<u>Matrices</u>

Observables are represented by Hermitian matrices.

$$A_{mn} = \int \psi_m^* A \psi_n \, d\tau$$

Matrix Multiplication:

$$(AB)_{mn} = \sum_{\ell} A_{m\ell} B_{\ell n}$$

This operation is called <u>Closure</u>

If A an observable

$$A_{m\ell} = A^*_{\ell m}$$

Nomenclature: Consider the matrix

$A \sim A_{nm}$ — nm element

a) The <u>transpose</u> of $A = \tilde{A} \sim A_{mn}$

b) " <u>conjugate</u> " " $= A^* \sim A^*_{nm}$

c) " Hermitian adjoint $= A^\dagger \sim A^*_{mn}$

A matrix is Hermitian if $A^\dagger = A$

$(A_{m\ell} = A^*_{\ell m})$

Suppose A & B are Hermitian

$$(AB)^*_{mn} = \sum_{\ell} A^*_{m\ell} B^*_{\ell n}$$

$$= \sum A_{\ell m} B_{n\ell}$$

$$= (BA)_{nm}$$

(AB) is not Hermitian

$$AB^{+} = BA$$
$$(AB)^{*} = (\tilde{BA})$$

The <u>symmetrical product</u> is Hermitian

$$(AB + BA)^{+} = BA + AB$$

The <u>commutator</u>

$$(AB - BA) = [AB]$$

$$[AB]^{+} = BA - AB = -[AB]$$

i.e $$-[AB]_{mn} = [AB]^{*}_{nm}$$

The commutator is <u>anti Hermitian</u>
The diagonal elements of the commutator are obviously pure imaginary

The basic relation of the Heisenberg theory is

$$[x p_x] = x p_x - p_x x = i\hbar \cdot 1$$

This is true in any representation as can be proved by a similarity transformation applied to both sides of the equation.

Assume A is diagonal

$$(AB)_{mn} = A_m B_{mn}$$
$$(BA)_{mn} = A_n B_{mn}$$

$$[AB]_{mn} = (A_m - A_n) B_{mn}$$

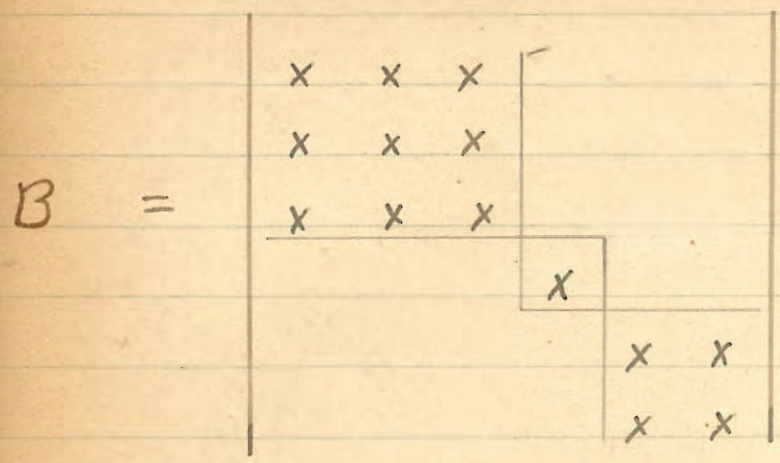
If B is not diagonal AB do not commute and we can have transitions between states

If $AB = BA$

$$[AB] = 0$$

and $B_{mn} = 0$ unless $A_m = A_n$

This will be the case if there are degeneracies. The B matrix may be constructed as indicated in the diagram. We can diagonalize each of the sub matrices independently.



Sets of Commuting Observables may be used to represent operators

x, y, z, coordinate rep.

p_x, p_y, p_z plane wave rep

Central field

$E\ M^2\ M_{\begin{pmatrix} z \\ x \\ y \end{pmatrix}}$

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I Development of Matrix Mechanics

Commutator.

$$qp - pq = ih$$

where q is the coordinate and p is the conjugate momentum.

1) $[qp^2] = qp^2 - p^2q$

$= qp^2 - pqp + pqp - p^2q$

$= (qp - pq)p + p(qp - pq)$

$= 2ikp$

(A q-number is a matrix)

2) $[qp^n] = nikp^{n-1} = ik(p^n)'$

If $f(p)$ can be expressed as a power series in p

3) $[q, f(p)] = ikf'(p)$

4) $[f(q), p] = ikF'(q)$

5) $[f(q)p^2] = ik(f'(q)p + pf'(q))$

6) $[f(q)p^3] = ik(f'p^2 + pfp + p^2f')$

Note 5 & 6 give symmetrical products.

Two important commutators are the following:

7) $[qH] = (qH - Hq)$

$$= -q\,ih\frac{\partial}{\partial t} + ih\frac{\partial}{\partial t}(q) = ih\frac{dq}{dt}$$

$$= ih\,H'^{p} = ih\frac{p}{m}$$

$$\frac{dq}{dt} = \frac{p}{m}$$

8) $[pH] = ih\frac{dp}{dt} = -ihH'^{q}$

$$\frac{dp}{dt} = -\frac{\partial V}{\partial q}$$

The Energy Representation (in which the energy is diagonal)

$$H_{kl} = E_k \delta_{kl}$$

9) $[qH]_{kl} = (qH - Hq)_{kl} = q_{kl}(E_l - E_k)$

$$= \frac{ih}{m} p_{kl}$$

$$\omega_{kl} \equiv \frac{E_l - E_k}{\hbar}$$

$$\underline{p_{kl} = -i m \omega_{kl} q_{kl}}$$

10) $$[pH]_{kl} = -i\hbar \left(\frac{\partial V}{\partial q}\right)_{kl}$$

$$= \hbar p_{kl} \omega_{kl}$$

$$\underline{\left(\frac{\partial V}{\partial q}\right)_{kl} = m \omega_{kl}^2 q_{kl}}$$

Sum Rule (Closure)

Observable matrices are Hermitian

$$\sum_l |q_{kl}|^2 = \sum_l q_{kl} q_{kl}^* = \sum_l q_{kl} q_{lk}$$

11) $$\sum_l |q_{kl}|^2 = (q^2)_{kk} = \langle q^2 \rangle_k$$

$$\sum_l |q_{kl}|^2 \omega_{kl} = \sum q_{lk} \frac{i p_{kl}}{m}$$

$$= \frac{i}{m} (pq)_{kk}$$

$$= \sum_l q_{kl} (-\omega_{lk}) q_{lk}$$

$$= -\frac{i}{m}\sum_s q_{ks} p_{sk} = -\frac{i}{m}(qp)_{kk}$$

$$(pq)_{kk} = -(qp)_{kk} = \sum_s |q_{ks}|^2 \omega_{ks}$$

2) $$\sum_s |q_{ks}|^2 \omega_{ks} = \frac{i}{2m}(pq - qp) = \frac{k}{2m}$$

This is the f sum rule.

$\sum_s |q_{ks}|^2 \omega_{ks}^2$ is related to the mean square energy. It enables us to determine probable fluctuations in the energy.

$$= -\sum q_{ks}\omega_{ks} q_{sk}\omega_{sk}$$
$$= -\left(\frac{i}{m}\right)^2 \sum_s p_{ks} p_{sk}$$

3) $$\sum_s |q_{ks}|^2 \omega_{ks}^2 = \frac{1}{m^2}(p^2)_{kk} = \frac{2}{m}(T)_{kk}$$

Virial Theorem

$$\sum_s q_{ks}\omega_{ks}^2 q_{sk} = \sum_s \frac{1}{m}\left(\frac{\partial V}{\partial q}\right)_{ks} q_{sk}$$

$$= \frac{1}{m}\left(\frac{\partial V}{\partial q} q\right)_{kk}$$

$$\langle 2T \rangle = \left\langle q \frac{\partial V}{\partial q} \right\rangle$$

A sum related to the optical transition probabilities is:

41) $$\sum_i |q_{kl}|^2 \omega_{kl}^3 = \sum_i q_{kl}^i \omega_{kl} q_{lk}^i \omega_{lk}^2$$

$$= \sum_i \frac{i}{m} p_{kl}^i \frac{i}{m} \left(\frac{\partial V}{\partial q}\right)_{lk}^i$$

$$= \frac{i}{m^2} \left(p \frac{\partial V}{\partial q}\right)_{kk} = -\frac{i}{m^2} \left(\frac{\partial V}{\partial q} p\right)_{kk}$$

Commutation of Angular Momentum

$$M_x = y p_z - z p_y$$

$$[x M_x] = 0$$

$$[y M_x] = -z i\hbar$$

$$[z M_x] = y i\hbar$$

$$[p_x M_x] = 0$$

$$[p_y M_x] = -p_z i\hbar$$

$$[p_z M_x] = p_y i\hbar$$

$$[M_x M_y] = [M_x, z p_x - x p_z]$$

$$= -i\hbar y p_x + i\hbar x p_y$$

$$= i\hbar M_z$$

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The commutator of any non commuting operator with the components of the angular momentum is:

$$[A_j M_k] = i\hbar A_l$$

where $j\,k\,l$ follow in the natural order.

Consider $[r^2 M_x]$

$$r^2 = x^2 + y^2 + z^2$$

$$[r^2 M_x] = (r^2 M_x - M_x r^2)$$
$$= [x^2 M_x] + y[y M_x) + [y M_x] y$$
$$+ z[z M_x] + [z M_x] z$$
$$= -2ihyz + 2ihzy$$
$$= 0$$

$$[r^2 \underline{M}] = 0$$
$$[p^2 \underline{M}] = 0$$
$$[M^2 \underline{M}] = 0$$

In general any function of r^2 and p^2 will commute with $\underline{M}$.

$$H = V(r^2) + \frac{p^2}{2m} = V(r^2) + T(p^2)$$

Relativistically $T(p^2) = \sqrt{p^2 + m^2 c^2}$

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

Therefore $\underline{M}$ is a constant of the motion. This follows from the fact that

$$[H A] = i\hbar \frac{dA}{dt}$$

Since H commutes with $\underline{M}$ and H is diagonal, this means the $\underline{M}$ must be diagonal in the sense that it can contain only elements between states of the same energy.

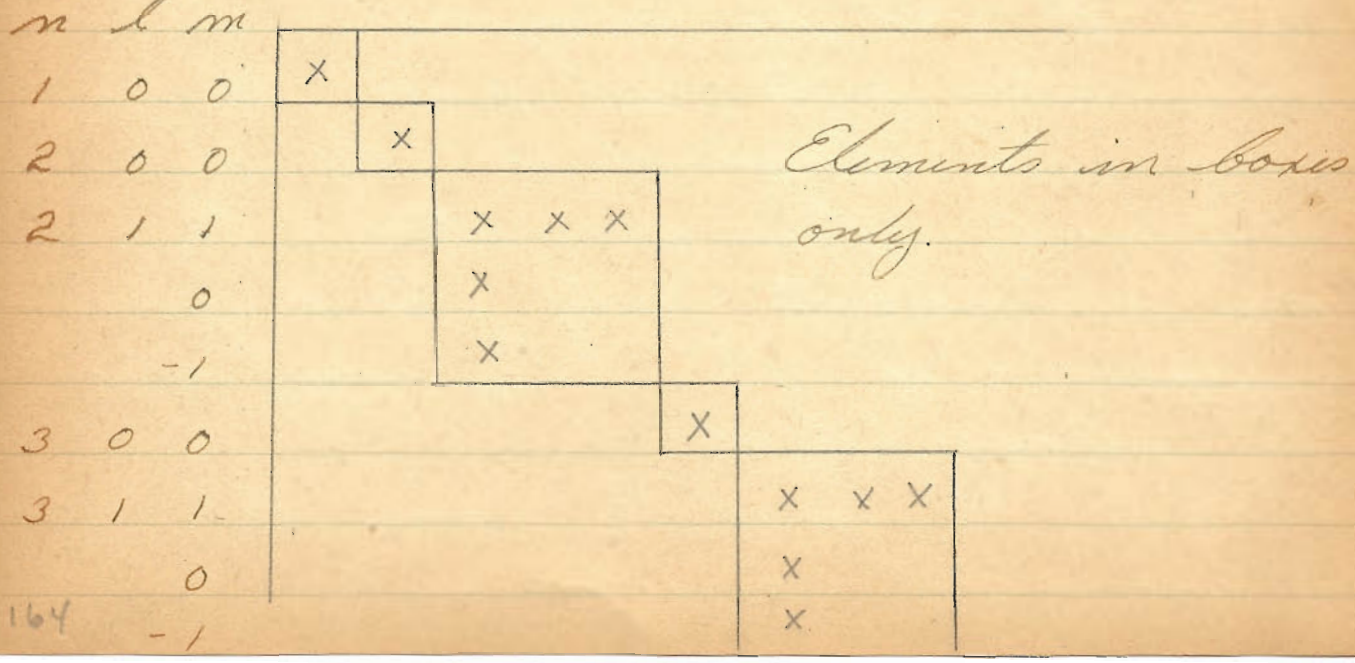
M_z commutes with M^2 and H. $E(H)$ is diagonal. M^2 commutes with E and therefore may be diagonalized by a similarity transformation. M_z has components only for a given eigenvalue of M^2. M_z may also be diagonalized.

E, M^2, and M_z can be diagonalized simultaneously.

We can use these three commuting variables to represent our system. They are related to the quantum numbers n, l, m already known to us:

$$n \sim E$$
$$l \sim M^2 = \hbar^2 l(l+1)$$
$$m \sim M_z = m\hbar$$

M_z does not commute with M_x, M_y
M_z does commute with E and M^2. M_x has elements only between states of the same n and l, but different m are possible.



The constants n, l, m are the constants of motion which describe the state of our particle.

Linear Harmonic Oscillator

$$\begin{cases} H = \frac{P^2}{2m} + \frac{1}{2} m\omega^2 X^2 \\ X P - P X = i\hbar \end{cases}$$

The solution of our problem lies in the solution of the above pair of matrix equations.

Let

$$X = a q$$
$$P = \hbar p / a$$

$$q p - p q = i$$

$$2H = \frac{\hbar^2}{m a^2} p^2 + m\omega^2 a^2 q^2$$

Let $\frac{\hbar^2}{m a^2} = m\omega^2 a^2$

$$a = \sqrt{\hbar / m\omega}$$

Also let $H = \hbar\omega\epsilon$

Then

$$\underline{2\epsilon = p^2 + q^2}$$

In the ϵ representation

$$q\epsilon - \epsilon q = ip$$
$$p\epsilon - \epsilon p = -iq$$
$$(q\epsilon - \epsilon q)_{mn} = ip_{mn} = q_{mn}(\epsilon_n - \epsilon_m)$$
$$(p\epsilon - \epsilon p)_{mn} = -iq_{mn} = p_{mn}(\epsilon_n - \epsilon_m)$$

$$\underline{q_{mn} = (\epsilon_n - \epsilon_m)^2 q_{mn}}$$

This tells us that $q_{mn} \neq 0$ only if $(\epsilon_n - \epsilon_m) = \pm 1$. We may write $\epsilon_n = n + \alpha$.

Notation

$$\left\{ \begin{aligned} (n|q|n-1) &= f(n) \\ (n|p|n-1) &= +if(n) \\ (n-1|q|n) &= f(n)^* \\ (n-1|p|n) &= -if(n)^* \end{aligned} \right\}$$

We wish to find:

$$\langle n|q^2|n\rangle = \sum_{n'} \langle n|q|n'\rangle\langle n'|q|n\rangle$$

$$= \langle n|q|n+1\rangle\langle n+1|q|n\rangle + \langle n|q|n-1\rangle\langle n-1|q|n\rangle$$

$$= f^*(n+1)\, f(n+1) + f(n)\, f^*(n)$$

$$= |f(n)|^2 + |f(n+1)|^2$$

Similarly

$$\langle n|p^2|n\rangle = |f(n)|^2 + |f(n+1)|^2$$

$$2\epsilon = 2\left[|f(n)|^2 + |f(n+1)|^2\right]$$

$$= (n+\alpha)2$$

A solution of the above functional equation yields

$$|f(n)|^2 = \tfrac{1}{2}(n+\alpha-\tfrac{1}{2})$$

Choosing $|f(0)|^2 = 0$ we obtain $\alpha = \tfrac{1}{2}$

$$\underline{\epsilon = n + \tfrac{1}{2}}$$

$(n|q|n-1) = \sqrt{\frac{1}{2}n}$

5/1/47

Application of the matrix method to the problem of determining the matrix elements and eigenvalues of the three commuting operators.

$$E,\ M^2,\ M_z$$

We assume a knowledge of the eigenvalues of M_z, $\hbar m$. (2/22/47)

$$[M_y M_z]_{mn} = i\hbar (M_x)_{mn}$$

$$\sum_{n'} (m|M_y|n')(n'|M_z|n) - \sum_{n'} (m|M_z|n')(n'|M_y|n) = i\hbar (m|M_x|n)$$

M_z diagonal: elements $\hbar m$

$$\hbar n (m|M_y|n) - \hbar m (m|M_y|n) = i\hbar (m|M_x|n)$$

$$(n-m)\langle m|M_y|n\rangle = i\langle m|M_x|n\rangle$$

From $[M_x M_z]_{mn} = ik(M_y)_{mn}$ we obtain

$$(n-m)\langle m|M_x|n\rangle = -i\langle m|M_y|n\rangle$$

$$(n-m)^2\langle m|M_x|n\rangle = \langle m|M_x|n\rangle$$

Therefore:

$\langle m|M_x|n\rangle \neq 0$ only if

$n - m = \pm 1$

Define

$$\langle m|M_x|m-1\rangle = k f(m)$$
$$\langle m-1|M_x|m\rangle = k f^*(m)$$

$\therefore$
$$\langle m|M_y|m-1\rangle = -ik f(m)$$
$$\langle m-1|M_y|m\rangle = ik f^*(m)$$

$$[M_x M_y] = ik M_z$$

$$\sum_{m'} \langle m|M_x|m'\rangle\langle m'|M_y|m\rangle - \sum_{m_1} \langle m|M_y|m'\rangle\langle m'|M_x|m\rangle$$

$$= ik\langle m|M_z|m\rangle = ik^2 m$$

$$(k f(m))(i k f^*(m)) - (-i k f(m))(k f^*(m))$$
$$+ (k f^*(m+1))(-i k f(m+1)) - (i k f^*(m+1))(k f(m+1))$$

$$= 2 i k^2 |f(m)|^2 - 2 i k^2 |f(m+1)|^2$$
$$= i k^2 m$$

$$2 (|f(m)|^2 - |f(m+1)|^2) = m$$

$$|f(m)|^2 = |f(0)|^2 - \frac{1}{2} \sum_{1}^{m-1} k$$

$$|f(m)|^2 = A - \frac{1}{4}(m(m-1))$$

where A is independent of m but may depend on E and M^2.

We now seek to determine how A depends on M^2.

$$M^2 = M_x^2 + M_y^2 + M_z^2$$

$$(m|M^2|m) = \sum_{m'} (m|M_x|m')(m'|M_x|m)$$

$$+ \sum_{m'} (m|M_y|m')(m'|M_y|m) + (m|M_z|m)^2.$$

$$h^{-2}(m|M^2|m) = m^2 + 2(|f(m)|^2 + |f(m+1)|^2)$$

$$= m^2 + 2A - \tfrac{1}{2}m(m-1) + 2A - \tfrac{1}{2}m(m+1)$$

$$M^2 = 4A$$

From $|f(m)|^2 = A - \frac{1}{4}m(m-1)$ we see that $A - \frac{1}{4}m(m-1)$ must be positive definite. This implies a maximum value of m for which $|f(m)|^2 \neq 0$. Let the maximum $m = j$.

$$|f(j+1)|^2 = 0 = \tfrac{1}{4}M^2 - \tfrac{1}{4}j(j+1)$$

$$M^2 = j(j+1)$$

Also

$$|f(-j)|^2 = 0 = \tfrac{1}{4}M^2 - \tfrac{1}{4}[-j(-j-1)]$$

Since the values of m must differ by an integer:

$$2j + 1 = \text{an integer}$$

j can be either an integer or a half integer. m must be an integer in order that the Φ function be single valued in space. Therefore if j is half integral it must be due to an intrinsic spin of the electron itself.

The eigenvalues of M^2 are

$$M^2 = \hbar^2 j(j+1)$$

$$A|f(m)|^2 = j(j+1) - m(m-1)$$

$$= (j+m)(j-m+1)$$

Hence:

$$\rightarrow \begin{cases} (m|M_x|m-1) = \frac{1}{2}\sqrt{(j+m)(j-m+1)}\,\hbar \\ (m|M_x|m+1) = \frac{1}{2}\sqrt{(j+m+1)(j-m)}\,\hbar \\ (m|M_y|m-1) = -\frac{i}{2}\sqrt{(j+m)(j-m+1)}\,\hbar \\ (m|M_y|m+1) = \frac{i}{2}\sqrt{(j+m+1)(j-m)}\,\hbar \end{cases}$$

The intrinsic angular momentum in the z direction is $\pm \frac{1}{2}$ for elementary particles:

$$M_z = \hbar \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}$$

Hence

$$M_x = \hbar \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix}$$

$$M_y = \hbar \begin{pmatrix} 0 & -\frac{i}{2} \\ \frac{i}{2} & 0 \end{pmatrix}$$

Knowing M_z the commutation relations give M_x and M_y. If we write $\underline{M} = \frac{1}{2}\hbar\,\underline{\sigma}$ we get:

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

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

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$\underline{\sigma}$ is the Pauli spin matrix.

$$\sigma_x \sigma_y - \sigma_y \sigma_x = 2i\sigma_z$$

$$\sigma_x \sigma_y = i\sigma_z$$

$$\sigma_y \sigma_x = -i\sigma_z$$

$$\sigma_x \sigma_y + \sigma_y \sigma_x = 0 \quad \text{anti commute}$$

The spin matrices do not act on the space coordinates. We introduce a spin coordinate, μ, which assumes only the two values $\pm \frac{1}{2}$.

$$\Psi = \Psi(x y z \mu t)$$

$$\psi = \begin{pmatrix} \psi_1(xyz) \\ \psi_2(xyz) \end{pmatrix}$$

$$\sigma_z \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \lambda \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$$

We find $\lambda^{(1)} = 1 \quad \psi^{(1)} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

$\lambda^{(2)} = -1 \quad \psi^{(2)} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

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I Spin Wave Function

The total wave function including the spin may be written in any of the following ways:

$$\Psi(xyz\mu t) = \begin{pmatrix} \psi_1(xyzt) \\ \psi_2(xyzt) \end{pmatrix}$$

$$= \begin{pmatrix} 1 \\ 0 \end{pmatrix} \psi_1 + \begin{pmatrix} 0 \\ 1 \end{pmatrix} \psi_2 = \alpha \psi_1 + \beta \psi_2$$

$$\alpha \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \beta \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

The complex conjugate of ψ is

$$\psi^* = (\psi_1^* \; \psi_2^*) = \alpha^* \psi_1^* + \beta^* \psi_2^*$$

$$\alpha^* \equiv (1, 0) \;, \quad \beta^* = (0, 1).$$

$$\psi^* \psi = (\psi_1^* \psi_2^*) \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \psi_1^* \psi_1 + \psi_2^* \psi_2$$

$$\phi^* \sigma_x \psi \equiv (\phi_1^* \phi_2^*) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$$

Any eigenfunction of the spin operator must be a linear combination of α and β. The coefficients are ψ_1 and ψ_2

Operations on α and β

$$\sigma_z \alpha = \alpha \; ; \; \sigma_x \alpha = \beta \; ; \; \sigma_y \alpha = i\beta$$
$$\sigma_z \beta = -\beta \; ; \; \sigma_x \beta = \alpha \; ; \; \sigma_y \beta = -i\alpha$$

Suppose we know that the spin is in the x direction. Then the eigenvalues of σ_x must be ± 1, and we have:

$$\sigma_x(\alpha+\beta) = (\alpha+\beta)$$
$$\sigma_x(\alpha-\beta) = -(\alpha-\beta)$$

If the spin is in the y direction

$$\sigma_y(\alpha+i\beta) = (\alpha+i\beta)$$
$$\sigma_y(\alpha-i\beta) = -(\alpha-i\beta)$$

Let us now investigate the case where the spin is in the direction of an arbitrary unit vector $\underline{S} = iS_x + jS_y + kS_z$

$$S^2 = S_x^2 + S_y^2 + S_z^2 = 1$$

We have

$$M_s\psi = \tfrac{1}{2}\hbar\psi$$

or

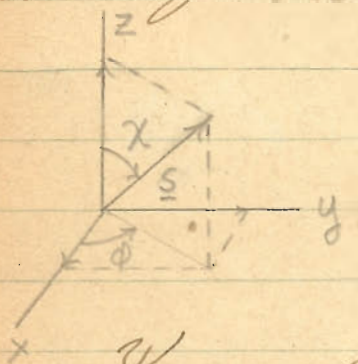
$$\frac{M_s}{\frac{1}{2}\hbar}\psi = (S_x\sigma_x + S_y\sigma_y + S_z\sigma_z)\psi = \sigma_s\psi$$

$$= \begin{pmatrix} S_z & S_x - iS_y \\ S_x + iS_y & -S_z \end{pmatrix}\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = \begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}$$

$$(S_z - 1)\psi_1 + (S_x - iS_y)\psi_2 = 0$$
$$(S_x + iS_y)\psi_1 - (S_z + 1)\psi_2$$

$$\frac{\psi_2}{\psi_1} = \frac{(S_x + iS_y)}{(S_z + 1)} = \frac{(1 - S_z)}{(S_x - iS_y)}$$

In spherical coordinates



$$S_z = \cos\chi$$
$$S_x = \sin\chi\cos\phi$$
$$S_y = \sin\chi\sin\phi$$

$$\frac{\psi_2}{\psi_1} = \frac{\sin\chi}{1 + \cos\chi} e^{i\phi} = \frac{1 - \cos\chi}{\sin\chi} e^{i\phi}$$

$$\frac{\psi_2}{\psi_1} = \tan\frac{\chi}{2} e^{i\phi}$$

$$\left|\frac{\psi_2}{\psi_1}\right| = \tan\frac{\chi}{2}$$

The phase of $\frac{\psi_2}{\psi_1}$ is ϕ. The phase is stationary if there is no preferred direction in space. However, if the energy of ψ_1 ≠ to the energy of ψ_2 (as in a magnetic field), the phase

may depend on the time. We shall now treat this case

$E_2 \sim$ energy ψ_2.
$E_1 \sim$ " ψ_1.

$$E_1 - E_2 = 2\mu H \qquad \mu = \frac{e\hbar}{2mc}(g)$$
$$= \frac{e\hbar g}{mc} H \qquad g = \frac{\mu}{S_{pin}}$$

$$\psi_1 \sim e^{-\frac{i}{\hbar}E_1 t} \; ; \; \psi_2 \sim e^{-\frac{i}{\hbar}E_2 t}$$

$$\frac{\psi_2}{\psi_1} \sim e^{\frac{i}{\hbar}(E_1 - E_2)t} = e^{i\left(\frac{eHg}{mc}\right)t}$$

$\left(\frac{eHg}{mc}\right) = \omega_n =$ Larmor Frequency

Effect of a rotation of axes

$$\psi_1 = \cos\frac{\chi}{2} e^{-i\phi/2}$$
$$\psi_2 = \sin\frac{\chi}{2} e^{i\phi/2}$$

II Spectra

Let Ψ be the total wave function of an atom plus its electrons.

$$(E - H)\Psi = 0$$

$$\sum_j \frac{\hbar^2}{2m_j} \nabla_j^2 \Psi + \left(E - \sum_j V(r_j)\right)\Psi = 0$$

$$\sum_j V(r_j) = -\sum_j \frac{Ze^2}{|r_j|} + \sum_{j=1}^{n} \sum_{k=j+1}^{n} \frac{e^2}{|r_{jk}|}$$

We shall use the Variational Method to solve the problem. An approx to the lowest eigenvalue of an operator, H, is:

$$W = \min \frac{\int f^* H f \, dx}{\int f^* f \, dx}$$

If f is chosen the eigenfunction of H, then W will be exactly the eigenvalue. To prove this let us derive the Schrodinger equation from the variational

equation.

Take $f = \psi + \epsilon\phi$

$$\frac{\int f^* H f}{\int f^* f} = \frac{\int \psi^* H \psi + \epsilon \int \psi^* H \phi + \epsilon \int \phi^* H \psi + \epsilon^2 \ldots}{\int \psi^* \psi + \epsilon \int \psi^* \phi + \epsilon \int \phi^* \psi + \epsilon^2 \ldots}$$

Since H is self adjoint, and

$$\left\{ \int \psi^* \psi + \epsilon \left[\int \psi^* \phi + \int \phi^* \psi \right] \right\}^{-1}$$

$$= \left\{ \int \psi^* \psi \right\}^{-1} \left\{ 1 - \epsilon [\ + \ ] / \int \psi^* \psi \right\}$$

$$= \frac{\int \psi^* H \psi}{\int \psi^* \psi} + \frac{\epsilon \left[\int \phi^* H \psi + \int \phi H \psi^* \right]}{\int \psi^* \psi}$$

$$- \frac{\epsilon \left[\int \psi^* \phi + \int \psi \phi^* \right] \int \psi^* H \psi}{\left[\int \psi^* \psi \right]^2} + O(\epsilon^2)$$

= We want δW to be zero

Hence

$$W_{min} = \frac{\int \psi^* H \psi}{\int \psi^* \psi}$$

and

$$\epsilon \left[\frac{\int \phi^* H \psi}{\int \psi^* \psi} - W \frac{\int \psi \phi^*}{\int \psi^* \psi} \right] + \epsilon(\text{conj}) = 0$$

$$\int \phi^* (H - W) \psi \, d\tau = 0$$

$$H\psi = W\psi$$

We assume the converse: that if Ψ a solution of the Schroedinger equation, it is also a solution of the variational equation.

In solving a problem, the procedure is to guess Ψ. Consider the Helium atom. The lowest state is spherically symmetric.

$$\Psi_{\text{guess}}(r_1, r_2, r_{12}) = e^{-\alpha(r_1+r_2)}\{1 + a_1(r_1+r_2)$$

$$+ a_2(r_1^2+r_2^2) + a_3 r_1 r_2 + a_4 r_{12} + a_5 r_{12}^2$$

$$+ a_6(r_1+r_2)r_{12} + \ldots\}$$

In the above equation α and the a's are constants the value of which is determined by the minimum (extremum) condition.

$BE_{He} = 1.80727\ Ry$

Using α only $= 24.46$ ev

	BE
	$1.695\ Ry$
3 terms	1.80488
6 "	1.80648
8 "	1.80749

Using 8 terms we over shoot the correct answer. This is impossible. If we apply a correction for motion of the center of mass and relativity, $-.00015$, we obtain:

$1.80734\ Ry$ and this is within the experimental error.

5/6/47

The above method of finding the eigenvalues is known as the Ritz method:

Ref: Hylleraas Zeits f. Phy.
48, 469 (1928)
54, 347 (1929)

Method of finding the higher eigenvalues. The total wave function can be written:

$$\Psi = \sum_n c_n \Psi_n$$

Hence

$$W = \frac{\int \Psi^* H \Psi}{\int \Psi^* \Psi} = \frac{\sum |c_n|^2 \int \Psi_n^* H \Psi_n}{\sum |c_n|^2}$$

$$= \frac{\sum |c_n|^2 E_n}{\sum |c_n|^2} \geq E_0$$

The Ψ_n are orthonormal.

E_0 = min. of W

E_1 = min of W with $\int \Psi_1^* \Psi_0 = 0$

E_n = min of W with $\int \Psi_j^* \Psi_n = 0$

for $j = 0, 1, 2, \ldots n-1$.

I Hartree Method

Assumes total wave function can be written as a product of the wave functions for the individual electrons

$$\Psi(r_1 \ldots r_n) = \prod_{j=1}^{n} \phi_j(r_j)$$

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

$$= -\frac{\hbar^2}{2m} \sum_j \prod_{k \neq j} \phi_k(r_k) \nabla^2 \phi_j(r_j) - \sum_j \prod_{k \neq j} \phi_k(r_k) \frac{Ze^2}{r_j} \phi_j(r_j) + \sum_{j<k} \frac{e^2}{r_{jk}} \prod_\ell \phi_\ell(r_\ell)$$

$$= E \prod_\ell \phi_\ell(r_\ell)$$

The ϕ's are orthonormal

$$\int \phi_j^* \phi_k \, d\tau = \delta_{jk}$$

$$\int \Psi^* \Psi \, d\tau = \prod_j \int \phi_j^* \phi_j \, d\tau = 1$$

$$\int \Psi^* H \Psi \, d\tau = -\frac{\hbar^2}{2m} \sum_j \int \phi_j \nabla^2 \phi_j \, d\tau_j - \sum_j \int \frac{e^2 Z}{r_j} \phi_j^* \phi_j \, d\tau_j + \sum_{j<k} \int \phi_j^* \phi_k^* \frac{e^2}{r_{jk}} \phi_j \phi_k \, d\tau_j \, d\tau_k$$

$$= \sum_{j=1}^{n} \int \phi_j^* \left\{ -\frac{\hbar^2}{2m}\nabla_j^2 - \frac{Ze^2}{r_j} + \sum_{k=j+1}^{n} \int \phi_k^* \frac{e^2}{r_{jk}} \phi_k \, d\tau_k \right\} \phi_j \, d\tau_j$$

$$= \sum_{j=1}^{n} \int \phi_j^* \left\{ -\frac{\hbar^2}{2m}\nabla_j^2 - \frac{Ze^2}{r_j} + V_j \right\} \phi_j \, d\tau_j - \sum_{j=1}^{n} \sum_{k=j+1}^{j=n} \int \frac{e^2}{r_{jk}} \phi_j^2 \phi_k^2 \, d\tau_j d\tau_k$$

where $V_j = e \sum_{k \neq j} \int \frac{\phi_k^* e \phi_k}{r_{jk}} d\tau_k$

$$= e \sum_{k \neq j} \int \frac{\rho_k}{r_{jk}} d\tau_k \quad \left\{ \text{See Next Lecture} \right.$$

V_j is found by the method of selfconsistant fields: Ref Lecture 38 Jan 23, 1947

E = min. of W

$$= \min \frac{\sum_j \int \phi_j^* \left[-\frac{\hbar^2}{2m}\nabla_j^2 - \frac{Ze^2}{r_j} + V_j \right] \phi_j \, d\tau_j}{\underbrace{\left[\prod_j \int \phi_j^* \phi_j \, d\tau_j \right]}_{1}} - \sum_{j=1}^{n} \sum_{k=j+1}^{n} \int \frac{e^2}{r_{jk}} \phi_j^2 \phi_k^2 \, d\tau_j d\tau_k$$

= eigenvalues of the equation

$$\left(-\frac{\hbar^2}{2m}\nabla_j^2 - \frac{Ze^2}{r_j} + V_j \right) \psi = E_j \psi$$

The ionization energy, $E_{n=2}$, for Helium

He $\left\{ \begin{array}{ll} 1.835 \, Ry & \text{Hartree} \\ 1.810 \cdot \; " & \text{Experiment of Ritz} \end{array} \right.$

5/18/47

Bethe

Explanation of Hartree eigenvalue for the energy.

Consider the case of the He atom.

We have $$W = \frac{\int \psi^* H \psi}{\int \psi^* \psi}$$

where $$H = -\frac{\hbar}{2m}(\nabla_1^2 + \nabla_2^2) - e^2 Z\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{r_{12}}$$

We assume $$\psi = \phi(1)\phi(2)$$

and $$\int |\psi|^2 d\tau = 1$$

$$H\psi = \phi(2)\left[-\frac{\hbar}{2m}\nabla_1^2 - \frac{e^2 Z}{r_1} + \frac{e^2}{r_{12}}\right]\phi(1)$$

$$+ \phi(1)\left[-\frac{\hbar}{2m}\nabla_2^2 - \frac{e^2 Z}{r_2} + \frac{e^2}{r_{12}}\right]\phi(2)$$

$$- \frac{e^2}{r_{12}}\phi(1)\phi(2)$$

$$\int \psi^* H \psi \, d\tau = \int \phi^2(2) d\tau_2 \int \phi^*(1)\left[-\frac{\hbar}{2m}\nabla_1^2 - \frac{e^2 Z}{r_1}\right]\phi(1) d\tau_1$$

$$+ \int\int \phi^2(2) \frac{e^2}{r_{12}} d\tau_2 \, \phi^2(1) d\tau_1$$

$$+ \text{ ditto (2)} - \int \frac{e^2}{r_{12}} \psi^2(1)\psi^2(2)\,d\tau_1\,d\tau_2$$

$$= \int \psi^*(1)\left[-\frac{h}{2m}\nabla_1^2 - \frac{Ze^2}{r_1} + U(r_1)\right]\psi(1)\,d\tau_1$$

$$+ \int \psi^*(2)\left[-\frac{h}{2m}\nabla_2^2 - \frac{Ze^2}{r_2} + U(r_2)\right]\psi(2)\,d\tau_2$$

$$- \int \frac{e^2}{r_{12}} \psi^2(1)\psi^2(2)\,d\tau_1\,d\tau_2$$

where $U(r_1) = \int \psi^2(2)\frac{e^2}{r_{12}}\,d\tau_2$

$\frac{Ze^2}{r_1} + U(r_1) = V(r_1) =$ Hartree potential for electron (1).

$$W = E_1 + E_2 - \int \frac{e^2}{r_{12}} \psi^2(1)\psi^2(2)\,d\tau_1\,d\tau_2$$

where E_1 and E_2 are the Hartree energies of the first and second electron, and $\int \frac{e^2}{r_{12}} \psi^2(1)\psi^2(2)\,d\tau_1\,d\tau_2$ is the electron interaction energy which must be subtracted off. For Helium $E_1 = E_2 = E$

$$W = 2E - \int \frac{e^2}{r_{12}} \psi^2(1)\psi^2(2)\,d\tau_1\,d\tau_2$$

For an atom containing Z electrons we would get

$$W = \sum_{1}^{Z} E_k - \sum_{j=1}^{Z} \sum_{k=j+1}^{Z} \int \frac{e^2}{r_{jk}} \psi^2(j)\, \psi^2(k)\, d\tau_j\, d\tau_k$$

Ionization energy for first He electron

$$W_{He\ atom} = -2.1.835 - 2.064$$
$$= -5.734$$
$$W_{He\ ion} = \underline{-4.000}$$
$$\text{Ionization } E = -1.734$$

This value is well above the measured value of 1.810. Even as crude a guess as $\psi = e^{-\alpha r}$ in the Ritz method gives a value for E of 1.687. The Hartree method is not much good in this case.

One may ask why the eigenvalues of H_j have any relation to the true eigenvalues.

Consider an atom. We want the ionization potential.

$$H_{atom} = H_{ion} + H_{electron}$$

$$H_{el} = -\frac{\hbar}{2m}\nabla_1^2 - \frac{Ze^2}{r_1} + \sum_{k=2}^{Z} \frac{e^2}{r_{1,k}}$$

Using the variational method we calculate $W_{atom} - W_{ion}$ with the atomic wave function

$$\int \psi_a^* H_a \psi_a - \int \psi_a^* H_i \psi_a = \int \psi_a^* (H_a - H_i) \psi$$

$$= \int \psi_a^* H_{el} \psi_a \, d\tau_a$$

$$= \int \phi^*(1) H_{el(1)}^{Hart} \phi(1) \, d\tau_1$$

$$H_{el(1)}^{Hart} \phi(1) = E_{el(1)}^{Hart} \phi(1)$$

This method will give a value of $E_{el(1)}^{Hart}$ which is too small because if W_{atom} is correct then W_{ion} will be too large and

the difference will be too small. We have seen that this is the case.

The Hartree method is a trial and error method. One assumes a potential. Then calculates the wave function. With this wave function one calculates a new potential. In practice it is a lot of work and only the Hartrees are really adept at it.

The results are usual given in terms of the effective nuclear charge, = the charge contained in a sphere of radius r

$$Z(r) = Z - Q(\text{electron cloud})$$

$$E = \frac{Z(r)e}{r^2}$$

$$V = -\int_{-\infty}^{r'} \frac{Z(r)e}{r^2}\, dr$$

Hartree gets $Z(r)$ constant to .01 of a unit.

References

1928 Camb Phil Soc. 24, 89

1933 Proc. Roy Soc 141 282 Cu^+, Cl^-

1934 " " " 143 506 $K^+ Cs^+$

1935 " " " 149 210 Be Ca Hg $Fl^- Rb^+$