[1] # Electron-Impact Collisions

$$e^- + A$$

$$=$$

ATOMIC STRUCTURE $\rightarrow$ $e^- + A$ $\rightarrow$ PLASMA DIAGNOSTICS

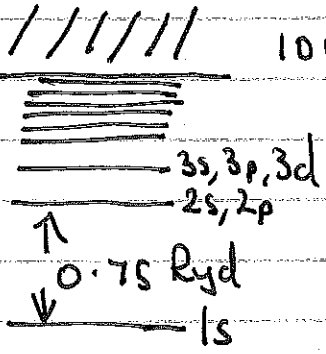
There are several electron-impact processes vital for astrophysical plasmas & magnetically-confined plasmas

1.0. Electron-impact processes

1.1 Electron-impact excitation where

an electron (free, + energy) collides with an atom/ion.

Eg Hydrogen



e^- +

If an electron has sufficient energy to excite a target electron (eg 1s) to an upper level then electron-impact excitation may occur.

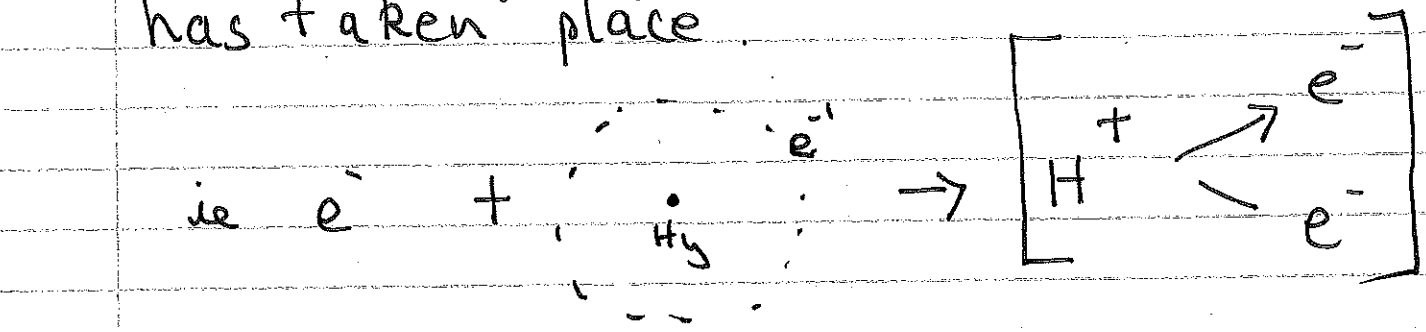
If the incident electron has insufficient energy to excite an atom/ion then

both the electron + target have the same energies before / after the collision. This is referred to an elastic scattering

1.2 Electron-impact ionisation (e2e)

$$e^- + A \rightarrow A^+ + e^- + e^-$$

If the incoming incident electron has sufficient energy to raise one of the target electrons into the continuum leaving the atomic target more charged, then ionisation has taken place



Of course if the electron is sufficient high double / triple ionisation is possible

1.3 Electron-impact recombination

1.3.1 Dielectronic Recombination

$$e^- + A^q \rightarrow A^{q**} \rightarrow A^{(q-1)} + h\nu$$

[compound resonance state]

Eg $e^- + 1s \rightarrow 2p\,\bar{n}\,\bar{l}$

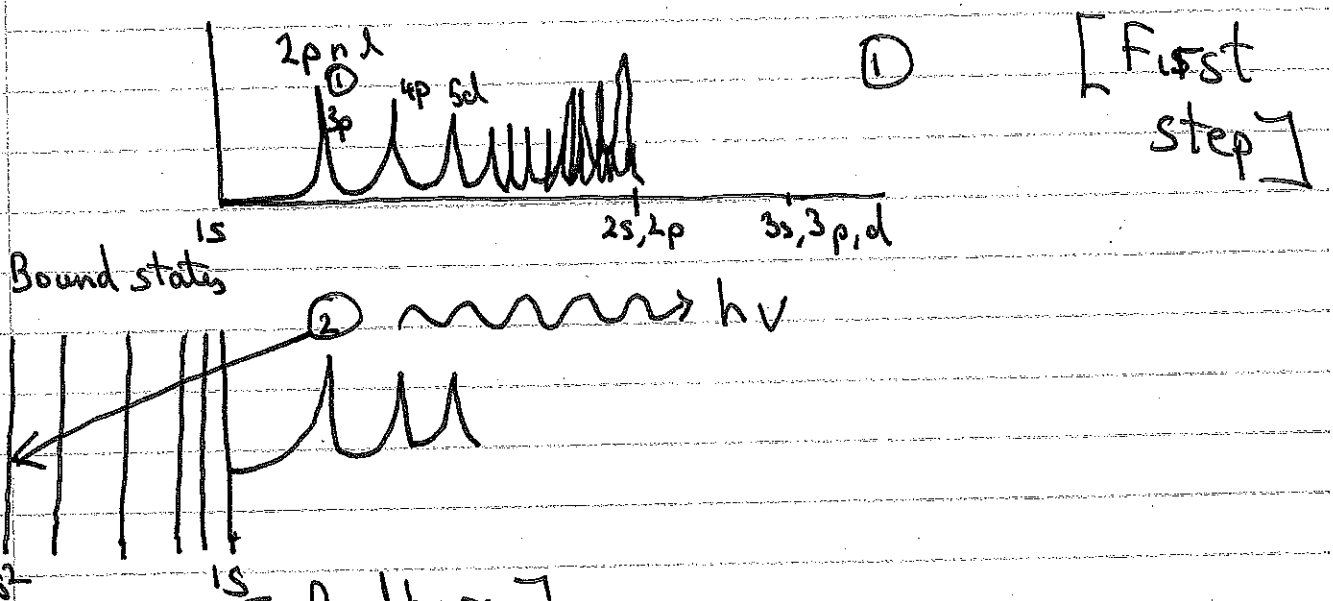
$\searrow\ 1s^2$

$1s\,n\,l$

where $\bar{n}\,\bar{l}$ refer to a particular Rydberg resonance

[Casual picture viewpoint]

$e^- + He^+(1s) \rightarrow He^{**}\ 2p\,n\,l$



① [First step]

The [Rydberg resonance] state from ① emits a photon and is captured into a bound state completing the process

1.3.2 Radiative recombination

As opposed to Dielectronic recombinat this does not occur via a resonanc there is simply the emission of a photon

1.4 Other collisional processes such as charge exchange also play an important role in plasma physics

$$A^{q+} + B \rightarrow B^{+} + A^{(q-1)+}$$

but we will not be considering it here.

Overview of Current Methods

2.1 Perturbative Methods

	Pro	Con
• Plane-wave Born	quick, good at high energy	Poor at low energy + near neutral targets
• Distorted Wave.		

As perturbative methods, by definition consider an initial and final state it is difficult to model the interactio of other states or the interaction between the incoming and outgoing electrons accurately.

2.2 Non-Perturbative Methods

- Convergent close coupling (CCC)
- Exterior Complex scaling
- R-matrix method (RMPS) ← [talk about later

2.3 Lattice or grid approch

We solve either the Schrödenger or Dirac equations on a numerical grid.

K.E. P.E.

ie $$i\hbar \frac{\partial}{\partial t}\Psi(x,t) = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi + V\Psi$$

$\Psi \equiv$ bomplex 1-dimensional wavefunction
$V \equiv V(x)$ 1-dimensional potential
$\hbar \equiv$ Planck's constant / 2π

or more compactly

$$i\hbar \frac{\partial \Psi}{\partial t} = \mathcal{H}\Psi \quad \text{where } \mathcal{H} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V$$

* $$\Psi(x,t) = \exp\left\{-\frac{i}{\hbar}\mathcal{H}t\right\}\Psi(x,0)$$

is a formal solution

* We discretize space + time

into increments of h + τ

$$\therefore\ i\hbar \frac{\Psi_j^{n+1} - \Psi_j^n}{\tau} = \frac{-\hbar^2}{2m}\frac{\Psi_{j+1}^n + \Psi_{j-1}^n - 2\Psi_j^n}{h^2} + V_j \Psi_j^n$$

or

[**] $$i\hbar \frac{\Psi_j^{n+1} - \Psi_j^n}{\tau} = \sum_{k=1}^{N} H_{jk}\Psi_k^n$$

where $$H_{jk} = \frac{-\hbar^2}{2m}\frac{\delta_{j+1,k} + \delta_{j-1,k} - 2\delta_{jk}}{h^2} + V_j \delta_{jk}.$$

[ie tridiagonal]

where $\underline{\underline{I}}$ = identity $= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

Re-arranging

[EXPLICIT] $$\Psi^{n+1} = \left(\underline{\underline{I}} - \frac{i\Upsilon}{\hbar}\underline{\underline{H}}\right)\Psi^{n}$$

or $$\begin{bmatrix} \psi_1^{n+1} \\ \\ \psi_N^{n+1} \end{bmatrix} = \begin{bmatrix} & & \\ & & \\ & & \end{bmatrix} \begin{bmatrix} \psi_1^{n} \\ \vdots \\ \psi_N^{n+1} \end{bmatrix}$$ } N grid points

ie it allows us to propagate the wavefunction from one time step to the next.

Or we can apply our Hamiltonian to a future Ψ

$$i\hbar \frac{\psi_j^{n+1} - \psi_j^{n}}{\Upsilon} = \sum_{k=1}^{N} H_{jk}\,\psi_k^{n+1}$$

$$\Rightarrow \underline{\Psi}^{n+1} = \underline{\Psi}^{n} - \frac{i\Upsilon}{\hbar}\underline{\underline{H}}\,\underline{\Psi}^{n+1}$$

$$\Rightarrow \left(\underline{\underline{I}} + \frac{i\Upsilon}{\hbar}\underline{\underline{H}}\right)\Psi^{n+1} = \Psi^{n}$$

[IMPLICIT] $$\Rightarrow \Psi^{n+1} = \left(\underline{\underline{I}} + \frac{i\Upsilon}{\hbar}\underline{\underline{H}}\right)^{-1}\Psi^{n}$$

Note: This requires the inversion of a complex matrix

Finally, the Crank-Nicolson scheme is a mixture of the implicit & explicit scheme.

$$i\hbar \frac{\psi_j^{n+1} - \psi_j^n}{\tau} = \frac{1}{2} \sum_{k=1}^{N} H_{jk} \left(\psi_k^n + \psi_k^{n+1} \right)$$

$$\Rightarrow \underline{\psi}^{n+1} = \underline{\psi}^n - \frac{i\tau}{2\hbar} \underline{\underline{H}} \left(\underline{\psi}^n + \underline{\psi}^{n+1} \right)$$

[Crank Nicolson] or $$\underline{\psi}^{n+1} = \left(\underline{\underline{I}} + \frac{i\tau}{2\hbar} \underline{\underline{H}} \right)^{-1} \left(\underline{\underline{I}} - \frac{i\tau}{2\hbar} \underline{\underline{H}} \right) \underline{\psi}^n$$

Pros Accurate time dependent solutions and if using the Crank-Nicolson gives very stable results

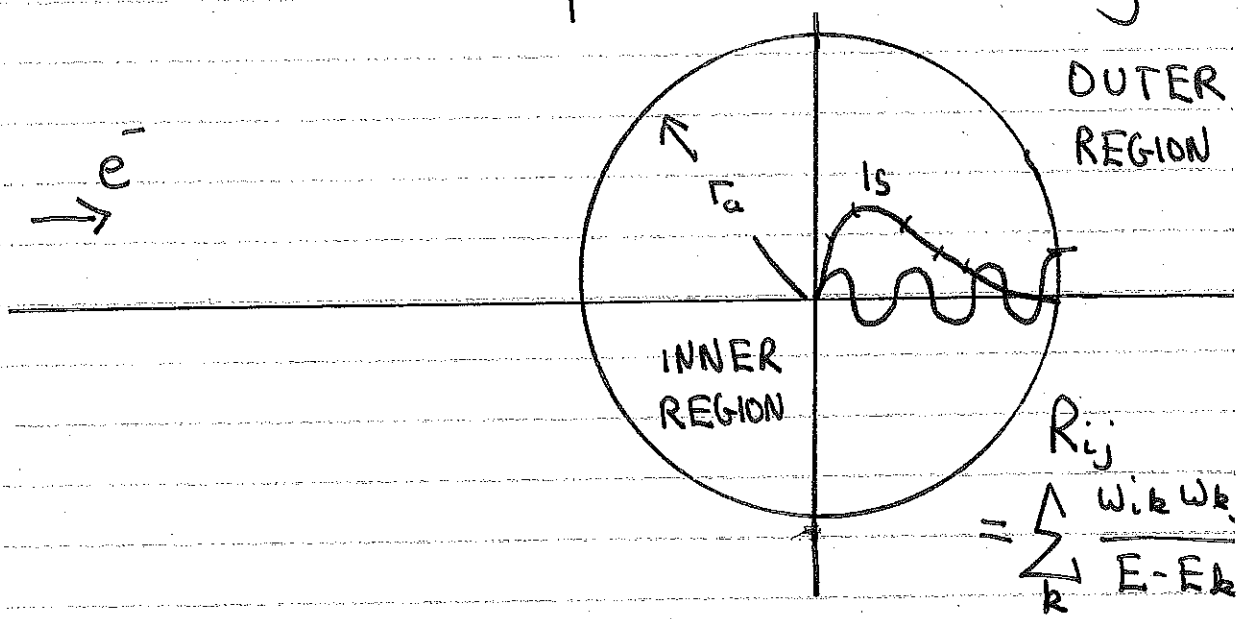
$$e^{-z} \approx \frac{1 - z}{1 + z}$$

Cons (i) Very time / computationally demanding beyond one dimension

(ii) Not very suitable for long lived resonance description

(iii) Does not provide many energy points compared to other methods

2.4. Overview of R-Matrix Theory



- We are back to considering

$$e^- + A_i \rightarrow e^- + A_j$$

→ Inelastic scattering : transition from state i to state j

→ We are considering CENTRAL POTENTIALS

$$V \equiv V(r)$$

The R-matrix approach (in its simplest form) partitions configuration space into two regions (INNER / OUTER)

2.4.1 Inner Region

The radial distance from the nucleus to some radial distance r_a, chosen to enclose the charge cloud of the atom. A simple choice is the radial extent of the most diffuse orbital (target)

Invariably, this is the highest principal quantum number orbital [at least for light systems] $Z < 10$.

ie H atom [1s, 2s, 2p, ..., 4f] electrons

4f would set the R-matrix boundary.

* Mathematically it can be larger, but this impacts the computational time.

* In the inner region, electron exchange & correlation effects between the scattered electron & target are important. Informally, the problem may be considered to some degree as a N+1 electron bound problem.

2.4.2 Outer Region

For $r > r_a$, the problem simplifies. Exchange of the incoming electron with the target is neglected. The scattered electron moves in the 'weak' long range potential of the target.

Okay, back to the very basics

[3] Basic Scattering Theory

Consider, the non-relativistic time-independent Schrödinger equation, describing the motion of a particle of mass [unit mass] in a central potential.

$$[3.1] \quad \left[-\frac{1}{2}\nabla^2 + V(r)\right]\Psi(\underline{r}) = E\,\Psi(\underline{r})$$

$\Rightarrow$ E = total energy
$\Rightarrow$ $V(r)$ = Central potential

a) short range i.e. $\to 0$ faster than $\frac{1}{r}$ at large distances

b) less singular than $\frac{1}{r^2}$ at $r=0$

Solution of [3.1] corresponding to an incident particle [i.e. an electron] on the scattering centre [i.e. nucleus] travelling initially along the z axis but scattered in the direction $\Omega \equiv (\theta, \phi)$ has the <u>asymptotic form</u>

$$[3.2] \quad \Psi(\underline{r}) \sim e^{ikz} + f(\theta,\phi)\frac{e^{-ikr}}{r}$$

$\Rightarrow$ $f(\theta,\phi)$ = scattering amplitude

$\Rightarrow$ k (wave number) related to the total energy

$$[3.3] \quad k^2 = 2E$$

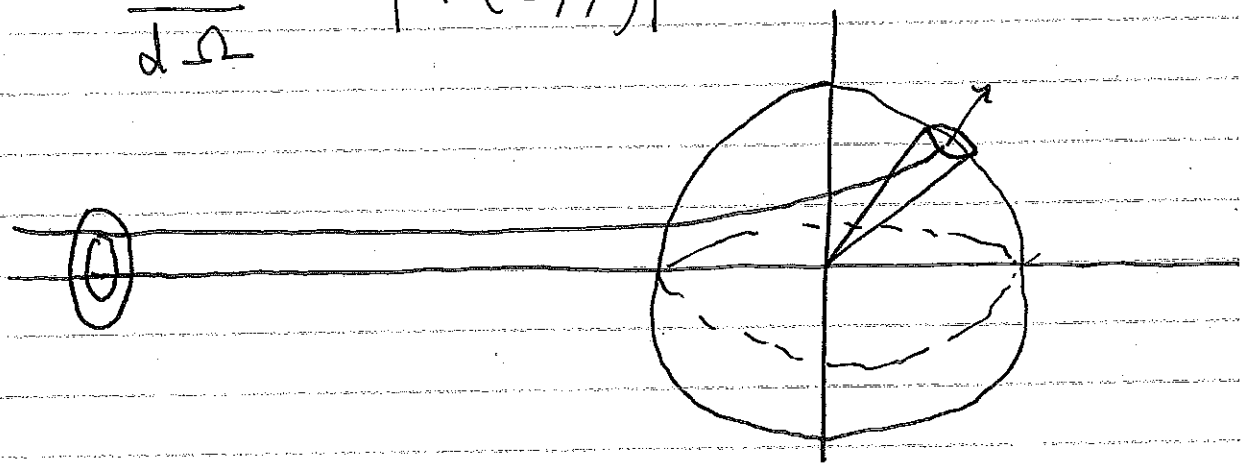
→ The asymptotic form of the scattered electron is different depending on whether the target is neutral (atom) or an ion.

→ If an ion, the Coulomb potential which behaves as $\frac{1}{r}$ at large distances must be accounted for. The Coulomb potential distorts the scattered wavefunction

→ Neutral systems (atoms) have a simpler asymptotic form and may be represented by spherical Bessel and Neumann functions

The differential cross section can be obtained from [3.2] by calculating the outward flux of electrons scattered through a spherical surface $r^2 d\Omega$ for large r divided by the incident flux and by the element of the solid angle $d\Omega$

$$\frac{d\sigma}{d\Omega} = |f(\theta, \phi)|^2 \qquad [3.4]$$



in units of a_0^2 per steradian, where a_0 = Bohr radius.

The <u>total cross section</u> is then obtained by integrating the differential cross section over all scattering angles

$$[3.5] \quad \sigma_{total} = \int_0^{2\pi} \int_0^{\pi} |f(\theta,\phi)|^2 \sin\theta \, d\theta \, d\phi$$

So how do we determine the scattering amplitude, solve [3.1] subject to [3.2]

This can be achieved by <u>partial wave expansion</u>

[3.6] Consider $U(r) \equiv 2V(r)$

Expand

$$[3.7] \quad \psi(r) = \sum_{l=0}^{\infty} B_l(k) \frac{1}{r} u_l(r) P_l(\cos\theta)$$

l = orbital angular momentum of incoming electron

$P_l(\cos\theta)$ = Legendre polynomial

$B_l(k)$ = coefficients determined by enforcing boundary conditions of [3.2]

The reduced radial wave function

$U_l(r)$ [which does not include the $\frac{1}{r}$] is determined by substituting [3.7] into [3.1], premultiplying by $P_l(\cos\theta)$ and integrating with respect to $\cos\theta$

[3.8] $$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - U(r) + k^2\right) U_l(r) = 0$$

$$\text{Effective potential} = -\left[\frac{l(l+1)}{r} + U(r)\right]$$

$\frac{l(l+1)}{r}$: repulsive centrifugal barrier; $U(r)$: reduced potential

As $U(r)$ is real, the energies (k^2) are real, we expect

$U_l(r)$ to be real also

[3.9] For [3.8] as $r \to 0 \Rightarrow U_l(r \to 0) \sim N r^{l+1}$

as $r \to \infty \Rightarrow S_l(kr) + C_l(kr) \times \tan\delta_l(k)$

where (i) N is a normalisation factor

(ii) $S_l(kr)$ & $C_l(kr)$ are the regular & irregular solutions to [1.8] without $U(r)$

It can be shown

[3.96] $S_\ell(kr) = kr\, j_\ell(kr) \rightarrow$ Spherical Bessel fn

$$= \left(\frac{\pi kr}{2}\right)^{\frac{1}{2}} J_{\ell+\frac{1}{2}}(kr)$$

$$\sim \sin\left(kr - \frac{\ell\pi}{2}\right)$$

and

$$C_\ell(kr) = -kr\, h_\ell(kr) \quad \text{— Neumann fn}$$

$$= (-1)^\ell \left(\frac{\pi kr}{2}\right)^{\frac{1}{2}} J_{-\ell-\frac{1}{2}}$$

$$\sim \cos\left(kr - \tfrac{1}{2}\ell\pi\right)$$

Let us return to [3.9], where we still have the remaining quantity $\delta_\ell(k)$ called the 'phase shift' to be determined.

$$\delta_\ell \approx \delta_\ell\underbrace{(k, E, \ell)}_{\text{ALL REAL}}$$

We can define an <u>S-matrix</u> in terms of the <u>phase shifts</u>

Consider [3.9] + [3.8]

$$* \quad u_\ell^N(r) \sim N\left[S_\ell(kr) + C_\ell(kr)\tan\delta_\ell(k)\right]$$

N is a <u>Normalisation</u> factor + [*] is still a solution of [1.8]

choose $N = -2i \cos\delta_\ell \exp(i\delta_\ell)$

Then [*] becomes

$$u_\ell(r) \underset{r\to\infty}{\sim} \exp(-i\theta_\ell) - \exp(i\theta_\ell) S_\ell$$

$[\theta_\ell = kr - \frac{\ell\pi}{2}]$

[3.10] where $S_\ell(k) = \exp[2i\delta_\ell(k)]$

$$= \frac{1 + iK_\ell(k)}{1 - iK_\ell(k)}$$

where $K_\ell(k) = \tan\delta_\ell(k)$

So informally/intuitively what is δ_ℓ ?

[It is a measure of how far u_ℓ deviates for the $U(r) \equiv 0$ solution]

*** We have not forgotten about $B_\ell(k)$ introduced in [3.7], but let us consider

First Born Approximation

Goal: Useful expression for K_ℓ & δ_ℓ

Consider the Schrödinger equation with $U(r) = 0$

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

choose $V_\ell(r)$ to be the regular solution $S_\ell(r)$

(i) Premultiply [3·8] by $v_l(r)$

(ii) Premultiply [3·11] by $u_l(r)$

(iii) Integrate (i) + (ii) from 0 to ∞, and subtract

$$\Rightarrow \int_0^\infty \left[v_l(r) \frac{d^2 u_l}{dr^2} - u_l(r) \frac{d^2 v_l}{dr^2} \right] dr$$

Apply Green's formula

$$= \int_0^\infty v_l(r)\, U(r)\, u_l(r)\, dr$$

Apply boundary conditions

$$\therefore K_l(k) = \tan \delta_l(k)$$

$$= -\int_0^\infty j_l(kr)\, U(r)\, u_l(r)\, r\, dr$$

If $U(r)$ is weak, or the electron is moving fast (whether it is appropriate or not) we replace $u_l(r)$ by $v_l(r)$

$$\Rightarrow K_l^B(k) = \tan \delta_l^B(k)$$

$$= -k \int_0^\infty U(r)\, j_l^2(kr)\, r^2\, dr$$

which is known as the <u>first Born approximation</u>

Returning to [3.8] solutions must follow orthonormality

$$\int_0^\infty \left[u_l^N(k,r)\right]^* u_l^N(k',r)\,dr = \delta(E-E')$$

$$u_l(k,r) \underset{r\to\infty}{\sim} \left(\frac{2}{\pi k}\right)^{\frac{1}{2}} \frac{\left[\sin\theta_l + \cos\theta_l K_l(k)\right]}{\left[1+K_l^2(k)\right]^{\frac{1}{2}}}$$

[3.13] Outgoing soln

$$u_l^+(k,r) \underset{r\to\infty}{\sim} \left(\frac{2}{\pi k}\right)^{\frac{1}{2}}\left[\sin\theta_l + \frac{1}{2i}\exp(i\theta_l)T_l(k)\right.$$

$$u_l^-(k,r) \underset{r\to\infty}{\sim} \left(\frac{2}{\pi k}\right)^{\frac{1}{2}}\left[\sin\theta_l - \frac{1}{2i}\exp(-i\theta_l)T_l^*(k)\right.$$

where $T_l(k) = \dfrac{2iK_l(k)}{1-iK_l(k)} = S_l(k) - 1$

so if $U(r)\equiv 0$, $S_l(k) = 1$ & $T_l(k) = 0$

If we return to the plane wave term in [3.2] in partial waves and equate it with the asymptotic form of [3.7]

[3.14]
$$e^{ikz} = \sum_{l=0}^{\infty} (2l+1)\,i^l\, j_l(kr)\, P_l(\cos\theta)$$

Using [3.9] & [3.96]

and by equating the coefficients $B_l(k)$ [3.7]

Explicitly

$$[3.7] \quad \psi(r) = \sum_{l=0}^{\infty} B_l(k) \frac{1}{r} u_l(r) P_l(\cos\theta)$$

$$e^{ikz} = \sum_{l=0}^{\infty} (2l+1)\, i^l j_l(kr) P_l(\cos\theta)$$

$\Rightarrow$

$$[3.15] \quad B_l(k) = k^{-1} (2l+1) i^l \cos\delta_l(k) \exp(i\delta_l)$$

Substitute [3.15] back into [3.7] and compare with [3.2]

$$[3.16] \quad f(\theta,\phi) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1) \left[e^{2i\delta_l} - 1 \right] P_l(\cos\theta)$$

Finally substituting [3.16] back into the expression for the total cross section

$$\sigma_{TOTAL} = \sum_{l=0}^{\infty} \sigma_l = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2\delta_l$$

[Wigner - Eisenbud]

Chapter 4 : Basic R-matrix Theory

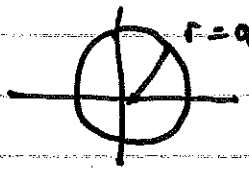
Consider again the short-range potential let $l = 0$, s wave model (Poet-Temkin)

The radial Schrödinger eqn

$$[4.1] \quad \left[\frac{d^2}{dr^2} - U(r) + k^2\right] u_0(r) = 0$$

where we assume $U(r) = 0 \quad r \geq a_0$

$a_0 \equiv$ R-matrix radius



So we have divided the range of r into an 'internal' & 'external' region

$0 \leq r \leq a_0$ [internal]
$a_0 \leq r < \infty$ [external]

We look for a solution of [a] subject to

$$[4.2] \quad u_0(0) = 0$$
$$u_0(r) = \sin(kr) + \cos(kr)\tan\delta_0(k)$$

The R-matrix, $R_0(E)$ is defined in terms of the solution $u_0(a_0)$ & its derivative on the boundary $r = a_0$

$$[4.3] \quad u_0(a_0) = R_0(E)\left[a_0 \frac{du_0}{dr} - b_0 u_0\right]_{r=a}$$

b_0 = arbitrary const (set = 0)

If so, [$\therefore R_0(E)$ is equal to the reciprocal of a_0 times the logarithmic derivative of $u_0(r)$ at $r = a_0$]

Consider a solution of [4.1] in the internal region in terms of a complete set of continuum basis orbitals.

$$[4.4] \quad \left[\frac{d}{dr^2} - U(r) + k_i^2\right] u_{0i} = 0 \qquad 0 \le r \le a_0$$

subject to $u_{0i} = 0$ if $r = 0$

$$[4.5] \quad \frac{a_0}{u_{0i}(r=a_0)} \left.\frac{du_{0i}}{dr}\right|_{r=a_0} = b_0 \qquad [b_0 \text{ also arbitrary}]$$

and <u>orthonormality</u> conditions

$$\int_0^{a_0} u_{0i} u_{0j}\, dr = \delta_{ij}$$

The solution of $u_0(r)$ of [4.1] at any energy $E = \frac{1}{2}k^2$ is then expanded in the terms of this basis

$$u_0(r) = \sum_{i=1}^{\infty} u_{0i}(r)\, c_i \qquad 0 \le r \le u_0$$

This expansion converges uniformly except on the boundary $r = a_0$ for all values of b_0

However, on the boundary this expansion CANNOT represent the derivative of the solution $u_0(r)$ except at the eigenenergies $E_i = \frac{1}{2} k_i^2$ of [4.4] & [4.5]

One way to proceed to the evaluation of the R-matrix given in [4.3] is to

(i) Premultiply [4.1] by $u_{0i}(r)$

(ii) Premultiply [4.4] by $u_0(r)$

(iii) Integrate between $r = 0$ to a_0 for both (i) & (ii), then subtract

$$[4.6] \quad \int_0^{a_0} \left(u_{0i} \frac{d^2 u_0}{dr^2} - u_0 \frac{d^2 u_{0i}}{dr^2} \right) dr = \left(k_i^2 - k^2 \right) \int_0^{a_0} u_{0i} u_0 \, dr$$

↓ Via Green's Theorem

↙ orthogonality

$$\left[u_{0i} \frac{du_0}{dr} - u_0 \frac{du_{0i}}{dr} \right]_{r=a_0} = \left(k_i^2 - k^2 \right) c_i$$

Using [4.5] i.e. boundary conditions

$$[4.7] \quad c_i = \frac{1}{a_0} \frac{u_{0i}(a_0)}{k_i^2 - k^2} \left(a_0 \frac{du_0}{dr} - b_0 u_0 \right)_{r=a_0}$$

Substituting c_i back into

$$u_0(r) = \sum_{i=1}^{\infty} u_{0i}\, c_i \qquad 0 \le r \le a_0$$

we get

$$u_0(r) = \frac{1}{a_0} \sum_{i=1}^{\infty} \frac{u_{0i}(r)\, u_{0i}(a_0)}{k_i^2 - k^2} \left(a_0 \frac{du_0}{dr} - b_0 u_0 \right)_{r=a_0}$$

→ By setting $r = a_0$ in the above equation & comparing with [4·3]

$$R_0(E) = \frac{1}{2a_0} \sum_{i=1}^{\infty} \frac{[u_{0i}(a_0)]^2}{E_i - E}$$

[R-matrix] [meromorphic function]

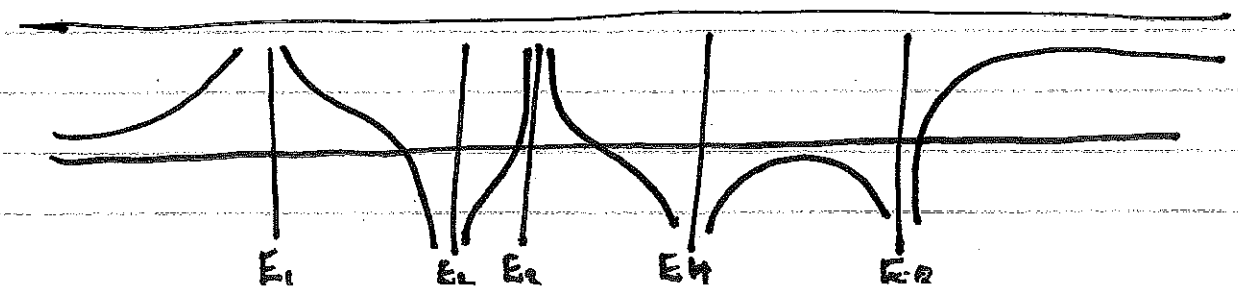
→ $E_i = k_i^2$ & $E = k^2$

Consider the above, [4·2] & [4·3]

We see

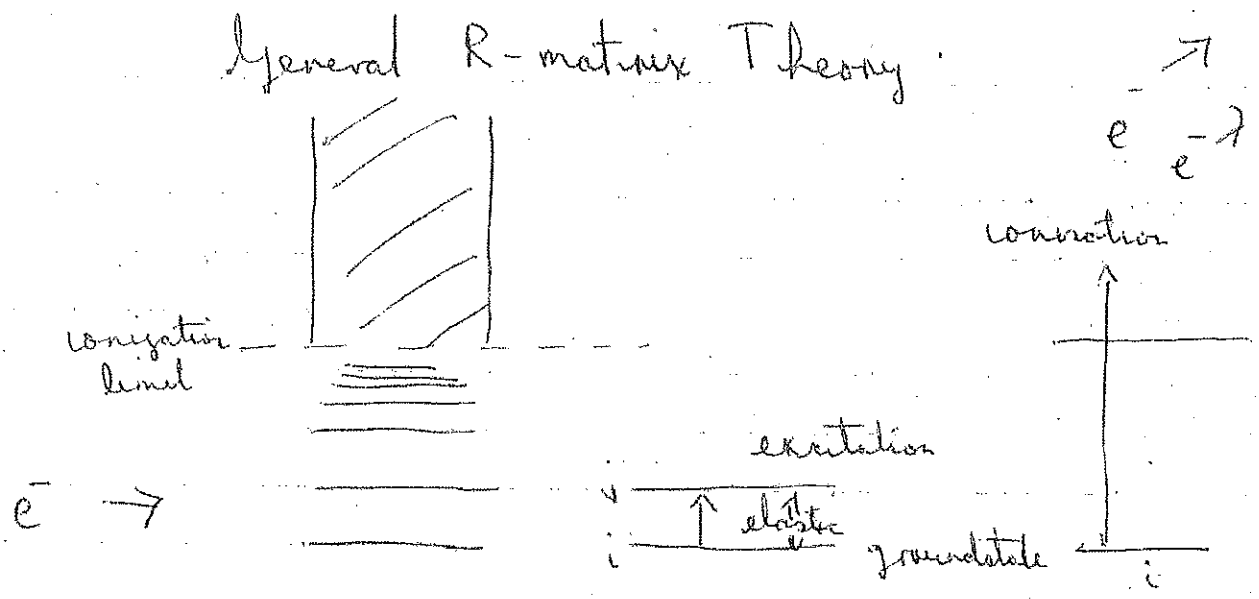
$$\tan \delta_0(k) = \frac{-\sin(ka_0) + R_0(E)[ka_0 \cos(ka_0) - b_0 \sin(ka_0)}{\cos(ka_0) + R_0(E)[ka_0 \sin(ka_0) + b_0 \cos(ka_0)}$$

From phase shift → K matrix
→ S matrix
→ total cross section



Chapter 5

General R-matrix Theory.



$$e^- + A_i \rightarrow A_j + e^-$$

where $A_{i,j}$ are both bound states of an atom or an ion, assumed to contain N electrons and has nuclear charge number Z.

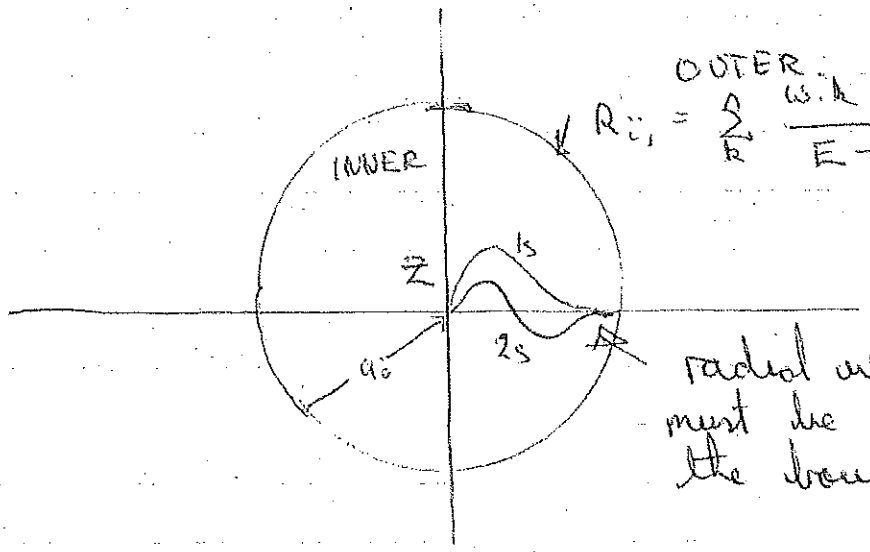
We shall solve the Time-Independent Schrodinger Equation for

$$H_{N+1}\,\Psi = E\Psi \qquad [1]$$

$$H_{N+1} = \sum_{i=1}^{N+1}\left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right) + \sum_{i>j}^{N+1}\frac{1}{r_{ij}} \qquad [9]$$

K.E. P.E. electron-electron repulsion

Initially, N electron (target bound)
1 electron (continuum)



radial wavefunction must be zero on the boundary

The R-matrix expansion of the inner region

[b] $$\chi^{\Gamma}_{j,E}(X_{N+1}) = \sum_{k=1}^{n_t} \psi^{\Gamma}_{k}(X_{N+1})\, A^{\Gamma}_{kj}(E)$$

Γ labels quantum numbers

$X_{N+1} = (r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2, \ldots r_{N+1}, \theta_{N+1}, \phi_{N+1})$ + spin

j labels the solns of [a]

$A^{\Gamma}_{kj}(E)$ = energy dependent expansion coefficients.

$\psi^{\Gamma}_{j,E}$ = energy independent basis function

Breathe deeply!

[c] $$\psi^{\Gamma}_{k}(X_{N+1}) = A \sum_{i=1}^{n} \sum_{j=1}^{n_c} \bar{\phi}^{\Gamma}_{i}(X_N; r_{N+1}\sigma_{N+1}) \frac{1}{r_{N+1}} \times u^{0}_{ij}(r_{N+1})\, a^{\Gamma}_{ij,k} + \sum_{i=1}^{m} \eta^{\Gamma}_{i}(X_{N+1})\, b^{\Gamma}_{ik} \quad k = 1, \ldots, n_t$$

n = number of channels

n_c = number of radial continuum basis orbitals for each channel ks, kp, kd, ...

m = number of square-integrable functions

$\bar{\phi}_i^{\Gamma}$ = channel function

$u_{ij}^{o}(r)$ = continuum functions which describe the motion of the scattered electron between $r = 0$ & a_0.

$\underbrace{a_{i,k}^{\Gamma} \quad + \quad b_{i,k}^{\Gamma}}_{C_{i,k}^{\Gamma}}$ = to efficient determined by diagonalizing H_{N+1} [real symmetric]

Give me an example!!

Consider H : 1s, 2s, 2p

$\rightarrow {}^2S^e(1s), {}^2S^e(2s), {}^2P^o(2p)$

$\bar{e}$ = arbitrary angular momentum l but either spin up or down

However say we chose $\Psi_k^{\Gamma}(X_{N+1}) = {}^1P^o$

$\therefore$ incoming electron must be spin down

Informally

$\Gamma = {}^1P^o = {}^2S^e(1s) + kp \quad$ } channels

$\quad\quad {}^2S^e(2s) + kp$

1 term but 2 channels $\left\langle \begin{array}{l} {}^2P^o(2p) + ks \\ {}^2P^o(2p) + kd \end{array} \right.$

target term + continuum

+ correlation $\begin{matrix} 1s\,2p \\ 2s\,2p \end{matrix}$ } correlation consists of only bound orbitals

When we diagonalise our Hamiltonian

[c] $\langle \Psi_k^\Gamma | H_{N+1} | \Psi_{k'}^\Gamma \rangle = E_k^\Gamma \delta_{kk'}$

Our 'Γ' = ${}^1P^o$ is described as a partial wave. ~~analysis~~ We need to sum over many partial waves to have a converged total cross section

ie ${}^{1,3}S^{e,o}$ / ${}^{1,3}P^{e,o}$ / ${}^{1,3}D^{e,o}$ / ${}^{1,3}F^{e,o}$ / ...

which is an indirect way of summing over the arbitrary k of the incoming electron, hence the 'k' in eqn [c]

The ks, kp, kd continuum fns are solved for each l in a similar fashion to the previous section. The extra constraint of ensuring orthogonality between the continuum basis and the spectroscopic orbitals is achieved by Lagrange multipliers

ie H case ks is orthogonal to 1s, 2s
kp is " " 2p.

The R-matrix itself acts as the interface between $0 - a_0$ and beyond.

$$R_{ij} = \frac{1}{2a} \sum_k \frac{W_{ik} W_{kj}}{E_k - E}$$

W_{ik} ← surface amplitudes

E_k ← Eigenvalues of H_{N+1}

$$W_{ik} = \sum C_{ikj} U_{ij}(r = a_0)$$

$U_{ij}(r=a_0)$ → continuum on the boundary

C_{ikj} ↓ eigenvectors of the N+1 Hamiltonian

a) Generate continuum basis $U_{ij}(r=a_0)$

b) Form and diagonalise the H_{N+1} Hamiltonian

→ ~~Eigk~~ C_{ikj} (Eigenvectors of Hamiltonian)

→ E_k (R-matrix poles or Eigenvalues of H_{N+1})

c) From (a) & (b) $\Rightarrow W_{ik}$

d) $W_{ik} \Rightarrow R_{ij}$

e) Connect to Outer Region

Outer Region

What have we so far

(i) $$R_{ij} = \frac{1}{2a} \sum_k \frac{w_{ik} w_{jk}}{E_k - E}$$

(ii) $$F_i(a) = \sum_j R_{ij}(E) \left(a \frac{dF_j}{dr} - bF_j \right)_{r=a}$$

In the outer region, we drop exchange and there we lose the asymmetrization of [c] and the second summation

By projecting this modified [c] back onto the Schrodinger eqn

$$\Rightarrow \left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{2Z}{r} + k_i^2 \right) F_i(r)$$

$$= 2 \sum_{j=1}^{n} V_{ij} F_j(r)$$

n = number of channels

V_{ij} is a weak multipole expansion

$$V_{ij} = \left\langle \phi_i^{\Gamma} \middle| \sum_{k=1}^{N} \frac{1}{r_{k,N+1}} \middle| \phi_j^{\Gamma} \right\rangle$$

Now connecting back with Kevin's lecture

$F_{ij} \underset{r\to\infty}{\sim} k_i^{-\frac{1}{2}} (\sin\theta_i + \cos\theta_i K_{ij})$ open

$\underset{r\to\infty}{\sim} 0$ closed

$K \rightarrow S$ matrix $\rightarrow \sigma$ [total cross section]

If perhaps I have presented this too informally ....

For hydrogen [c] can be expressed

$$\psi^{LS\Pi}_{n_1 l_1 n_2 l_2}(\hat{r}_1, \hat{r}_2)$$

$$= \frac{1}{\sqrt{2}}\left[\frac{1}{r_1} u_{n_1 l_1}(r_1)\frac{1}{r_2} u_{n_2 l_2}(r_2) \mathcal{Y}_{l_1 l_2 L M_L}(\hat{r}_1, \hat{r}_2)\right.$$

$$\left. + (-1)^{L+S+l_1+l_2}\frac{1}{r_1} u_{n_2 l_2}(r_1)\frac{1}{r_2} u_{n_1 l_1}(r_2)\right.$$

$$\left.\mathcal{Y}_{l_2 l_1 L M}(\hat{r}_1, \hat{r}_2)\right]$$

for $n_1 l_1 \neq n_2 l_2$ and

$$\psi^{LS\Pi}_{n_1 l_1 n_2 l_2}(\hat{r}_1, \hat{r}_2) = \frac{1}{r_1} u_{n_1 l_1}(r_1)\frac{1}{r_2} u_{n_2 l_2}(r_2)$$

$$\mathcal{Y}_{l_1 l_2 L M_L}(\hat{r}_1, \hat{r}_2)$$

where $u_{nl} \in \{1s, 2s, 2p, 3s, 3p, 3d, \ldots\}$

$LS\Pi = {}^1P^o$

$$\mathcal{Y}_{l_1 l_2 L M}(\hat{r}_1, \hat{r}_2) = \sum_{m_1, m_2} \underbrace{(l_1 m_1, l_2 m_2 : L M_L)}_{\text{Clebsch-Gordan coeff.}}$$

$$\times Y_{l_1 m_1}(\hat{r}_1) Y_{l_2 m_2}(\hat{r}_2)$$

with $u^c_{nl}(r)$ satisfying

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + V(r) + k^2_{nl}\right) u^c_{nl}(r)$$

$$= \sum_{n'} \lambda_{nn'l}\, u^b_{n'l}(r)$$

Lagrange multiplier — bound orbital

$$\left.\begin{aligned} u^c_{nl}(0) &= 0 \\ \frac{a}{c}\frac{du^c_{nl}}{dr}\bigg|_{r=a} &= b \end{aligned}\right\} \text{ condition}$$

$$\int_0^a u^c_{nl}(r)\, u^b_{n'l'}(r)\, dr = 0 \quad \forall\, n', n, l$$