Collision theory

- partial wave expansion
- Wigner threshold law, generalizations
- effective range theory
  & the scattering length
- long-range interactions
- multichannel quantum defect theory

  Rydberg states

  ultracold collisions and
  Fano - Feshbach resonances

  Frame transformations

Single-channel scattering theory

This theory applies to the following two scenarios:

(1) Scattering of an incident particle of mass m from an infinitely-massive center, with potential energy $V(r)$

or

(2) Scattering of 2 particles in their center-of-mass frame, if the potential energy depends only on their separation, $V(r)$.

$\Rightarrow$ Then mathematically these two problems look the same, provided that, in case (2), the reduced mass is used in the radial Schrödinger equation, i.e.

$$m = \frac{m_1 m_2}{m_1 + m_2}$$

- For now we will assume that the particles are <u>structureless</u>, i.e. with no internal states that might get excited in an inelastic collision

$$\Rightarrow \quad V = V(|\vec{r}_1 - \vec{r}_2|) = V(r), \quad r = |\vec{r}_1 - \vec{r}_2|$$

Also, assume for now that $V(r)$ is of <u>finite range</u>, such that $V(r) = 0$ at $r > r_0$.

- Initially consider this from a time-independent stationary-state point of view $\Rightarrow$ fixed energy E

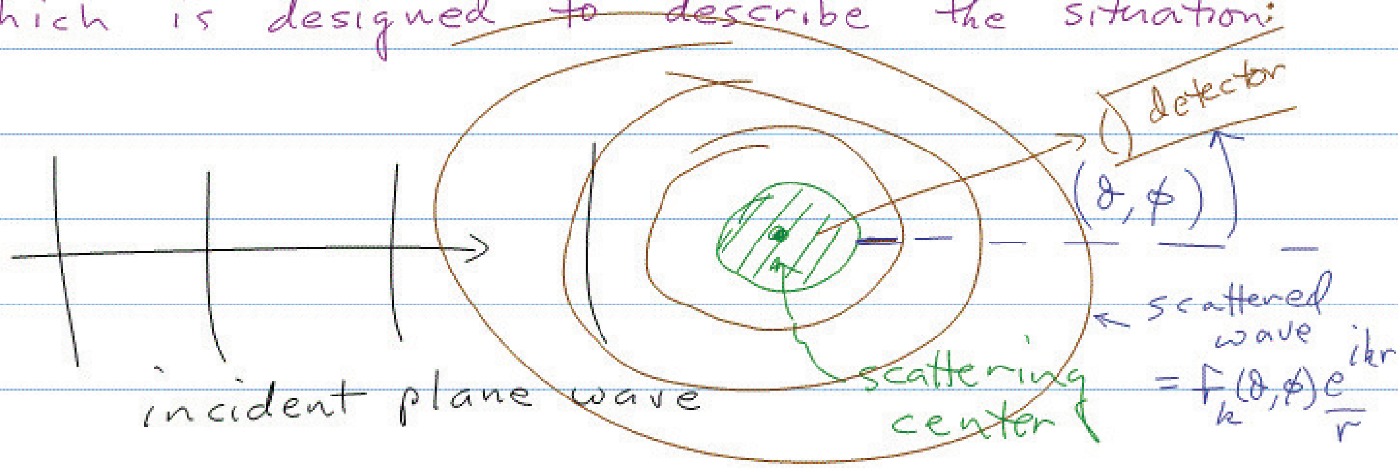
$\Rightarrow$ Our goal is to solve the time-indep. Schrödinger equation, subject to scattering boundary conditions (B.C.s), namely

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

i.e., with BCs:

$$\psi_{\vec{k}}(\vec{r}) \xrightarrow[r\to\infty]{} e^{i\vec{k}\cdot\vec{r}} + f_k(\theta,\phi)\frac{e^{ikr}}{r}$$

which is designed to describe the situation:



and of course the de Broglie wavenumber is $k = \left(\frac{2mE}{\hbar^2}\right)^{1/2}$

Aside: If you prefer to see this as a time-dependent wavepacket, just carry out the appropriate Fourier analysis:

$$\Rightarrow \Psi(\vec{r},t) = \int d^3k \, e^{-i\frac{\hbar k^2}{2m}t} \psi_{\vec{k}}(\vec{r}) A_{\vec{k}}$$

and you will see a Gaussian "blob" coming in from $r=\infty$ and then "scattered blobs" moving outward from the scattering center

Partial wave treatment – best at low energy

=> Assume that the scattering potential has the form

$$V(r) = \begin{cases} \text{complicated}, & r < r_0 \\ 0, & r > r_0 \end{cases}$$

(This treatment readily generalizes to long-range decaying potentials, exponentially or power-law decreases, but for now we will ignore these subtleties.)

Now, because $V = V(r)$, we know that separable solutions exist in spherical coordinates and a Complete Set of Commuting Observables (C.S.C.O.) is $H, \vec{L}^2, L_z \longrightarrow E, l, m$ and a generic separable solution is

$$\psi_{Elm}(\vec{r}) = Y_{lm}(\theta,\phi)\, R_{El}(r)$$

and the radial equation for $u_{El}(r) = r\, R_{El}(r)$ is

$$-\frac{\hbar^2}{2m} u''_{El}(r) + \left[\frac{l(l+1)\hbar^2}{2mr^2} + V(r) - E \right] u_{El}(r) = 0$$

Our goal is to derive a scattering amplitude for observing a particle scattered into (θ, ϕ) which amounts to an "observation" of θ, ϕ.

$\Rightarrow$ Because this "observable" does not commute with $\vec{L}^2, L_z$, we anticipate that we will have to coherently superpose the separable solutions $\psi_{E\ell m}(\vec{r})$ in order to impose the scattering boundary conditions.

[In fact, for a plane wave incident along the z-axis, L_z is conserved since

$$[L_z, P_z] = 0,$$

whereby only one m will be needed. However ℓ is not definite, so our superposition will only involve a sum over ℓ, finally]

Keeping everything general for now, our scattering solution must be representable as

$$\Psi_E(r,\theta,\phi) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} A_{\ell m} \frac{u_{E\ell}(r)}{r} Y_{\ell m}(\theta,\phi)$$

At distances beyond r_0, the radial Sch. Eqn is

$$-\frac{\hbar^2}{2m} u''_{E\ell}(r) + \left[\frac{\ell(\ell+1)\hbar^2}{2mr^2} - \frac{\hbar^2 k^2}{2m}\right] u_{E\ell}(r) = 0$$

and of course this equation has 2 linearly-independent solutions for each ℓ, k:

"regular at $r=0$" $\quad F_{E\ell}(r) = \left(\frac{2m}{\pi\hbar^2 k}\right)^{1/2} kr\, j_\ell(kr)$

and "irregular at $r=0$" $\quad g_{E\ell}(r) = \left(\frac{2m}{\pi\hbar^2 k}\right)^{1/2} kr\, n_\ell(kr)$

$y_\ell(kr)$ in some references

The constant factors $(\ )^{1/2}$ have been chosen such that these solutions are "energy-normalized", e.g.

$$\int_0^\infty F_{E\ell}(r)\, F_{E'\ell}(r)\, dr = \delta(E-E')$$

units check: $\left[\frac{m}{(pr)p}\right]^{1/2} \left[\frac{m}{(pr)p}\right]^{1/2} [r] = \left[\frac{m}{p^2}\right] = [E]^{-1}$ ✓

We will need the small-r and large-r forms, namely

$$kr\, j_\ell(kr) \xrightarrow[kr \gg \ell]{} \sin\left(kr - \frac{\ell\pi}{2}\right)$$

$$kr\, n_\ell(kr) \xrightarrow[kr \gg \ell]{} -\cos\left(kr - \frac{\ell\pi}{2}\right)$$

and

$$kr\, j_\ell(kr) \xrightarrow[kr \ll \ell]{} \frac{(kr)^{\ell+1}}{(2\ell+1)!!}$$

$$kr\, n_\ell(kr) \xrightarrow[kr \ll \ell]{} -(kr)^{-\ell}\,(2\ell-1)!!$$

(note: $(-1)!! \equiv 1$)

Now, the most general solution to the radial Sch. Equation at $r > r_0$ can be written as a <u>linear</u> <u>combination</u>, i.e. as:

$$u_{E\ell}(r) = a_\ell f_{E\ell}(r) + b_\ell g_{E\ell}(r), \quad r \geq r_0$$

or replacing a_ℓ, b_ℓ by two equivalent constants $A_\ell = \sqrt{a_\ell^2 + b_\ell^2}$

and $\delta_\ell = \tan^{-1}\left(\frac{-b_\ell}{a_\ell}\right)$, gives

$$u_{E\ell}(r) = A_\ell \left[f_{E\ell}(r)\cos\delta_\ell - g_{E\ell}(r)\sin\delta_\ell\right], \quad r \geq r_0$$

$$\xrightarrow[\substack{r > r_0 \\ kr \gg \ell}]{} A_\ell \left(\frac{2m}{\pi\hbar^2 k}\right)^{1/2} \sin\left(kr - \frac{\ell\pi}{2} + \delta_\ell\right)$$

To determine the crucial energy-dependent scattering phaseshifts $\delta_\ell(E)$ here, we must solve the radial Schrödinger equation in the presence of the full potential $V(r)$ out to any radius $r \geq r_0$, which determines $u_{E\ell}(r)$ and $u'_{E\ell}(r)$ for $0 \leq r \leq r_0$ subject to the B.C. $u_{E\ell}(0) = 0$. Since $u_{E\ell}$ and $u_{E\ell}'$ must be continuous, their ratio must be continuous, namely the "logarithmic derivative",

$$\left.\frac{d}{dr} \ln u_{E\ell}(r)\right|_{r_0} = \frac{u'_{E\ell}(r_0)}{u_{E\ell}(r_0)} = \frac{f'_{E\ell}(r_0)\cos\delta_\ell - g'_{E\ell}(r_0)\sin\delta_\ell}{f_{E\ell}(r_0)\cos\delta_\ell - g_{E\ell}(r_0)\sin\delta_\ell}$$

This is readily solved for $\tan\delta_\ell$:

$$\tan\delta_\ell(E) = \left.\frac{W[f_{E\ell}, u_{E\ell}]}{W[g_{E\ell}, u_{E\ell}]}\right|_{r \geq r_0}$$

where the Wronskian of any 2 solutions is defined as $W(a,b) \equiv a b' - a' b$

Returning to our scattering problem, the general stationary state solution looks like:

$$\Psi_E = r^{-1} \sum_{\ell m} A_{\ell m} Y_{\ell m}(\hat{r}) \left[f_{E\ell}(r) \cos\delta_\ell - g_{E\ell}(r) \sin\delta_\ell \right]$$

at $r \geq r_0$

and its asymptotic form is

$$\Psi_E \xrightarrow[\substack{kr \gg \ell \\ r > r_0}]{} r^{-1} \sum_{\ell m} A_{\ell m} Y_{\ell m}(\hat{r}) \left(\frac{2m}{\pi \hbar^2 k} \right)^{1/2} \sin\left(kr - \frac{\ell\pi}{2} + \delta_\ell\right)$$

Continuing toward our goal of deriving the differential scattering cross section $\frac{d\sigma}{d\Omega}$, we need now a crucial identity, the spherical expansion of a plane wave,

$$e^{i\vec{k}\cdot\vec{r}} = \sum_{\ell m} i^\ell \, 4\pi \, Y^*_{\ell m}(\hat{k}) \, Y_{\ell m}(\hat{r}) \, j_\ell(kr)$$

This can be viewed in Dirac's bra-ket notation as

$$e^{i\vec{k}\cdot\vec{r}} \xrightarrow[kr\to\infty]{} \sum_{lm} i^l 4\pi \langle\hat{r}|lm\rangle\langle lm|\hat{k}\rangle \frac{\sin(kr - \frac{l\pi}{2})}{kr}$$

(where the $kr\to\infty$ form of $j_l(kr)$ has been inserted)

The next step is to impose the scattering B.C.,

$$\Psi \xrightarrow[kr\to\infty]{} e^{i\vec{k}\cdot\vec{r}} + f(\hat{k}',\hat{k})\frac{e^{ikr}}{r}$$

(setting $\hat{k}' = \hat{r}$ at $r\to\infty$)

and the SCATTERING AMPLITUDE here has the structure

$$f(\hat{k}',\hat{k}) \equiv \langle\hat{k}'|f|\hat{k}\rangle$$

Plugging this into the equation on p.4 gives

$$\langle\hat{k}'|f|\hat{k}\rangle\frac{e^{ikr}}{r} = r^{-1}\sum_{lm}\langle\hat{k}'|lm\rangle\Big[A_{lm}\left(\frac{2m}{\pi\hbar^2 k}\right)^{1/2}\sin(kr - \tfrac{l\pi}{2} + \delta_l) - 4\pi i^l \frac{\langle lm|\hat{k}\rangle}{k}\sin(kr - \tfrac{l\pi}{2})\Big]$$

Since the LHS (left-hand side) has only an OUTGOING radial wave, the coefficient of $\frac{e^{-ikr}}{r}$ on the RHS must <u>vanish</u>, whereby

$$A_{lm} = 4\pi i^l e^{i\delta_l}\langle lm|\hat{k}\rangle\left(\frac{2m}{\pi\hbar^2 k}\right)^{-1/2}$$

Plugging this back in now gives the key desired formula for the scattering amplitude,

$$\boxed{\begin{aligned} \langle \hat{k}' | F | \hat{k} \rangle &= \sum_{lm} \langle \hat{k}' | lm \rangle \frac{4\pi}{2ik} \left(e^{2i\delta_l} - 1 \right) \langle lm | \hat{k} \rangle \\ &= \frac{1}{2ik} \sum_{l=0} (2l+1) P_l(\hat{k}\cdot\hat{k}') \left(e^{2i\delta_l} - 1 \right) \end{aligned}}$$

and this is the well-known partial-wave expansion for the scattering amplitude.

Matrices relevant to scattering

It is informative to write the above formulas in terms of a TRANSITION MATRIX, in part because this simplifies our discussion later of more complicated inelastic scattering processes. When there are many possible outcomes, the use of matrix algebra becomes essential.

Hence we can write

$$\langle \hat{k}' | F | \hat{k} \rangle = \frac{4\pi}{k} \sum_{l,m} \langle \hat{k}' | l'm' \rangle \langle l'm' | T | lm \rangle \langle lm | \hat{k} \rangle$$

where T is the "transition operator", which is particularly simple for the present problem, namely diagonal in l, m:

$$\langle l'm'|T|lm\rangle = \delta_{ll'}\delta_{mm'}\frac{e^{2i\delta_l}-1}{2i} \equiv T_{l'm',lm}$$

Or it is sometimes written in terms of the SCATTERING OPERATOR S as

$$\langle l'm'|T|lm\rangle = \langle l'm'|\frac{S-1}{2i}|lm\rangle$$

The scattering matrix $\langle l'm'|S|lm\rangle$ is also diagonal in an angular momentum representation, for elastic scattering by a spherically-symmetric potential, and equal to

$$\delta_{ll'}\delta_{mm'}e^{2i\delta_l} = S_{l'm',lm}$$

which is unitary since δ_l = real here

Some other matrices of interest include

REACTION MATRIX

$$K = -i\frac{S-1}{S+1} \rightarrow \tan\delta_l$$ for a spherically-symm. single-channel problem

or $\langle \hat{k}' | K | \hat{k} \rangle = \sum_{lm} \langle \hat{k}' | lm \rangle \tan\delta_l \langle lm | \hat{k} \rangle$

TIME DELAY MATRIX

$$\underline{Q} = i\hbar\, \underline{S}(E) \frac{d}{dE} S^{+}(E)$$

which simplifies to $Q \to 2\hbar \dfrac{d\delta_l}{dE}$ if $S \to e^{2i\delta_l(E)}$

Phaseshift matrix

Formally, $\underline{\delta} = \tan^{-1}(\underline{K}) = \frac{1}{2i} \ln \underline{S}$

Don't forget that the tangent (or arctangent) of a matrix is not formed by simply taking the tangent of every element!

CROSS SECTIONS

The differential scattering cross section in 3D is the ratio of the scattered flux j_s in $f(\theta,\phi)\dfrac{e^{ikr}}{r}$ to the incident flux j_{inc} in $e^{i\vec{k}_0\cdot\vec{r}}$, with an additional factor of r^2 so that the ratio will approach a constant as $r \to \infty$

i.e.

$$\frac{d\sigma}{d\Omega} = \lim_{r\to\infty} \frac{r^2 \hat{r}\cdot\vec{j}_s}{|j_{inc}|}$$

Here $\vec{j}$ is the usual quantum probability flux, defined as

$$\vec{j} = \frac{\hbar}{2im}\left(\psi^* \nabla\psi - \psi\nabla\psi^*\right)$$

$$= \frac{1}{m} \mathrm{Re}\left(\psi^* \vec{p}\,\psi\right)$$

where $\vec{p} = -i\hbar\nabla$ is the momentum operator

giving $\frac{d\sigma}{d\Omega} = |f(\hat{k}', \hat{k})|^2$

For an incident beam directed along $\hat{z}$, i.e. $\hat{k}\to\hat{z}$, the scattering amplitude f depends only on θ

$$\Rightarrow f(\hat{k}',\hat{k}) \to f(\theta)$$

and $\sigma_{elastic} = \int d\Omega \frac{d\sigma}{d\Omega} = \int \sin\theta\, d\theta \int d\phi\, |f(\theta)|^2$

$$= \int d\hat{k}' \left| \sum_{lm} \langle \hat{k}'|lm\rangle \left(e^{2i\delta_l}-1\right)\langle lm|\hat{k}\rangle \frac{4\pi}{2ik}\right|^2$$

which simplifies upon inserting $\langle\hat{k}'|lm\rangle = Y_{lm}(\hat{k}')$ to

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