electron and atom scattering - basic principles

We will discuss a few of the basic theoretical methods, following Ch. 4 of Friedrich closely, but omitting some topics.

The topic of long-range (or ultracold) collisions will be treated in more detail in about two weeks. For now, we keep things general, but fairly superficial.

I. **Elastic scattering** (short-range potential)

A. Nomenclature, specification of the problem:

Ordinarily we can

i) Reduce to a one-body scattering from a potential, using a reduced mass.

ii) Solve the time-independent Schrödinger equation for scattering a steady flux.

\[ V = \frac{k^2}{2} \]

\[
\text{incoming plane wave} \quad \text{spherical wave (amplitude may vary with } \theta, \phi \text{)}
\]

Look for solutions of asymptotic form,

\[ \psi = e^{ikz} + f(\theta, \phi) \frac{e^{ikr}}{r} \]

"scattering amplitude"

to the Schrödinger equation,

\[ \left( -\frac{k^2}{2\mu} \nabla^2 + V(r) \right) \psi(r) = E \psi(r), \]

in the presence a short-range potential (will do Coulomb later)

\[ \lim_{r \to 0} r^2 V(r) = 0 \]
particle density \( \rho = \frac{|\gamma|^2}{2} \) (\( = 1 \) for incoming wave) \( \tag{4} \)

current density \( \vec{j} = \frac{k}{2i\mu} \left( \gamma \times \vec{\gamma} \times \gamma^* \right) \) \( \tag{5} \)

\( (= \frac{k}{\mu} \frac{\gamma^2}{2} \) for incoming wave) \( \)

For the outgoing spherical wave, \( \vec{j}_{\text{out}} = \frac{k}{\mu} |f(\varphi, \omega)|^2 \frac{\mu^2}{v^2} + O \left( \frac{1}{r^3} \right) \) \( \tag{6} \)

The asymptotic flux through a surface \( r^2 \, d\omega \) will be \( |\vec{j}_{\text{out}}| \, r^2 \, d\omega \). The ratio of this flux scattered into solid angle \( d\omega \) to the incoming current density is the differential scattering cross section,

\[ d\sigma = |f(\varphi, \omega)|^2 \, d\omega \] (or \( \frac{d\sigma}{d\omega} = |f(\varphi, \omega)|^2 \)) \( \tag{7} \)

The total elastic cross section is

\[ \sigma = \int d\sigma = \int |f(\varphi, \omega)|^2 \sin \theta \, d\varphi \, d\omega \] \( \tag{8} \)

The continuity equation (flux conservation) is

\[ \nabla \cdot \vec{j} = 0 \] \( \tag{9} \)

But in the asymptotic solution \( \vec{j}_{\text{in}} \), if we evaluate \( \oint_{\partial S} \vec{j} \cdot d\vec{s} = 0 \) (for the surface of a sphere), the \( \vec{j}_{\text{in}} \) term contributes 0, while the outgoing term contributes,

\[ \vec{j}_{\text{out}} = \int_{\partial S} \vec{j}_{\text{out}} \cdot d\vec{s} = \frac{k}{\mu} \int |f(\varphi, \omega)|^2 \, d\omega \, d\varphi = \frac{k}{\mu} \sigma \] \( \tag{10} \)

This must be cancelled by the interference terms.

It turns out only the interference for \( \theta = 0 \) matters (Problem 4.1 of Friedrich), leading to the optical theorem,

\[ \frac{1}{2i} \left( f(\theta = 0) - f^*(\theta = 0) \right) = \frac{k}{4\pi} \sigma \] \( \tag{11} \)

\( \sigma \) is forward scattering amplitude.
Finally, we can rephrase the problem in integral form using a Green's function.

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

Using \(G(r, r') = -\frac{\hbar}{2\pi\epsilon_0^2} \frac{e^{ik|r-r'|}}{|r-r'|}\)

\(\psi = \lim_{\epsilon \to 0} \frac{1}{E - \frac{\hbar^2 \nabla^2}{2m} + i\epsilon}\)

\(\Rightarrow\) outgoing spherical wave.

The "solution" can now be written as

\[\psi(r) = e^{ikz} + \int G(r, r') V(r') \psi(r') \, dr',\]

the Lippman-Schwinger equation.

If the potential can be treated as a perturbation, we can make the Born approximation

\[\psi(r) \Rightarrow e^{ikz} \text{ in } \text{(i)}\]

The scattering amplitude becomes, using \(\lim_{\epsilon \to 0} G(r, r') = \frac{-\hbar}{2\pi\epsilon_0^2} \frac{e^{ikr} - e^{-ikr}}{r}\)

\[f_{\text{Born}} = \frac{-\hbar}{2\pi\epsilon_0^2} \langle \tilde{\Psi}_f | V | \tilde{\psi} \rangle = \frac{-\hbar}{2\pi\epsilon_0^2} \int e^{-i\tilde{k} \cdot \tilde{r}} V(\tilde{r}) \tilde{\psi}(\tilde{r}) \, d\tilde{r} \]

where \(\tilde{\psi} = k (\tilde{r} - \tilde{z})\)

\(\text{direction of scattering}\)

This vastly simplifies calculations but is often not a good approximation. (It applies at high energies.)
B. Spherically symmetric potentials

Now the problem has cylindrical symmetry, so $\ell \neq 0$ is a good quantum number.

Expand $\psi(r)$ in partial waves,

$$\psi(r) = \sum_{\ell} \phi_{\ell}(r) \sqrt{\frac{2\ell+1}{4\pi}} P_\ell \cos \theta \quad (17)$$

Using $e^{ikr} = \sum \ell \frac{\ell}{\ell} i^\ell j_\ell(kr) P_\ell \cos \theta$

and $f(r) = \sum \ell f_\ell P_\ell \cos \theta$,

the asymptotic wave function for large $r$ becomes

$$\psi(r) \sim \sum_{\ell} \left( (2\ell+1) \frac{i^\ell}{\ell} j_\ell(kr) + f_\ell \frac{e^{ikr}}{r} \right) P_\ell \cos \theta \quad (18)$$

But we also require that as $r \to \infty$, the solutions must approach $\sin(kr - \frac{\pi}{2} + d_\ell)$.

Expanding $j_\ell(kr)$ and matching coefficients, we get

$$\psi(r) = \sum_{\ell} \frac{i^\ell e^{i\phi}}{\ell} \frac{2\ell+1}{kr} \sin(kr - \frac{\pi}{2} + d_\ell) P_\ell \cos \theta$$

and

$$0 = \frac{4\pi}{k^2} \sum (2\ell+1) \sin^2 \phi \quad (19)$$

$\phi$ is the phase shift and $\sqrt{\Delta}$ is the transition amplitude.

If $\psi(r)$ falls off exponentially for large $r$,

the threshold behavior near $kr = 0$ can be determined using $j_\ell(kr) \to (kr)^\ell$, or by phase space arguments:

$$\Delta(\ell) = n\pi - \alpha_\ell K^{2\ell+1} \quad (20)$$

At threshold, $\alpha = 0$ dominates, and we define the scattering length,

$$\lim_{\ell \to 0} \Delta = 4\pi a^2 \quad (a = \alpha_0 = \frac{\Delta}{K}) \quad (21)$$
Fig. 4.2. Phase shifts for elastic scattering of electrons by neon. The crosses show experimental data from [Wil79]. The solid lines were obtained by solving the radial Schrödinger equation with a simple local potential consisting of the electrostatic terms plus a polarization potential (4.41) which merges into a constant for separations smaller than a phenomenological parameter $r_0$. The polarizability was taken to be the experimental value $\alpha_d = 2.66a_0^3$ [TP71] and the value of $r_0$ was 0.974$a_0$ for $l = 0$, 1.033$a_0$ for $l = 1$ and 1.11$a_0$ for $l = 2$. (From [IF92])
Fig. 4.3. Scattering length $a$ for an electron with low kinetic energy in an attractive, spherically symmetric potential of radius $r_0$. Since the value of $a$ is defined as the abscissa of the intercept, the scattering length shown is negative. (Adapted from Fermi [6].)
FIG. 5. The upper panel illustrates the long de Broglie wave at long range, on the scale of 1 μm. The lower panel shows an enlargement of the short range wave function for the case of three different potentials, with three different scattering lengths, negative, zero, and positive.

For potentials that fall off as $\frac{1}{r^n}$ ($n > 2$), (2) can still be used, but (20) becomes more complex. See p. 206 of Friedrich for an expression found using “effective range theory.”

Resonances in elastic scattering are much the same as for photoabsorption (and in fact, MQDT can be used to calculate them, among other methods.) For an isolated resonance, the phase rapidly changes by $\pi$ while the cross section exhibits a Beutler-Fano lineshape. Page 5-9 shows a simple example for electron scattering from He.

C. Coulomb potential

If $V = -\frac{2e^2}{r}$, a substantial modification is needed. We still need the asymptotic form of Eq. (1). A superposition of Coulomb functions that does this is given by Friedrich,

$$\Psi_c = e^{-\frac{m}{2}} \Gamma(1+i\eta) e^{i\frac{kz}{r}} F(-i\nu, 1; ik(r-z))$$

with $\eta = \frac{-1}{ka}$ as on p. C-2, $a$ = Bohr radius.

($\Gamma$ = gamma func., $F$ = confluent hypergeometric func.)

For large $k(r-z)$,

$$\Psi_c \rightarrow e^{ikz + i\frac{\eta}{2} K(r-z)} \left( 1 + \frac{\eta^2}{ik(r-z)} + \cdots \right)$$

incomng plane wave + $f_c(0) \frac{e^{ikr - i\frac{\eta}{2} K(r-z)}}{r} \left( 1 + \frac{(1+i\eta)^2}{ik(r-z)} + \cdots \right)$

outgoing spherical wave

with $f_c(0) \equiv -\frac{\eta}{2k^{1/2}} e^{-i(\xi_0^2 + \eta^2/4)} e^{-i(\xi_0^2 \sin^2 \theta/2) - 2\xi_0}$

$\sigma_0 \equiv \text{arg} [\Gamma(1+i\eta)]$
Fig. 8.1. Resonances in $e$–He elastic scattering. (a) Scattered intensity as a function of incident energy. (From Kuyatt et al. [1].) (b) Original observation of the $(1s2s^2)^2S$ resonance in $e$–He elastic scattering at $72^\circ$. See Fig. 1.5a for later data at different angles. (From Schulz [2].)
The current density becomes
\[ J_{\text{out}} = \frac{e^2}{\hbar} |f_c(\theta)|^2 \frac{r}{r^3} + O(\frac{1}{r^3}) \] (25)

And the differential cross section is
\[ \frac{d\sigma}{d\Omega} = |f_c(\theta)|^2 = \frac{\pi^2}{4k^2 \sin^2 \theta} = \frac{4}{a^2 q^4} \] (26)

with \( q = \kappa (r - \hat{r}) \), \( q = 2k \sin \frac{\theta}{2} \), as in (16)

This is just the standard Rutherford formula.

Because of the strong forward peaking, \( J_{\text{out}} \to \infty \).

By coincidence, the same result is obtained in the Born approximation, and even in a WKB semiclassical analysis.

D. Distorted wave approximation

If the short-range potential is complicated, but the long-range potential is Coulombic, the incoming plane wave must be modified. See Friedrich, pp. 217 ff., for a description. At high energies the Born approximation is valid, leading to the distorted wave Born approximation.

E. Spin and polarization

See Friedrich, pp. 223–231. This works much as for atomic structure and radiative transitions, but is more complex because of the additional degrees of freedom in scattering problems.
II. Inelastic Scattering

A. Definitions and Terminology; Lippman-Schwinger eqn

Here the target undergoes a change in its internal state. (Note that fragmentation is even more complicated; see, for example, Friedrich's account of (e, 2e) reactive scattering.

Inelastic scattering is intrinsically a multichannel process, so (start with a coupled channel approach)

\[
\left(-\frac{\hbar^2}{2\mu} \nabla^2 + V_{ii}\right) \Psi_i(\vec{r}) + \sum_{j \neq i} V_{ij} \Psi_j(\vec{r}) = (E - E_i) \Psi_i(\vec{r})
\]

\(\vec{r}\) = coordinate of projectile (electron for e- - atom scatt.),

\((i, j)\) label open channels, with \(\Psi^{(i)}\) specifying the internal target atom state.

If the reactions are short-ranged, then asymptotically

\[
\Psi_j(\vec{r}) \sim \frac{\gamma_j}{r} e^{ik_j r} + \frac{e^{ik_j}}{r} f_{ji}(0,0)
\]

with \(k_j = \sqrt{\frac{2\mu(E - E_j)}{\hbar^2}}\)

As before, the differential elastic cross section is

\[
\frac{d\sigma_{ii}}{d\Omega} = \left|f_{ii}(\theta, \phi)\right|^2
\]

But for the inelastic scattering,

\[
\frac{d\sigma_{ij}}{d\Omega} = \frac{k_j}{K_i} \left|f_{ji}(\theta, \phi)\right|^2
\]

can get from (1) Golden rule or (2) \(V_{ii} = \frac{\hbar k_i}{\mu}\)

\[
\left\{ \begin{aligned}
\Delta m &= \frac{\hbar k_j}{\mu} \left|f_{ji}\right|^2 \frac{r}{\hbar^2} + \ldots \\
\end{aligned} \right.
\]
The integrated cross sections are then,

$$\sigma_{i \rightarrow j} = \frac{k_i}{k_i} \int |f_{ji}|^2 \, d\Omega$$  \hspace{1cm} (51)$$

and the total cross section is

$$\sigma = \sigma_{ii} + \sum_{j \neq i} \sigma_{ij} + \sigma_{\text{abs}}$$  \hspace{1cm} (52)$$

As for elastic scattering, an integral form is again possible. Write

$$\left( -\frac{\hbar^2}{2\mu} \nabla^2 + \frac{E - E_i}{\hbar} \right) \psi = \hat{V} \psi$$  \hspace{1cm} (53)$$

matrix with 

$E-E_i$ on diagonals

matrix of $V_{ij}$'s,

$$V_{ij} = \langle \psi_j^{(i)} | H_{\text{interaction}} | \psi_i^{(j)} \rangle$$

internal state $i$ of target

The matrix of free-particle Green's functions,

$$G = \begin{pmatrix}
G_{11} & 0 & \cdots \\
0 & G_{22} & \cdots \\
\vdots & \vdots & \ddots
\end{pmatrix}$$

$$G_{ii} = \frac{\epsilon^{ik_i \cdot (r-r_i)}}{2\pi \hbar}$$  \hspace{1cm} (54)$$

plays the role of (12) on p. 5-3, leading to

$$\psi = \psi_{\text{homogeneous}} + \hat{G} \hat{V} \psi$$

If $\psi_{\text{homogeneous}}$ has components $\psi_i = e^{ik_i \cdot z}$ and $\psi_j = 0$, $j \neq i$ (incoming plane wave in channel $i$),

Then $\psi_j(r) = c_{ij} e^{ik_i \cdot z} + \sum_n G_{nj}(r-r_n) \sum \psi_n(r_n) e^{ik_n \cdot z}$

(a multi-channel Lippman-Schwinger equation),

and $f_{ji}(\theta, \varphi) = -\frac{\hbar}{2\pi \epsilon^2} \sum_n \int e^{-ik_i r \cdot} V_{jn} \psi_n(r) \, d^2r$,
As before, take \( \psi_n \rightarrow \sum \epsilon_{ki} e^{i k_i z'} \) for the
Born Approximation,

\[
f^{\text{Born}}_{ji} = -\frac{\mu}{2\pi \hbar^2} \int e^{-ik_j z'} V_{ji} e^{ik_i z'} \, d^3 r' = -\frac{\mu}{2\pi \hbar^2} \left< \psi_{n0j} \mid V \mid \psi_{nim} \right> \tag{27}
\]

This can be simplified further for e\(^{-}\) - atom
or e\(^{-}\) - ion scattering; see Friedrich.

B. Partial wave expansion:

Choose the internal states \( \psi_{nim} \) of the target
to be eigenstates of \( \hat{J}_z \), with
quantum number \( J_z, M_z \). (we can no
longer take \( m, M_i = 0 \) in general)

Expand \( \psi_i (\vec{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{\phi_{ilm}}{r} Y_{lm}(\theta, \phi) \) \tag{38}

The potentials will not conserve orbital
angular momentum, so write

\[
V_{ij} Y_{l_1 m_1} = \sum_{lm} Y_{lm} V_{ij}^{rad} (l_1 m_1, l_2 m_2)
\]

"radial potentials"

Insertion into (27) gives the coupled radial equations

\[
\left( \frac{-\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\lambda (\ell_i r)}{2mr^2} \right) \phi_{ilm} (r) + \sum_{lj, l_1 m_1} V_{ij}^{rad} (l_1 m_1, l_2 m_2) \phi_{lj, l_1 m_1} (r) = (E_i - E_j) \phi_{ilm} (r) \tag{39}
\]

These equations come in blocks for each value of
the (conserved) total angular momentum. Each
such block of \( N \) equations has \( N \) linearly
independent vectors \( \Phi \) of channel wave functions \( \Phi_{ilm} \)
that solve the equations.
Asymptotically, for short-range potentials the radial wave functions must be superpositions of

\[ \Phi_{i,k}^s = \sqrt{\frac{2M}{\pi \hbar^2 k_i}} \sin\left( k_i r - \frac{\pi}{2} \right) \]

and \[ \Phi_{i,k}^c = \sqrt{\frac{2M}{\pi \hbar^2 k_i}} \cos\left( k_i r - \frac{\pi}{2} \right) \]

One very common basis of vectors \( \Phi^{(i\ell m)} \) of solutions is defined by

\[ \lim_{r \to 0} \Phi_{j \ell m} = \delta_{ij} \delta_{k' k} \delta_{m m'} \Phi_{i,k}^s \]

\[ + R_{i \ell m j \ell m'} \Phi_{j,k'}^c \]

Reactance matrix or \( K \) matrix

If spherical waves are used in place of (40), we instead get the \( S \)-matrix related to \( K \) by

\[ S = \frac{1 + i \frac{\partial}{\partial E}}{1 - i \frac{\partial}{\partial E}} \]

Hermitean if \( V \) is unitary.

For a given energy \( E \), \( S \) can be diagonalized. The corresponding linear combinations of channels are eigenchannels, the eigenvalues \( \rho \) of \( S \) are real, \( \rho = \tan \rho \), where \( \rho \) is the coefficient in front of \( \Phi_{i,k}^c \) for each of the functions (40) in the solution (all have same coefficient) asymptotic.
At a scattering resonance, \( P(E) \) will increase suddenly by \( \pi \) as a function of energy, as in previous cases.

Finally, \( R \) or \( S \) matrix can be connected to the scattering amplitude using the asymptotic form (28).

After some manipulation,

\[
\begin{align*}
\pi \sqrt{k_1 k_2} f_{ij}(\theta, \phi) &= \sum_{\ell m} \psi_{\ell m}(\theta, \phi) \sum_{\ell' m'} \frac{i \ell' e^{i \ell' \theta}}{\ell'! (2\ell'!)} \times \\
&\left( \delta_{\ell 0} \delta_{m 0} - \frac{\ell'}{2} \delta_{\ell' 0} \delta_{m 0} \right)
\end{align*}
\]

Modification for Coulomb scattering:

Replace (28) with distorted waves. Now \( R \) represents the influence of short-range deviations from a pure Coulomb potential.

\[ \Lambda \]

Scattering quantum defect theory \( \Lambda \)

\( R \)-matrix MQDT, as introduced without proof before.

Actual calculations may focus either on \( R \)-matrix or on close-coupling methods where equations like (27) are solved directly (computationally) using a large basis set.
C. Threshold laws for inelastic scattering.

For Coulomb scattering, we converge back on MADT for Rydberg-continuum coupling.

For short-range potentials, examine (30),

$$\frac{d\sigma}{d\Omega} = \frac{k_f}{k_i} \left| f_{ij}(\theta, \phi) \right|^2$$

At a channel threshold $E = E_j$, generally $f_{ij}$ will be finite and slowly varying, given by (30). If $l$ is the lowest partial wave in the exit channel, and we expand $e^{-ik_{j'}r}$ in Bessel functions, using $j_l(k_{j'}r) \rightarrow k_{j'}^l j_l$, then we have the Wigner law for inelastic cross sections,

$$\sigma_{ij}(E) \propto \left( \sqrt{E - E_j} \right)^{2l+1}$$

(Short-range potential, threshold energy $E_j$)

The opening of channel $j$ will in general also affect the other cross sections;
see Friedrich for a description of the cusp often seen in the total elastic scattering.

What if $E_i$ in entrance channel is $> E_j$? This is superelastic scattering (or an exothermic reaction), and the cross sections diverge at threshold.

For examples of $e^- + H$ scattering (from Friedrich, see following page).
Fig. 4.10. Integrated cross sections for inelastic electron scattering by hydrogen just above the inelastic threshold (10.20 eV). The upper curve shows the $1s \rightarrow 2p$ excitation, the lower curve shows the $1s \rightarrow 2s$ excitation. The dots are the experimental data of Williams and the solid lines are the theoretical results from [Cal82], which have been smoothed a little in order to simulate finite experimental resolution. (From [Wil88])

Fig. 4.11. Integrated cross sections for inelastic electron scattering by hydrogen just below the threshold for $n = 3$ excitations of the hydrogen atom (12.09 eV). The upper curve shows the $1s \rightarrow 2p$ excitation, the lower curve shows the $1s \rightarrow 2s$ excitation. The dots are the experimental data of Williams and the solid lines are the theoretical results from [Cal82], which have been smoothed a little in order to simulate finite experimental resolution. The vertical lines above the abscissa show the positions of a number of Feshbach resonances. (From [Wil88])