
Collisions

Atoms and molecules are excited and deexcited by collisions with particles. In ionized or moderately ionized environments, the colliding particles are most commonly electrons, since electrons are the lightest and therefore fastest moving particles around. Collisions with protons and other ions can be important for some processes, such as $2s - 2p$ in H, or in some energetic environments. In molecular environments, collisions with a variety of abundant species may be important. In what follows, the colliding particle will be taken for simplicity and definiteness to be an electron, although much of what is said generalizes immediately to other colliders.

If the colliding particles are nonrelativistic, their velocity distribution is almost invariably Maxwellian, since cross-sections for momentum-changing elastic collisions — for charged particles, these are Coulomb collisions — between like particles (or particles of similar mass) are generally much larger than cross-sections for inelastic collisions. Elastic collisions are those in which the atom or molecule remains in the same atomic eigenstate (although its momentum is changed), while inelastic collisions are those in which the atom or molecule changes its eigenstate.

1. Detailed Balance between Excitation and Deexcitation

Consider the mutually inverse processes of collisional excitation and deexcitation between lower ($L$) and upper ($U$) states of an atom X by colliding electrons

$$e + X_L \leftrightarrow e + X_U . \quad (1.1)$$

For simplicity, assume that the colliding electrons are nondegenerate and nonrelativistic. The generalizations to the cases of partially degenerate and partially relativistic electrons are the subjects of Questions 1.1 and 1.2 at the end of this section. The collisional excitation and deexcitation rate coefficients $C_\uparrow$ and $C_\downarrow$, with units volume/time, are defined so that

$$\frac{\text{number of excitations}}{\text{time} \cdot \text{volume}} = n_en_LC_\uparrow \quad (1.2)$$

$$\frac{\text{number of deexcitations}}{\text{time} \cdot \text{volume}} = n_en_UC_\downarrow \quad (1.3)$$

where $n_e$ is the number density of electrons, and $n_L$ and $n_U$ are the number densities of atoms in the lower and upper levels.

The principle of detailed balance, or microscopic reversibility, is a statement of time-reversal invariance, or $T$ symmetry. It asserts that the rate at which a system in a state $A$ transforms into another state $B$ is equal to the inverse rate at which the time-reversed state $B^*$ transforms into the time-reversed state $A^*$

$$\text{rate}(A \rightarrow B) = \text{rate}(A^* \rightarrow B^*) . \quad (1.4)$$
The time-reversed states differ from the originals by a change of sign of all momentum and spin components\(^1\). An equivalent statement is that when a system is in thermodynamic equilibrium, all processes are individually precisely balanced by their inverses.

Consider then collisions between electrons and atoms in mutual thermodynamic equilibrium at temperature \(T\). In thermodynamic equilibrium, the number of excitations balances the number of deexcitations, so that

\[
n_e n_L C_u(T) = n_e n_U C_l(T) .
\]

But in thermodynamic equilibrium the ratio of number densities in the upper and lower states is

\[
\frac{n_U}{n_L} = \frac{g_U}{g_L} e^{-\Delta E / kT} \tag{1.6}
\]

where \(g_U\) and \(g_L\) are the degeneracies of the upper and lower levels, and \(\Delta E = E_U - E_L\) is their energy difference. It follows from equations (1.5) and (1.6) that the ratio of excitation to deexcitation rate coefficients by collisions with a population in thermodynamic equilibrium at temperature \(T\) is

\[
\frac{C_u(T)}{C_l(T)} = \frac{g_U}{g_L} e^{-\Delta E / kT} \tag{1.7}
\]

Equation (1.7) is the detailed balance relation between the collisional excitation and deexcitation rate coefficients in the case where the colliding particles are nondegenerate and nonrelativistic, i.e. they have a Maxwellian distribution of collision velocities. The relation (1.7) is independent of the actual number densities of atoms in the upper and lower levels, or of the number density of electrons.

Detailed balance requires that the balance between excitation and deexcitation hold not just averaged over thermal populations, as in equation (1.5), but in detail. In thermodynamic equilibrium, the distribution of electron and atomic velocities is a joint Maxwellian

\[
\frac{d n_e d n_X}{dV} = n_e n_X \frac{2}{\pi} \left( \frac{m_e}{kT} \right)^{3/2} \left( \frac{m_X}{kT} \right)^{3/2} e^{-m_e v_e^2 / 2kT} v_e^2 e^{-m_X v_X^2 / 2kT} v_X^2 dV \tag{1.8}
\]

\[
= n_e n_X \frac{2}{\pi} \left( \frac{m}{kT} \right)^{3/2} \left( \frac{M}{kT} \right)^{3/2} e^{-mv^2 / 2kT} v^2 dV e^{-MV^2 / 2kT} V^2 dV \tag{1.9}
\]

\(^1\)It is of interest here to note that while \(T\) symmetry is found experimentally to be respected by the electromagnetic and strong interactions, there is a small violation of \(T\) symmetry in the quark sector of the weak interactions, manifested in the decay of \(K\) and \(B\) mesons. The \(T\) violation occurs in the mass matrix which couples the three different quark flavors, and is associated with the interaction of the quarks with the Higgs field which breaks the electroweak symmetry, and which gives the quark flavors their different masses. Although \(T\) symmetry is thus sometimes violated, a theorem of relativistic quantum field theory asserts that the combination \(CPT\) is always a good symmetry. The operation \(C\) represents charge conjugation, the change of sign of all charges, while \(P\) represents parity reversal, the change of sign of all spatial coordinates. The \(CP\)-conjugate of a particle \(A\) is its anti-particle, denoted \(\bar{A}\). Thus \(CPT\) symmetry asserts that the rate at which a state \(A\) transforms into another state \(B\) is equal to the inverse rate at which the time-reversed state of the antiparticle, \(\bar{B}^*\), transforms into the time-reversed state of the antiparticle, \(\bar{A}^*\),

\[
rate(A \rightarrow B) = rate(\bar{A}^* \rightarrow \bar{B}^*) .
\]
where \( m \equiv m_e m_X/(m_e + m_X) \) and \( M \equiv m_e + m_X \) are the reduced and total masses of the colliding pair, \( \mathbf{v} \equiv \mathbf{v}_e - \mathbf{v}_X \) is the collision velocity, and \( \mathbf{V} \equiv (m_e \mathbf{v}_e + m_X \mathbf{v}_X)/(m_e + m_X) \) is the velocity of the center of mass. The (de)excitation rate coefficients can depend only on the collision velocity \( \mathbf{v} \), not on the velocity \( \mathbf{V} \) of the center of mass. Thus in thermodynamic equilibrium, the rate of excitation of \( X_L \) by electrons which enter at collision velocity \( \mathbf{v}_\uparrow \) relative to the atom and exit at velocity \( \mathbf{v}_\downarrow \), must precisely balance the rate of deexcitation of \( X_U \) by electrons which enter at velocity \( -\mathbf{v}_\uparrow \) and exit at velocity \( -\mathbf{v}_\downarrow \). If the electron and atom have no preferred direction in space, or if one is interested only in the (de)excitation rates averaged over orientations of the electron and atom, then the (de)excitation rate will depend only on the magnitudes \( v_\uparrow \) and \( v_\downarrow \) of the collision velocities. In general however an orientation may be set by the spin of the incident electron, or by the total angular momentum of the atom, or by an externally applied field, and in this case the direction of the collision velocity may be relevant. Energy conservation requires that the collision excitation and deexcitation energies \( E_\uparrow \equiv m v_\uparrow^2/2 \) and \( E_\downarrow \equiv m v_\downarrow^2/2 \) differ by the excitation energy \( \Delta E = E_U - E_L \)

\[
E_\uparrow = E_\downarrow + \Delta E .
\]  

(1.10)

Thus detailed balance requires

\[
\frac{d n_e d n_L}{dE} C_\uparrow(\mathbf{v}_\uparrow) = \frac{d n_e d n_U}{dE} C_\downarrow(\mathbf{v}_\downarrow) .
\]  

(1.11)

Correctly, the energy \( E \) is the collision energy in the center of mass frame of the colliding electron and atom. For nonrelativistic particles, \( E = m v^2/2 \) where \( m \equiv m_e m_X/(m_e + m_X) \) is the reduced mass and \( v \) is the relative velocity of the colliding particles. Usually the electron mass is much less than the atomic mass, \( m_e m_X \), so the reduced mass \( m \) and collision velocity \( v \) are nearly equal to the electron mass and velocity, \( m \approx m_e \) and \( v \approx v_e \). In any case, the distribution of collision energies is a Maxwellian

\[
d n_e = n_e \left( \frac{2}{\pi} \right)^{1/2} \left( \frac{m}{kT} \right)^{3/2} e^{-mv^2/2kT} dv .
\]  

(1.12)

It follows from equation (1.12) that ratio of number of collisions at energy \( E + \Delta E \) to those at energy \( E \) is

\[
\frac{d n_e(E + \Delta E)/dE}{d n_e(E)/dE} = \frac{v_\uparrow}{v_\downarrow} e^{-\Delta E/kT} .
\]  

(1.13)

where \( v_\uparrow \) and \( v_\downarrow \) are the excitation and deexcitation collision velocities, corresponding to collision energies \( E + \Delta E \) and \( E \)

\[
v_\uparrow \equiv \left( \frac{2(E + \Delta E)}{m} \right)^{1/2}, \quad v_\downarrow \equiv \left( \frac{2E}{m} \right)^{1/2} .
\]  

(1.14)

It follows from the balance equation (1.11), together with (1.6) and (1.13), that the ratio of excitation to deexcitation rate coefficients is

\[
\frac{C_\uparrow(E + \Delta E)}{C_\downarrow(E)} = \frac{v_\downarrow g_U}{v_\uparrow g_L} .
\]  

(1.15)
Again, equation (1.15) is a relation between the excitation and deexcitation rate coefficients, and is true independent of the actual number densities of atoms in the lower and upper levels, and irrespective of whether or not the colliding particles are in thermodynamic equilibrium.

**Question 1.1:** In the more general case where the colliding electrons are partially degenerate, argue that the rates for (de)excitation of particles X by electrons with initial and final velocities \( v_i \) and \( v_f \) should be modified to

\[
\frac{\text{number of excitations}}{\text{time} \cdot \text{volume}} = n_e(v_i) [1 - N_e(v_f)] n_X C(v_i)
\]

where \( N_e(v) \) is the occupation number of electrons at velocity \( v \). Show that in thermodynamic equilibrium, detailed balance implies the same relation (1.7) between collisional excitation and deexcitation rates as before.

**Question 1.2:** Show that if the electrons are partially relativistic, then equation (1.15) is modified to

\[
\frac{C_i(v_i)}{C_i(v_f)} = \frac{v_i \gamma_i^2 g_U}{v_f \gamma_f^2 g_L}
\]

where \( \gamma = (1 - v^2/c^2)^{-1/2} \) is the relativistic gamma factor.

2. Collision Strength

The rate coefficient \( C(v) \) for excitation or deexcitation is the product of the collision velocity \( v \) with an appropriate collisional cross-section \( \sigma \)

\[
C = v \sigma.
\]

Collisional rate coefficients are frequently quoted in terms of the dimensionless **collision strength** \( \Omega \) defined by

\[
\sigma_i(v_f) = \pi \left( \frac{\hbar}{mv_f} \right)^2 \frac{\Omega_i(v_f)}{g_U}, \quad \sigma_i(v) = \pi \left( \frac{\hbar}{mv} \right)^2 \frac{\Omega_i(v)}{g_L}
\]

which is so defined that \( \Omega \) is essentially the same quantity for both excitations and deexcitations, in view of the detailed balance relation (1.15),

\[
\Omega_i(v_f) = \Omega_i(v_f).
\]

The quantity \( \hbar/mv = \lambda/2\pi \) in the definition (2.2) can be recognized as the de Broglie wavelength \( \lambda \) of the collision momentum divided by \( 2\pi \).

For collisions with a population in thermodynamic equilibrium at temperature \( T \), the collision strength \( \Omega(T) \) is defined analogously by

\[
C_i(T) = \langle v_i \sigma(v_i) \rangle = \pi \left( \frac{\hbar}{m} \right)^2 \frac{\langle v_i^{-1} \rangle \Omega_i(T)}{g_L} = \frac{\hbar^2 (2\pi)^{1/2}}{m^{3/2} (kT)^{1/2}} \frac{\Omega_i(T)}{g_L}
\]

where the mean inverse collision velocity \( \langle v^{-1} \rangle = (2m/\pi kT)^{1/2} \) is an average over a Maxwellian distribution.
3. Born Approximation

Calculation of collision cross-sections is in general complicated. However, if the path of the colliding electron is only mildly perturbed by the collision, then the collision process can be treated by perturbation theory. The result is the Born approximation to collision cross-sections. The Born approximation applies to both elastic and inelastic collisions. The condition for the Born approximation to hold is that the collision velocity \( v_i \) change by a small amount

\[
\Delta v \equiv |v_f - v_i| \ll v_i .
\]  

(3.1)

In the standard Born approximation, the initial and final wavefunctions \( \chi_i \) and \( \chi_f \) of the colliding particle are taken to be those of free particles.

In first order perturbation theory, the rate, the number of transitions per unit time, at which an atom in eigenstate \( \phi_i \) transforms into eigenstate \( \phi_f \) as the result of collisions with electrons which start in eigenstate \( \chi_i \) and finish in eigenstate \( \chi_f \) is given by Fermi’s Golden Rule (see the notes on Perturbation Theory):

\[
\nu \sigma = \frac{2\pi}{\hbar} \frac{dn(E_f)}{dE} |\langle \phi_f \chi_f | V_{\text{int}} | \phi_i \chi_i \rangle|^2 .
\]  

(3.2)

The interaction potential energy \( V_{\text{int}} \) here is the electrostatic Coulomb energy between the colliding electron and the nucleus and electrons of the atom. For an atom with nuclear charge \( Z \), the interaction energy is

\[
V_{\text{int}} = \frac{-Ze^2}{|r - r_Z|} + \sum_{\text{atomic electrons} a} \frac{e^2}{|r - r_a|} .
\]  

(3.3)

where \( r, r_Z, \) and \( r_a \) are the positions respectively of the colliding electron, the nucleus, and the atomic electrons. In the Born approximation, the eigenstates \( \chi \) of the initial and final states of the colliding electron are taken to be free wavefunctions

\[
\chi = e^{ik \cdot r}
\]  

(3.4)

with momentum \( p = \hbar k \) and energy \( E = p^2/2m \). The normalization of the free wavefunctions (3.4) is such that the number density \( n \) of particles is unity

\[
n = V^{-1} \int_V |\chi|^2 d^3 r = 1
\]  

(3.5)

the integration being taken over some (large) volume \( V \). Note that the total number of colliding particles tends to infinity as the volume \( V \to \infty \). In other words there is an infinite train of particles incident on the atom, with a constant finite flux of \( n v = v \) (since \( n = 1 \)) colliders per unit area per unit time. The normalization of the free wavefunctions (3.4) with respect to momenta is, in the limit of infinite volume,

\[
\int \chi^{* \prime} \chi d^3 r = \int e^{-ik' \cdot r} e^{ik \cdot r} d^3 r = (2\pi)^3 \delta(k' - k) .
\]  

(3.6)
which means that there is one particle per interval \(d^3 k/(2\pi)^3\) of momentum, so the number of states in an interval of momenta is

\[
dn = \frac{d^3 k}{(2\pi)^3} = \frac{d^3 p}{h^3} = \frac{m^2 v}{h^3} dE \, do
\]

(3.7)

Fermi’s Golden Rule (3.2) with \(n = 1\) on the left hand side from equation (3.5), and number of states \(dn/dE = m^2 v_f/do/h^3\) on the right hand side from equation (3.7), thus implies that the differential cross-section \(d\sigma\) for scattering electrons into an interval \(do\) of solid angle is, in the Born approximation,

\[
d\sigma = \frac{m^2}{(2\pi)^2 h^4 v_i} \left| \langle \phi_f \chi_f \left| \frac{-Ze^2}{|r - r_Z|} + \sum_{\text{atomic electrons } a} \frac{e^2}{|r - r_a|} \phi_i \chi_i \right| \right|^2 \cdot \frac{1}{v_f}
\]

(3.8)

The part of the matrix element in (3.8) involving the free wavefunctions \(\chi\) can be done analytically:

\[
\int \frac{1}{|r - r_a|} \chi_i \, d^3 r = \int \frac{1}{|r - r_a|} e^{ik \cdot r} \, d^3 r = \int \frac{e^{-iq \cdot r}}{|r - r_a|} \, d^3 r = \frac{4\pi}{q^2} e^{-iq \cdot r}
\]

(3.9)

where \(q\) is the momentum transfer \(q\) defined by

\[
q = k_f - k_i \cdot \frac{1}{v_f}
\]

(3.10)

Equation (3.10) implies that \(q^2 = k_f^2 + k_i^2 - 2k_f k_i \cos \theta\), so that the interval of solid angle \(do\) can be expressed in terms of an interval \(dq\) of momentum transfer

\[
do = 2\pi \sin \theta \, dq = \frac{2\pi q \, dq}{k_f k_i} = \frac{2\pi h^2 q \, dq}{m^2 v_f v_i}.
\]

(3.11)

Thus the differential cross-section (3.8) may be rewritten

\[
d\sigma = 8\pi \left( \frac{e^2}{h v_i} \right)^2 \frac{dq}{q^2} \left| \phi_f \right|^2 \left( -Z + \sum_{\text{atomic electrons } a} e^{-iq \cdot r_a} \phi_i \right|^2
\]

(3.12)

where the nucleus has been taken to lie at the center of mass, the origin, \(r_Z = 0\). The total collision cross-section is an integral over the differential cross-section (3.12)

\[
\sigma = 8\pi \left( \frac{e^2}{h v_i} \right)^2 \int_{q_{\text{max}}}^{q_{\text{min}}} \frac{dq}{q^2} \left| \phi_f \right|^2 \left( -Z + \sum_{\text{atomic electrons } a} e^{-iq \cdot r_a} \phi_i \right|^2
\]

(3.13)
where \( q_- \) and \( q_+ \) are the minimum and maximum momentum transfers

\[
q_{\pm} = |k_f \pm k_i| = \frac{m}{\hbar} |v_f \pm v_i| = \left( \frac{2m}{\hbar} \right)^{1/2} \left| E_f^{1/2} \pm E_i^{1/2} \right|
\]  

(3.14)

The Born approximation is valid for small momentum transfer \( q \), equation (3.1). Taylor expanding the exponentials \( e^{-i q \cdot r_a} \) in the matrix elements of the Born cross-sections (3.12) and (3.13) gives

\[
\langle \phi_f | e^{-i q \cdot r_a} | \phi_i \rangle = \langle \phi_f | 1 - i q \cdot r_a + \ldots | \phi_i \rangle = \langle \phi_f | \phi_i \rangle - i q \langle \phi_f | r_a | \phi_i \rangle + \ldots
\]  

(3.15)

The condition for the leading order terms of the Taylor expansion (3.15) to dominate is that \( q \ll (r_a)^{-1} \), or equivalently

\[
\Delta v \equiv |v_f - v_i| \ll v_{atom}
\]  

(3.16)

where \( v_{atom} \sim Zc/137 \) is the characteristic velocity of electrons in the atom.

The condition (3.16) is not necessarily the same as the condition \( \Delta v \ll v_i \), equation (3.1), for the validity of the Born approximation. In particular, if the collision velocity is much larger than the characteristic velocity of atomic electrons, \( v_i \gg v_{atom} \), then the Born approximation cross-section (3.12) remains valid for collisions of moderate momentum transfer, \( v_{atom} \lesssim \Delta v \ll v_i \), but the exponentials \( e^{-i q \cdot r_a} \) in the matrix element are not dominated by the leading terms of the Taylor expansion (3.15).

Collision with momentum transfer exceeding the typical momentum of atomic electrons, \( \Delta v \gtrsim v_{atom} \), are usually associated with close collisions of the colliding electron either with the nucleus or with one of the atomic electrons. In the latter case, the atomic electron may well be knocked out of the atom, i.e. the atom is ionized. Close collisions between fast electrons and one of the atomic electrons are called knock-on collisions, and their cross-section approximates that of Coulomb collisions between free electrons.

4. ELASTIC SCATTERING

For elastic collisions, the initial and final atomic wavefunctions are the same, \( \phi_i = \phi_f \). Here the \( Z \) (nuclear) term in the matrix element in the cross-section (3.12) simplifies to \( \langle \phi_i | Z | \phi_i \rangle = -Z \). Thus the Born approximation to the differential cross-section (3.12) for elastic scattering may be written

\[
d\sigma_{\text{elastic}} = 8\pi \left( \frac{e^2}{\hbar \nu i} \right)^2 \frac{d\sigma}{dq} \left| Z - F(q) \right|^2
\]  

(4.1)

where \( F(q) \) is the atomic form factor

\[
F(q) \equiv \left\langle \phi_i \left| \sum_{\text{atomic electrons} \ a} e^{-i q \cdot r_a} \right| \phi_i \right\rangle
\]  

(4.2)

which is independent of the direction \( \hat{q} \) of the momentum transfer if the atom is randomly oriented.
For small momentum transfer $q$, the exponentials in the matrix element (4.2) are dominated by the leading term in their Taylor expansion, $\langle \phi|e^{-iq\cdot r}\rangle \phi_i \approx \langle \phi|\phi_i \rangle = 1$, so that the form factor approximates the number of electrons in the atom

$$F(q) \rightarrow N_{\text{elec}} \quad (\Delta v \ll v_{\text{atom}}).$$

Thus for small momentum transfer the differential cross-section (4.1) for elastic scattering approximates

$$d\sigma_{\text{elastic}} \rightarrow 8\pi \left( \frac{Z_{\infty} e^2}{\hbar v_i} \right)^2 \frac{dq}{q^3} \quad (\Delta v \ll v_{\text{atom}})$$

where $Z_{\infty} \equiv Z - N_{\text{elec}}$ is the net charge of the atom as seen at infinity. The cross-section (4.4) coincides exactly\(^2\) with the classical Coulomb collision cross-section for an electron scattering off a charge $Z_{\infty}e$.

In the opposite limit of large momentum transfer $q$, the exponentials in (4.2) are rapidly oscillating and the form factor tends to zero

$$F(q) \rightarrow 0 \quad (v_{\text{atom}} \ll \Delta v \ll v_i).$$

Here the cross-section goes over to that of Coulomb scattering of an electron off a charge $Ze$:

$$d\sigma_{\text{elastic}} \rightarrow 8\pi \left( \frac{Ze^2}{\hbar v_i} \right)^2 \frac{dq}{q^3} \quad (\Delta v \gg v_{\text{atom}}).$$

Physically, elastic collisions with small momentum transfer correspond to distant collisions in which the colliding electron feels only the net charge $Z_{\infty}$ at infinity, while elastic collisions with large momentum transfer correspond to close collisions with the nucleus of the atom.

Evidently the form factor $F(q)$ is a measure of the distribution of charge inside the atom. The form factor can be measured experimentally, providing a probe of the charge distribution.

5. **INELASTIC COLLISIONS**

For inelastic collisions, the initial and final atomic wavefunctions are different. Among other things, this means that the $Z$ (nuclear) term in the Born approximation cross-section (3.12) vanishes, $\langle \phi_f | Z | \phi_i \rangle = 0$, because of the orthogonality of the atomic wavefunctions, $\langle \phi_f | \phi_i \rangle = 0$. For inelastic collisions, one often sees the Born collisional cross-section (3.13) written in the form

$$\sigma_{\text{inelastic}} = \frac{2\pi e^4}{E_i \Delta E} \int_{q_-}^{q_+} f(q) \frac{dq}{q}$$

\(^2\)It is remarkable that the classical, Born approximation, and exact nonrelativistic cross-sections for Coulomb scattering are all the same.
where $E_i = \frac{1}{2}m_v v_i^2$ is the collision energy, and $f(q)$ is the dimensionless generalized oscillator strength (not to be confused with the form factor [4.2]) defined by

$$f(q) \equiv \sum_i \frac{2m_e \Delta E}{\hbar^2 q^2} \left| \frac{\langle \phi_f | \hat{r}_z | \phi_i \rangle}{\sum_{\text{atomic electrons } a} e^{-i q \cdot r_a}} \right|^2$$

(5.2)

which is averaged over initial states $i$ and summed over final states $f$.

The generalized oscillator strength is so-called because, in the limit of small momentum transfers $q$, it goes over to the usual absorption oscillator strength $f$ for radiative dipole transitions

$$f(q) \to f \equiv \sum_i \frac{2m_e \Delta E}{\hbar^2} \left| \langle \phi_f | \hat{r}_z | \phi_i \rangle \right|^2 \quad (\Delta v \ll v_{\text{atom}})$$

(5.3)

again averaged over initial states $i$ and summed over final states $f$. For dipole forbidden transitions, the oscillator strength between the initial and final atomic states is zero, $f = 0$, and it is necessary to go to the next order in the expansion of the matrix element in (5.2) to get a finite result.

The collision cross-section in the limit of collision energies much greater than the transition energy, $E_i \gg \Delta E$, is called the Bethe-Born approximation. For $E_i \gg \Delta E$, the minimum and maximum momentum transfers $q_-$ and $q_+$, equation (3.14), are

$$q_- \approx \frac{\Delta E}{\hbar v_i}, \quad q_+ \approx \frac{2m_e v_i}{\hbar}.$$  

(5.4)

With $r_0 \sim \hbar/(m_e v_{\text{atom}}) \sim \hbar/(m_e \Delta E)^{1/2}$, one has $q_- r_0 \sim (\Delta E/E_i)^{1/2} \ll 1$, so the minimum momentum transfer $q_-$ is small enough that equation (5.3) is satisfied.

If the small momentum transfer limit (5.3) were taken as valid over the full range of momentum transfers $q_-$ to $q_+$ (which is not true), then the integrated cross-section (5.1) would be

$$\sigma = \frac{2\pi e^4}{E_i \Delta E} \int \ln \left( \frac{q_+}{q_-} \right) = \frac{\pi e^4}{E_i \Delta E} \int \ln \left( \frac{4E_i}{\Delta E} \right)$$

(5.5)

where the last equality follows because equation (5.4) implies that $q_+/q_- = 4E_i/\Delta E$ for $E_i \gg \Delta E$. Now in reality equation (5.3) breaks down for larger momentum transfers. Conventionally, the difference between the true integral (5.1) and the approximation (5.5) is allowed for by introducing an extra factor of $C$ into the argument of the logarithm. Thus the Bethe-Born approximation is typically written

$$\sigma_{\text{Bethe-Born}} = \frac{\pi e^4}{E_i \Delta E} \int \ln \left( \frac{4CE_i}{\Delta E} \right).$$

(5.6)

In the Bethe-Born approximation, the collision cross-section is proportional to the dipole oscillator strength $f$ of the transition, multiplied by a logarithmic factor.
6. More

Collision theory is a complicated subject. A few of the simpler developments are as follows.

If the atom is charged (an ion), so that the electric potential at far distances from the ion approximates a Coulomb field, $\propto 1/r$, then a better approximation is to take the initial and final wavefunctions of the collider to be unbound Coulomb functions. This is called the **Coulomb-Born approximation**.

Including the effects of exchange between the colliding and atomic electrons leads to the **Born-Ochkur approximation**. This is important for example in collisions that change the spin of the atom, which can only occur through electron exchange. It can be shown that the cross-section for collisions with exchange goes as $\sigma \propto E_i^{-3}$ for $E_i \gg \Delta E$, in contrast to the normal $\sigma \propto E_i^{-1}$ high energy behavior of collisions without exchange.