

Appendixes

A. Delta Functions

To represent the deterministic processes discussed in Chapter 2 we introduce the concept of a delta function, $\delta(x - x_0)$. By definition,

$$\delta(x - x_0) = \begin{cases} 0, & x \neq x_0 \\ +\infty, & x = x_0 \end{cases}$$

and

$$\int_{-x}^x \delta(x - x_0) dx = 1$$

such that

$$\int_{-x}^x f(x) \delta(x - x_0) dx = f(x_0) \quad (\text{A.1})$$

There are a number of mathematical representations of $\delta(x - x_0)$ using functions symmetric about x_0 which have finite widths and which are used by taking the limit as this width goes to zero, e.g.,

$$\begin{aligned} \delta(x - x_0) &= \frac{1}{\pi} \lim_{\varepsilon \rightarrow +0} \varepsilon / [(x - x_0)^2 + \varepsilon^2] \\ &= \lim_{\Delta \rightarrow +0} (2\pi\Delta)^{-1/2} \exp[-(x - x_0)^2/2\Delta] \\ &= \frac{1}{\pi} \lim_{L \rightarrow \infty} \frac{\sin L(x - x_0)}{(x - x_0)} \end{aligned} \quad (\text{A.2})$$

An often used expression from Fourier analysis, which we employ in Chapters 3 and 4, is

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(ikx) dk \quad (\text{A.3})$$

For further discussion [see A. Messiah, *Quantum Mechanics*, Vol. 1, North-Holland, Amsterdam (1961), p. 468].

The integral property of the one-dimensional delta function for a variable defined on $(-\infty, +\infty)$, as in Eq. (A.1), is often modified in practice to $\int_{W_-}^{W_+} f(w)\delta(w - W_0) dw = f(W_0)$, if $W_+ > W_0 > W_-$. For the classical collision probability of Eq. (2.31), $p_{AB}(b, \theta) = (1/2\pi)\delta[\cos\theta - \cos\Theta(b)]$ with $\cos\theta$ defined on $(-1, 1)$, the total collision probability is

$$P_{AB}(b) = 2\pi \int_{-1}^1 p_{AB}(b, \theta) d\cos\theta = 1$$

B. CM Deflection Function and Semiclassical Phase Shift

In the classical impulse approximation of Chapter 2, Eq. (2.57a), we have

$$\chi(b) \simeq -\frac{d}{dR_0} \left\{ \frac{1}{2E} \int_{-\infty}^{\infty} V(R) dZ \right\} \quad (\text{B.1})$$

in which $R^2 = R_0^2 + Z^2$, where for distant collisions $R_0 \simeq b$. Similarly, in Chapter 3, Eq. (3.52), the quantum impulse approximation or Born approximation gives the semiclassical phase shift as

$$\eta^{\text{SC}}(b) \simeq -(m/\hbar p_0) \int_{-\infty}^{\infty} V(R) dZ \quad (\text{B.2})$$

for the straight-line trajectory, $Z = p_0 t/m$. Together, Eqs. (B.2) and (B.1) confirm the semiclassical relationship, $\chi(b) = (2\hbar/p_0)\partial\eta^{\text{SC}}/\partial b$, of Eq. (3.47). The integral in Eqs. (B.1) and (B.2) evaluated for the screened potentials, $V(R) = C_n \exp(-\beta R)/R^n$ of Eq. (3.63), becomes

$$\int_{-\infty}^{\infty} V dZ = C_n (-1)^{1-n} \cdot 2 \frac{\partial^{1-n}}{\partial \beta^{1-n}} K_0(\beta b) \quad \text{for } n \leq 1, n \text{ integer} \quad (\text{B.3})$$

where $K_0(z)$ is a modified Bessel function of zero order [see Eq. (D.8)]. For large impact parameters ($b \gg \beta^{-1}$) and arbitrary n , we have

$$\int_{-\infty}^{\infty} V dZ \rightarrow \frac{2C_n}{b^{n-1}} \left(\frac{\pi}{2\beta b} \right)^{1/2} e^{-\beta b} \quad (\text{B.4})$$

In the limit $\beta \rightarrow 0$, the simple power-law potentials yield

$$\begin{aligned} \int_{-\infty}^{\infty} V dZ &= \frac{C_n}{b^{n-1}} \cdot 2 \int_0^{\infty} dx/(1+x^2)^{n/2} \\ &= \frac{C_n}{b^{n-1}} \left[\Gamma(1/2) \frac{\Gamma[(n-1)/2]}{\Gamma(n/2)} \right], \quad n > 1 \end{aligned} \quad (\text{B.5})$$

which is used to obtain Eq. (2.58), with $b \sim R_0$ and Eq. (5.1). Here $\Gamma(x)$ is defined as $\Gamma(x) = \int_0^{\infty} t^{x-1} e^{-t} dt$ and has the properties $\Gamma(x+1) = x\Gamma(x)$, $\Gamma(x+1) = x!$ for x integer, and $\Gamma(1/2) = (\pi)^{1/2}$. For other values, $\Gamma(x)$ is tabulated.

The exact classical deflection function is most easily evaluated using the Gauss-Mehler quadrature

$$\int_{-1}^1 dx f(x)/(1-x^2)^{1/2} \simeq \sum_{i=1}^n w_i f(x_i) \quad (\text{B.6})$$

where $x_i = \cos [(2i-1)\pi/2n]$ and $w_i = \pi/n$. With the change of variable $x = R_0/R$, Eq. (2.55) becomes

$$\chi(b) = \pi - 2\beta \int_0^{\infty} dx/[1 - (x\beta)^2 - V/E]^{1/2}, \quad \beta = b/R_0 \quad (\text{B.7})$$

which, when V/E is small, is close in form to Eq. (B.6). Using Eq. (B.6) with $f(x) = \beta\{(1-x^2)/[1-(x\beta)^2 - V/E]\}^{1/2}$ and $n = 2m$, as $f(x)$ is an even function, we have

$$\chi(b) \simeq \pi \left[1 - 1/m \sum_{i=1}^m f(x_i) \right] \quad (\text{B.8})$$

To evaluate the semiclassical action in Eq. (3.50a) or the radial phase shift in Eq. (3.50b), the integration procedure above may be used or a related integration expression

$$\int_{-1}^1 f(x)(1-x^2)^{1/2} dx \simeq \sum_{i=1}^n w_i f(x_i)$$

with $w_i = [\pi/(n+1)] \sin^2 [i\pi/(n+1)]$, $x_i = \cos [i\pi/(n+1)]$, and $f(x)$ determined from Eqs. (3.50).

For further information on the modified Bessel functions, the gamma functions, or these integration techniques, see, for instance, M. Abramowitz and I. A. Stegun, eds., *Handbook of Mathematical Functions*, National Bureau of Standards, U.S. Government Printing Office, Washington, D.C. (1964).

C. Collision with an Oscillator

The equation of motion for a harmonically bound charge of mass M_i in the field of a passing atom or ion is

$$M_i \ddot{\mathbf{r}} = -M_i \Gamma \dot{\mathbf{r}} - \mathbf{k}\mathbf{r} + \mathbf{F}_i(t) \quad (\text{C.1})$$

in which the terms on the right are a damping force, the binding force approximated as in Eq. (3.73), and the outside force on i , $\mathbf{F}_i(t)$, due to the passing particle, A, where \mathbf{r} is the position of the bound charge, i , in the target B. The total work done on the charge by A is

$$Q_i = \int_{-\infty}^{\infty} \dot{\mathbf{r}} \cdot \mathbf{F}_i(t) dt \quad (\text{C.2})$$

which can be evaluated using Fourier transforms. Taking the Fourier transform of Eq. (C.1) and solving for $\mathbf{r}(\omega)$ [the transform of $\mathbf{r}(t)$] in terms of $\mathbf{F}(\omega)$ [the transform of $\mathbf{F}(t)$] and substituting these into Eq. (C.2) we obtain

$$Q_i = (\pi/M_i) \int_{-\infty}^{\infty} |\mathbf{F}(\omega)|^2 g(\omega) d\omega \quad (\text{C.3})$$

in which $g(\omega) = (1/\pi)\{\omega^2 \Gamma / [(\omega^2 - \omega_0^2)^2 + \omega^2 \Gamma^2]\}$, with $\omega_0^2 = k/M_i$. In the limit that the damping disappears (i.e., $\Gamma \rightarrow 0$), $g(\omega)$ becomes a delta function (Appendix A), $\delta(\omega - \omega_0)$. Hence, as $\Gamma \rightarrow 0$, using Eq. (A.1), we obtain

$$Q_i = (\pi/M_i) |\mathbf{F}(\omega_0)|^2 \quad (\text{C.4})$$

The force between a particle A of charge Z_A and a bound electron on B is the coulomb force $\mathbf{F} = -Z_A e^2 (\mathbf{R} - \mathbf{r}) / |\mathbf{R} - \mathbf{r}|^3$ [cf. Eq. (4.4)]. If, in addition, A is assumed to be moving in a straight line, $R^2 = v^2 t^2 + b^2$ and $r \ll R$ [as in Eq. (4.10a)], then

$$F_{\perp}(\omega) \simeq (Z_A e^2 / bv) (2/\pi)^{1/2} [(\omega b/v) K_1(\omega b/v)]$$

and

$$F_{\parallel}(\omega) \simeq -i(Z_A e^2 / bv) (2/\pi)^{1/2} [(\omega b/v) K_0(\omega b/v)].$$

As in Appendix B, the K_ν are modified Bessel functions and we used

$$\int_{-\infty}^{\infty} \frac{e^{i\alpha x} dx}{(1+x^2)^{3/2}} = 2\alpha K_1(\alpha) \quad \text{and} \quad \int_{-\infty}^{\infty} \frac{x e^{i\alpha x} dx}{(1+x^2)^{3/2}} = -2i\alpha K_0(\alpha)$$

Substituting these expressions in Eq. (C.4), we obtain ($M_i \rightarrow m_e$)

$$Q_e \simeq \frac{2Z_A^2 e^4}{m_e v^2} \frac{1}{b^2} [\omega b/v]^2 [K_1^2(\omega b/v) + K_0^2(\omega b/v)] \quad (\text{C.5a})$$

The asymptotic expressions for K_ν (cf. Appendix B),

$$K_\nu \xrightarrow{z \rightarrow 0} \frac{1}{2} \Gamma(\nu) (Z/2)^{-\nu}, \quad \nu \neq 0$$

$$K_0(z) \xrightarrow{z \rightarrow 0} -\ln(1.123/z)$$

and

$$K_\nu(z) \xrightarrow{z \rightarrow \infty} (\pi/2z)^{1/2} e^{-z}$$

when used in Eq. (C.5a), yield

$$Q_e(b, \omega) \rightarrow \frac{2Z_A^2 e^4}{m_e v^2} \frac{1}{b^2} \begin{cases} 1 & , \quad \omega b/v \ll 1 \\ \pi(\omega b/v) e^{-2\omega b/v} & , \quad \omega b/v \gg 1 \end{cases} \quad (\text{C.5b})$$

Defining b/v to be the collision time, we see that $\omega b/v \ll 1$ is the classical BEA limit of Chapter 2 in which the electron's bound motion is slow compared to the incident-particle motion, and $\omega b/v \gg 1$ is the adiabatic limit of Chapter 4.

The energy transfer to the electrons can be used to calculate the stopping power $(dE/dx)_e$. That is, using Eq. (2.71), we have

$$-(dE/dx)_e = \sum_i f_i n_B 2\pi \int_{b_{\min}}^{b_{\max}} Q_e(b, \omega_i) b db \quad (\text{C.6})$$

where f_i is the oscillator strength of Eqs. (4.19) and (4.20). The integral in Eq. (C.6), on substituting Eq. (C.5), yields

$$-(dE/dx)_e = n_B (4\pi Z_A^2 e^4 / m_e v^2) \sum_i f_i [B_{\min} - B_{\max}] \quad (\text{C.7})$$

where $B = (\omega b/v) K_1(\omega b/v) K_0(\omega b/v)$. Estimates for b_{\min} and b_{\max} can be made using the arguments in Chapters 2 and 5. Letting $b_{\max} \rightarrow \infty$ (i.e., $v/\omega \ll d$, the distance to the neighboring target atom), and $b_{\min} \ll v/\omega$, we have

$$-(dE/dx)_e \simeq n_B (4\pi Z_A^2 e^4 / m_e v^2) \ln(1.123v/\bar{\omega} b_{\min}) \quad (\text{C.8})$$

where $n_B \ln(\hbar\bar{\omega}) = \sum_i f_i \ln(\hbar\omega_i) \simeq \sum_j f_j \ln(I_{Bj})$. Comparing this to earlier discussions, we see that $\hbar\bar{\omega} = \bar{I}_B$ is the mean ionization energy of Eq. (5.22). The quantity b_{\min} in Eq. (C.8) is the larger of $Z_A e^2 / mv^2$ and \hbar/mv , the classical and quantum limits in impact parameter.

If A is an incident neutral atom, which interacts with the electrons on B via a screened coulomb potential $V = (Z_A e^2 / R) e^{-\beta R}$, then a similar expression for Q_e is obtained. Using the integral

$$\int_{-\infty}^{\infty} \frac{e^{-\beta R}}{R} e^{i\omega t} dt = \frac{2K_0(b\beta')}{v} \quad (\text{C.9})$$

where $\beta'^2 = \beta^2 + (\omega/v)^2$, we find that the energy transfer becomes

$$Q_e = \frac{2Z_A^2 e^4}{m_e v^2} \frac{1}{b^2} [(\beta'b)^2 K_1^2(\beta'b) + (\omega b/v)^2 K_0^2(\beta'b)] \quad (\text{C.10})$$

where we used $(\partial/\partial z)K_0(z) = -K_1(z)$ [see Eq. (D.8)]. This reduces to Eq. (C.5) when $\beta \rightarrow 0$. The stopping power now becomes, using $b_{\max} \rightarrow \infty$,

$$\left| \frac{dE}{dx} \right|_e = n_B \frac{4\pi Z_A^2 e^4}{m_e v^2} \sum f_i \{ (\beta'b_{\min}) K_1(\beta'b_{\min}) K_0(\beta'b_{\min}) - \frac{1}{2} (\beta b_{\min})^2 [K_1^2(\beta'b_{\min}) - K_0^2(\beta'b_{\min})] \} \quad (\text{C.11})$$

In the limit $\beta'b_{\min} \ll 1$,

$$\left| \frac{dE}{dx} \right|_e \sim n_B \frac{4\pi Z_A^2 e^4}{m_e v^2} \sum f_i \left[\ln \frac{1.123}{\beta'b_{\min}} - \frac{1}{2} \left(\frac{\beta}{\beta'} \right)^2 \right] \quad (\text{C.12})$$

For very fast collisions, $\beta = \beta'$, the term in brackets becomes a constant and $(dE/dx)_e$ goes as $1/E$ (e.g., BEA). Therefore, the screening length acts like a large b (small energy transfer) cutoff on the interaction as stated at the end of Chapter 2. Compare these expressions to Eqs. (5.18), (5.22), (5.29), and (2.72).

Additional information on these topics is contained in J. D. Jackson, *Classical Electrodynamics*, Chapter 13, Wiley, New York (1963).

D. Born-Approximation Cross Section and Transition Probabilities

The first Born approximation to the elastic scattering amplitude, $f(\chi)$, was given in Eq. (3.59) as

$$f^{(1)}(\chi) = \frac{-m}{2\pi\hbar^2} \int d^3R \exp[i(\mathbf{K}_0 - \mathbf{K}_f) \cdot \mathbf{R}] V(\mathbf{R}) \quad (\text{D.1})$$

If the potential depends only on R , then the angular integrations can be performed, giving

$$f^{(1)}(\chi) = -\frac{2m}{\hbar^2} \int \frac{\sin(\Delta p R/\hbar)}{(\Delta p R/\hbar)} V(R) R^2 dR \quad (\text{D.2})$$

For the screened power-law potentials, $V(R) = (C_n/R^n)e^{-\beta R}$, the scattering amplitude scales as

$$f^{(1)}(\chi) = -\frac{2m}{\hbar^2} \left(\frac{\hbar}{\Delta p} \right)^{3-n} C_n \int_0^\infty \frac{\sin x}{x^{n-1}} e^{-\gamma x} dx \quad (\text{D.3})$$

where $\gamma = \beta\hbar/\Delta p$. In the limit $\gamma \rightarrow 0$ the expression for the power laws in Eq. (3.61) is obtained. The integrals in Eqs. (D.2) and (D.3) are fourier-sine

integrals which are given in A. Erdelyi, *Tables of Integral Transforms*, Volume 1, McGraw-Hill, New York (1954). For the screened potential, for $n < 3$ and $\gamma < 0$, we have

$$f^{(1)}(\chi) = \frac{-2m}{\hbar^2} \left(\frac{\hbar}{\Delta p} \right)^{3-n} C_n g_n(\gamma),$$

$$g_n(\gamma) = \Gamma(2-n) \sin[(2-n) \cot^{-1}(\gamma)] / (1+\gamma^2)^{1-n/2} \quad (\text{D.4})$$

This expression is valid for power laws (i.e., $\gamma = 0$) only for $1 \leq n < 3$. The function $\Gamma(x)$ is the tabulated gamma function defined, for $x > 0$, as

$$\Gamma(x) = \int_0^\infty t^{x-1} e^{-t} dt \quad (\text{D.5})$$

For $x < 0$, see p. 255.

The first-order transition amplitudes in the impact parameter method are given in Eq. (4.51) as

$$C_{0f}^1(\infty) = \frac{1}{i\hbar} \int_{-\infty}^{\infty} V_{f0}(R) \exp(i\omega_{f0} t) dt \quad (\text{D.6})$$

with $R^2 = b^2 + v^2 t^2$. Using the wave functions for the $\text{H}^+ + \text{H}(1s) \rightarrow \text{H}^+ + \text{H}(2s)$ transition, the reader can verify that $V_{1s,2s} = -2^{3/2} \cdot (2+3R)e^{-3/2R}/27$. Therefore, we are generally interested in potentials of the form $V_{f0} = A_n R^n e^{-\beta R}$. Using Eq. (C.9), we see that the coefficients have a form like that in Eq. (B.3),

$$C_{0f}^1(\infty) = \frac{2A_n}{i\hbar v} (-1)^{n+1} \frac{\partial^{n+1}}{\partial \beta^{n+1}} K_0(b\beta') \quad (\text{D.7})$$

where $\beta'^2 = \beta^2 + (\omega_{f0}/v)^2$. The recursion relations for the modified Bessel functions are

$$\frac{\partial K_0(z)}{\partial z} = -K_1(z) \quad (\text{D.8})$$

$$2nK_n(z) = -z(K_{n-1} - K_{n+1}) \quad 2 \frac{\partial K_n(z)}{\partial z} = -(K_{n-1} + K_{n+1})$$

E. Transport Equations

In Chapters 1 and 2 various transport equations are considered either with regard to the discussion of collision cascades or to chemical kinetics and diffusion. These equations are simply conservation equations that account for all losses and gains in a small volume of the material. The local rate of change of the density of a species, $\partial n_i / \partial t$, in a given volume element

is due to the difference in the flow into and out of the volume element and any production rates (sources), P_i , or loss rates (sinks), L_i , within this volume:

$$\frac{\partial n_i}{\partial t} = \text{Change due to flow} + P_i - L_i \quad (\text{E.1})$$

If the flow is uniform, the change in density due to the flow is zero. However, if there is a gradient (e.g., more “in” one side than “out” the other), then n_i is affected. Writing the flow as $n_i \mathbf{w}_i$, Eq. (E.1) can be written

$$\frac{\partial n_i}{\partial t} = -\nabla n_i \mathbf{w}_i + P_i - L_i \quad (\text{E.2})$$

where the reader should confirm the negative sign. This is referred to, generally, as the continuity equation.

The time-independent radiation cascade equation can be developed from the expression in Eq. (1.1). If the radiation intensity $I_i(\mathbf{p}, z)$ defined in the text is used, then $I_i(\mathbf{p}, z)(\hat{p} \cdot \hat{z})d^3p$ is the number of particles per unit area per unit time of type i with momentum between \mathbf{p} and $\mathbf{p} + d\mathbf{p}$ crossing a surface at depth z . Here $\hat{p} \cdot \hat{z}$ is the cosine between the incident direction \hat{p} and the surface normal. As I_i is assumed uniform across the surface in our model, the total number of particles crossing the surface is

$$A \int I_i(\mathbf{p}, z)(\hat{p} \cdot \hat{z})d^3p$$

where A is the surface area. If $\omega(\mathbf{p}, \mathbf{p}')d^3p'$ is the probability per unit path length of a collision occurring in which $\mathbf{p} \rightarrow \mathbf{p}'$, then $\int \omega_i(\mathbf{p}, \mathbf{p}')\Delta z/(\hat{p} \cdot \hat{z})d^3p'$ is the total probability of particles \mathbf{p} changing their momentum when crossing a slab Δz thick. The path length through the slab is, of course, $\Delta z/(\hat{p} \cdot \hat{z})$. Using these definitions, we see that the change in flux across a slab Δz thick, as defined in Eq. (1.1), becomes

$$\begin{aligned} & [I_i(\mathbf{p}, z + \Delta z) - I_i(\mathbf{p}, z)](\hat{p} \cdot \hat{z})d^3p \\ &= -I_i(\mathbf{p}, z)(\hat{p} \cdot \hat{z})d^3p \int \omega_i(\mathbf{p}, \mathbf{p}') \left(\frac{\Delta z}{\hat{p} \cdot \hat{z}} \right) d^3p' \\ &+ \left[\int I_i(\mathbf{p}', z)(\hat{p}' \cdot \hat{z})\omega_i(\mathbf{p}', \mathbf{p}) \left(\frac{\Delta z}{\hat{p}' \cdot \hat{z}} \right) d^3p' \right] d^3p \\ &+ \mathcal{S}_i(\mathbf{p}, z)\Delta z d^3p \end{aligned} \quad (\text{E.3})$$

The first term on the right is the loss due to scatterings of i type particles of momentum \mathbf{p} , where $(\Delta z/\hat{p} \cdot \hat{z})$ is their path length through the slab. The second term is the addition to the flux of particles of type (i, \mathbf{p}') by scattering from \mathbf{p}' into the interval \mathbf{p} to $\mathbf{p} + d\mathbf{p}$, where the path length for the \mathbf{p}'

particles through the slab is $\Delta z/\hat{p}' \cdot \hat{z}$. The last term accounts for all other sources and sinks for particles of type (i, \mathbf{p}) , that is, the probability of an absorption, ionization, nuclear reaction, etc. in the slab. This last term obviously contains a considerable amount of physics of the processes occurring in materials. The integral equation (E.3) can be converted into an integral-differential equation by writing

$$I_i(\mathbf{p}, z + \Delta z) \simeq I_i(\mathbf{p}, z) + \Delta z \frac{\partial I_i}{\partial z}(\mathbf{p}, z) \quad (\text{E.4})$$

Using Eq. (E.4) and canceling the Δz and angular factors ($\hat{p} \cdot \hat{z}$), we see that Eq. (E.3) becomes

$$-\cos \theta \frac{\partial I_i}{\partial z}(\mathbf{p}, z) = \int [I_i(\mathbf{p}, z)\omega_i(\mathbf{p}, \mathbf{p}') - I_i(\mathbf{p}', z)\omega_i(\mathbf{p}', \mathbf{p})] d^3 p' - \mathcal{S}_i(\mathbf{p}, z) \quad (\text{E.5})$$

where we have defined $\cos \theta = \hat{p} \cdot \hat{z}$. This is the expression used in Eq. (1.2). This result is related to that in Eq. (E.2) if the momenta are randomly oriented, so $\int I_i(\mathbf{p}, z) d^3 p = 0$, and the net flow $(n\mathbf{w})_i = \int I_i(\mathbf{p}, z) \cos \theta d^3 p$. Integrating Eq. (E.5) over all momenta, we see that the collision terms cancel (as many are scattered into any direction as out of) and the time-dependent continuity equation in one dimension is recovered: $\partial(n\mathbf{w})_i/\partial z = \mathcal{S}_i$. Here $\mathcal{S}_i = \int \mathcal{S}_i(\mathbf{p}, z) d^3 p = P_i - L_i$.

In Chapter 2 we discuss the collision-cross-section differential in angle rather than the $\omega(\mathbf{p}, \mathbf{p}')$. These are related by $(d\sigma/d\Omega) d\Omega \delta[\mathbf{p}' - \mathbf{p}'(\Omega, \mathbf{p})] d^3 p' = (1/n_T)\omega(\mathbf{p}, \mathbf{p}') d^3 p'$ where n_T is the target number density, generally written n_B in Chapter 2, where B identifies the target atoms or molecules. The quantity Ω indicates the solid angle associated with the scattered momentum direction \hat{p}' , as measured from the incident direction, here \hat{p} (viz. Figure 2.6), and $\mathbf{p}'(\Omega, \mathbf{p})$ is the final momentum calculated by classical kinematics. The delta function is discussed in Chapter 2 and in Appendix A. The reader is also referred to Eq. (6.17) and the following discussion.

F. The Stationary-Phase Approximation

The stationary-phase approximation is used extensively in Chapters 3 and 4 to evaluate integrals of oscillatory functions having the general form

$$I = \int_{-\infty}^{\infty} A(x) \exp[i\alpha(x)] dx \quad (\text{F.1})$$

where $A(x)$ is a slowly varying quantity. If the phase, $\alpha(x)$, changes rapidly (or randomly) with x , then the contributions to I tend to cancel. On the

other hand, if $\alpha(x)$ has a stationary point, x_0 , i.e., $\alpha' = d\alpha/dx|_{x=x_0} = 0$, then α will be slowly varying over a region of x about x_0 , and a significant contribution to I may accrue, as indicated in Figure 3.6. Writing $\alpha(x) \simeq \alpha(x_0) + [(x - x_0)^2/2]\alpha''$ in a region about x_0 having extent Δx , we can approximate the integral by zero outside this region, and

$$I \approx \exp[i\alpha(x_0)] \int_{x_0 - \Delta x/2}^{x_0 + \Delta x/2} A(x) \exp\left[\frac{i\alpha''}{2}(x - x_0)^2\right] dx \quad (\text{F.2})$$

The slowly varying function $A(x)$ is replaced by its value $A(x_0)$ in this region. The remaining integral is now evaluated by extending the limits of integration to infinity,

$$I \approx \exp[i\alpha(x_0)] A(x_0) \int_{-\infty}^{\infty} \exp\left[\frac{i\alpha''}{2}(x - x_0)^2\right] dx \quad (\text{F.3})$$

This extension is valid since, when $|\Delta x| \gg |x_0|$, the integral in Eq. (F.3) oscillates rapidly as x changes, producing cancellation, and the primary contribution again comes from a small region about x_0 . The correct procedure for evaluating the integral in Eq. (D.3) is to use complex integration methods. However, noting that $\int_{-\infty}^{\infty} \exp[-\beta(x - x_0)^2] dx = (\pi/\beta)^{1/2}$ and writing $\beta = \varepsilon - i\alpha''/2$, we see that the integral becomes, in the limit $\varepsilon \rightarrow 0$,

$$I \approx A(x_0) \exp[i\alpha(x_0)] [\pi/(-i\alpha''/2)]^{1/2}$$

or

$$I \approx (2\pi/\alpha''(x_0))^{1/2} A(x_0) \exp\{i[\alpha(x_0) + \pi/4]\} \quad (\text{F.4})$$

This is the approximation used in Chapters 3 and 4.

G. Atomic State Labels

The wave function for the one-electron atom in Eq. (3.71) has the form $\psi_{nlm_l} = \mathcal{R}_{nl} Y_{lm_l}$, where the label n is an energy index, l ($l = 0, 1, 2, \dots$) is the angular momentum index, and m_l ($m_l = l, l - 1, \dots, -l + 1, -l$), is an index for the angular momentum along the arbitrary axis through the atom. The latter is important only when the electron is in an applied field or the field of another electron or nucleus. Each electron also has a spin, which is another angular momentum quantity. As there are two possible spin orientations, the angular momentum labeling is $s = \frac{1}{2}$ and $m_s = \pm \frac{1}{2}$, by analogy with l and m_l . For a multielectron atom, the total angular momentum of a given atomic state is the only observable quantity. However, for light atoms, which we will concentrate on here, it is useful to imagine the atomic state as being built up from single-electron states. Each such state has a given angular momentum and spin, with the orbital and spin angular mo-

momentum combining separately. This assumes that the electrons in the atom orbit independently in the field of the nucleus and the average field of the other electrons.

The atomic-orbital method, based on the Pauli principle, assigns labels n and l for each electron orbital and allows each orbit type to be filled with only that number of electrons determined by the m_l values for each l and the two possible spin orientations. Each such orbital or shell, therefore, can contain at most $2(2l + 1)$ electrons. Using the spectroscopic notation (i.e., s , p , d , f , g , ... corresponds to $l = 0, 1, 2, 3, 4, \dots$), one often labels a ground state hydrogen atom $(1s)$, where one is the energy index n , and s is the angular momentum index, $l = 0$. Helium becomes $(1s)^2$, implying that the two electrons have different spin orientations. Lithium, with three electrons, becomes $(1s)^2(2s)$; carbon, with six electrons, becomes $(1s)^2(2s)^2(2p)^2$; and neon completes the $n = 2$ shell with 10 electrons, $(1s)^2(2s)^2(2p)^6$.

The individual angular momenta combine to give a total orbital angular momentum, L , and spin angular momentum, S . Again the spectroscopic notation S , P , D , for sharp, principal, and diffuse lines, which were found to correspond to $L = 0, 1, 2$, is generally used to label the states. As the lines were often observed to be split slightly, each state was found to have a multiplicity related to the total spin, $(2S + 1)$. Hence hydrogen is labeled $(1s) ^2S$ or just 2S , where the superscript is the spin multiplicity.

Helium is $(1s)^2 ^1S$ and lithium $(1s)^2(2s) ^2S$. The carbon atom has a number of angular-momentum states corresponding to $(1s)^2(2s)^2(2p)^2$ because of the vector addition of the angular momenta associated with the $(2p)$ electrons. By the so-called Hund's rules for angular-momentum coupling, the state lowest in energy has been found to be the one with the highest multiplicity and the lowest L , here 3P . Neon has only one total angular-momentum state corresponding to the closed-shell configuration, $(1s)^2(2s)^2(2p)^6 ^1S$. The reader is referred to any one of the many modern physics or quantum-chemistry text for further information on the labeling of atomic states. The material presented above is adequate for understanding any references to atomic states in this text.

H. Thomas–Fermi Interaction: Results

Bohr, Firsov, Lindhard, and others have used the Thomas–Fermi model for calculating charge distributions to determine “universal” interaction potentials between atoms. The potential is written in the form

$$V_{AB}(R) = \frac{Z_A Z_B e^2}{R} \Phi \left(\frac{R}{a_{AB}} \right) \quad (\text{H.1})$$

where the function Φ does not depend on Z_A and Z_B explicitly. The vari-

able is expressed as the internuclear separation scaled by the screening constant, a_{AB} [viz. Eq. (4.8)]. The Thomas–Fermi model is a statistical model for describing the electronic charge distribution. In this model the electrons are treated as a gas in which the uncertainty principle restricts the number of electrons having a given momentum in any volume of space. Lindhard and co-workers obtained an extensively used numerical solution for $\Phi(R/a_{AB})$, in which the screening length is $a_{AB}^L = 0.8853a_0(Z_A^{2/3} + Z_B^{2/3})^{-1/2}$. Lenz and Jensen earlier had obtained a variational solution to a similar interaction model,

$$\Phi_{LJ} = (1 + b_1 y + b_2 y^2 + b_3 y^3 + b_4 y^4)e^{-y} \quad (\text{H.2})$$

where $y = (9.67R/a_{AB}^L)^{1/2}$, and $b_1 = 1$, $b_2 = 0.3344$, $b_3 = 0.0485$, and $b_4 = 0.002647$. These were employed in the comparison in Figure 5.6. Recent experimental evidence* suggests $b_1 = 0.9839$, $b_2 = 0.4272$, $b_3 = 0.01150$, and $b_4 = 0.01288$ for certain ion–atom collisions. Lindhard and co-workers used the Thomas–Fermi screening function to obtain a general form for the differential cross section to describe collisions involving many-electron atoms. In scaled units we have

$$\frac{d\sigma_{AB}}{dt} = \frac{\pi(a_{AB}^L)^2 f(t^{1/2})}{(2t^{3/2})} \quad (\text{H.3})$$

where $t = \varepsilon^2 T/T_{\max}$, with $\varepsilon = Ea_{AB}^L/Z_A Z_B e^2$, E is the CM energy, and $T_{\max} = \gamma E_A$. The function $f(t^{1/2})$ is well approximated by $f(t^{1/2}) \simeq \lambda t^{1/6}/[1 + (2\lambda t^{2/3})^{2/3}]^{3/2}$, where $\lambda = 1.309$. Using this expression, we see that the corresponding nuclear component of the stopping cross section, S_n , in reduced units [$S_n = \pi(a_{AB}^L)^2 (T_{\max}/\varepsilon) S_n(\varepsilon)$] is

$$s_n(\varepsilon) \simeq \frac{9}{8\varepsilon} \{ \ln [A + (1 + A^2)^{1/2}] - A/(1 + A^2)^{1/2} \} \quad (\text{H.4})$$

with $A = (2\lambda)^{1/3} \varepsilon^{4/9}$.

For background on this material see the following: W. Lenz, *Z. Phys.* **77**, 713 (1932); H. Jensen, *Z. Phys.* **77**, 722 (1932); O. B. Firsov, *Sov. Phys. JETP* **5**, 1192 (1957); J. Lindhard, V. Nielsen, and M. Scharff, *Dan. Vidensk. Selsk. Mat. Fys. Medd.* **36**, No. 10 (1968); P. Sigmund, in *Physics of Ionized Gases*, ed. M. Kurepa, (1972), p. 137; and J. Lindhard and M. Scharff, *Phys. Rev.* **124**, 128 (1961). For a discussion of the Thomas–Fermi interaction see I. M. Torrens, *Interatomic Potentials*, Academic Press, New York (1972), Chapter 3, and P. Gombás, *Handbuch der Physik*, XXXVI (1956).

I. Low Energy, Inelastic Cross Sections

Those inelastic cross sections which can be described by two states at low velocities often have simple analytic forms. From Eq. (2.24) and (4.61a),

* P. Lottager, F. Besenbacher, O. S. Jensen, and V. S. Sørensen, *Phys. Rev. A*, **20**, 1443 (1979).

(4.59), or (4.62), the cross sections can be written as

$$\sigma_{0 \rightarrow f}^{(v)} \approx 2\pi \int_0^\infty \bar{P}_{0f} \cdot 2 \sin^2(\Delta\varphi_{0f}) b db \quad (\text{I.1})$$

where $\Delta\varphi_{0f}$ is the net phase change. This integral requires numerical evaluation unless the random phase approximation on the oscillatory part can be used and $2 \sin^2(\Delta\varphi_{0f})$ can be replaced by one. Firsov [O. Firsov, *Zh. Eksp. Teor. Fiz.* **21**, 1001 (1951)] makes this replacement for impact parameters less than that (b^*) at which the change in phase first becomes $\sim 1/\pi$. For an exponential interaction such that

$$(\Delta\varphi_{0f}) \sim \left(\frac{1}{\hbar} \int_{-\infty}^\infty V_{0f} dt \right),$$

and using Eq. (B.4) then b^* is estimated from

$$V_{0f}(b^*)(2\pi b^*/\beta)^{1/2}/v \approx 1/\pi. \quad (\text{I.2})$$

For symmetric resonant, charge exchange [Eq. (4.62)] (Eq. I.1) becomes

$$\sigma_{c.t.}(v) \approx \pi b^{*2}/2. \quad (\text{I.3})$$

For inelastic collisions the cross section in (Eq. I.1) becomes

$$\sigma_{0 \rightarrow f} \approx \pi R^{*2} P_{0 \rightarrow f}(v) \quad (\text{I.4})$$

as in Eq. (2.11), where for the LZS approximation [Eq. (4.59)] $R^* = R_x$ and for the Demkov approximation [Eq. (4.61c)] R^* is the lesser of b^* and R_x . For the LZS case the reader can verify that

$$P_{0 \rightarrow f} \approx 4 \left(1 - \frac{V_{00}(R_x)}{E} \right) [E_3(\xi) - E_3(2\xi)] \quad (\text{I.5})$$

where $E_3(\xi)$, the exponential integral $\int_1^\infty e^{-\xi x}/x^3$, is tabulated (Reference in appendix B) and $\xi = \tau_x/\tau_{0f}$ of Eq. (4.57) evaluated at $b = 0$. The Demkov (Eq. 4.61c) expression has a similar form

$$P_{0 \rightarrow f} \approx 4(1 - V_{00}(R_x)/E) \int_1^\infty dx e^{-2\xi'x}/(1 + e^{-2\xi'x})^2 \quad (\text{I.6})$$

where $\xi' = (\xi/2\hbar\beta) \cdot \Delta E_{0f}/v'$, where $v' = v[1 - V_{00}(R_x)/E]^{1/2}$ and $\Delta E_{0f} = \varepsilon_f + V_{ff} - \varepsilon_0 - V_{00}|_{R_x}$ the energy splitting at R_x , defined by $V_{0f}(R_x) = (1/2)\Delta E_{0f}$. Evaluating $P_{0 \rightarrow f}$, with exponential coupling and constant ΔE_{0f} by numerically integrating the two state equations Olson [R. E. Olson, *Phys. Rev. A* **6**, 1822 (1972)] gives a numerical result which is more accurate than that in Eq. (I.6). Writing $P_{0 \rightarrow f}(v) = (1 - V_{00}(R_x)/E)\tilde{P}$, values of \tilde{P} are given in Table I.1.

When $b^* < R_x$, the Demkov (or Rozen-Zener) cross section has the

Table I.1. Values of p

$(\zeta')^{-1}$	\bar{P}	$(\zeta')^{-1}$	\bar{P}
0.5	0.015	3.0	0.54
1.0	0.15	3.5	0.53
1.5	0.33	4.0	0.52
2.0	0.48	4.5	0.51
2.5	0.52	5.0	0.50

form of Eq. (I.3), i.e., $\bar{P}_{0f} \rightarrow \frac{1}{2}$ in Eq. (I.1). For all these expressions the semiempirical coupling potential $V_{0f} = (I_0 I_f)^{1/2} (\beta R) e^{-.86\beta R}$ gives reasonable results where $\beta = 0.5 [(2I_0)^{1/2} + (2I_f)^{1/2}]$ with I_0 and I_f the binding energy of the electron in atomic units [R. E. Olson, F. T. Smith, and E. Bauer, *App. Optics* **10**, 1848 (1971)]. Smirnov [B. M. Smirnov, *Sov. Phys.-JETP* **20**, 345 (1965)] gives a more accurate expression for the symmetric resonant case.

When the initial state potential curve crosses a continuum or near continuum of final states [e.g., $A^{+n} + B \rightarrow A^{+(n-1)} + B^+$ or the Langerin process, Eq. (5.35)] then the total reaction cross section has the form of Eq. (I.4) with $P_{0 \rightarrow f} \rightarrow 1$. This is referred to as an absorbing sphere model and R^* is determined by that distance at which the reaction probability first becomes "significant": $\tau_x/\tau_{0f} \sim 0.15$ [R. E. Olson and A. Salop, *Phys. Rev. A.*, **14**, 579 (1976)]. For determining R^* as a tunneling problem see T. P. Grozdanov and R. Janer, *Phys. Rev. A.*, **17**, 880 (1978).

J. Constants and Units

Table A1. Physical Constants^a

Designation of quantity	Symbol	Value	Units	
			SI	Other
Avogadro's number	N_A	6.0222	$10^{26} \text{ kmol}^{-1}$	10^{23} mol^{-1}
Atomic mass unit ($^{12}\text{C} = 12$)	amu	1.6605	10^{-27} kg	10^{-24} g
Electron charge/mass ratio	e/m_e	1.7588	$10^{11} \text{ C kg}^{-1}$	10^7 emu g^{-1}
Electron charge	e	1.6022	10^{-19} C	10^{-20} emu
Electron mass	m_e	9.1096	10^{-31} kg	10^{-28} g
Bohr radius (a.u.)	a_0	5.2918	10^{-11} m	10^{-9} cm
Rydberg constant	R_∞	1.097373	10^7 m^{-1}	10^5 cm^{-1}
Speed of light in a vacuum	c	2.99792	10^8 m s^{-1}	$10^{10} \text{ cm s}^{-1}$
Planck's constant	h	6.6262	10^{-34} J s	10^{-27} erg s
Dirac's \hbar ($h/2\pi$)	\hbar	1.0546	10^{-34} J s	10^{-27} erg s
Hartree (a.u.)	a.u.	4.3594	10^{-18} J	10^{-11} erg
Gas constant	R	8.314	$10^3 \text{ J kmol}^{-1} \text{ K}^{-1}$	$10^7 \text{ erg mol}^{-1} \text{ K}^{-1}$
Boltzmann's constant (R/N_A)	k	1.3806	$10^{-23} \text{ J K}^{-1}$	$10^{-16} \text{ erg K}^{-1}$

^a From R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamic*, Oxford University Press, Oxford (1974).

Table A2. Atomic Units (a.u.)

Mass: $m_e = 1$, 1 amu = 1823 (based on $^{12}\text{C} = 12$ amu)
Charge: $e = 1$
Angular momentum: $\hbar = 1$
1 a.u. of length: $\hbar^2/(m_e e^2) = 0.529 \times 10^{-8} \text{ cm} = a_0 = \text{Bohr radius of H}$
1 a.u. (energy, $m_e e^4/\hbar^2$) = 27.2 eV = 1 hartree = ($2 \times$ ground-state energy of H)
1 a.u. (velocity, e^2/\hbar) = $2.19 \times 10^8 \text{ cm/s} = c/137.0 =$ (speed of light \times fine-structure constant)
1 a.u. (time, $\hbar^3/m_e e^4$) = $0.242 \times 10^{-16} \text{ s} =$ (period of electron in ground state of H/ 2π)

Table A3. Approximate) Energy Conversion Factors^a

	erg	J	cal	eV	a.u.	cm ⁻¹	Hz	K	kJ mol ⁻¹	kcal mol ⁻¹
1 erg =	1	1.000(-7)	2.39(-8)	6.24(+11)	2.29(+10)	5.03(+15)	1.509(+26)	7.24(+15)	6.02(+13)	1.440(+13)
1 joule (J) =	1.000(+7)	1	2.39(-1)	6.24(+18)	2.29(+17)	5.03(+22)	1.509(+33)	7.24(+22)	6.02(+20)	1.440(+20)
1 cal =	4.184(+7)	4.184	1	2.61(+19)	9.58(+17)	2.10(+23)	6.31(+33)	3.03(+23)	2.52(+21)	6.02(+20)
1 eV =	1.602(-12)	1.602(-19)	3.83(-20)	1	3.68(-2)	8.07(+3)	2.42(+14)	1.161(+4)	9.65(+1)	2.31(+1)
1 hartree										
(au) =	4.36(-11)	4.36(-18)	1.042(-18)	2.72(+1)	1	2.19(+5)	6.58(+15)	3.16(+5)	2.63(+3)	6.28(+2)
1 cm ⁻¹ =	1.986(-16)	1.986(-23)	4.75(-24)	1.240(-4)	4.56(-6)	1	3.00(+10)	1.439	1.200(-2)	2.86(-3)
1 Hz =	6.63(-27)	6.63(-34)	1.585(-34)	4.14(-15)	1.520(-16)	3.34(-11)	1	4.80(-11)	3.99(-13)	9.54(-14)
1°K (K) =	1.380(-16)	1.380(-23)	3.30(-24)	8.62(-5)	3.17(-6)	6.95(-1)	2.08(+10)	1	8.32(-3)	1.988(-3)
1 kJ mol ⁻¹ =	1.659(-14)	1.659(-21)	3.97(-22)	1.035(-2)	3.81(-4)	8.36(+1)	2.50(+12)	1.202(+2)	1	2.39(-1)
1 kcal										
mol ⁻¹ =	6.94(-14)	6.94(-21)	1.661(-21)	4.33(-2)	1.593(-3)	3.50(+2)	1.048(+13)	5.03(+2)	4.184	1

^a Numbers in parentheses denote powers of ten by which the entry is to be multiplied. From R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics*, Oxford University Press, Oxford (1974).

Table J.4

Elements	Z	M(a.m.u)	I (eV)	Term	Elements	Z	M (a.m.u)	I (eV)	Term
H	1	1.01	13.60	² S	Cu	29	63.55	7.72	² S
He	2	4.00	24.58	¹ S	Zn	30	65.38	9.39	¹ S
Li	3	6.94	5.39	² S	Ga	31	69.72	6.00	² P
Be	4	9.01	9.32	¹ S	Ge	32	72.60	7.88	³ P
B	5	10.81	8.30	² P	As	33	74.92	9.81	⁴ S
C	6	12.01	11.26	³ P	Se	34	78.96	9.75	³ P
N	7	14.01	14.54	⁴ S	Br	35	79.90	11.84	² P
O	8	16.00	13.61	³ P	Kr	36	83.80	14.00	¹ S
F	9	19.00	17.42	² P	Rb	37	85.47	4.18	² S
Ne	10	20.18	21.56	¹ S	Sr	38	87.62	5.69	¹ S
Na	11	22.99	5.14	² S	Y	39	88.91	6.38	² D
Mg	12	24.31	7.64	¹ S	Zr	40	91.22	6.84	³ F
Al	13	26.98	5.98	² P	Nb	41	92.91	6.88	⁶ D
Si	14	28.09	8.14	³ P	Mo	42	95.94	7.10	⁷ S
P	15	30.98	10.55	⁴ S	Tc	43	98.91	7.28	⁶ S
S	16	32.06	10.36	³ P	Ru	44	101.1	7.36	⁵ F
Cl	17	35.45	13.01	² P	Rh	45	102.91	7.28	⁶ S
Ar	18	39.95	15.76	¹ S	Pd	46	106.4	8.33	¹ S
K	19	39.10	4.34	² S	Ag	47	107.87	7.57	² S
Ca	20	40.08	6.11	¹ S	Cd	48	112.40	8.99	¹ S
Sc	21	44.96	6.56	² D	In	49	114.82	5.78	² P
Ti	22	47.90	6.83	³ F	Sn	50	118.69	7.33	³ P
V	23	50.94	6.74	⁴ F	Sb	51	121.75	8.64	⁴ S
Cr	24	52.00	6.76	⁷ S	Te	52	127.60	9.01	³ P
Mn	25	54.94	7.43	⁶ S	I	53	126.90	10.44	² P
Fe	26	55.85	7.90	⁵ D	Xe	54	131.30	12.13	¹ S
Co	27	58.93	7.86	⁴ F	Cs	55	132.91	3.89	² S
Ni	28	58.71	7.63	³ F	Ba	56	137.34	5.21	¹ S