Oscillator strength

Oscillator strength is a very important parameter in spectroscopy. It is defined in a dimensionless form and gives the probability of absorption or emission of radiation in transitions between energy levels of an atom or a molecule

$$f_{fi} = \frac{2m\omega_{fi}}{3\hbar} |\langle f|\vec{r}|i\rangle|^2 \qquad \omega_{fi} = \frac{E_f - E_i}{\hbar}$$

where the dipole matrix elements are

$$|\langle f|\vec{r}|i\rangle|^2 \equiv |\langle f|x|i\rangle|^2 + |\langle f|y|i\rangle|^2 + |\langle f|z|i\rangle|^2$$

Oscillator strenghts obey the so-called Thomas-Reiche-Kuhn sum rule

$$\sum_f f_{fi} = 1$$

Obviously $f_{if} < 1$

Ther above sum rule can be derived as follows

$$\langle i|[x, p_x]|i\rangle = i\hbar \quad \leftarrow \text{basic commutator relation}$$

We may write it as

$$\sum_f \langle i|x|f\rangle\langle f|p_x|i\rangle - \langle i|p_x|f\rangle\langle f|x|i\rangle = i\hbar$$

Now, if the Hamiltonian is such that

$$H = \frac{p^2}{2m} + V(\vec{r}) = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + V(\vec{r})$$ we can

represent $\vec{p}$ as

$$p_x = \frac{im}{\hbar}[H, x] \qquad \left(\text{check: } [x, p_x^2] = [x, p_x]p_x + p_x[x, p_x] = = 2i\hbar p_x\right)$$

Hence, $\langle f|p_x|i\rangle = \frac{im}{\hbar}\langle f|(Hx - xH)|i\rangle$

Because both $|f\rangle$ and $|i\rangle$ are eigenfunctions of H we obtain

$$\langle f|p_x|i\rangle = -\frac{im}{\hbar}(E_i - E_f)\langle f|x|i\rangle$$

or simply

$$\langle f|p_x|i\rangle = +im\omega_{fi}\langle f|x|i\rangle$$

With that

$$\sum_f{}' \langle i|x|f\rangle\langle f|p_x|i\rangle - \langle i|p_x|f\rangle\langle f|x|i\rangle = i\hbar$$

becomes

$$\sum_f{}' [im\omega_{fi}|\langle f|x|i\rangle|^2 + im\omega_{fi}|\langle f|x|i\rangle|^2 = i\hbar$$

or

$$\sum_f \frac{2m\omega_{fi}}{\hbar}|\langle f|x|i\rangle|^2 = 1$$

The same result follows with x replaced by y or z. When we combine them we get

$$\sum_f \frac{2m\omega}{3\hbar}|\langle f|\vec{r}|i\rangle|^2 = \sum_f f_{fi} = 1$$

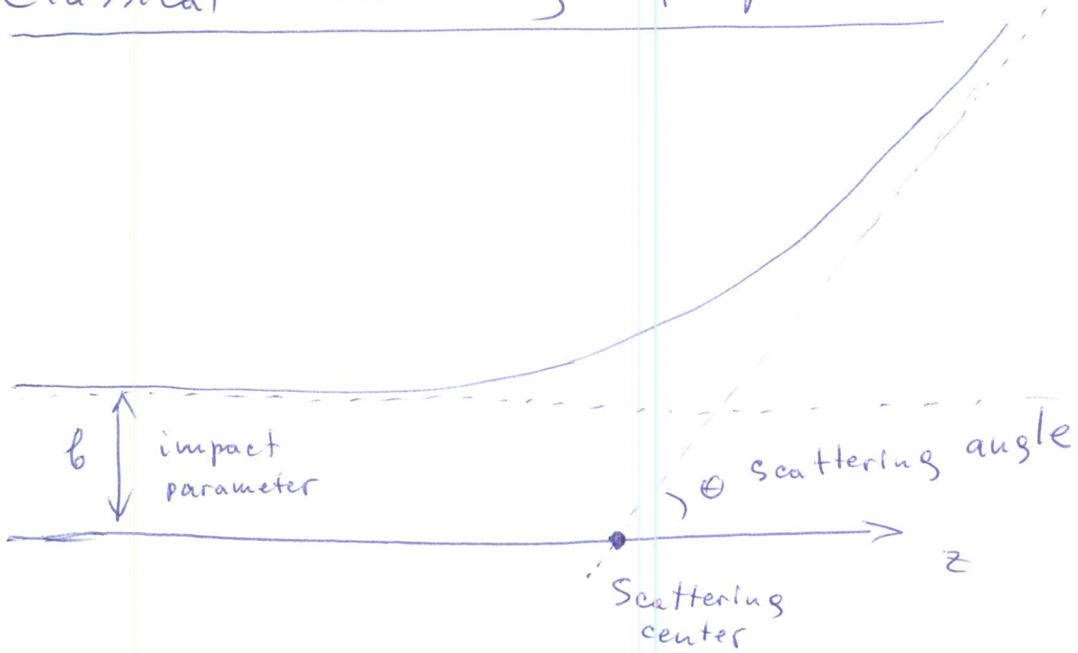
For an atom with Z electrons we make a replacemen

$$\langle f|\vec{r}|i\rangle \longrightarrow \langle f|\sum_{i=1}^{Z}\vec{r}_i|i\rangle$$

and then

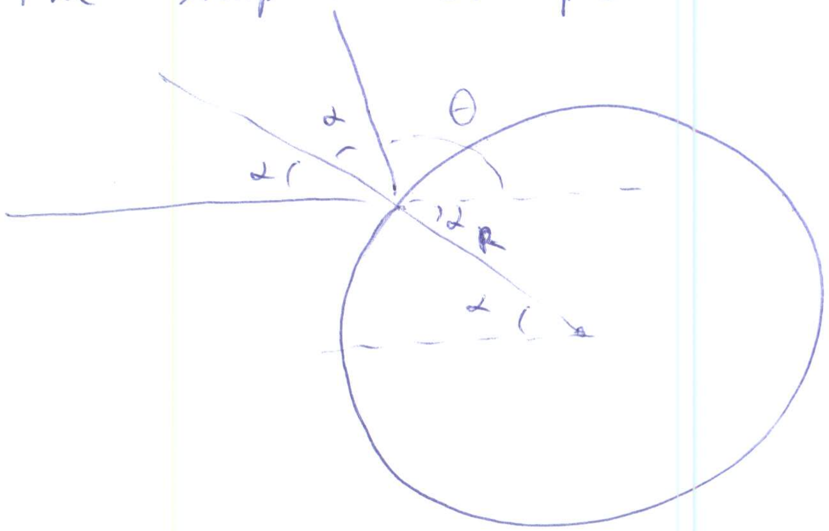
$$\sum_f{}' f_{fi} = Z$$

Classical scattering of particles



Let us consider a particle incident on some scattering center. The particle has some initial energy, E, and impact parameter, b. Eventually it scatters at some scattering angle θ. For simplicity we will assume that the target's potential is spherically symmetric. Then the trajectory lies in a single plain. Our task is to compute θ given b.

The simplest example is a hard-sphere potential



$$b = R\sin\alpha$$

$$\theta = \pi - 2\alpha$$

$$b = R\sin\left(\frac{\pi}{2} - \frac{\theta}{2}\right) = R\cos\theta$$

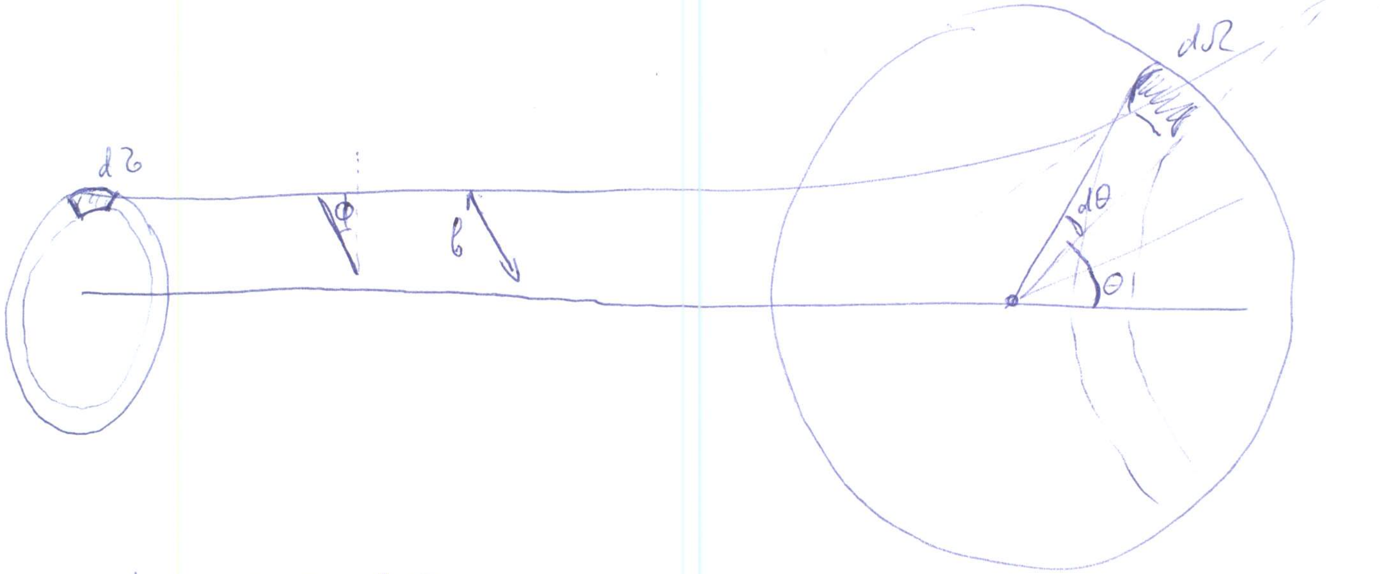
$$\theta = \begin{cases} 2\arccos\frac{b}{R} & , b < R \\ 0 & , b \geq R \end{cases}$$

Differential cross section

$$D(\theta) = \frac{d\sigma}{d\Omega}$$

$d\sigma$ – crossectional area

$d\Omega$ – solid angle



$$d\sigma = D(\theta)\, d\Omega$$

$$d\sigma = b\, db\, d\phi \qquad d\Omega = \sin\theta\, d\theta\, d\phi$$

$$D(\theta) = \frac{b}{\sin\theta}\left|\frac{db}{d\theta}\right|$$

For a hard sphere

$$\frac{db}{d\theta} = -\frac{1}{2} R \sin\frac{\theta}{2}$$

and $$D(\theta) = \frac{R\cos\frac{\theta}{2}}{\sin\theta}\left(\frac{R\sin\frac{\theta}{2}}{2}\right) = \frac{R^2}{4}$$

The total cross-section is the integral of $D(\theta)$ over all solid angles:

$$\sigma \equiv \int D(\theta)\, d\Omega$$

For a hard sphere $\sigma = \frac{R^2}{4}\int d\Omega = \pi R^2$

If we have a beam of incident particles with uniform intensity (luminocity)

$\mathcal{L}$ – # particles per unit area per unit time

then the number of particles going through area $d\sigma$ (and scattered into solid angle $d\Omega$) per unit time is

$$dN = \mathcal{L}\, d\sigma = \mathcal{L}\, D(\theta)\, d\Omega$$

So

$$D(\theta) = \frac{1}{\mathcal{L}} \frac{dN}{d\Omega}$$

This is taken as the definition of the differential cross section because it makes reference only to quantities easily measured in the experiment.

As a model to practice let us consider a Coulomb system of charges q_1 and q_2 and masses $m_1 = m$ and $M_2 =$ infinity.

Conservation of energy gives $E = \frac{1}{2} m(\dot r + r^2 \dot\varphi^2) + V(r)$

where $V(r) = \frac{q_1 q_2}{4\pi\varepsilon_0} \frac{1}{r}$

Conservation of angular momentum: $L = m r^2 \dot\varphi$ So $\dot\varphi = \frac{L}{mr^2}$

$$\dot r^2 + \frac{L^2}{mr^2} = \frac{2}{m}(E - V)$$

let $u \equiv \frac{1}{r}$ then

$$\dot r = \frac{dr}{dt} = \frac{dr}{du}\frac{du}{d\varphi}\frac{d\varphi}{dt} =$$

$$= -\frac{1}{u^2}\frac{du}{d\varphi}\frac{L}{m}u^2 = -\frac{L}{m}\frac{du}{d\varphi}$$