# MOLECULAR PROCESSES I

Jimena D. Gorfinkiel
School of Physical Sciences
The Open University

These two sessions

- Focus on electron scattering and theoretical/computational approaches

- What processes are possible for molecules

- Information required

- High energy approaches

- Quantum mechanical basics

- Low energy approaches

- R-matrix method

- Some examples

Molecules make everything more complicate (and more interesting!)

- Additional degrees of freedom mean more processes can take place

- Loss of symmetry means harder to model

- I will focus mainly on electrons as projectiles and calculations

- Which processes are possible depend on the **target** and **projectile** and on the scattering **energy:** let's look at an electron collision
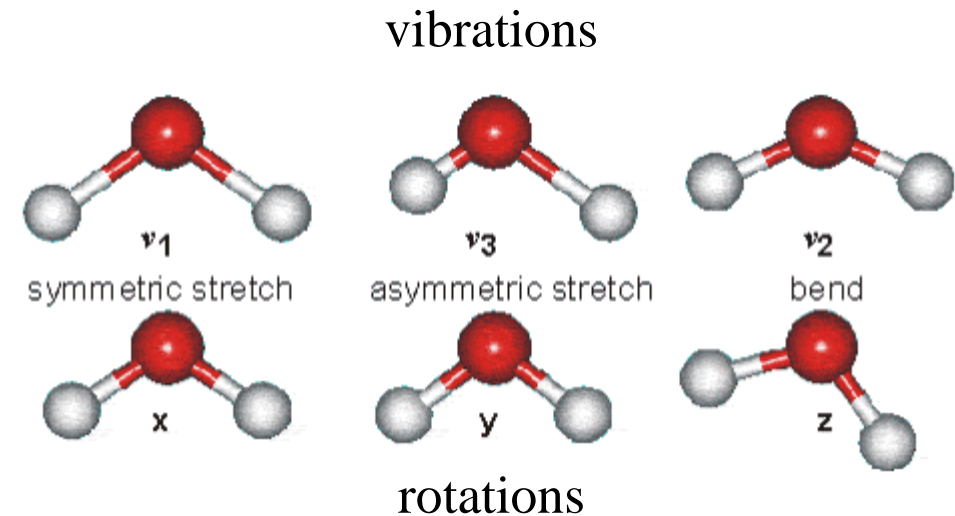
vibrations

symmetric stretch ν_1

asymmetric stretch ν_3

bend ν_2

x

y

z

rotations

Processes

And combinations of these! E.g. vibronic excitation, dissociative ionization and more…

* Dissociative recombination for an ion. Photorecombination also possible

Elastic scattering

$$AB + e \longrightarrow AB + e$$

Rotational excitation

$$AB(J'') + e \longrightarrow AB(J') + e$$

Vibrational excitation

$$AB(v''=0) + e \longrightarrow AB(v') + e$$

Dissociative attachment *

$$AB + e \longrightarrow A^- + B$$

Electronic excitation

$$AB + e \longrightarrow AB* + e$$

Impact dissociation

$$AB + e \longrightarrow A + B + e$$

Ionization

$$AB + e \longrightarrow AB^+ + e + e$$

Ion pair formation

$$AB + e \longrightarrow A^- + B^+ + e$$

Energy

What do the processes entail?

Elastic scattering

$$AB + e \longrightarrow AB + e$$
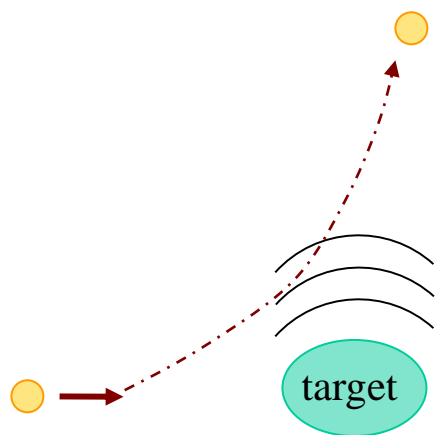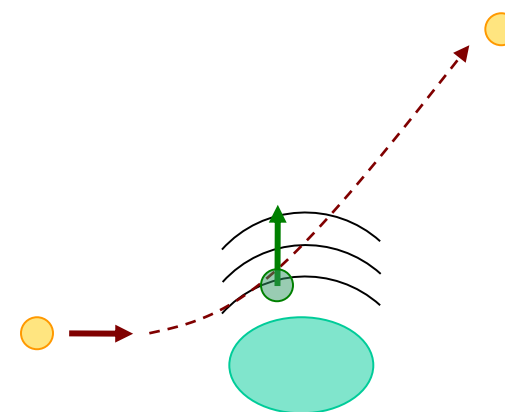
Simplest possible process
Outcome: change in direction of projectile
Occurs for any projectile kinetic energy

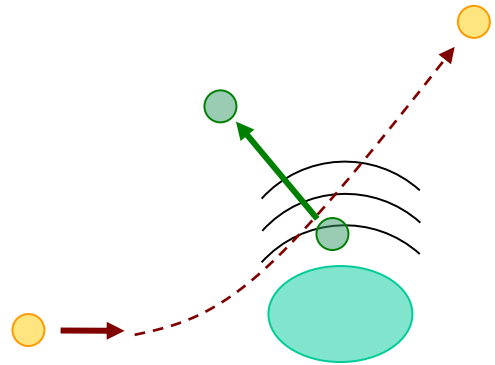**Excitation**

$$AB(J'', v'', i) + e \longrightarrow AB(J,v', j) + e$$

Outcome: change internal state of the target molecule, and kinetic energy and direction of projectile
Different processes have different **thresholds**
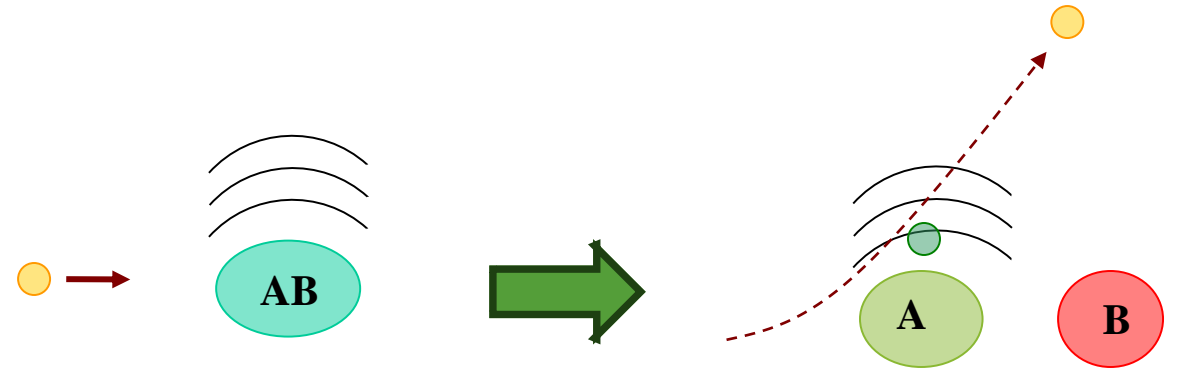
What do the processes entail?

Ionization

$$AB + e \longrightarrow AB^+ + e + e$$

Outcome: target losses one electron, so now 2 electrons in the continuum; kinetic energy and direction of projectile change
Thresholded

Impact dissociation

$$AB + e \longrightarrow A + B + e$$

Outcome: two or more molecular fragments with kinetic energy and direction; kinetic energy and direction of projectile change
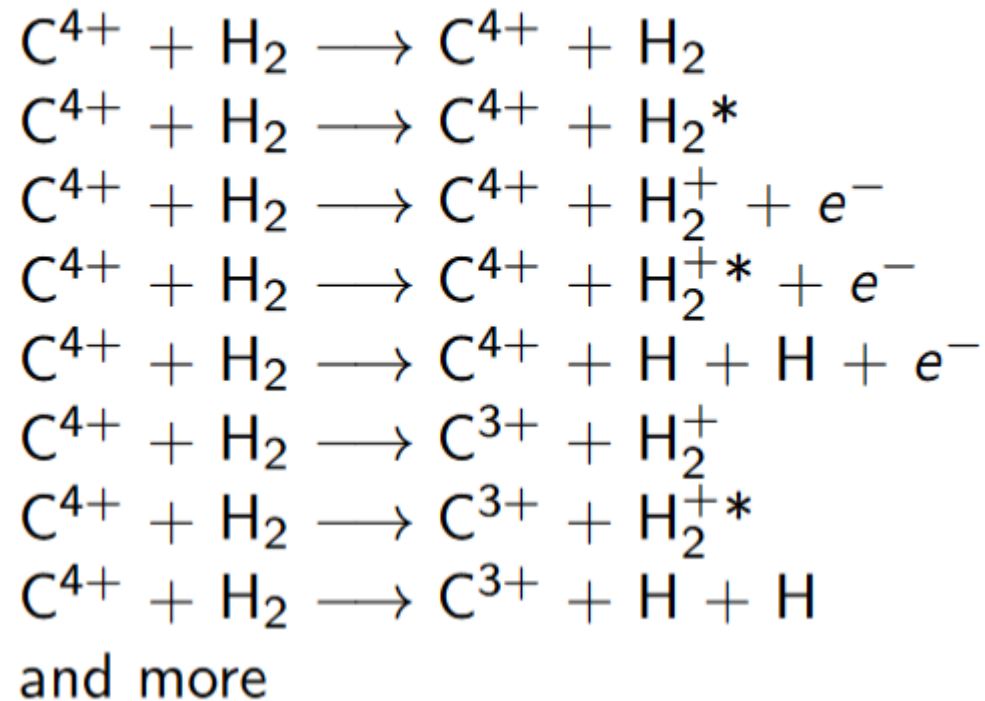Thresholded

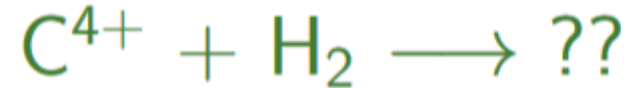# Example: electron scattering from CO

$$CO + e^- \longrightarrow ??$$

Example: electron scattering from CO

$$CO + e^- \longrightarrow ??$$

$CO + e^- \rightarrow CO + e^-$	Elastic Scattering
$CO(j'') + e^- \rightarrow CO(j') + e^-$	Rotational Excitation
$CO(v''=0) + e^- \rightarrow CO(v') + e^-$	Vibrational Excitation
$CO + e^- \rightarrow C + O^-$	Dissociative attachment
$CO + e^- \rightarrow CO^* + e^-$	Electronic Excitation
$CO + e^- \rightarrow C + O + e^-$	Impact dissociation
$CO + e^- \rightarrow CO^+ + e^- + e^-$	Ionisation
$CO + e^- \rightarrow C^+ + O^- + e^-$	Ion pair formation

What if the projectile is an ion?

$$C^{4+} + H_2 \longrightarrow ??$$

$$C^{4+} + H_2 \longrightarrow C^{4+} + H_2$$
$$C^{4+} + H_2 \longrightarrow C^{4+} + H_2*$$
$$C^{4+} + H_2 \longrightarrow C^{4+} + H_2^+ + e^-$$
$$C^{4+} + H_2 \longrightarrow C^{4+} + H_2^+* + e^-$$
$$C^{4+} + H_2 \longrightarrow C^{4+} + H + H + e^-$$
$$C^{4+} + H_2 \longrightarrow C^{3+} + H_2^+$$
$$C^{4+} + H_2 \longrightarrow C^{3+} + H_2^+*$$
$$C^{4+} + H_2 \longrightarrow C^{3+} + H + H$$

and more

Many of the processes induced by electron scattering also take place

Charge transfer!!!

How do we quantify the process?

- Probabilities are normally quantified as cross sections.

- Cross section can be seen as an effective area, normal to the direction of incidence, provided by a target to an incoming projectile. A constant of proportionality between incident and scattered particles. It has units of area.

- Absolute measurements not easy or impossible: radicals, excited targets, etc.. Experiments sometimes provide yields or relative values

- Validation of complete sets through electron swarm data through Boltzmann analysis

- Cross section for each processes that can take place

- We need to specify one or several below:
  - *final internal state of the target, including charge*
  - *kinetic energy of projectile and ejected particle(s)*
  - *direction of projectile and products (ions, neutrals, additional free electrons)*

Integral cross sections

For example, the integral cross section for electronic excitation is the constant of proportionality between the number of incident particles per unit time and area and the number of excited targets produced per unit time.
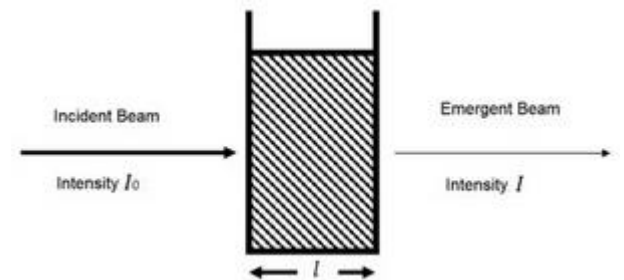
$$\text{Beer-Lambert Law: } I = I_0 e^{\sigma n l}$$

I_0: number of incident particles per unit area ($\perp$ to beam) per unit time

$I(l)$: number of particles lost from the beam

n: number of target particles per unit volume

l length of the interaction path

σ: integral cross sections

Incident Beam

Intensity I_0

Emergent Beam

Intensity I

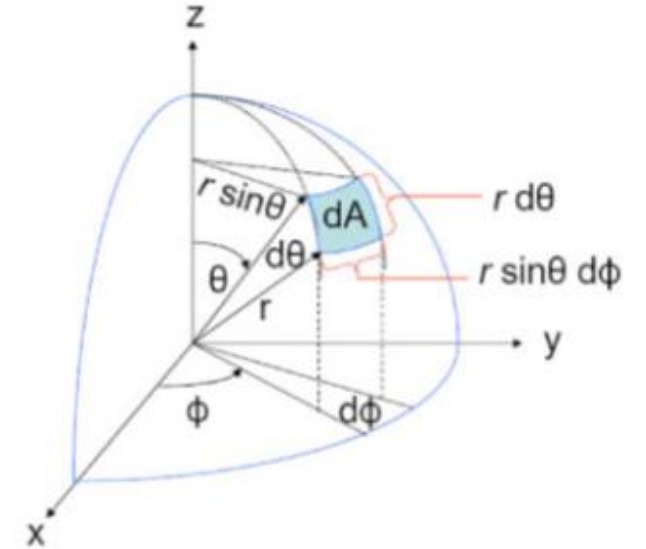$\leftarrow l \rightarrow$

Differential cross sections (DCS)

Particle flux scattered, by each target, into solid angle $d\Omega \sin = \theta d\theta d\phi$ divided by the incoming intensity

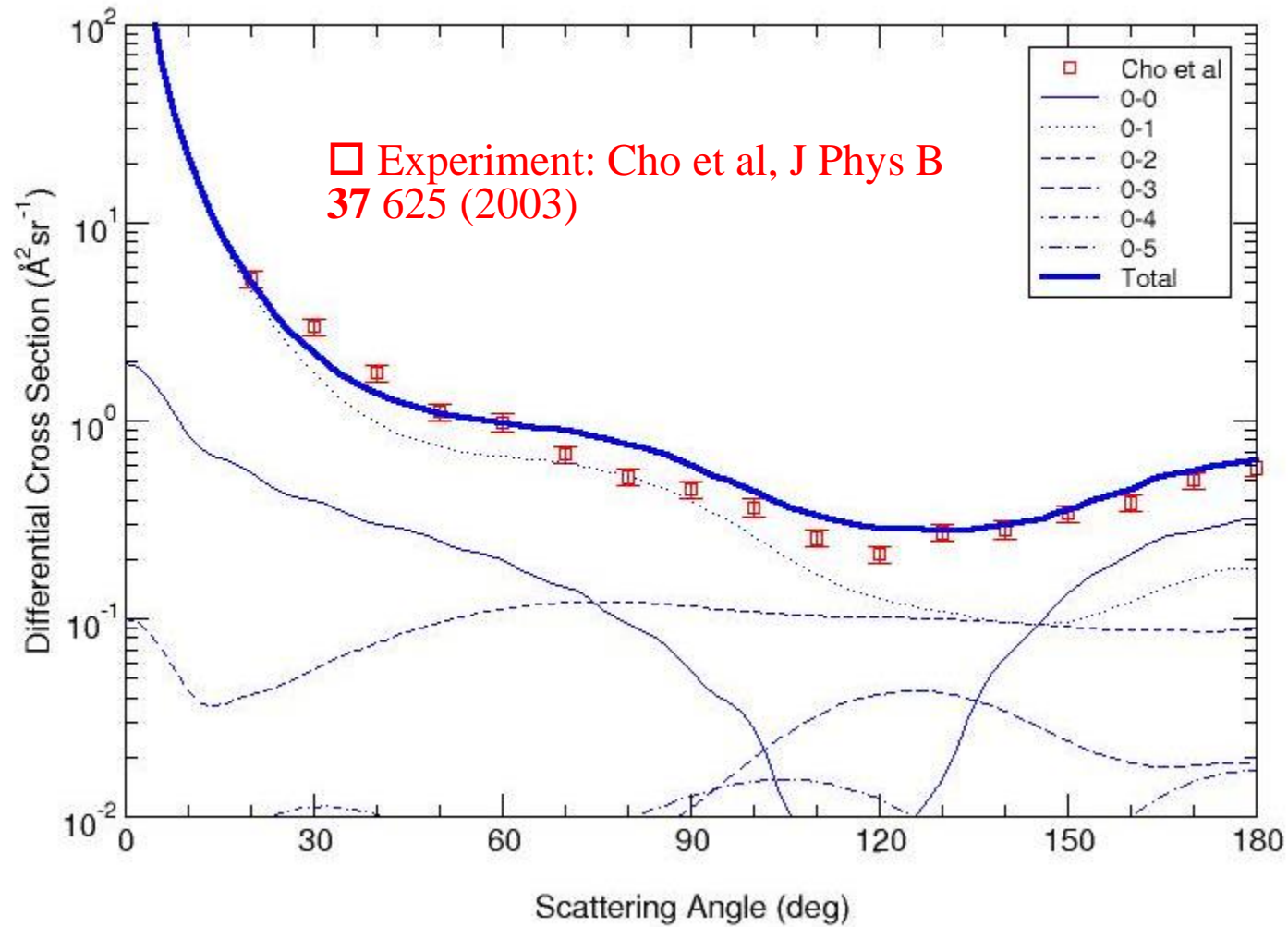$$\frac{I(\theta, \phi)}{I_0} \propto \frac{d\sigma}{d\Omega}(E, \theta, \phi)$$

$$\sigma(E) = \int_\Omega \frac{d\sigma}{d\Omega}(E, \theta, \phi) d\Omega$$

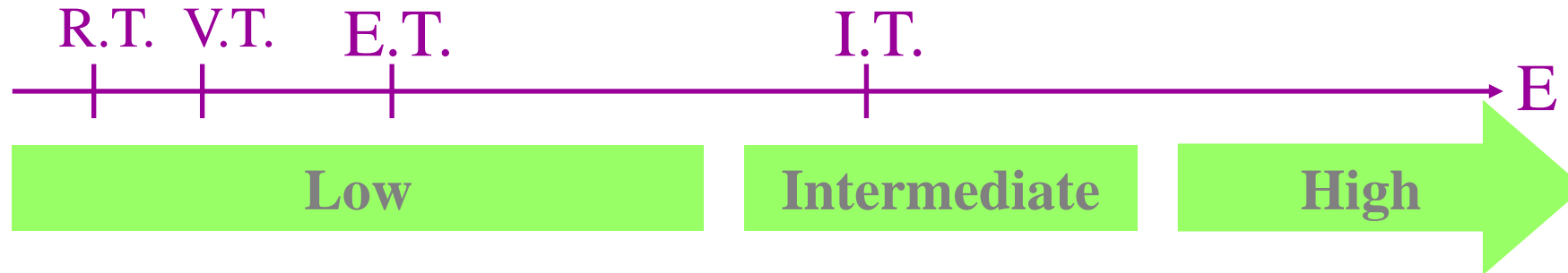$d\sigma/d\,\Omega$ = **differential cross section**

units of area / steradians

DCS example: H_2O, elastic scattering, 4 eV

Experiment: Cho et al, J Phys B **37** 625 (2003)

Faure et al., JPB **37** (2004) 1

How to model electron-molecule scattering?

Different energy regimes have different requirements

- High energies: collisions are effectively impulsive. Simplified calculations are accurate: e.g. use of perturbative methods, neglect of some interactions...
- Low energies: detailed description of the internal state of the target and full quantum mechanical treatment usually required. Approximations usually used.
- Intermediated energies: quantum mechanical methods are too costly to apply. Higher energy approaches sometimes work.

Complete sets are a community effort
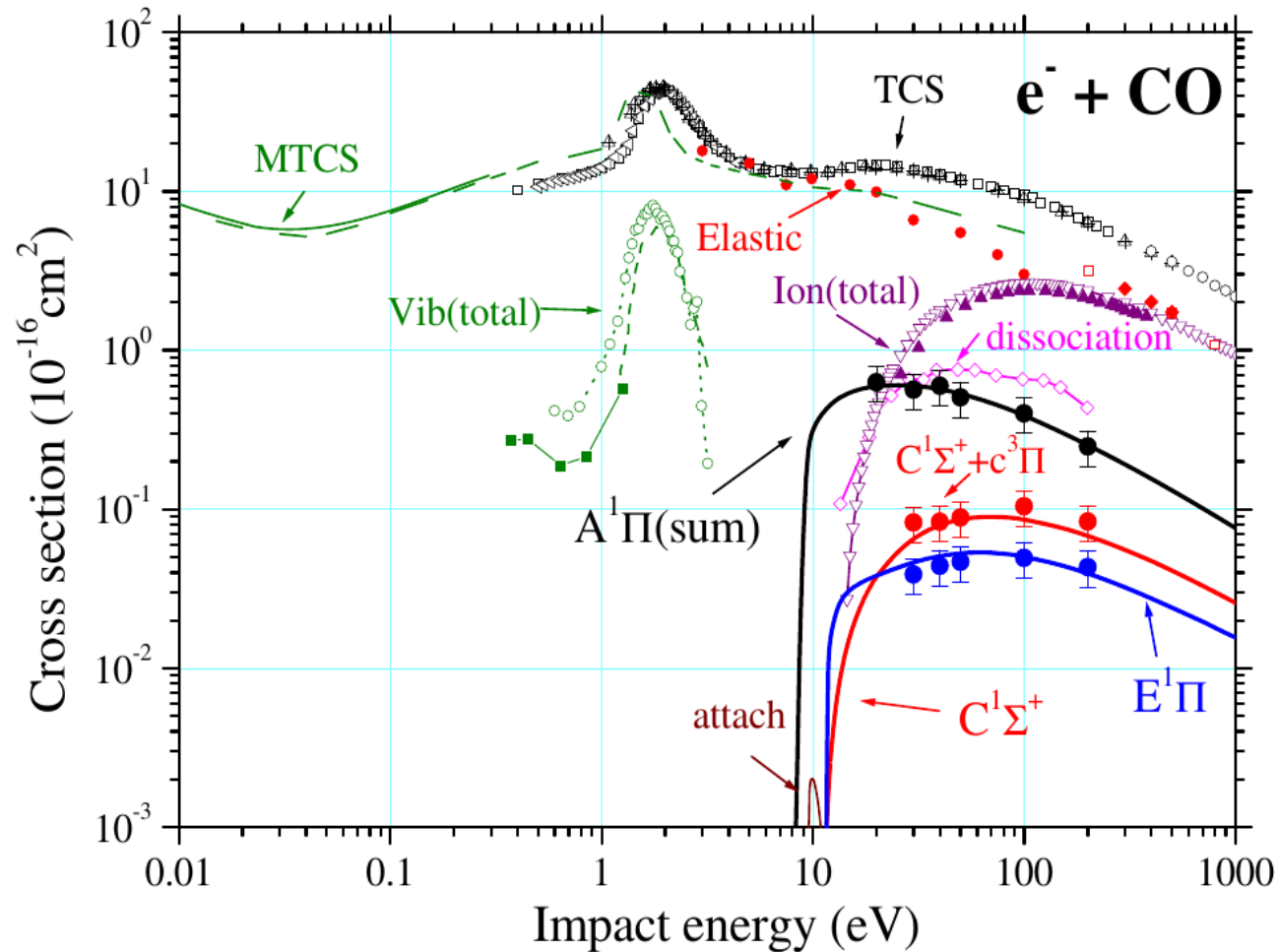
- **MTCS: momentum transfer cross section.** The average momentum transferred by the projectile when it collides

- **TCS:** total cross section

- **Ion:** ionization cross section

- **dissociation:** all dissociation processes

- **attach:** electron attachment

- **A, C, E:** excitation into specific electron states

High-energy electron scattering

- Simplified approaches that lead to analytical expressions

- These depend on:

    - adjustable parameters or

    - calculated or measured quantities: binding energies, oscillator strengths

- Usually tailored to a specific process (electron excitation, ionization, dissociative ionization….)

- Some (e.g. IAM-SCAR, independent atom model with screening corrected additivity rule, Garcia and coll) can model many processes

- We will use diatomic molecules as an example

High-energy: electronic excitation

Many based on high-energy Born cross sections. Valid when interaction is very week (V is very small and one can assume plane wave)

Generalized oscillator strength for a given bondlength

$$\sigma^{\text{Born}}(E) = \frac{2\pi e^2}{a_0 k_i^2} \int_{K_{\min}^2}^{K_{\max}^2} \frac{G(K;\ R)}{\Delta E} d\ln(K^2)$$

Initial momentum $= \sqrt{\dfrac{2mE}{\hbar^2}}$

transferred momentum $= |\boldsymbol{k}_i - \boldsymbol{k}_f|$

$$G(K;\ R) = \frac{2m}{\hbar^2 K^2} \Delta E_{i,j}(R) \int \frac{d\hat{R}}{4\pi} |\langle j| \sum_q e^{(iK \cdot r_q)} |i\rangle|^2$$

for given *i* and *j*

High-energy: electronic excitation

BEf scaling

- Improves lower energy behaviour

- Based on Born plane wave theory; introduces a scaling factor that depends on the binding energy of the electron B and the excitation energy ΔE

- Vibrationally resolved possible

$$\sigma_{\mathrm{BE}}(E) = \frac{E}{E + B + \Delta E} \sigma^{\mathrm{Born}}(E)$$

$$= \frac{E}{E + B + \Delta E} \frac{2\pi e^2}{a_0 k_i^2} \int_{K_{\min}^2 = (ki-kf)^2}^{K_{\max}^2 = (ki+kf)^2} \frac{G(K; R)}{\Delta E} d \ln(K^2)$$

G(K; R) is hard to calculated so employ a simplified expression with adjustable parameters f_m

$$G(x) = \frac{1}{(1 + x)^6} \left[\sum_{m=0}^{\infty} \frac{f_m x^m}{(1 + x)^m} \right]$$

High-energy: electronic excitation

Dipole-Born approximation

- Expressing generalized oscillator strength as a power series in K and retaining only first order (dipole) leads to simplified expression:

$$\sigma^{\text{Born}}(E) = \frac{8\pi}{3a_0^2 k_i^2} |<v_f|D_{i,j}(R)|v_i>|^2 \ln \frac{k_f + k_i}{|k_f - k_i|}$$

Converges to the right experimental behaviour at very high E

e x $D_{i,j}$ (R) = $M_{i,j}$ (R) electronic transition dipole

υ Indicate vibrational wavefunctions

Can be further simplified, so that behaviour as a function of E is improved for example:

$$\sigma^{\text{Born}}(E) = \frac{4\pi}{3a_0^2 k_i^2} |<v_f|D_{i,j}(R)|v_i>|^2 \ln \frac{4IE}{\Delta E^2}$$

I : ionization potential

High-energy: ionization

- Several approaches, many originating in the Thomson classical cross section

$$\sigma^{\text{ion}}(E) = \sum_i \sigma_i(E) = \sum_i 4\pi a_0^2 N_i \left(\frac{Ry}{B}\right)^2 f(E/B) \text{ with } f(E/B) = \frac{E/B - 1}{(E/B)^2}$$

- Gryzinski method

- Universal function method

- Deutsch-Mark (DM) formalism

- Binary encounter approaches that combine high and lower energy earlier methods

High-energy: ionization

Binary-encounter-Bethe (BEB) model

- https://physics.nist.gov/PhysRefData/Ionization/intro.html
- Expression for singly differential cross sections also available

$$\sigma_{\mathrm{BEB}} = \frac{S}{t + (u+1)/n} \left[\frac{Q \ln t}{2} \left(1 - \frac{1}{t^2} \right) + (2 - Q) \left(1 - \frac{1}{t} - \frac{\ln t}{t+1} \right) \right]$$

B= orbital binding energy

U= orbital kinetic energy

T= scattering electron's kinetic energy

$t = T/B$ $u = U/B$

n=1 for neutral molecules, 2 if singly charged molecular ions

$S = 4\pi a_0^2 N (Ryd/B)^2$ N= occupation number

Q can be approximated to 1 or calculated from the oscillator strength

An example of BEB

From NIST website:

e^- on H_2O

| Data set	Source
——	BEB Y.-K. Kim and M.E. Rudd, Phys. Rev. A **50**, 3954 (1994); W. Hwang, Y.-K. Kim and M.E. Rudd, J. Chem. Phys. **104**, 2956 (1996); and Y.-K. Kim and M.E. Rudd, Comments At. Mol. Phys. **34**, 293 (1999).
●	N. Lj. Duric, I. M. Cadez, and M. V. Kurepa, Int. J. Mass. Spectrom. Ion Processes **83**, R7 (1988).
■	J. Schutten, F. J. de Heer, H. R. Moustafa, A. J. H. Boerboom and J. Kistenmaker, J. Chem. Phys. **44**, 3924 (1966).
◆	M. A. Bolorizadeh and M. E. Rudd, Phys. Rev. A **33**, 882 (1985).
▲	M. V. V. S. Rao, I. Iga and S. K. Srivastava, J. Geophys. Res. **100**, 26421 (1995).
✳	S. P. Khare and W. J. Meath, J. Phys. B **20**, 2101 (1987), and references therein (theory).
▼	H. C. Straub, B. G. Lindsay, K. A. Smith, and R. F. Stebbings, J. Chem. Phys. **108**, 109 (1998).
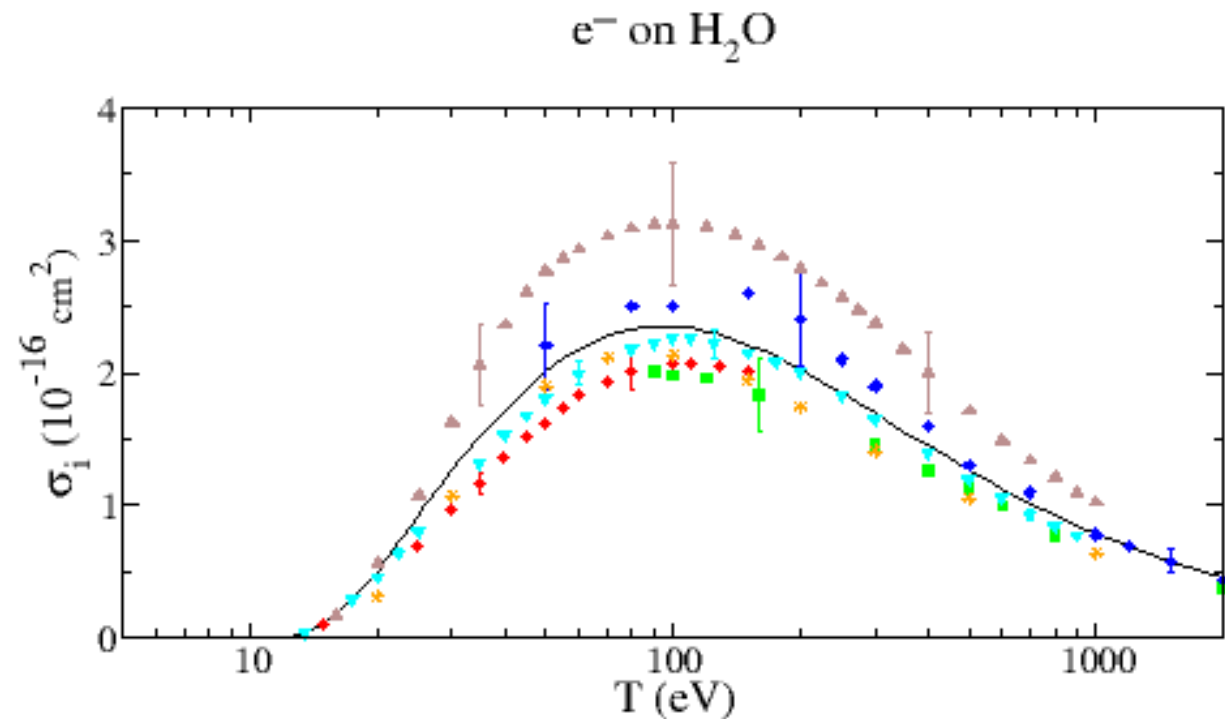
Mol. Orbital	B (eV)	U (eV)	N	Q
$2a_1$	36.88	70.71	2	1
$1b_2$	19.83	48.36	2	1
$3a_1$	15.57	59.52	2	1
$1b_1$	12.61	61.91	2	1

B: Binding Energy
U: Average Kinetic Energy
N: Electron Occupation Number
Q: Dipole Constant

More BEB ionization cross sections

- Cross sections have a similar shape with a maximum around 100-200 eV
- Different lines correspond to different calculated input parameters
- Agreement with experiment is very good
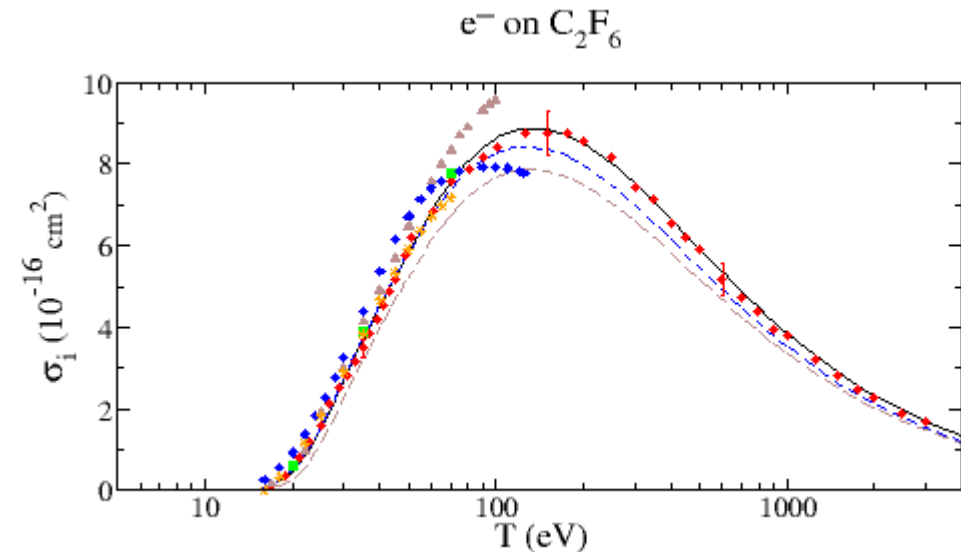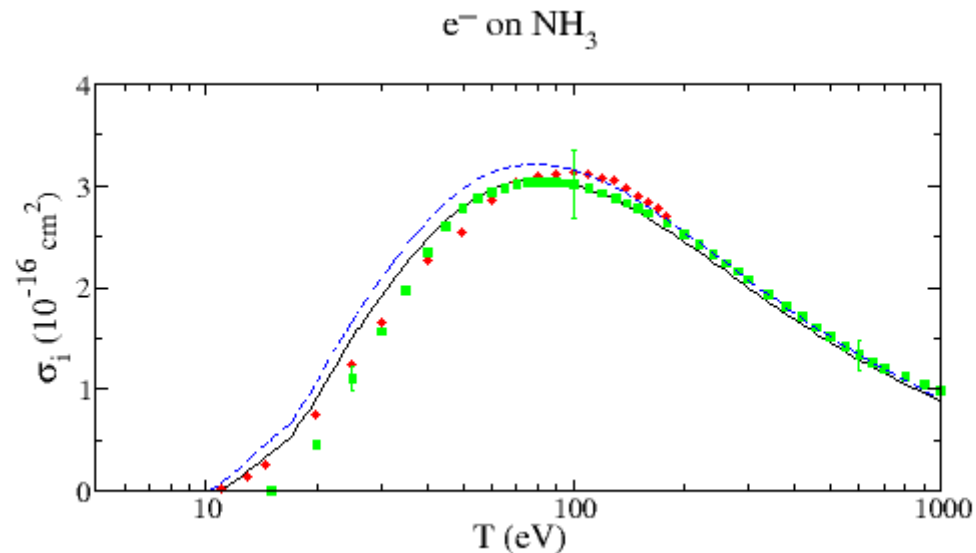
Quantum mechanical treatment

Let's look at a simple system:

- ▶ two particles with masses m_1 and m_2 so $\mu = \frac{m_1 \, m_2}{m_1 + m_2}$
- ▶ particles interacting through a potential $V(r)$ where r is the distance between the particles. This is a **central** or **spherically symmetric** potential.
- ▶ **no external forces are acting on the system.**
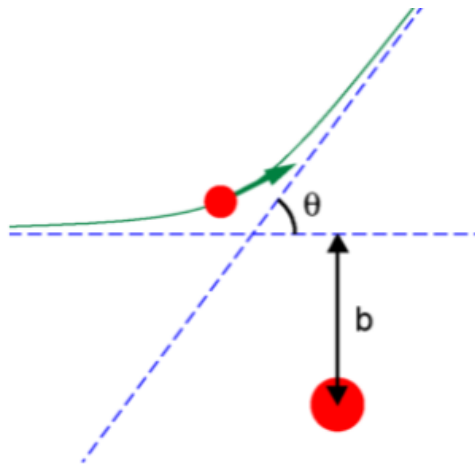
incident particle along z

Cylindrical symmetry: no dependence on ϕ of cross sections

Quantum mechanical treatment

Scattering processes can be studied using the time-independent Schrödinger equation

$$\underbrace{\left(-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right)}_{\hat{H}} \Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

$\Psi(\mathbf{r})$ is the wavefunction that describe the system (internal motion)
E is the energy of this motion (K.E. of C.M. excluded)

Example: H

In this case reduced mass $\mu \approx m_e$

$$V(r) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}$$ or, in atomic units $$V(r) = -\frac{1}{r}$$

Example: H (e^- + H^+ collision)

► If $E < 0$; $\Psi_{nlm}(\mathbf{r})$ with associated discrete eigenvalues:

$$E = -\frac{1}{2n^2}$$

correspond to the 1s, 2s, 2p, 3p...states of H. Also:

$$\int_{allspace} |\Psi_{nlm}(\mathbf{r})|^2 dV = 1 \qquad \text{assuming } \Psi_{nlm} \text{ is normalized}$$

► If $E > 0$: $\Psi_{Elm}(\mathbf{r})$ are associated to a continuum spectrum for E and correspond to $e^- + H^+$. Also:

$$\int_{allspace} |\Psi_{Elm}(\mathbf{r})|^2 dV \qquad \text{diverges}$$

Quantum mechanical treatment

The asymptotic boundary condition for a scattering process :

$$\Psi(\mathbf{r}) \overset{r \to \infty}{\longrightarrow} \underbrace{e^{ikz}}_{} + \underbrace{f(\theta)\frac{e^{ikr}}{r}}_{}$$

incident particles   scattered particles
plane wave   spherical waves
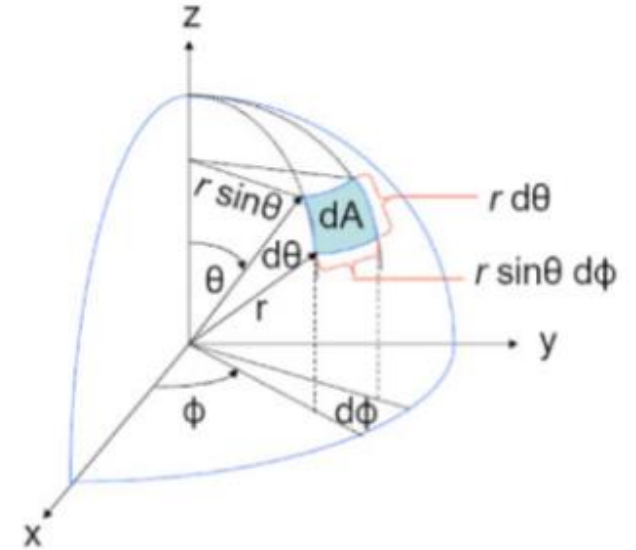
with $k = \frac{\sqrt{2\mu E}}{\hbar}$.

$f(\theta)$ is the **scattering amplitude** that contains all the information about the collision. It can be shown:

$$\frac{d\sigma}{d\Omega}(E, \theta, \phi) = |f(\theta)|^2$$

Angular behaviour

The Schrödinger equation is separable in spherical coordinates:

$$\nabla^2 = r^2\left(\frac{\partial}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \underbrace{\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]}_{L^2}$$

The eigenfunctions of L^2 are *spherical harmonics*:

$$L^2 Y_{lm}(\theta,\phi) = l(l+1) Y_{lm}(\theta,\phi)$$

$Y_{lm}(\theta,\phi) = N_{lm} P_l^{|m|}(\cos\theta)e^{im\phi}$ l and m angular and magnetic momentum quantum numbers

Any function that depends on θ and ϕ can be expressed as a liner combination of Y_{lm}.

Radial equation

$$\Psi(\mathbf{r}) = R(r)\, Y_{lm}(\theta, \phi)$$

For the radial part of the wave function:

$$\frac{d^2 R_l}{dr^2} + \frac{2}{r}\frac{dR_l}{dr} - \left(\frac{l(l+1)}{r^2} + \frac{2\mu}{\hbar^2}V(r)\right)R_l = ER_l$$

Setting $U(r) = \frac{2\mu}{\hbar^2}V(r)$ and $R_l(r) = \frac{S_l(r)}{r}$

$$\frac{d^2 S_l}{dr^2} - \left(\frac{l(l+1)}{r^2} + U(r) - k^2\right)S_l = 0$$

$S_l(r)$ must satisfy the boundary condition so $R_l(r)$ is well behaved:

$$S_l(r) = 0 \qquad \text{at} \qquad r = 0$$

Partial wave expansion

We know the form of the solutions:

$$\Psi(\mathbf{r}) = \sum_{l=0}^{\infty} \frac{S_l(r)}{r} Y_{lm}(\theta, \phi)$$

In our case $\Psi(\mathbf{r})$ does not depend on ϕ so:

$$\Psi(\mathbf{r}) = \sum_{l=0}^{\infty} d_l \frac{S_l(r)}{r} P_l(\cos \theta)$$

$P_l(\cos \theta)$: Legendre polynomials of degree l
d_l: coefficients to be determined (using boundary condition)
$S_l(r)$ solution to radial Schrödinger equation.
It is known as the lth **partial wave**. Partial wave expansion used
for non-spherically symmetric problems too.

Quantum mechanical treatment

In our case, asymptotically:

$$\frac{S_l(r)}{r} = R_l(r) \xrightarrow{r \to \infty} c_l \left[j_l(kr) + b_l n_l(kr) \right]$$

$j_l(kr)$: spherical Bessel function of order l
$n_l(kr)$: spherical Neumann function of order l
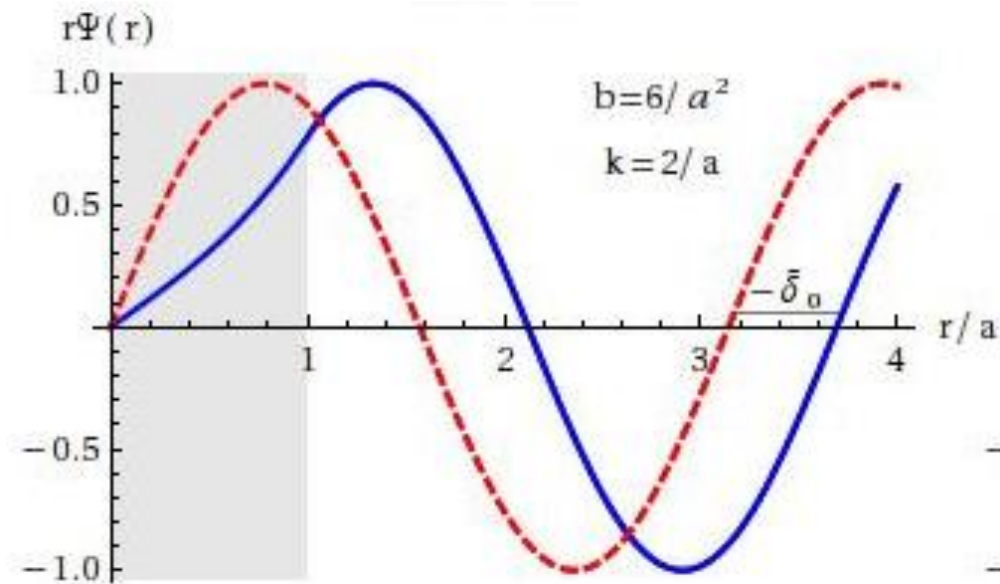It can be shown that one can therefore write

$$R_l(r) \xrightarrow{r \to \infty} \frac{1}{r} \sin(kr - -\frac{1}{2}l\pi + \eta_l)$$

η_l is the **phase shift** of the lth partial wave. Matching:

$$\sum_{l=0}^{\infty} d_l \frac{S_l(r)}{r} P_l(\cos\theta) \xrightarrow{r \to \infty} \sum_{l=0}^{\infty} \frac{d_l}{r} \sin(kr - \frac{1}{2}l\pi + \eta_l) P_l(\cos\theta)$$

Quantum mechanical treatment

Phase shift

We can derive an expression for $f(\theta)$ in terms of the η_l

$$f(\theta) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)e^{i\eta_l}\sin(\eta_l)P_l(\cos\theta)$$

Quantum mechanical treatment

$$\frac{d\sigma}{d\Omega}(E, \theta, \phi) = |f(\theta)|^2$$

$$\sigma(E) = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l + 1) \sin^2 \eta_l$$

- ► Partial wave expansion converges more rapidly at low energies: just a few l required. Centrifugal barrier increases with l: more energy needed to overcome it.

- ► Converges when

$$V(r) \propto \frac{A}{r^p} \qquad \text{with } p > 2 \qquad \text{as} \qquad r \to \infty$$

- ► At very low energies, s-wave scattering

- ► Partial wave expansion can be impractical at higher energies