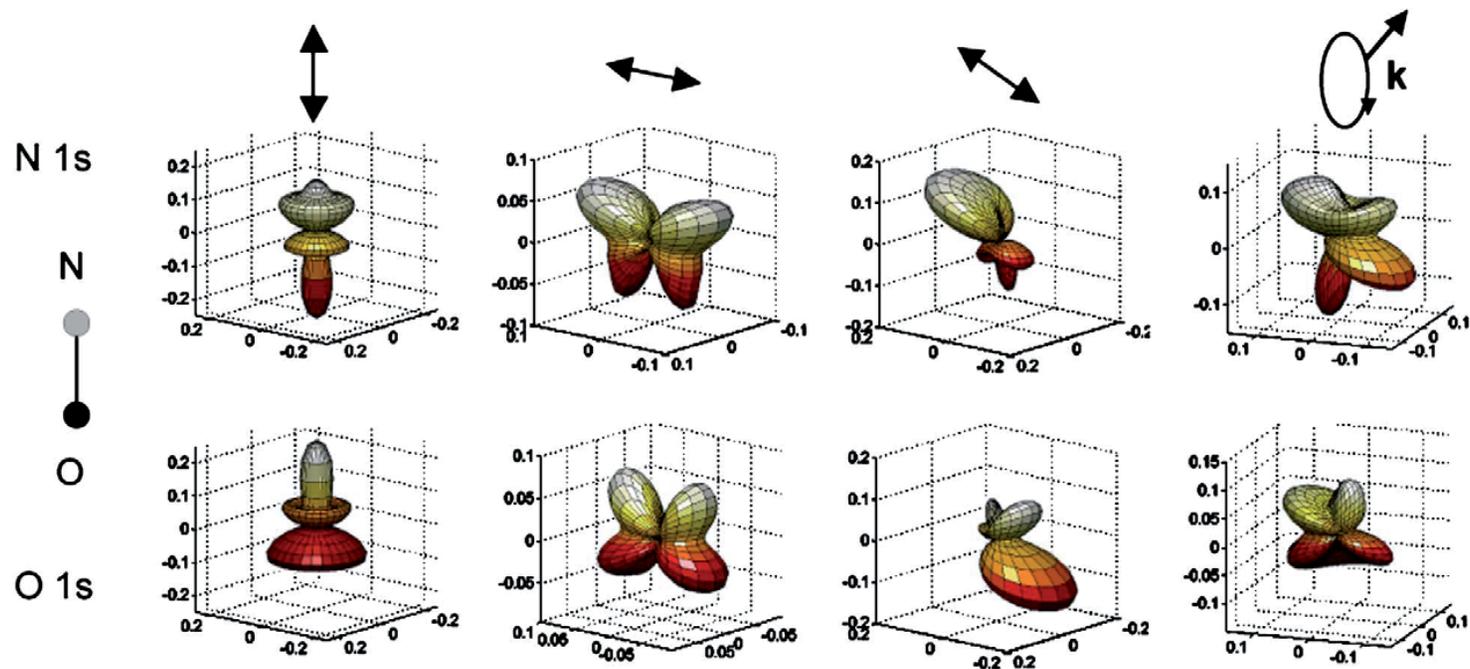


Photoelectron Angular Distributions Seminar Series

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W. B. Li, R. Montuoro, J. C. Houver, L. Journal, A. Haouas, M. Simon, R. R. Lucchese and D. Doweck, Physical Review A (Atomic, Molecular, and Optical Physics), **75** 052718 2007.

contents/aims

Part I - Very Brief Introduction to Scattering Theory

- Scattering theory overview (stationary-state picture).
- Partial wave expansion.
- Radial continuum wavefunctions for Coulombic and non-Coulombic potentials.
- The importance of the scattering phase shift.

Part II - Very Brief Introduction to Angular Momentum

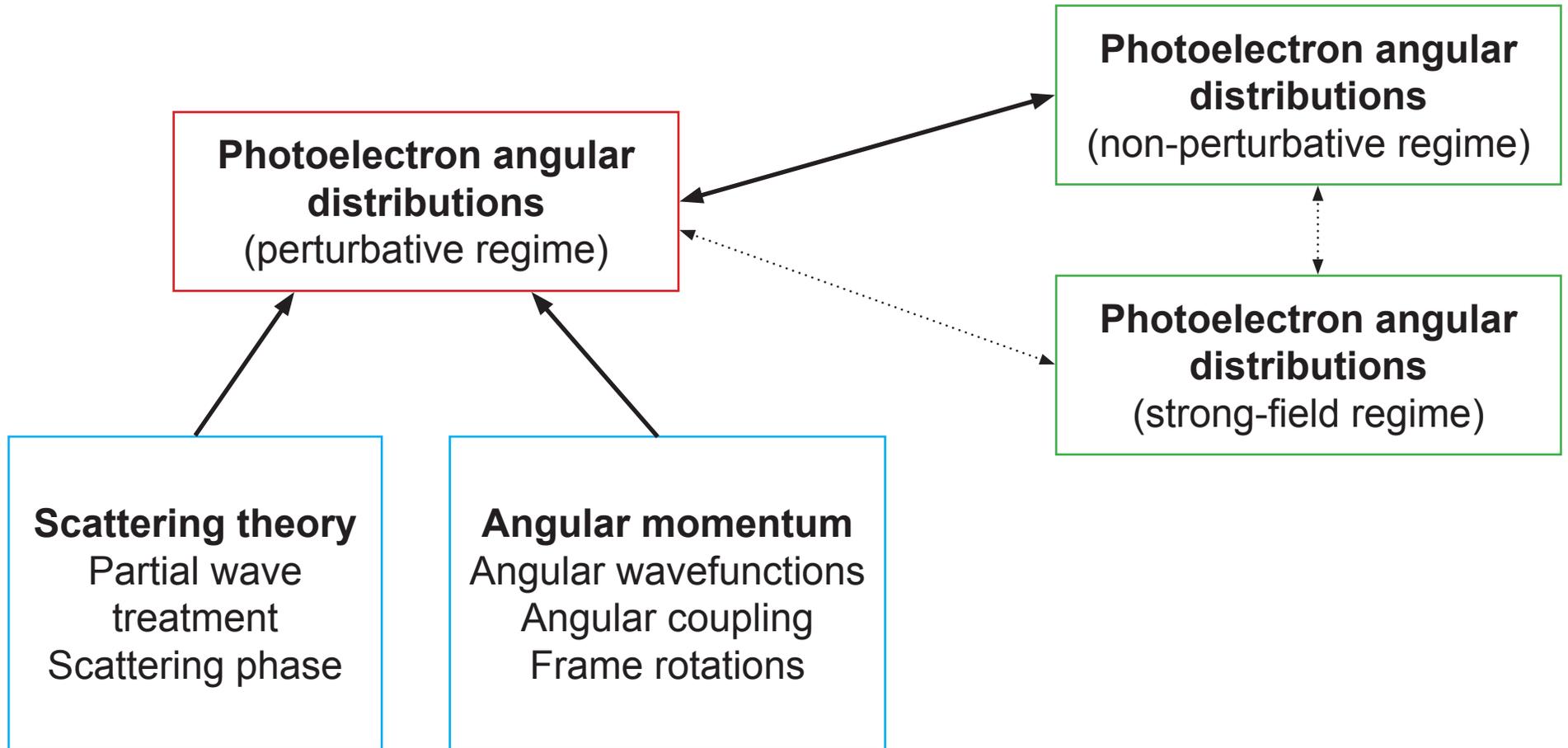
- Angular momentum overview - what is angular momentum?
- Angular momentum wavefunctions - the spherical harmonics.
- Angular momentum coupling - Clebsch-Gordan coefficients and Wigner $3j$ symbols.
- Transformation under rotation - rotation matrix elements.
- Angular part of the scattering problem.

Part III - Very Brief Introduction to Photoionization & Photoelectron Angular Distributions

- Dipole approximation, dipole matrix elements, explicit formulation of matrix elements from bound and continuum wavefunctions.
- Integrated and differential cross-sections, including exact result for 1-electron system (Cooper & Zare).
- Examples of PADs from atomic systems, in particular case of O^- photodetachment and s-d wave interference.
- Examples of PADs from molecular systems - case of many partial wave components due to non-central potentials, l-mixing/scattering etc.

Written notes will be available at the end of the seminars!

background road map

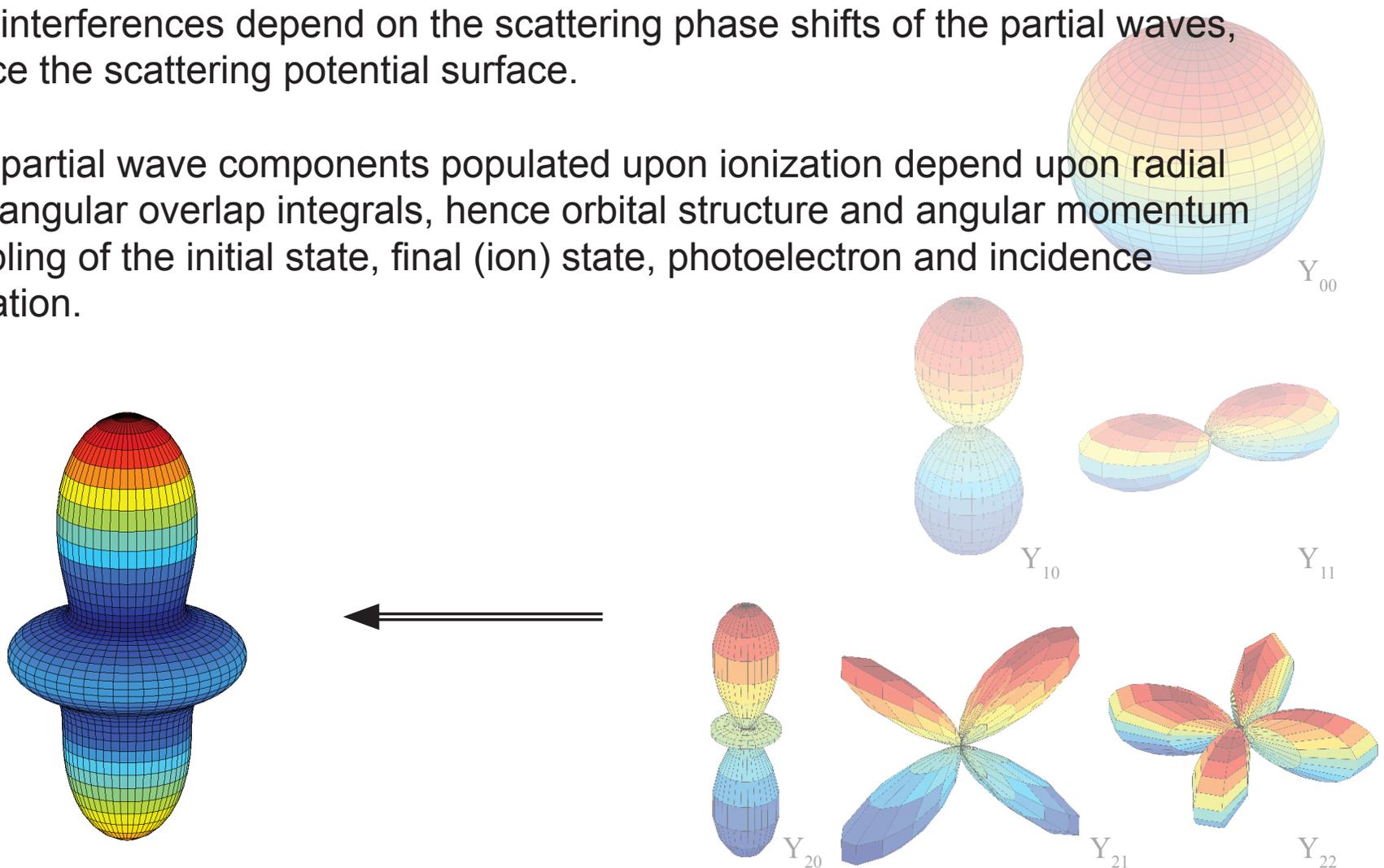


preview...

Photoelectron angular distributions (PADs) are angular interference patterns arising from interference between different partial wave components of the photoelectron wavefunction.

The interferences depend on the scattering phase shifts of the partial waves, hence the scattering potential surface.

The partial wave components populated upon ionization depend upon radial and angular overlap integrals, hence orbital structure and angular momentum coupling of the initial state, final (ion) state, photoelectron and incidence radiation.



overview of scattering

Scattering from a point target

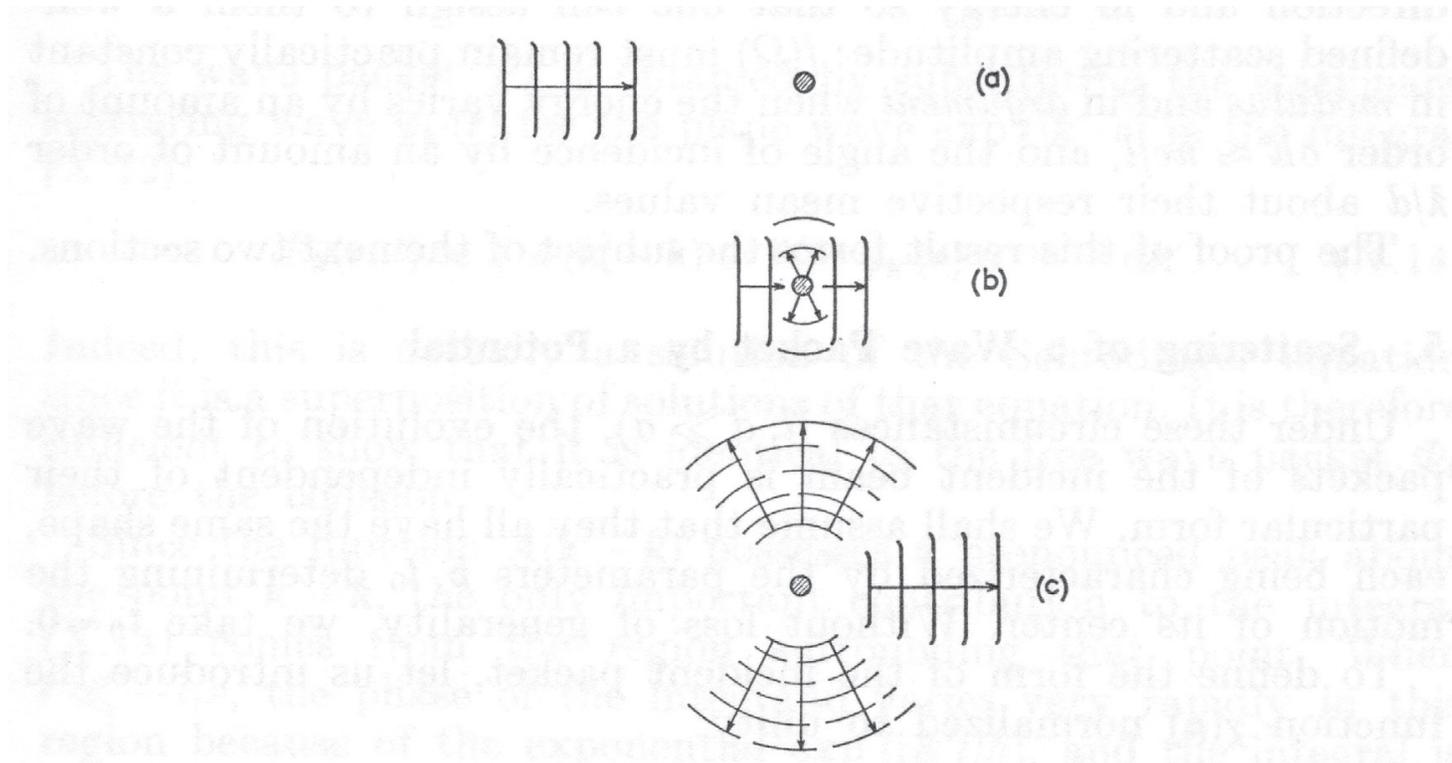
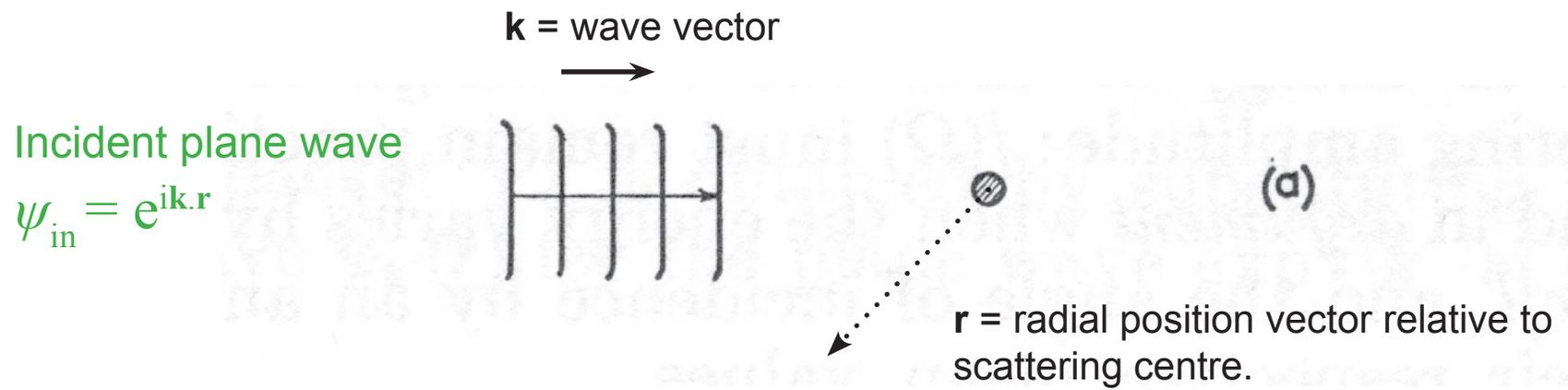


Fig. X.2. Stages of the scattering phenomenon of a wave packet: (a) before collision; (b) during collision; (c) after collision.

incident wave



transmitted wave

Transmitted plane wave

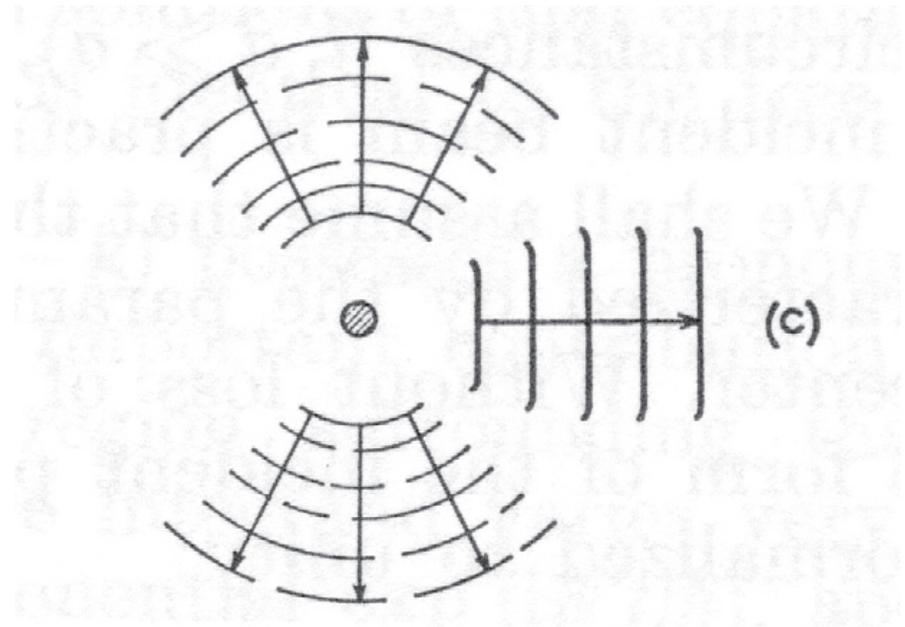
$$\psi_t = e^{ik \cdot r}$$

Scattered spherical wave

$$\psi_s = (e^{ikr}/r) f(\theta, \phi)$$



Scattering amplitude



scattering theory

Stationary scattering state:

$$\Phi = \psi_{incident} + \psi_{transmitted} + \psi_{scattered}$$

In the region of the scattering centre the exact form of these functions may be very complicated, reflecting the precise details of the scattering centre.

However, asymptotically, as $r \rightarrow \infty$, these functions must reflect a plane wave and a spherical scattered wave:

$$\Phi(\mathbf{r}) \xrightarrow{r \rightarrow \infty} A \left[e^{i\mathbf{k}\cdot\mathbf{r}} + \int_k (\theta, \phi) \frac{e^{ikr}}{r} \right]$$

scattering theory definitions

The differential, or angle-resolved, scattering cross-section is given by:

$$\frac{d\sigma}{d\Omega} = \left| \underset{k}{f}(\theta, \phi) \right|^2$$

The total, angle-integrated cross-section is given by:

$$\sigma = \int \frac{d\sigma}{d\Omega} d\Omega = \int_0^\pi \int_0^{2\pi} \left| \underset{k}{f}(\theta, \phi) \right|^2 \sin \theta d\theta d\phi$$

So, we want to understand $\underset{k}{f}(\theta, \phi)$

scattering theory summary

The main task in scattering theory is to apply these very general results to a specific problem of interest, and determine the functional form of $f_k(\theta, \phi)$.

This will depend on the boundary conditions imposed on the scattering system, and the precise details of the scattering centre.

References for scattering theory:

Atkins, Molecular Quantum Mechanics - Short treatment of scattering.

Rae, Quantum Mechanics - Short treatment.

Messiah, Quantum Mechanics (Vol. 1) - Longer treatment, very good source.

Rodberg & Thaler, Introduction to the Quantum Theory of Scattering - Comprehensive!

partial wave expansion

The time-independent Schrödinger equation for scattering can be written:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + U(r) \right] \Phi(\mathbf{r}) = E\Phi(\mathbf{r})$$

It will turn out that by using spherical polar coordinates this can be written in terms of radial and angular components, and solved in terms of radial functions and angular functions.

partial waves - angular part

Expand kinetic energy operator in spherical polars:

$$\begin{aligned}\nabla^2 &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \\ &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{1}{\hbar^2 r^2} \hat{L}^2(\theta, \phi)\end{aligned}$$

This is the angular part of the expansion.

Angular momentum operator (to be discussed further next time).
Eigenfunctions given by spherical harmonics:

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

partial waves - radial part

Solutions to the radial part of the scattering SE are more complicated. They must satisfy the equation:

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

Effective potential

Kinetic energy

Radial eigenfunctions

partial waves - effective potential

Centrifugal barrier

Angular momentum dependent

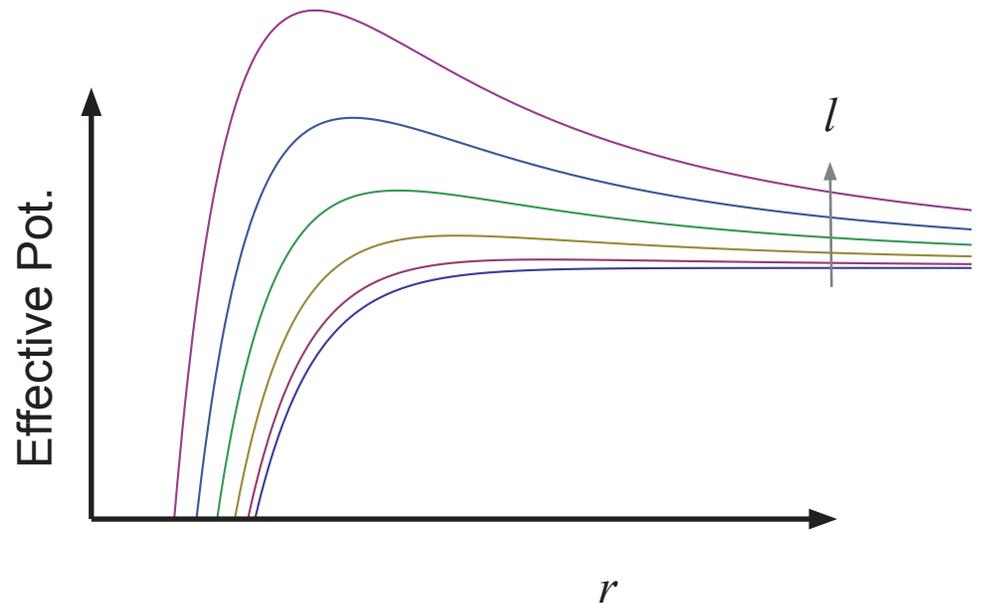
Scattering potential

$$k^2 - \frac{l(l+1)}{r^2} - \frac{2m}{\hbar^2}U(r)$$

Momentum (scalar)

Energy dependent

Effective potential for scattering mixes angular quantum numbers with radial potential.



partial waves - general form

Putting the radial and angular solutions together gives:

$$\Phi(\mathbf{r}) = \sum_{lm} A_l \chi_l(r) Y_{lm}(\theta, \phi) = \sum_{lm} \psi_{lm}(\mathbf{r})$$

Partial waves

l-dependent pre-factor

Radial eigenfunctions

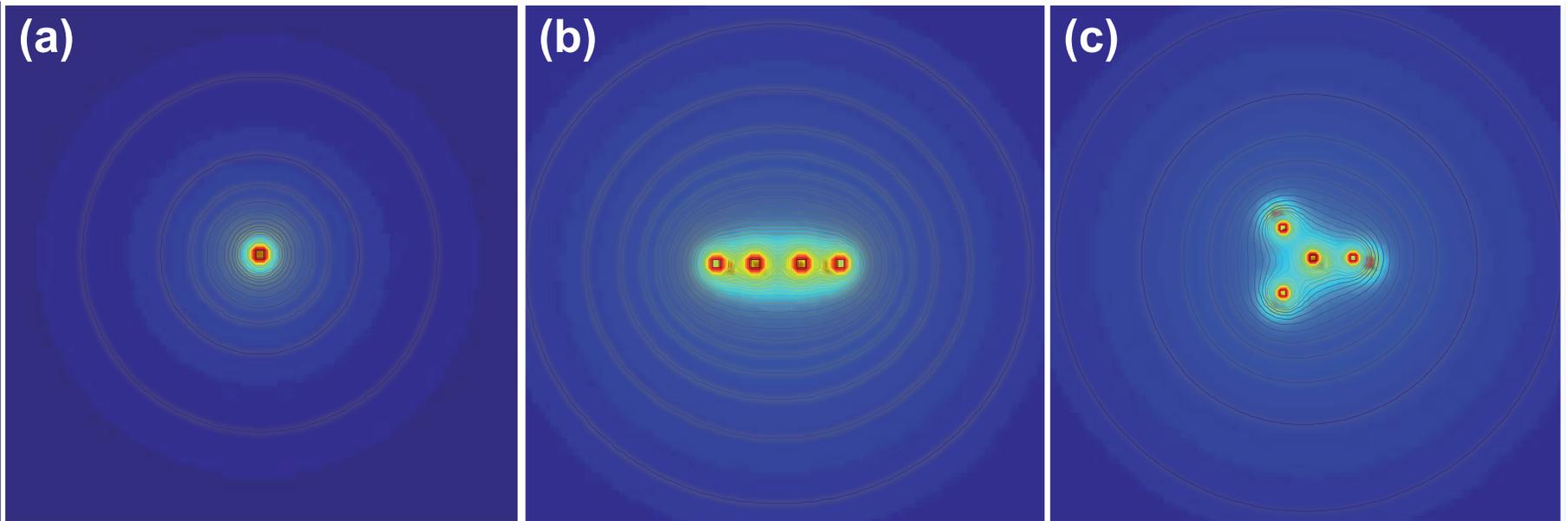
Angular eigenfunctions

In the asymptotic limit each partial wave is an independent scattering channel.

radial eigenfunctions

Q: What do $\chi_l(r)$ look like?

A: Depends on potential...



Coulombic

$$U(r) \propto Z_1 Z_2 / r$$

Non-coulombic... but can describe as Coulombic (long-range) part plus short range part

$$U(r \geq r_c)$$

$$U'(r < r_c)$$

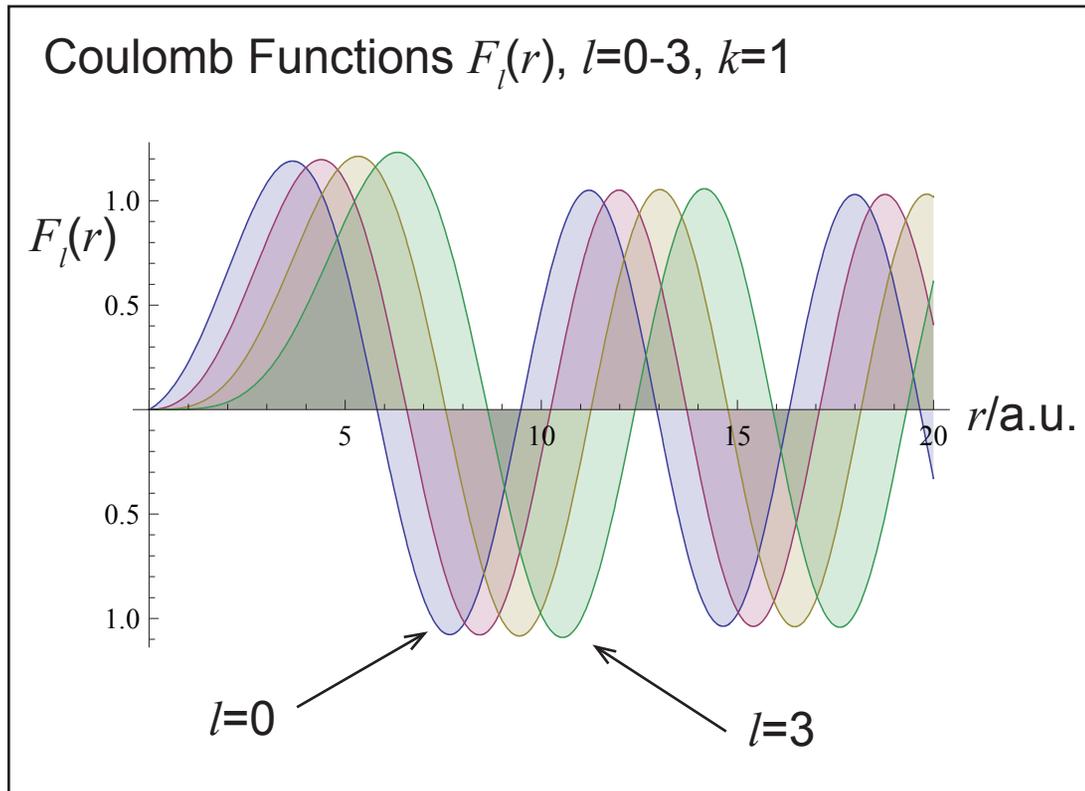
radial eigenfunctions - coulombic

Solutions given by (**regular**) **Coulomb functions** $F_l(r)$:

$$\chi_l(r) = F_l(r) \xrightarrow{r \rightarrow \infty} \sin \left[kr - \frac{\pi l}{2} - \frac{Z_1 Z_2}{k} \ln(2kr) + \sigma_l \right]$$

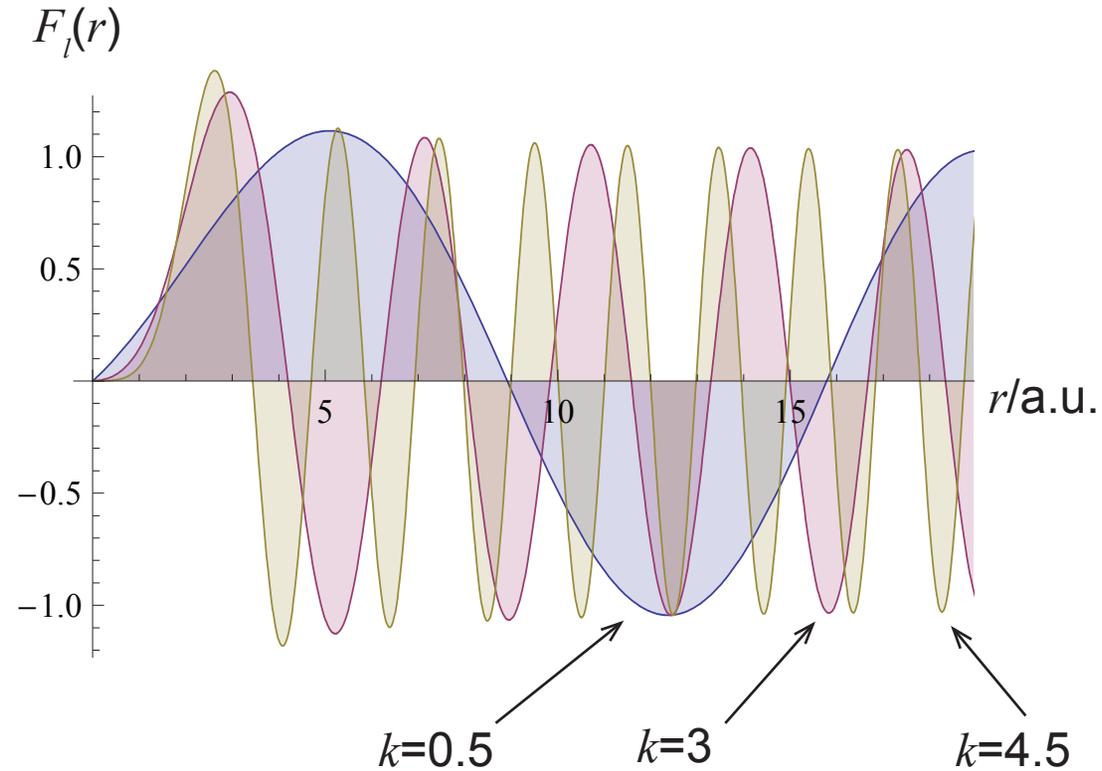
Coulomb phase

$$\sigma_l = \arg \Gamma \left[l + 1 - i \frac{Z_1 Z_2}{k} \right]$$

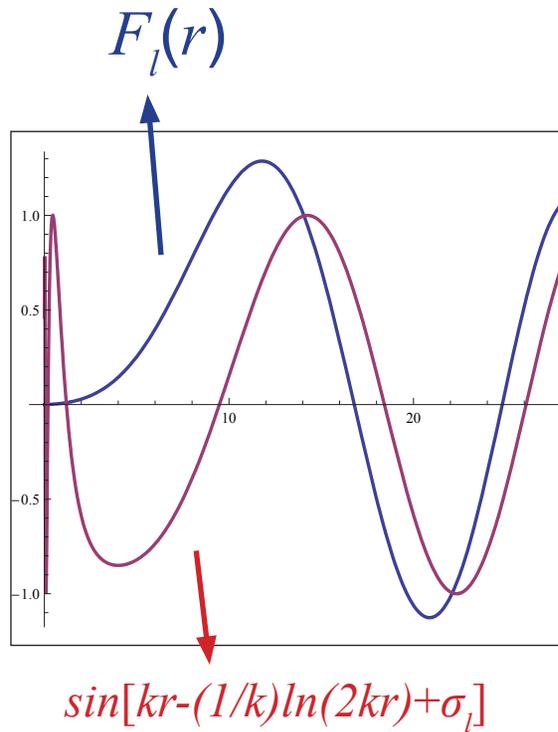


radial eigenfunctions - coulombic

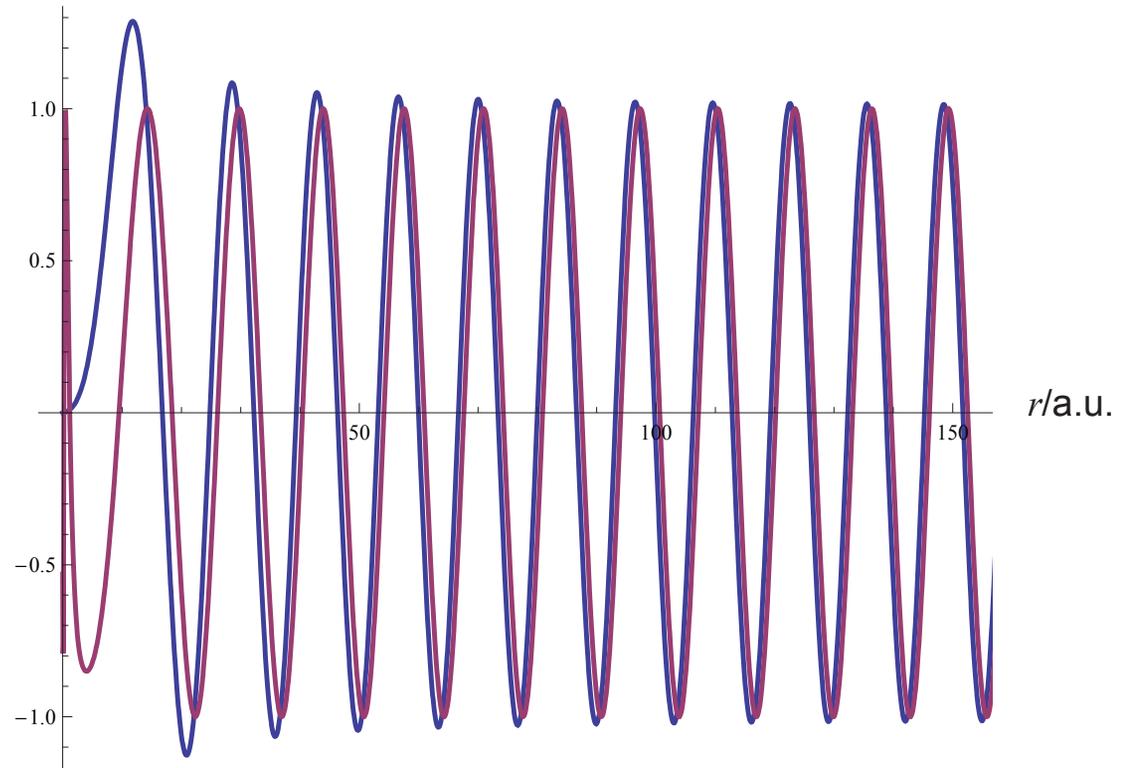
Coulomb Functions $F_l(r)$, $l=0$, $k=0.5, 3, 4.5$ a.u.



radial eigenfunctions - coulombic

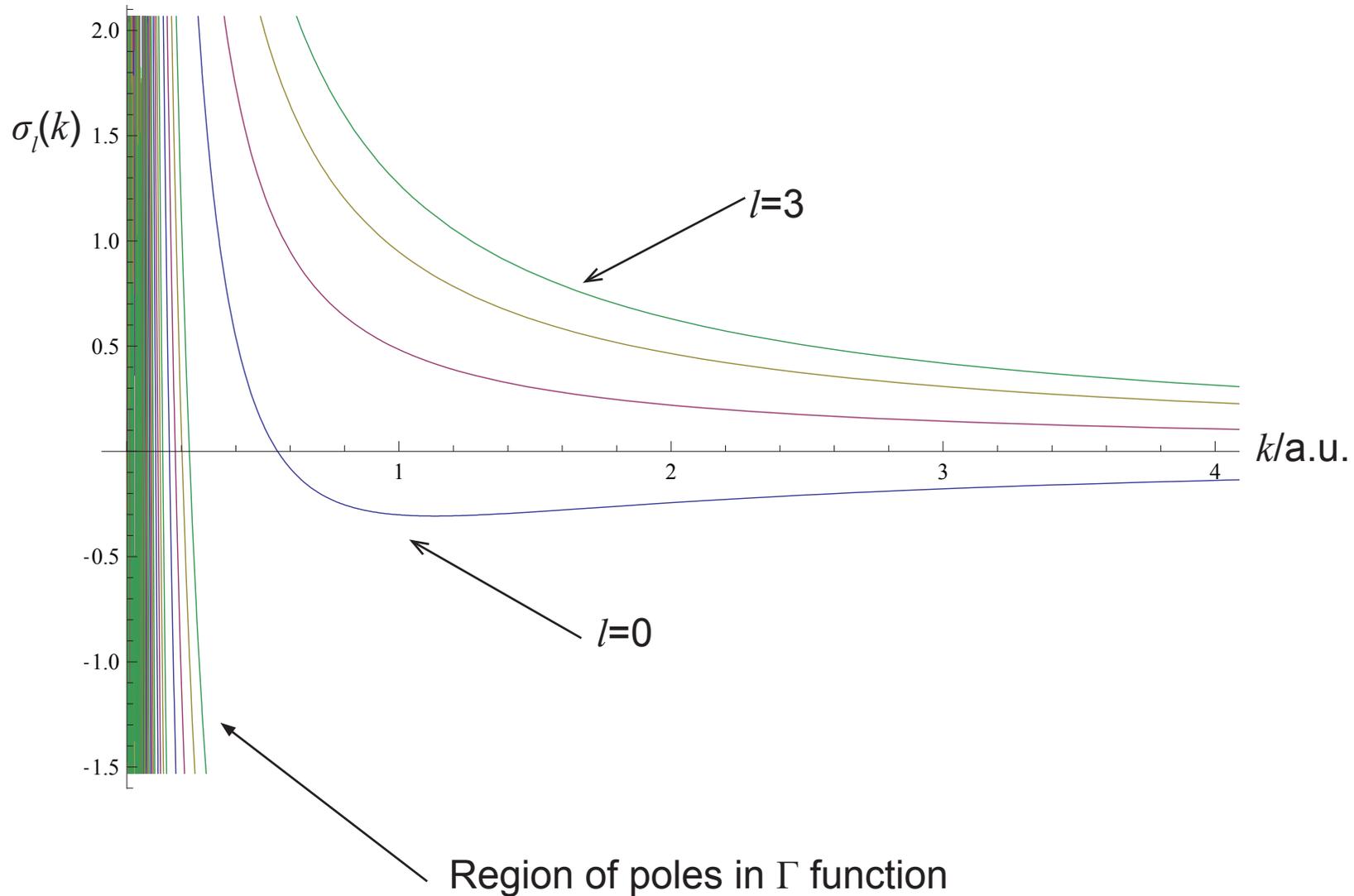


Asymptotic form



radial eigenfunctions - coulombic

Coulomb Phase $\sigma_l(k)$, $l=0-3$

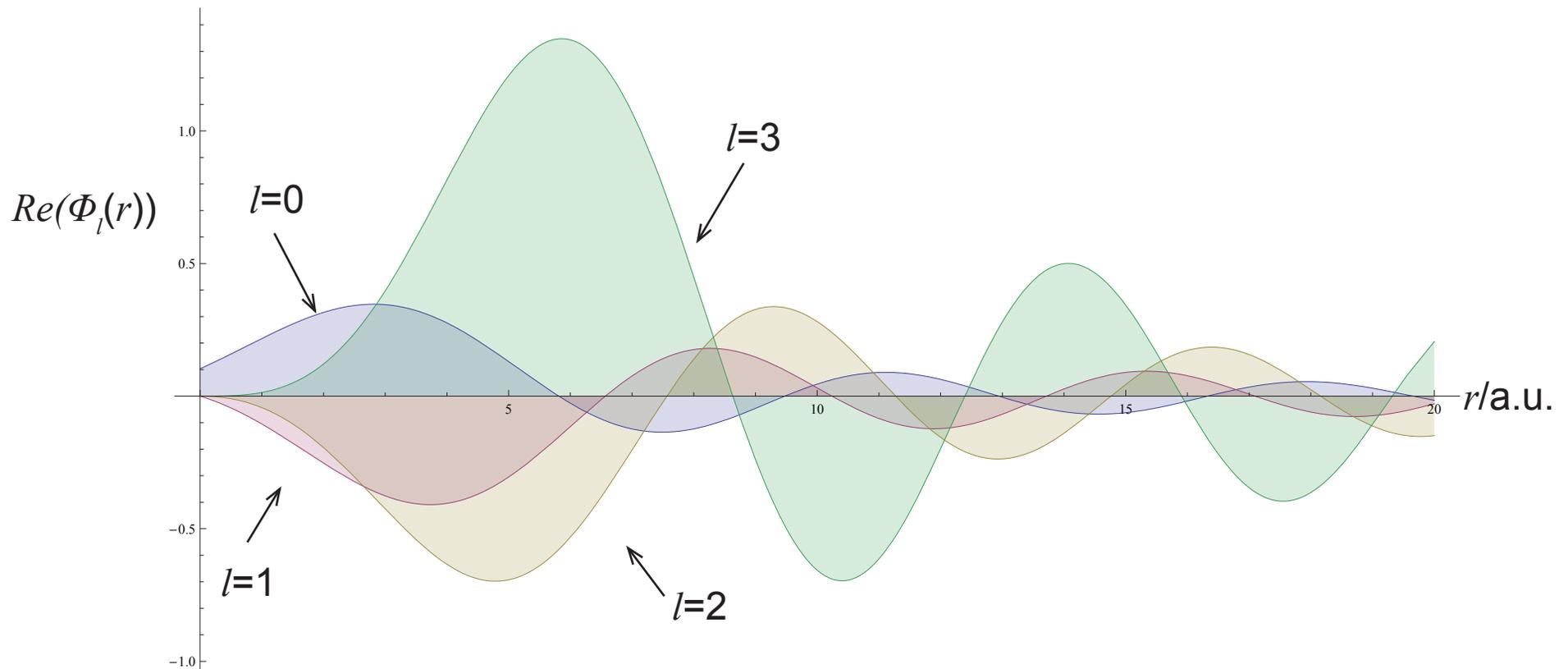


radial eigenfunctions - coulombic

To determine the complete radial wavefunction we also need:

$$A_l = \frac{2l + 1}{kr} i^l e^{i\sigma_l}$$

$\Phi_l(r)$, $l=0-3$, $k=1$ a.u.



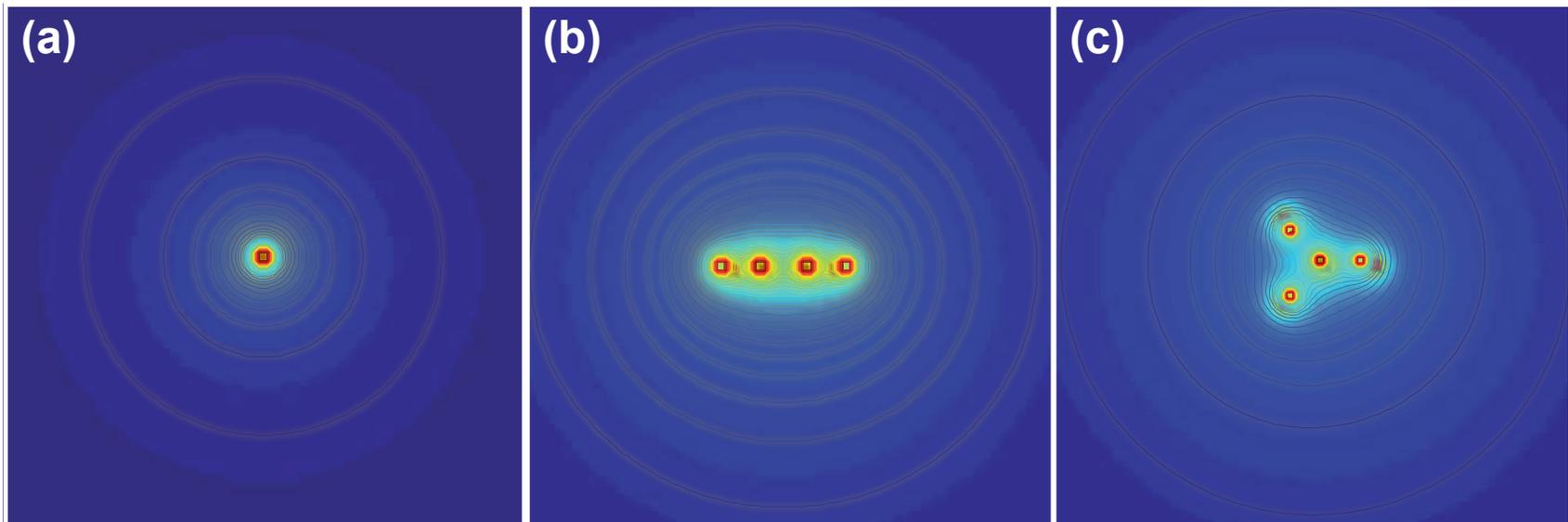
radial eigenfns - non-coulombic

The Coulomb potential is the exact form for a point charge, more generally a scattering system may have an additional short-range contribution to the potential (one which scales as $1/r^n$, where $n > 1$), and this contribution may be non-centrally symmetric (anisotropic).

The strength of these short-range interactions and multi-polar contributions to the potential will fall to zero much faster than the Coulombic term, and we can define a boundary, r_c , beyond which the potential is purely Coulombic.

Coulombic

Non-coulombic



radial eigenfns - non-coulombic

In the Coulombic region the radial wavefunction still has an analytic form, and is now described by:

$$\chi_l(r \geq r_c) = \cos(\delta_{lm})F_l(r) + \sin(\delta_{lm})G_l(r)$$

$$G_l(r) \xrightarrow{r \rightarrow \infty} \cos \left[kr - \frac{\pi l}{2} - \frac{Z_1 Z_2}{k} \ln(2kr) + \sigma_l \right]$$

$$A_l = \frac{2l + 1}{kr} i^l e^{i(\sigma_l + \delta_{lm})}$$

Irregular Coulomb function

Short-range or scattering phase shift

In the non-Coulombic region l -channels may be mixed by the potential, but they are still good asymptotically.

radial eigenfns - non-coulombic

The additional phase shift defines the mixing of the regular and irregular Coulomb functions, and this mixing also determines the total asymptotic phase shift:

$$\chi_l \xrightarrow{r \rightarrow \infty} \sin \left[kr - \frac{\pi l}{2} - \frac{Z_1 Z_2}{k} \ln(2kr) + \sigma_l + \delta_{lm} \right]$$

Hence the scattering phase δ_{lm} describes the effect of the non-Coulombic part of the potential, $U(r)$, and is labelled with m to show that this may affect different components of each l -wave differently in an anisotropic scattering system.

scattering phase shift

Compare:

$$\chi_l \xrightarrow{r \rightarrow \infty} \sin \left[kr - \frac{\pi l}{2} - \frac{Z_1 Z_2}{k} \ln(2kr) + \sigma_l + \delta_{lm} \right]$$

To: $\Psi = \sin(kr)$ Free-particle wavefunction

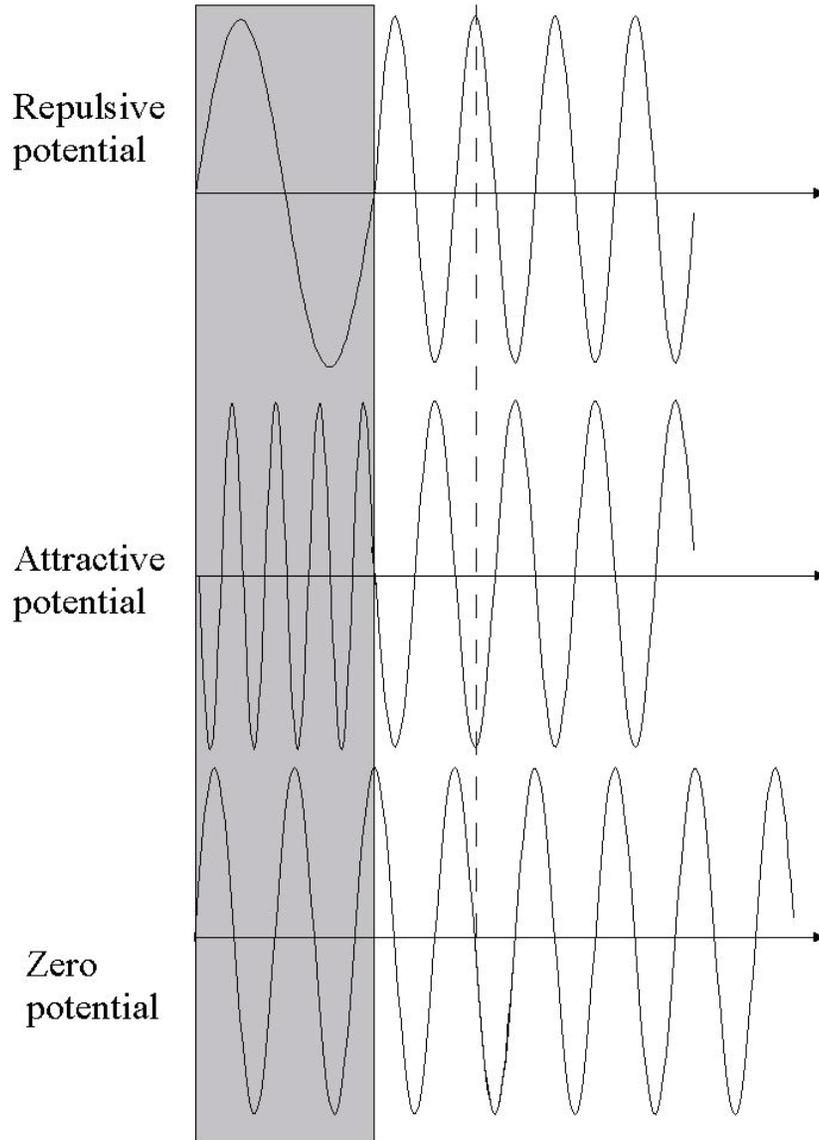
It is clear that there is a phase shift in the asymptotic form of the radial wavefunction, with contributions from several terms.

The Coulomb and scattering phase-shifts in particular are important - they carry all of the information on the scattering potential $U(r)+U'(r)$.

[Note - this is clearer in the S and K matrix form of scattering theory, see refs for details]

scattering phase shift

A scattering potential shifts the phase of the scattered wave at points beyond the scattering region



For an attractive potential the phase shift will be negative, and the outgoing wave retarded relative to a free particle.

For a repulsive potential the outgoing wave is advanced relative to a free particle.

scattering phase shift

Although we don't have an analytic solution for the wavefunction for $r < r_c$, all of the information on the potential is carried in the short-range phase shift.

Hence: if we can measure the scattering phases we obtain all possible information on the scattering potential. We will see later that PADs are uniquely sensitive to the scattering phase shifts...

summary

In this session we have covered:

- General formulation of scattering problems.
- Partial wave expansion of the stationary scattering state wavefunction in spherical polar coordinates, which allows the separation of the radial and angular components of the wavefunction.
- Solution of the radial wavefunctions for a Coulomb potential, and a more general potential with additional 'short range' terms.
- The phase shift of the asymptotic solution. This carries all of the information on the strength of the scattering potential.

NEXT TIME - Angular momentum...