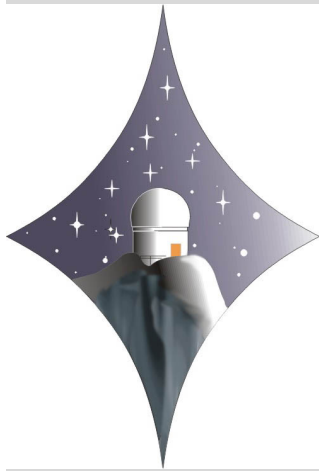
Atomic data

Atomic Data from 31st July 2007

Keith Butler
Universitätssternwarte
Munich



A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

Scattering theory

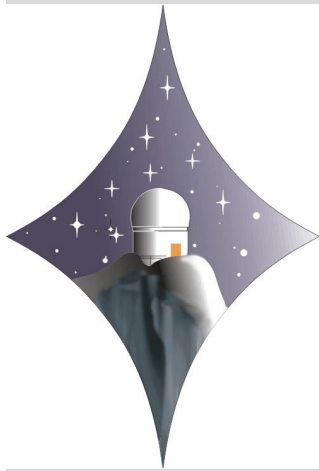
The close-coupling expansion

R-Matrix method

Intermediate energies

Outline

1. Introduction
2. Hydrogen wavefunctions
3. The Quantum Defect Method
4. Many electron systems
5. Scattering theory
6. The close-coupling expansion
7. R-Matrix method
8. Intermediate energies



A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies

Fermi's Golden Rule

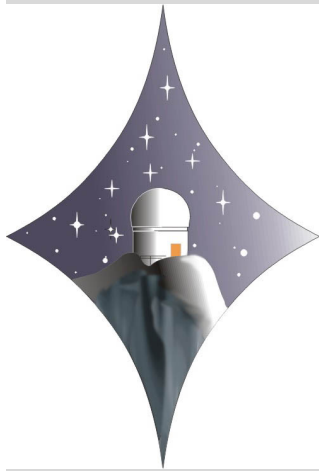
Time dependent perturbation theory gives us Fermi's Golden Rule

$$W_{ba} = \frac{dP_{ba}}{dt} = 2\pi |\langle \Psi_b | V | \Psi_a \rangle|^2.$$

which describes a transition from state a to state b caused by a perturbation V.
So if we know V and the wavefunctions we can calculate the transition probability.
Examples are

- Oscillator strengths $V = \mathbf{r}$
- Born approximation for Coulomb potential $V = 1/r$

So how do we get the wavefunctions?



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

Hydrogen wavefunctions

The Schrödinger equation for a central potential is

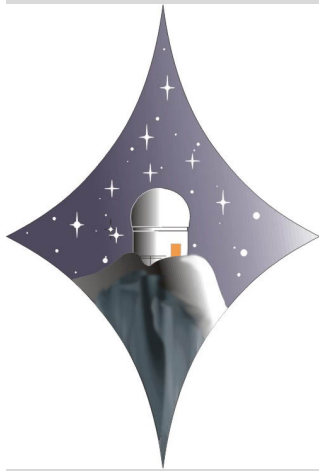
$$\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}).$$

Solutions of the hydrogenic Schrödinger equation ($V(r) = -z/r$) in spherical coordinates are

$$\Psi = Y_{lm}(\theta,\phi)R_{nl}(r).$$

- finite mass gives $\mu = m_e M/(m_e + M)$
- nlm are the quantum numbers
- $n > l$, $m = -l \ldots l$
- n and l are integers
l	=	0	1	2	3	4	...
		s	p	d	f	g	....
- Y_{lm} are spherical harmonics
- R_{nl} are the radial functions (Lagrange polynomials)

The angular functions give us selection rules.



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

Negative energies

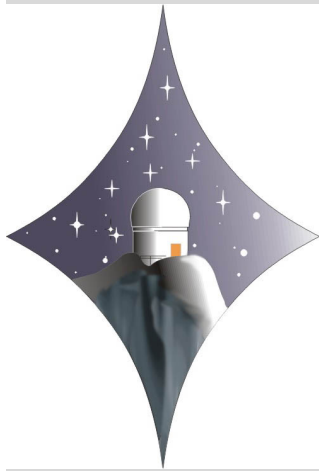
Setting $u = rR$ the radial equation simplifies to

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V\right] u = \frac{E}{2}u.$$

atomic units ($e = \hbar = m = 1$), E in Rydberg units
Hydrogenic $V = -z/r$. If $\rho = zr$ and $\varepsilon = -\lambda^2 = E/z^2$, gives

$$\left[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{2}{\rho} - \lambda^2\right] u = 0.$$

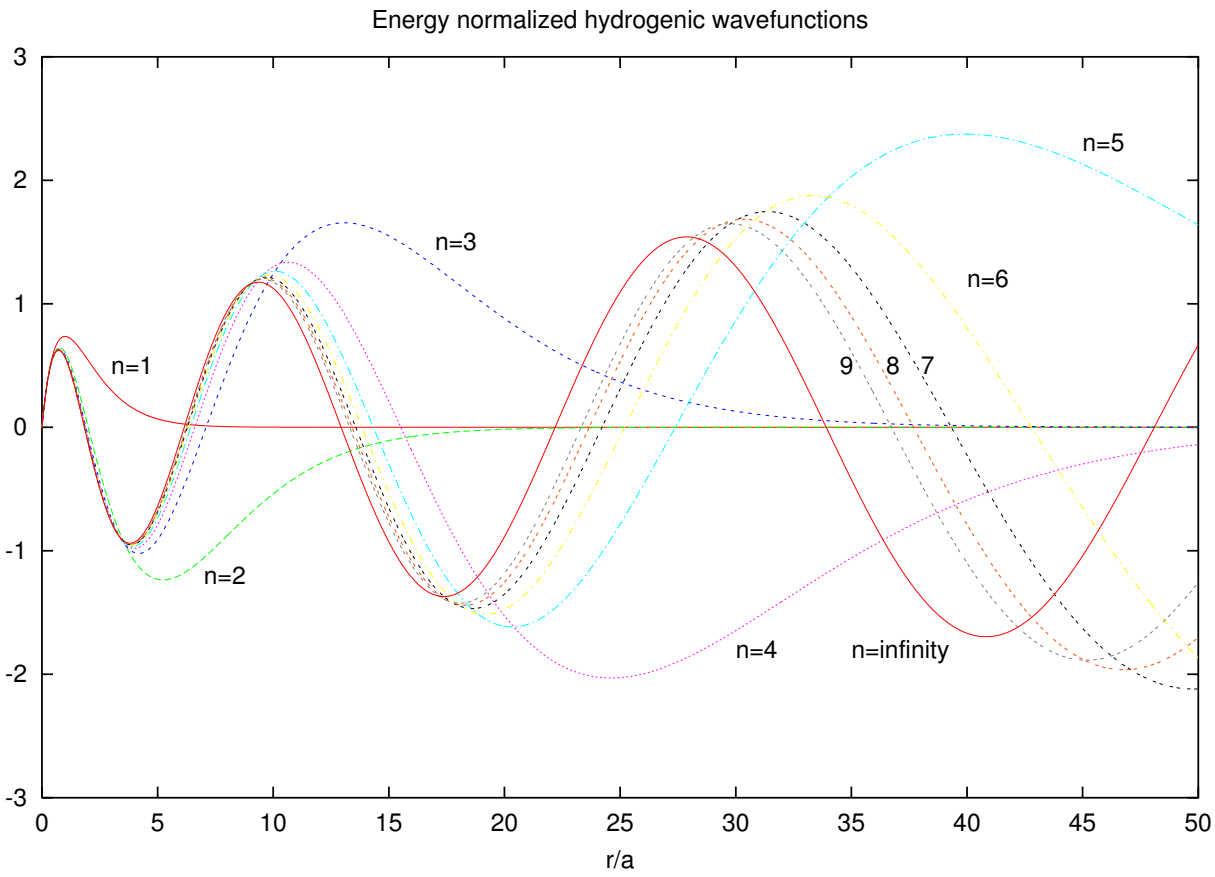
So all hydrogenic atoms satisfy the same wave equation provided we decrease the size of the atom by a factor z and at the same time increase the ionization energies by a factor z^2.

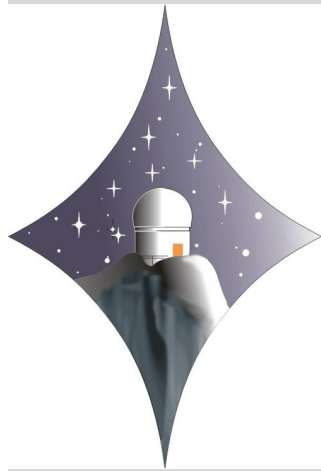


A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

Hydrogen wavefunctions

What do the radial wavefunctions look like?





A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies

Expectation values

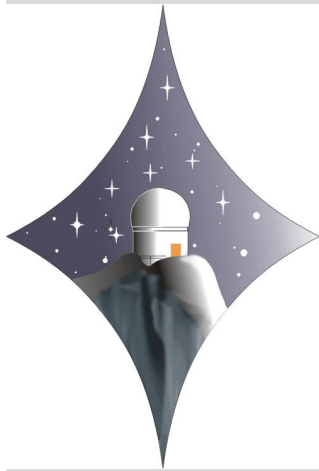
Now we have them we can calculate things with them

$$\begin{aligned}
\langle r \rangle_{nlm} &= \frac{n^2}{z}\left\{1+\frac{1}{2}\left[1-\frac{l(l+1)}{n^2}\right]\right\} \\
\langle r^2 \rangle_{nlm} &= \frac{n^4}{z^2}\left\{1+\frac{3}{2}\left[1-\frac{l(l+1)-1/3}{n^2}\right]\right\} \\
\left\langle \frac{1}{r} \right\rangle_{nlm} &= \frac{z}{n^2} \\
\left\langle \frac{1}{r^2} \right\rangle_{nlm} &= \frac{z^2}{n^3(l+\frac{1}{2})} \\
\left\langle \frac{1}{r^3} \right\rangle_{nlm} &= \frac{z^3}{n^3(l(l+\frac{1}{2})(l+1)}
\end{aligned}$$

and oscillator strengths/photoionization cross sections

$$f_{if} = \frac{2\Delta E_{fi}}{3}|\langle\phi_f|\mathbf{r}|\phi_i\rangle|^2 \qquad \sigma_\nu \sim \frac{df}{dE}$$

oscillator strengths independent of z



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

Positive energies

Let $\varepsilon = k^2$, $l = 0$ and $z = 0$ then

$$\frac{d^2u}{d\rho^2} = -k^2 u$$

solutions are $e^{\pm ik\rho}$ or $\cos k\rho, \sin k\rho$. A general solution is a linear combination

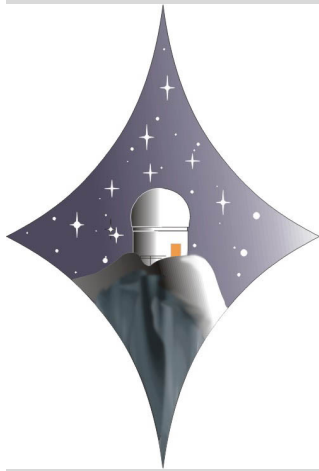
$$u = A \sin k\rho + B \cos k\rho$$

or

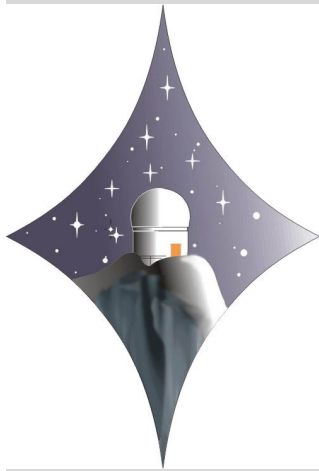
$$u = \sqrt{A^2 + B^2}(\cos\delta\phi_s + \sin\delta\phi_c).$$

(writing ϕ_s for the sine and ϕ_c for the cosine solutions) and

$$\tan\delta = B/A.$$



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies



Thus

$$u = \sqrt{A^2 + B^2}\sin(k\rho + \delta).$$

δ is called the phase shift. We can find A and B if we know the function and its derivative at some value of $\rho = \rho_0$

$$\begin{aligned} u(\rho_0) &= A\sin(k\rho_0) + B\cos(k\rho_0) \\ u'(\rho_0) &= A\cos(k\rho_0) - B\sin(k\rho_0) \end{aligned}$$

Once we have A and B we have the wavefunction from ρ_0 to ∞. For $l \neq 0$ but still with $z = 0$ $k\rho$ is replaced with $(k\rho - \frac{l\pi}{2})$. The full Coulomb equation then has

$$\left(k\rho - \frac{1}{k}\ln 2k\rho - \frac{l\pi}{2} + \arg(l + 1 - \frac{i}{k})\right)$$

More complicated but still just sine and cosine.

A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

Scattering theory

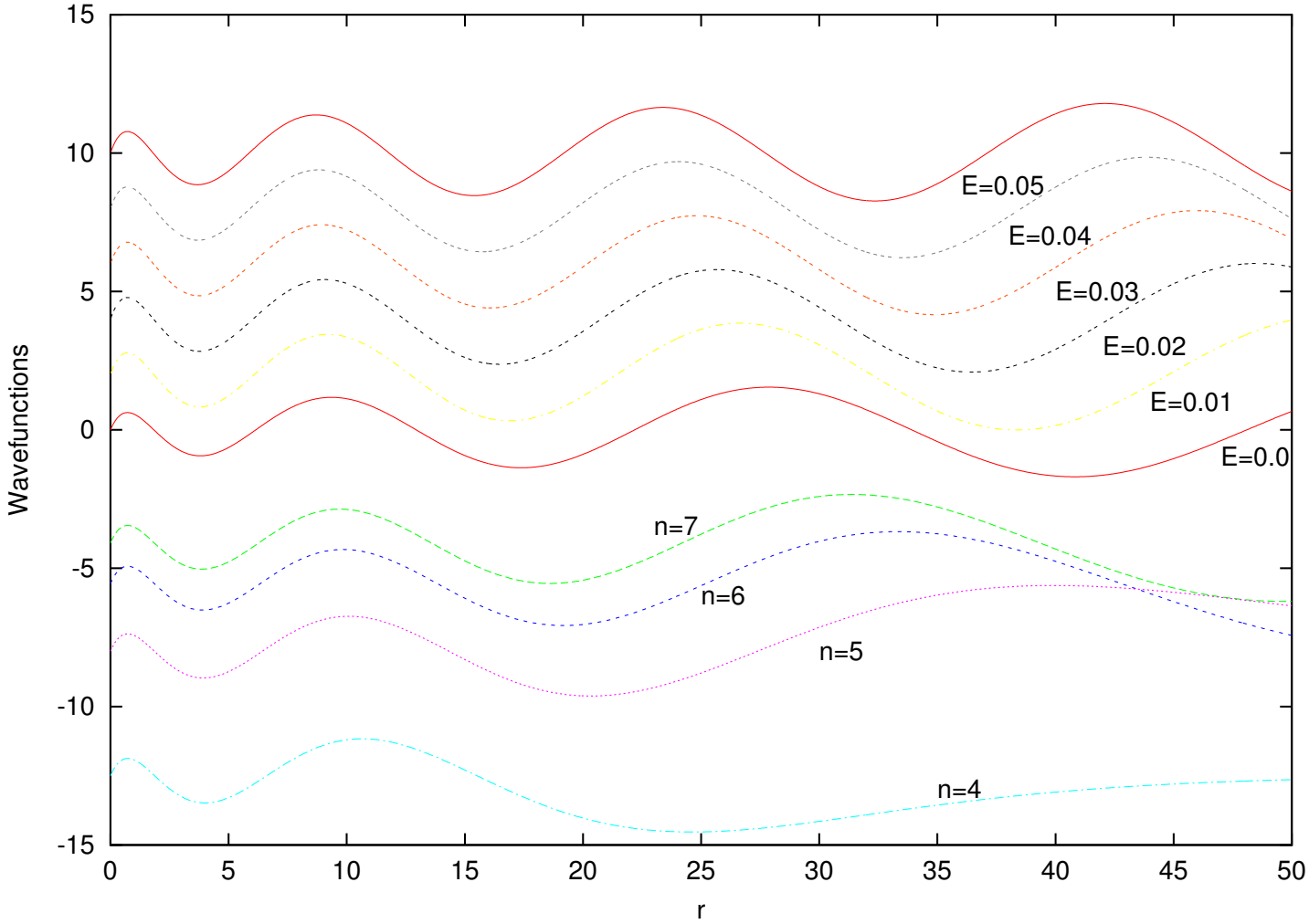
The close-coupling expansion

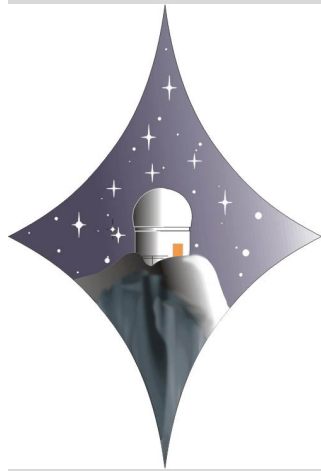
R-Matrix method

Intermediate energies

Energy normalized wavefunctions

There is continuity from bound states $n \rightarrow \infty$ to the free states $E = 0$





A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

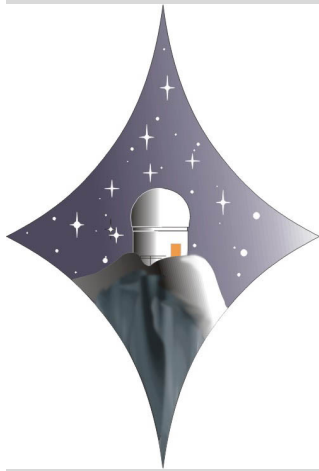
Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies

The Quantum Defect Method



For hydrogen-like ions, the energy levels are $E_n = -R_H z^2/n^2$
R_H Rydberg constant for H (109677 cm^{-1})
Observations show that for more complicated systems the energies are

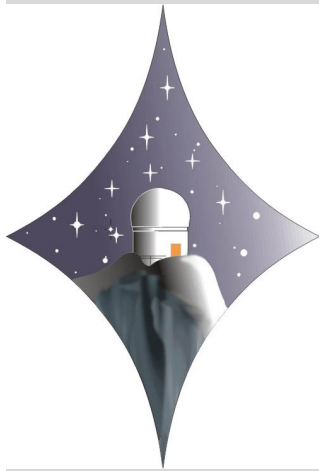
$$E_n = -\frac{Rz^2}{(n-\mu_{nl})^2}.$$

The Rydberg constant is

$$R = \frac{R_\infty (= 109737.312 \mathrm{cm}^{-1})}{1 + 1/1836 * AW}$$

- Atomic weight (AW) because of reduced mass main
- quantum defect μ_{nl} slowly varying function of the energy (E),
- large for small values of l
- large l hydrogenic, μ_{nl} small

A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies



Seaton (1958) shows that the phase shift at positive energies is related to the quantum defect at negative energies via

$$\delta_l = \pi\mu_l$$

and that bound states can occur at energies where

$$\tan[\pi(\nu+\mu)] = 0$$

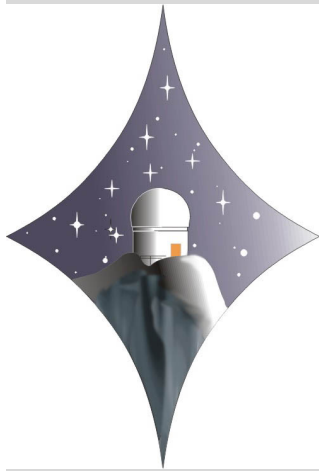
i.e. $\nu+\mu$ is an integer
This illustrates the continuity of physical variables across ionization thresholds. It can be put to practical use.

- bound state energies give quantum defects. Use to
- infer the energies of unobserved bound state energies
- deduce values of phase shifts - photoionization

A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

Quantum defects for C IV s states. The ionization energy is 520178.4 cm^{-1} (Moore C.E., NSRDS-NBS 3, Sect. 3)

nl	E(cm^{-1})	n^*	μ
2s	.00	1.837	.163
3s	302849.00	2.842	.158
4s	401348.09	3.844	.156
5s	445368.50	4.844	.156
6s	468784.00	5.845	.155
7s	482706.00	6.845	.155
8s	491650.81	7.845	.155
9s	497736.69	8.845	.155



A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

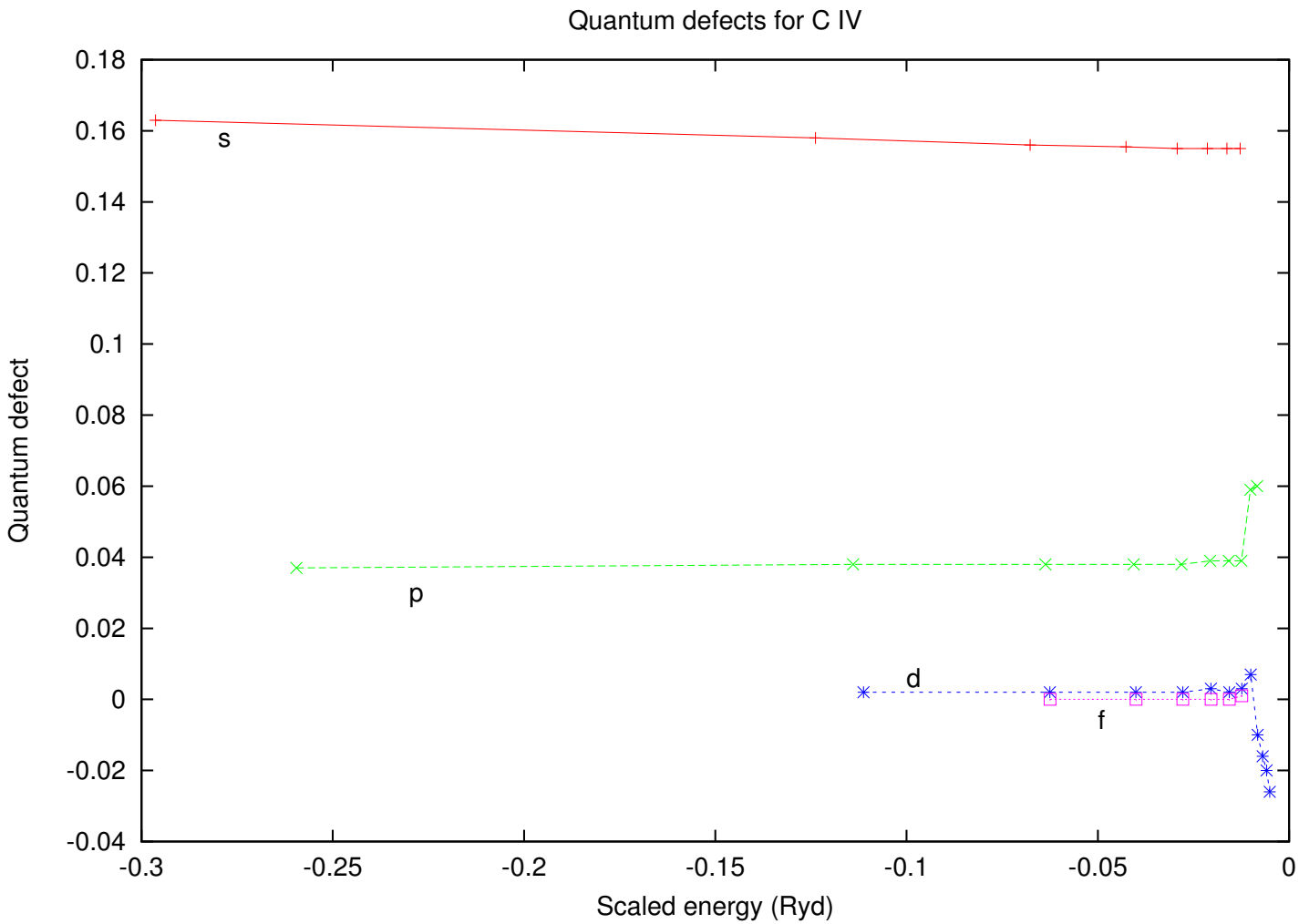
Scattering theory

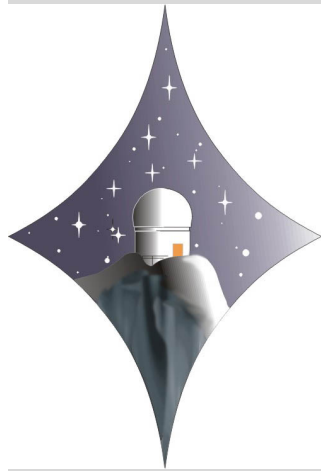
The close-coupling expansion

R-Matrix method

Intermediate energies

Quantum defects for C IV





A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

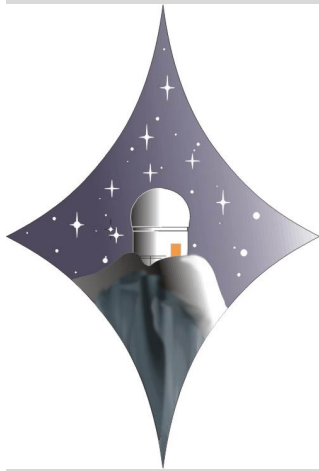
Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies



- Can go in both directions so that calculated or observed phase shifts may be used to find bound state energies etc.
- Theory can be used to calculate oscillator strengths cheaply (Bates and Damgaard, 1950)
- Functions will not be correct for small r but integral weights large r

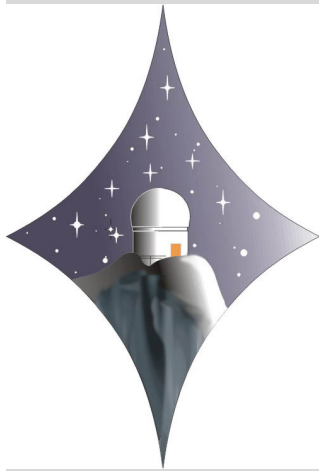
$$|\langle\phi_f|\mathbf{r}|\phi_i\rangle|^2 \equiv \left|\int \phi_f^* \mathbf{r} \phi_i \, d\mathbf{r}\right|^2$$

- Method works well for one electron systems and cases in which a single electron does all the work.

A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

Quantum defect oscillator strengths for C IV.

Lower	Upper	f_{QD}	f_{RM}
2s	2p	.2857	0.2855
2s	3p	.1993	0.203
2s	4p	.0600	0.061
2s	5p	.0265	0.0270
2s	6p	.0142	0.0145
2s	7p	.0085	0.0087
2s	8p	.0055	0.00565
2s	9p	.0038	0.0039
2s	10p	.0029	0.0028
2s	11p	.0022	—



A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

Scattering theory

The close-coupling expansion

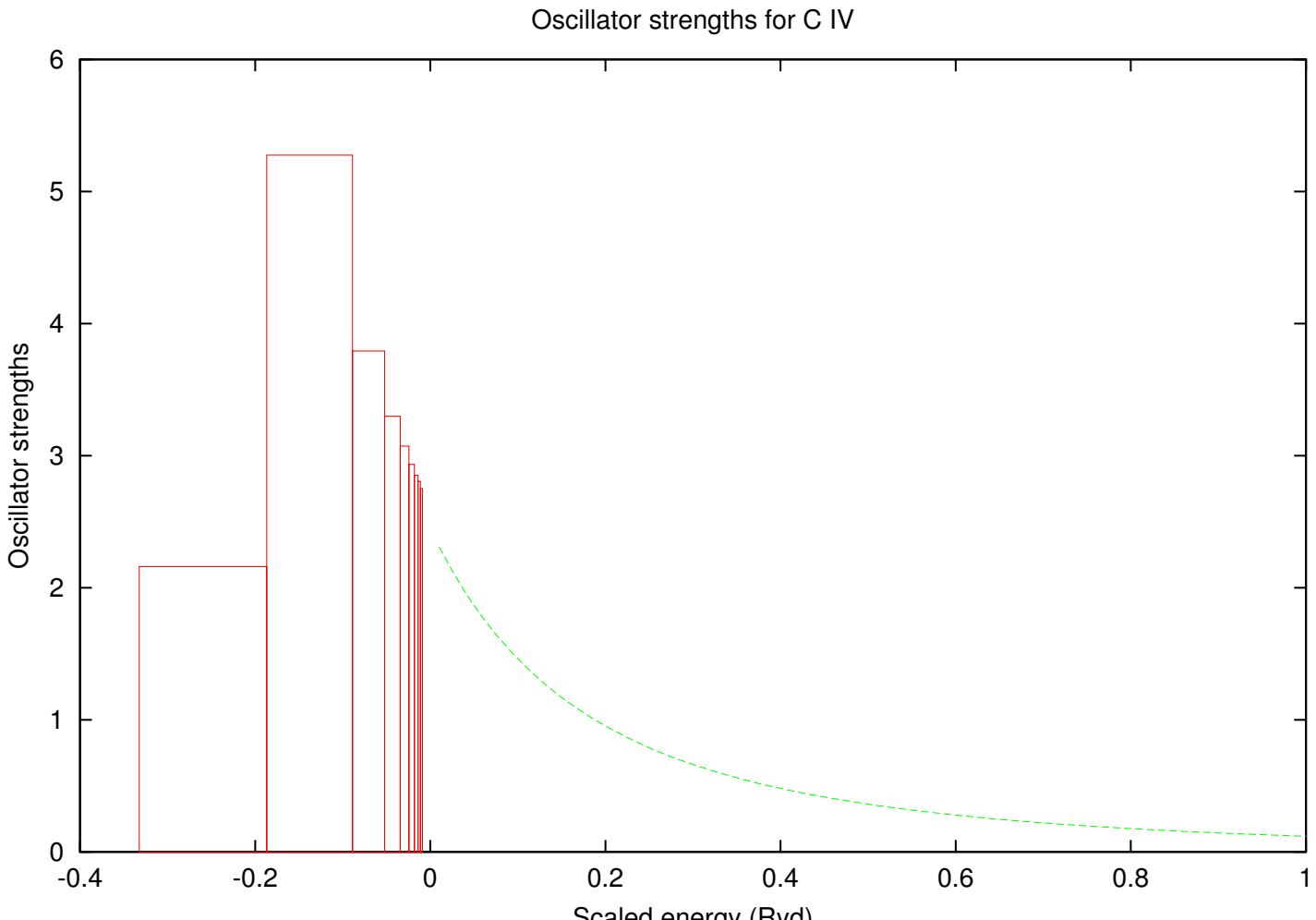
R-Matrix method

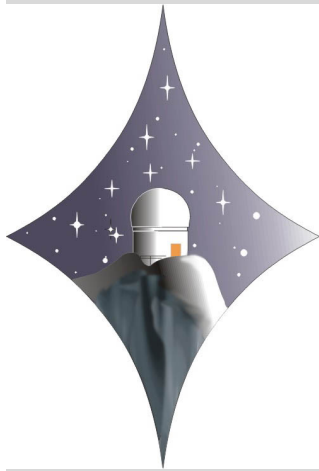
Intermediate energies

Photoionization Cross Sections

Can be applied to photoionization cross sections (Burgess and Seaton 1964)

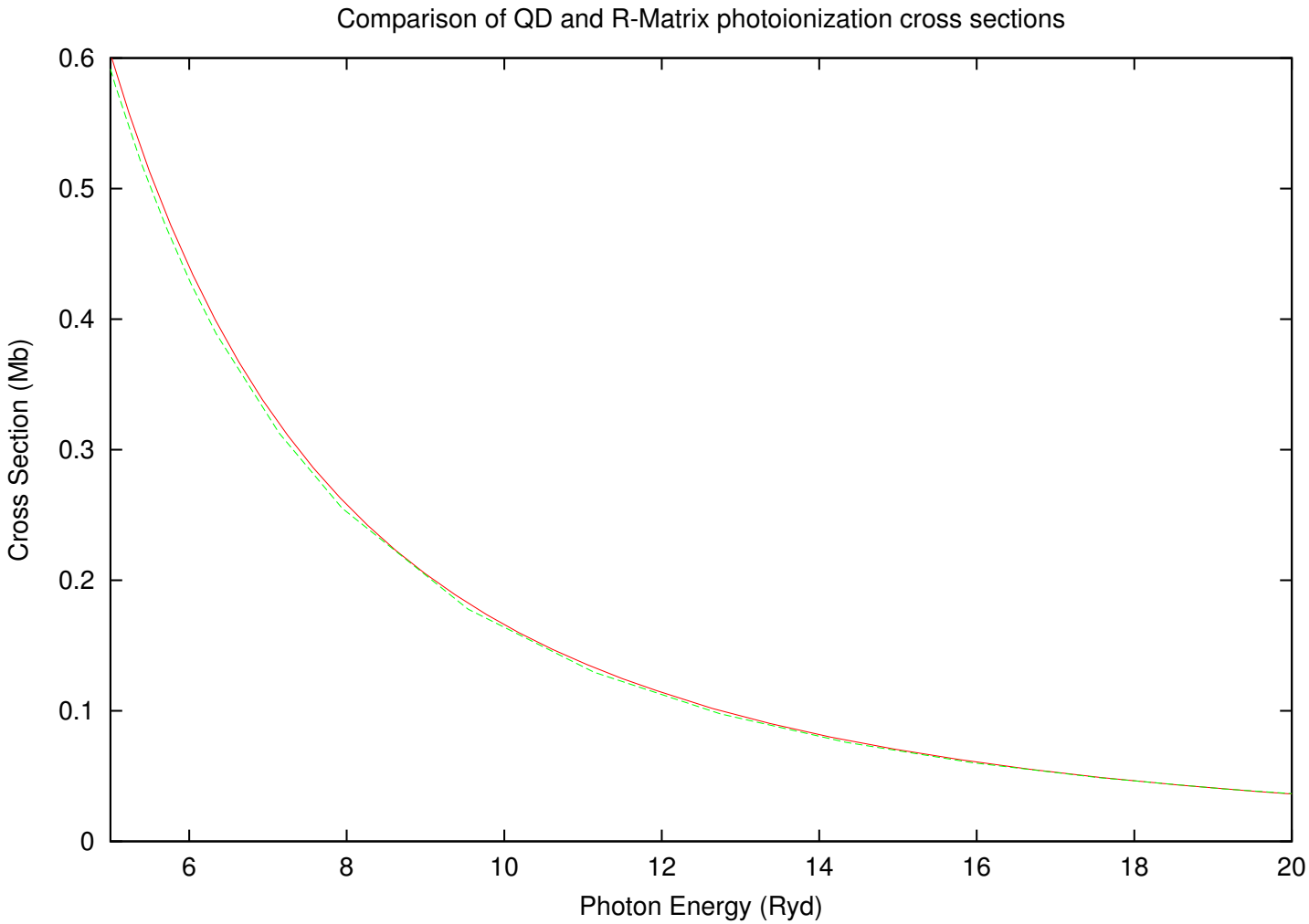
Extrapolate the known quantum defects to positive energies to obtain estimates of the phase shifts.

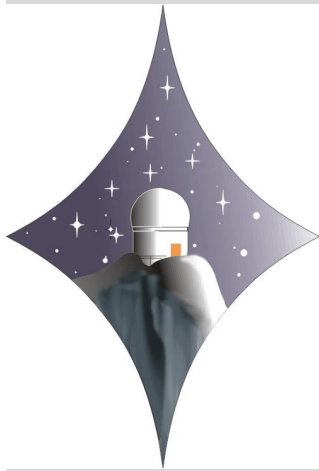




A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

Comparison QDT vs. R-matrix for C IV





A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies

Helium - Two electron atoms

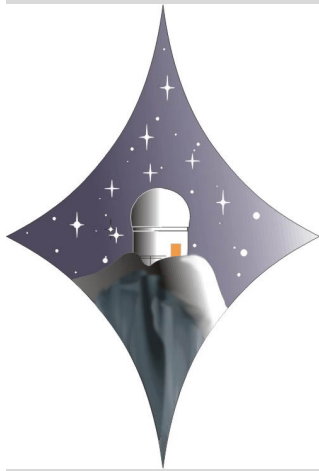
The next simplest system is an atom with two electrons, Helium. The Hamiltonian

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}_1} - \frac{1}{2}\nabla^2_{\mathbf{r}_2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right]\Psi(\mathbf{r}_1,\mathbf{r}_2) = E\Psi(\mathbf{r}_1,\mathbf{r}_2).$$

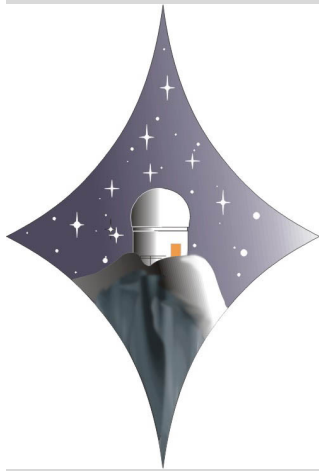
Since the Hamiltonian does not change when $\mathbf{r}_1$ and $\mathbf{r}_2$ are interchanged

$$\Psi(\mathbf{r}_1,\mathbf{r}_2) = \pm\Psi(\mathbf{r}_2,\mathbf{r}_1).$$

When the $+$ sign applies Ψ is said to be space symmetric, denoted by Ψ_+. The $-$ holds for space antisymmetric functions Ψ_-.



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies



Must take spins into account so

$$\Psi(\mathbf{q}_1, \mathbf{q}_2) = \Psi(\mathbf{r}_1, \mathbf{r}_2)\chi(1,2).$$

These must be antisymmetric (Pauli) - gives singlets and triplets.

A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

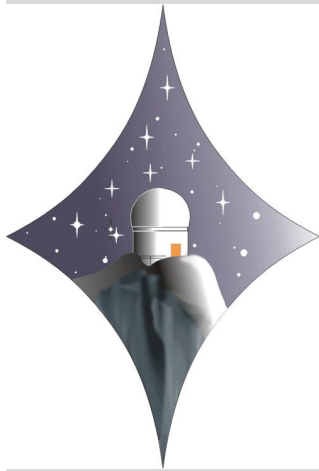
Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies



If the total orbital angular momentum is **L** with eigenvalues L, M_L, an energy term with a particular value of S and L is normally written ${}^{2S+1}L$ since for light elements LS-coupling is a good approximation. Here first the ls are coupled to give L and ss to give S and then the sum $L+S$ is taken. The term has multiplicity $(2S+1)$ and L is denoted by a letter

L	=	0	1	2	3	4	...
		S	P	D	F	G	....

When relativistic effects are taken into account, the levels of the terms are subject to fine-structure splitting. L, S are then no longer good quantum numbers, constants of the motion, but the total angular momentum $J = L+S$ is. Such a level is represented by

$$ {}^{2S+1}L_J. $$

A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies

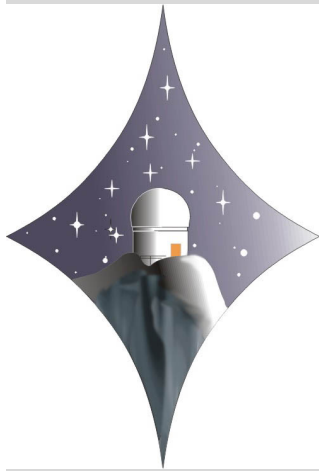
Independent Particle Model

What are the energy levels of Helium.

- Three-body system so must approximate.
- treat the two electrons separately
- couple them later.
- Very simplest is to $H = H_0 + H'$ with

$$\begin{aligned} H_0 &= -\frac{1}{2}\nabla^2_{\mathbf{r}_1} - \frac{Z}{r_1} - \frac{1}{2}\nabla^2_{\mathbf{r}_2} - \frac{Z}{r_2} \equiv h_1 + h_2 \\ H' &= \frac{1}{r_{12}}. \end{aligned}$$

- h_1 and h_2 are both hydrogenic



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

- Energies are

$$E^0_{n_1 n_2} = -\frac{Z^2}{2}\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)$$

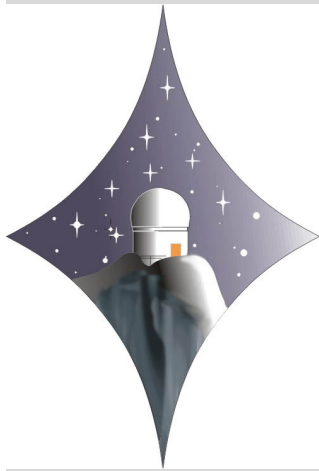
- ground state energy $-Z^2 = -4$ a.u. observed -2.90 a.u.
- singlet and triplet states are degenerate.
- must include $1/r_{12}$

Next simplest is

$$\begin{aligned} H_0 &= -\frac{1}{2}\nabla^2_{\mathbf{r}_1} + V(r_1) - \frac{1}{2}\nabla^2_{\mathbf{r}_2} + V(r_2) \equiv h'_1 + h'_2 \\ H' &= \frac{1}{r_{12}} - \frac{Z}{r_1} - V(r_1) - \frac{Z}{r_2} - V(r_2). \end{aligned}$$

We have simply rearranged the terms.

- Guess $V(r) = -(Z-s)/r \equiv Z_e/r$.
- Screening constant s allows for the electron shielding
- Energies are hydrogenic with effective charge Z_e.
- Ground state $-Z_e^2$. $s = 0.3$ reproduces observed value
- Just a fit



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

N-electron systems

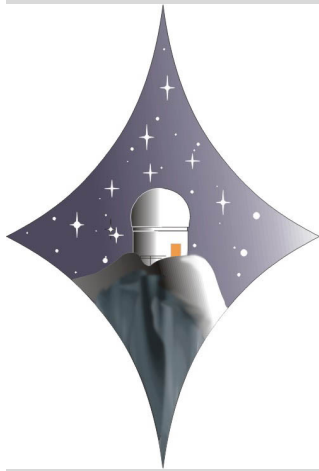
The Hamiltonian for an N-electron system is a straightforward generalization of that for Helium, namely

$$H = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla^2_{\mathbf{r}_i} + \frac{Z}{r_i} \right) + \sum_{j>i=1}^{N} \frac{1}{r_{ij}}.$$

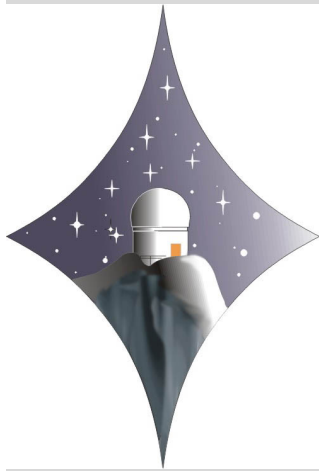
and the N-electron wavefunction

$$\Psi(\mathbf{q}_1, \mathbf{q}_2 \ldots \mathbf{q}_N) = \Psi(\mathbf{r}_1, \mathbf{r}_2 \ldots \mathbf{r}_N)\chi(1, 2, \ldots N)$$

must be antisymmetric so that the Pauli exclusion principle is satisfied. The independent particle approximation can be made for the N-electron system in the same way as for the two-electron system. Each electron then moves in an effective potential that describes the average effect of its interaction with the other $(N-1)$ electrons. They in turn 'screen' the nuclear charge.



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies



- $1/r_{12}$ behaves like $1/r_>$
- potential looks like

$$V(r_i) = -\frac{Z}{r_i} + S(r_i).$$

- r_i largest $r_> = r_i$ and

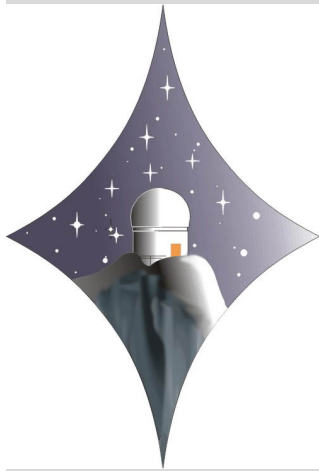
$$V(r) = -\frac{Z}{r_i} + \sum_{j=1}^{N-1} \frac{1}{r_i} = -\frac{Z-N+1}{r_i}.$$

- r_i is smallest

$$V(r_i) \approx -\frac{Z}{r_i} + \left\langle \sum_{j=1}^{N-1} \frac{1}{r_j} \right\rangle = -\frac{Z}{r_i} + \text{a constant}$$

- the electron "sees" full nuclear charge.

A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies



In between, $S(r_i)$ will be a complicated function. Bearing these considerations in mind, we rearrange the Hamiltonian once more

$$\begin{aligned} H &= H_C + H_1 \\ H_C &= \sum_{i=1}^{N} \left(\frac{1}{2}\nabla^2_{\mathbf{r}_i} + V(r_i) \right) \equiv \sum_{i=1}^{N} h_i \\ H_1 &= \sum_{j>i=1}^{N} \frac{1}{r_{ij}} - \sum_i \left(\frac{Z}{r_i} + V(r_i) \right) \\ &= \sum_{j>i=1} \frac{1}{r_{ij}} - \sum_i S(r_i). \end{aligned}$$

The advantage in doing this is that H_1 is now (hopefully) small and can be treated using perturbation theory.

A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

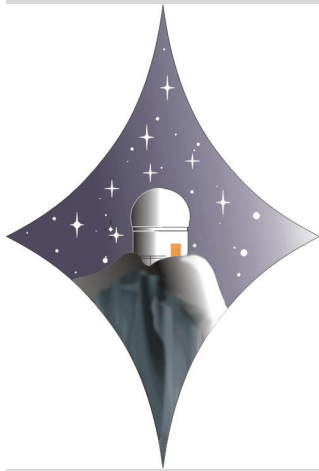
Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies



- Each orbital solution of

$$[-\frac{1}{2}\nabla^2_{\mathbf{r}} + V(r)]\psi_{nlm_l}(\mathbf{r}) = E_{nl}\psi_{nlm_l}(\mathbf{r})$$

- looks like

$$\psi_{nlm_lm_s}(\mathbf{q}) = R_{nl}(r)\,Y_{lm_l}(\theta,\phi)\chi_{\frac{1}{2},m_s}$$

- No two electrons can have same set of 4 quantum numbers (Pauli).

A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

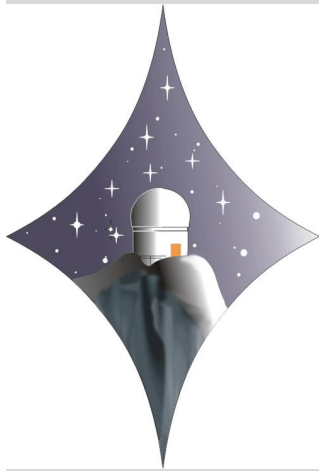
Intermediate energies

Configurations, shells, sub-shells

- Total energy is sum of one-electron contributions

$$E = \sum_{nl} E_{nl},$$

- Distribution of the electrons among the orbitals is a configuration, written as $(n_1 l_1)^{t_1}(n_2 l_2)^{t_2}\ldots(n_v l_v)^{t_v}$.
- E.g. Ground configuration (the energetically lowest) O is $1s^2 2s^2 2p^4$
- Abbreviated to $2p^4$ with 2 1s, 2 2s and 4 2p electrons.
- This is based on central field approximation.
- The electrons are indistinguishable. No 1s electron.
- Electrons with same value of nl belong to same sub-shell (equivalent)
- same n belong to same shell.
- two values of m_s, $(2l+1)$ values of m_l give maximum occupancy of a sub-shell is $2(2l+1)$. e.g. $2p^6$



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

Configuration Interaction

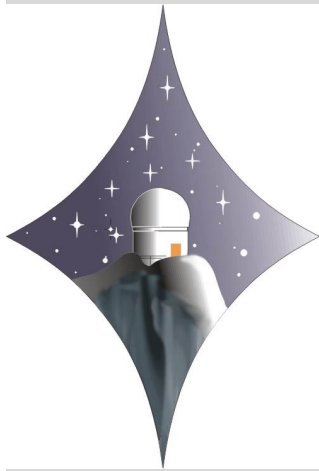
- independent particle model good $\Longrightarrow$ single configuration good.
- H_1 mixes configurations and terms with same L and S values.
- e.g. ground state of He I is $\Psi_g = 1s^2\ {}^1S$. Corrections give

$$\Psi_g = a_1(1s^2) + a_2(1s2s) + a_3(1s3s) + \cdots + a_k(2s^2) + \cdots$$

  with $\sum_{i=1}^{\infty} a_i^2 = 1$.
- 1s2s wavefunction will be

$$\Psi_{1s2s} = b_1(1s^2) + b_2(1s2s) + b_3(1s3s) + \cdots .$$

- Independent particle model and single configuration make sense if single coefficient is close to 1.



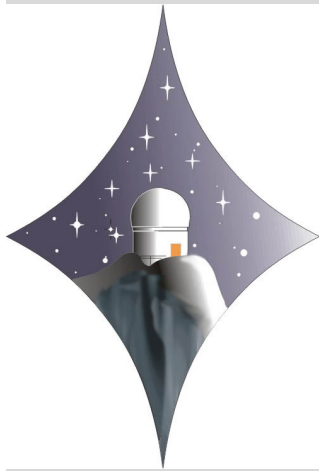
A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

Wavefunctions are optimized

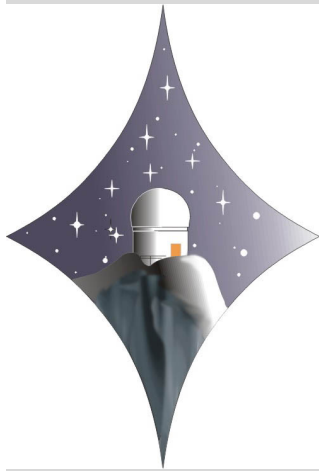
- Configuration interaction uses

$$\Psi = \sum_i c_i \Phi_i .$$

- 1. Choose a set of the Φ_i.
- 2. Choose a set of one-electron orbitals (adjustable parameters).
- 3. Calculate the Hamiltonian matrix $H_{ij} = \langle \Psi_i | H | \Psi_j \rangle$.
- 4. Diagonalize for eigenvalues E_n and coefficients c_i.
- 5. Calculate the weighted sum $\sum_{n=1}^{N} g_n E_n$, g_n is weighting factor, e.g. the statistical weight or 1.
- 6. Go back to 2 and adjust the parameters until this sum is a minimum.



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies



- Sum over i runs over all bound and free states. Must be truncated to fit into computer. Balance between doable and desireable.
- Normally LS-coupling $\Longrightarrow$ low-Z ions.
- Relativistic effects via perturbation theory
- GRASP is fully relativistic but more difficult.
- Calculations along isoelectronic sequence (e.g. C I, N II, O III...) cheaply if "algebra" is stored.

A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

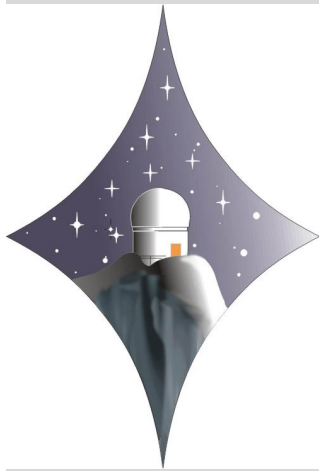
Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

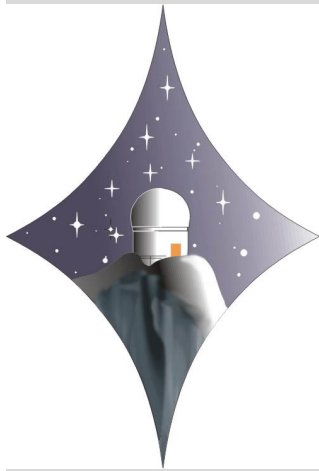
Intermediate energies



Look out for

- Cowan and ZEALOT. Matrix elements H_{ij} are sums of integrals. Least squares fits to observed energies give these integrals and then radiative data (Cowan). Kurucz uses this. The data are ideal for opacity calculations because of completeness. Data for individual ions and transitions can also be good. ZEALOT works similarly, used by Fawcett for ions of iron.
- Multi-Channel-Hartree-Fock (MCHF). A generalization of the Hartree-Fock approach to configuration interaction. The one-electron orbitals are adjusted to give a self-consistent solution to the problem. Gives best solution for any given set of configurations and one-electron orbitals. Atomic data are of high-quality.

A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies



- CIV3 and AUTOSTRUCTURE. Major difference is the radial wavefunctions. In CIV3, these are analytical 'Slater-type orbitals' (STOs)

$$P_{n_i l_i}(r) = \sum_j b_{ij} \frac{(2\xi_{ij})^{l_{ij}+\frac{1}{2}}}{\sqrt{2l_{ij}!}} r^{l_{ij}} e^{-\xi_{ij} r}$$

essentially asymptotic hydrogenic functions. Radial integrals computed extremely quickly.
In AUTOSTRUCTURE potential chosen is Thomas-Fermi-Dirac-Amaldi which 'smears' out the contributions of the electrons. They are used in the calculation of 'target' wavefunctions for scattering calculations to which we turn next.

A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

Cross sections

Consider a typical experiment. Ideally, we have a uniform, monoenergetic beam consisting of N particles per unit time per unit area perpendicular to the beam. If the density in the target n is low enough in each collision only a single particle is involved. If the target is thin enough multiple scatterings will not occur. dN' is the number of particles scattered into the solid angle $d\Omega$ centred about a direction Ω

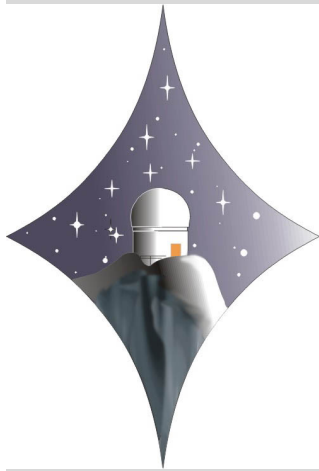
The number of scattered particles will be proportional to N, n and $d\Omega$ with a constant of proportionality defined by

$$dN' = Nn\frac{d\sigma}{d\Omega}(\theta,\phi)d\Omega,$$

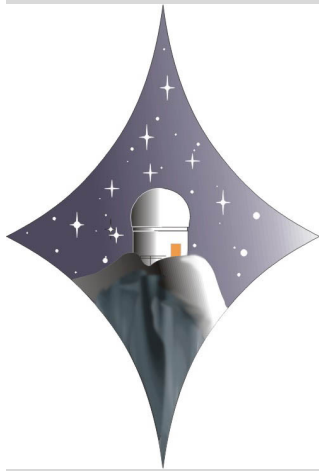
the differential cross section. It is the ratio of the number of scattered particles dN' to the flux of incident particles with respect to the target and has the dimensions of an area.

The total cross section is the integral of the differential cross section over all angles

$$\sigma_{\text{tot}} = \int \frac{d\sigma}{d\Omega}(\theta,\phi)d\Omega$$



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies



Simple scattering theory

Scattering by a potential allows us to define such quantities as the cross section, the collision amplitude and so on. We begin with the Schrödinger equation in its time dependent form

$$\left[-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right]\Psi(\mathbf{r},t) = i\frac{\partial}{\partial t}\Psi(\mathbf{r},t).$$

We assume $V(\mathbf{r})$ to be real and time-independent so that

$$\Psi(\mathbf{r},t) = \psi(\mathbf{r})e^{-iEt}$$

and

$$\left[-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}).$$

E, the energy is written as $\frac{1}{2}k^2 = \frac{1}{2}v^2$ and we also assume that V is of short range (atoms only, no Coulomb potential). For large r we have to solve

$$(\nabla^2 + k^2)\psi(\mathbf{r}) = 0$$

and we write

$$\psi(\mathbf{r}) \underset{r\to\infty}{\sim} \psi_{\text{inc}}(\mathbf{r}) + \psi_{sc}(\mathbf{r}).$$

A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

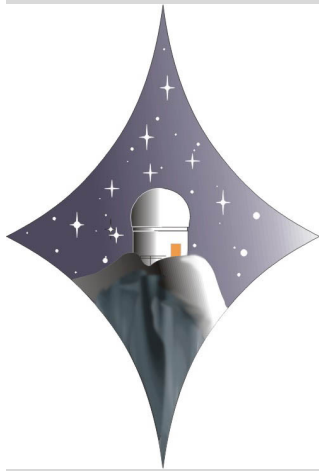
Many electron systems

Scattering theory

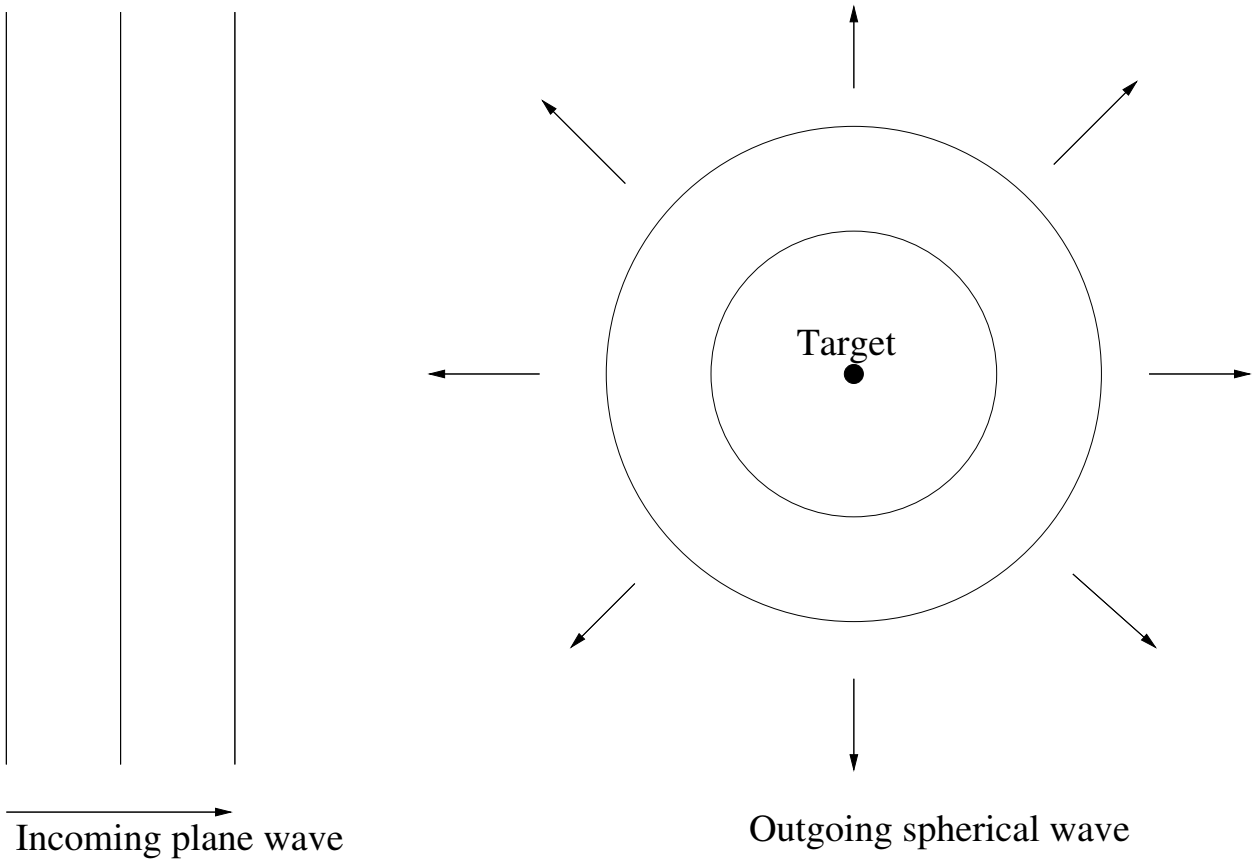
The close-coupling expansion

R-Matrix method

Intermediate energies

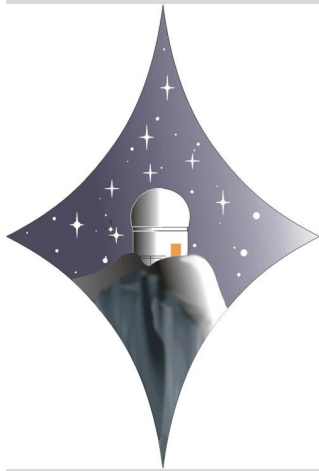


This representation is intended to describe the situation shown



A monoenergetic incident beam strikes the target atom. The beam is scattered by our target particle into a solid angle $d\Omega$ where it is detected. As with water waves striking a rock, the outgoing waves will be spherically symmetric and different fractions will be scattered into the different directions.

A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies



The monoenergetic incident beam can be described by the plane wave

$$\psi_{\text{inc}}(\mathbf{r}) = Ae^{i\mathbf{k}\cdot\mathbf{r}}$$

(A is a constant) while the scattered beam is

$$\psi_{\text{sc}}(\mathbf{r}) = Af(k,\theta,\phi)\frac{e^{ikr}}{r}.$$

$f(k,\theta,\phi)$ is known as the scattering amplitude. The differential cross section is

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

with a total cross section

$$\sigma_{\text{tot}} = \int \frac{d\sigma}{d\Omega}\, d\Omega.$$

A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies

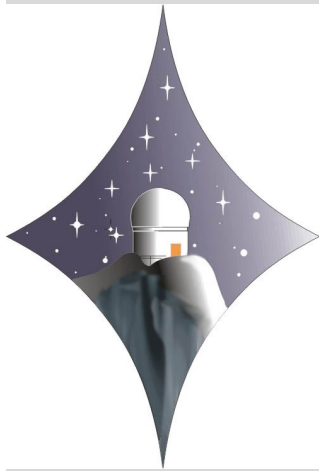
The close-coupling expansion

The close-coupling expansion is an attempt to mimic the scattering experiment as closely as possible. H is simplest example.

- stationary target atom has wfn. $\psi(a|\mathbf{r}_1)$ with $a \equiv nlm$
- scatters electron with wavefunction $F(a|\mathbf{r}_2)$.
- close-coupling expansion is

$$\Psi(\mathbf{r}_1, \mathbf{r}) = \sum \psi(a|\mathbf{r}_1) F(a|\mathbf{r}).$$

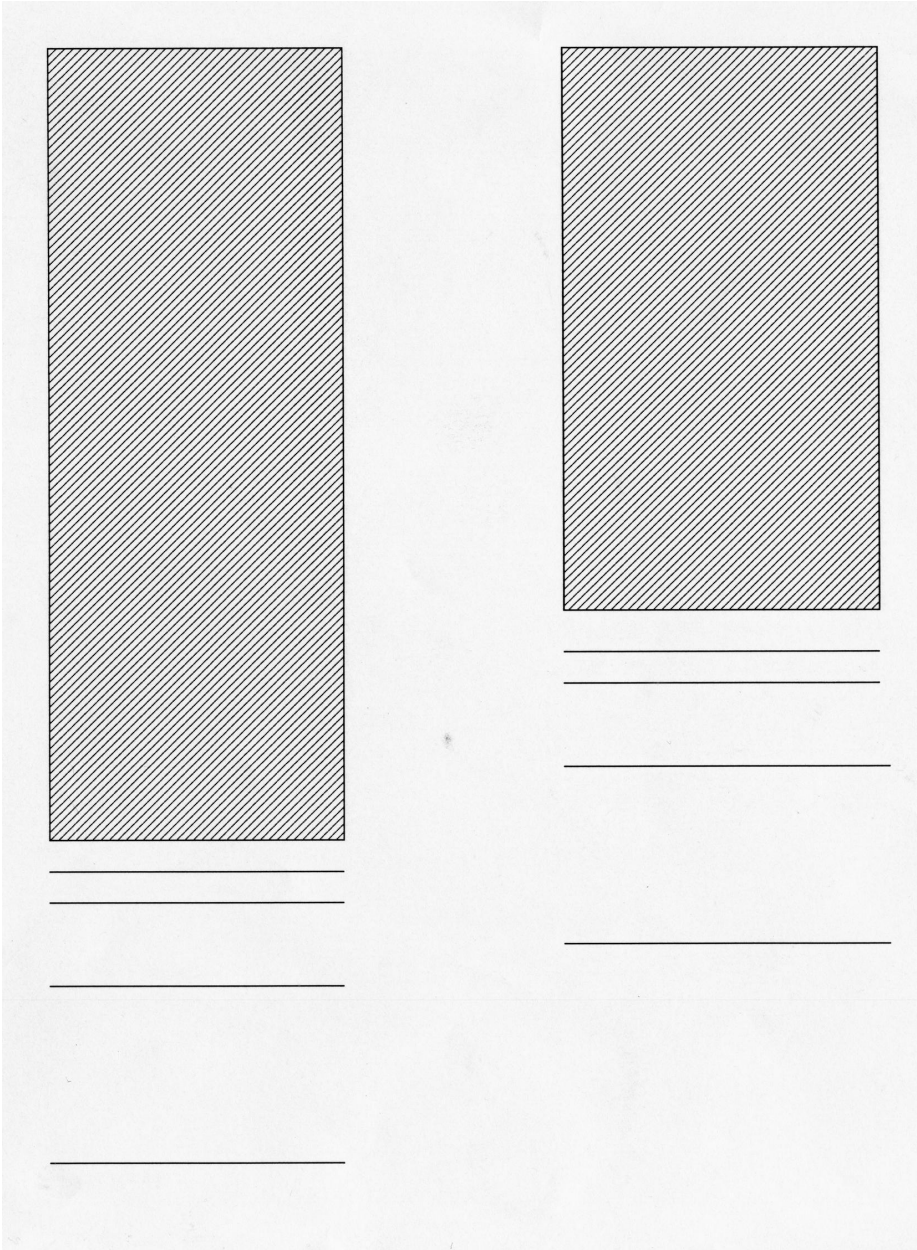
- each pair is a channel, atom and electron in definite states during the collision.
- bound states retain their character during the collisional process
- sum so that all channels on equal footing
- note the similarity to CI

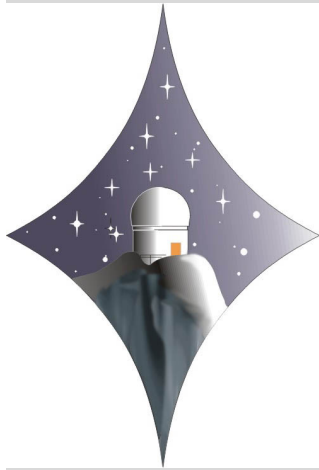


A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

Resonances

Channel mixing gives resonances





A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

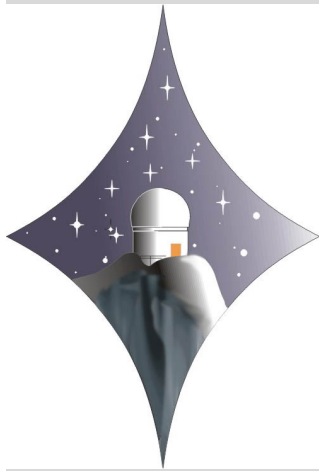
Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies



The close-coupling equations may be derived as follows. The functions satisfy the identity

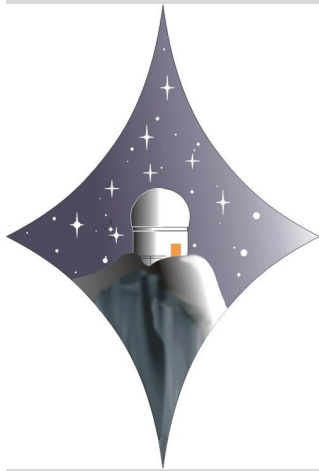
$$\int \psi^*(a|\mathbf{r}_1)[H-E]\Psi(\mathbf{r}_1,\mathbf{r})\,d^3\mathbf{r}_1 = 0$$

since $H\Psi = E\Psi$. A bit of algebra later...

$$[\nabla^2 + k_a^2]F(a|\mathbf{r}) = 2\sum_{a'} V_{aa'}(\mathbf{r})F(a'|\mathbf{r})$$

- $E = E_a + \frac{1}{2}k_a^2$.
- $\frac{1}{2}k_a^2$ is the channel energy
- if positive the channel is *open*, negative the channel is *closed*.
- $V_{aa'}$ is shorthand for $\int \psi^*(a|\mathbf{r}_1)V\psi(a'|\mathbf{r}_1)\,d^3\mathbf{r}_1$

A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies



- set of coupled differential equations
- with exchange

$$[\nabla^2 + k_a^2]F^{\pm}(a|\mathbf{r}) = 2\sum_{a'}[V_{aa'}(\mathbf{r}) \pm W_{aa'}(\mathbf{r})]F^{\pm}(a'|\mathbf{r}).$$

- exchange much more complicated as

$$W_{aa'}(\mathbf{r})F(a'|\mathbf{r}) = \int \psi^*(a|\mathbf{r}_1)[H(\mathbf{r}_1,\mathbf{r}_2) - E]F(a'|\mathbf{r}_1)\, d^3\mathbf{r}_1 \psi(a'|\mathbf{r}).$$

- F under the integral $\Longrightarrow$ coupled integro-differential equations.
- Solve using standard techniques
- Exchange small for large r
- Exchange small for large l
- Exchange small for large z
- Exchange small for large E

A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies

Weak Coupling

We can now look at simpler approximations. Remember

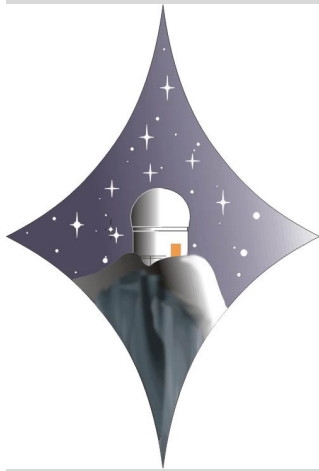
- $$F(j,i) \underset{r\to\infty}{\sim} e^{i\mathbf{k}_i\cdot\mathbf{r}}\delta_{ji} + \frac{e^{ik_j r}}{r} f(j,i)$$
- $$[\nabla^2 + k_j^2]F(j,i|\mathbf{r}) = 2\sum_{j'} V_{jj'}(\mathbf{r})F(j',i|\mathbf{r}). \qquad (1)$$
- now have two boundary conditions
- k_j^2 large so

  $$F(j,i) \simeq e^{i\mathbf{k}_i\cdot\mathbf{r}}\delta_{ji}$$

  an incoming plane wave. Put this into the RHS of (1) to obtain the first Born approximation

  $$[\nabla^2 + k_j^2]F_{B1}(j,i) = 2V_{ji}(\mathbf{r})e^{i\mathbf{k}_i\cdot\mathbf{r}}.$$

- $$f_{B1}(j,i) = -\frac{1}{2\pi}(\mathbf{k}_j|V_{ji}|\mathbf{k}_i)$$
- How large must the energy be? Who knows.



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

Distorted Wave

- distorted wave approximation assumes all except for V_{ji} are negligible. Have

$$\begin{aligned}[\nabla^2 + k_i^2]F(i,i) &= 2V_{ii}F(i,i) \\ [\nabla^2 + k_j^2]F(j,i) &= 2V_{jj}F(j,i) + 2V_{ji}F(i,i)\end{aligned}$$

- Solution is

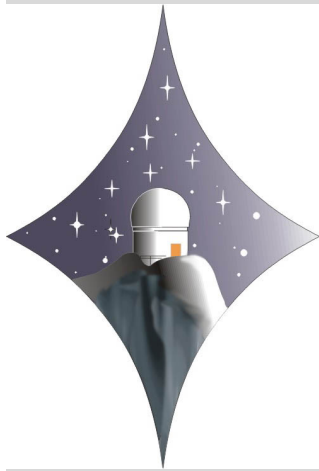
$$f_{DW}(j,i) = -\frac{1}{2\pi}\int \mathcal{F}(j,-\mathbf{k}_j)V_{ji}\mathcal{F}(i,\mathbf{k}_i)\,d^3\mathbf{r}$$

where

$$[\nabla^2 - 2V_{ii} + k_i^2]\mathcal{F}(i,i) = 0$$

$$\mathcal{F}(i,\mathbf{k}_i) \underset{r\to\infty}{\sim} e^{i\mathbf{k}_i\cdot\mathbf{r}}\delta_{ji} + \frac{e^{ik_i r}}{r} f_{DW}.$$

- Distorted wave with exchange – replace V by $V \pm W$
- Can also use Coulomb functions for ions



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

Bethe approximation

- Start with DW approximation

$$\sigma(i \to j) = \frac{1}{4\pi^2 g_i} \frac{k_j}{k_i} \int |(\mathbf{k}_j | V_{ji} | \mathbf{k}_i)|^2 \, d\mathbf{k}_j$$

- note that

$$V_{ji} = -\frac{1}{r_2} + \frac{1}{r_{12}}.$$

- expand $1/r_{12}$

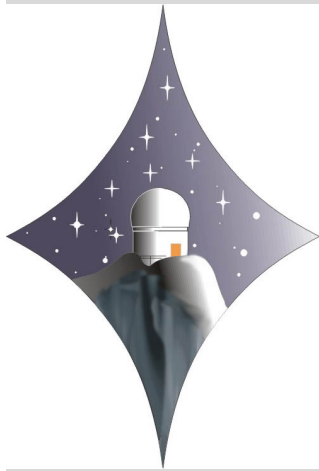
$$\frac{1}{r_{12}} = \frac{1}{r_2} + \frac{\mathbf{r}_1 \cdot \mathbf{r}_2}{r_2^3}.$$

- Integrate over $\mathbf{r}_1$,

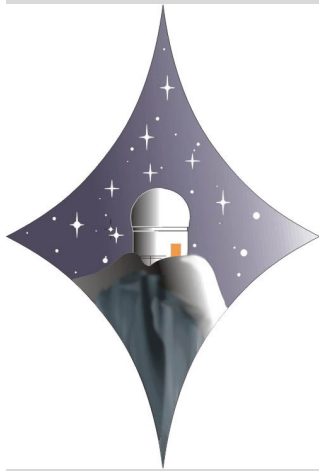
$$V_{ji}(r_2) = \frac{\mathbf{r}_2 \cdot (j|\mathbf{r}_1|i)}{r_2^3}$$

- cross section is

$$\sigma(i \to j) = \frac{1}{4\pi^2} \frac{k_j}{k_i} \int |(\mathbf{k}_j | \mathbf{r}_2 / r_2^3 | \mathbf{k}_i)|^2 \, d\mathbf{k}_j \times \frac{1}{3g_i} |(j|\mathbf{r}_1|i)|^2$$



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies



- Oscillator strength is

$$\frac{1}{3g_i}|(j|\mathbf{r}_1|i)|^2 = \frac{f_{ji}}{2\Delta E}$$

- free-free Gaunt factor

$$\int \left|(\mathbf{k}_j \left| \frac{\mathbf{r}_2}{r_2^3} \right| \mathbf{k}_i)\right|^2 d\mathbf{k}_j = \frac{32\pi^4}{k_i k_j \sqrt{3}} g(k_j, k_i).$$

- so cross section is

$$\sigma(i \to j) = \frac{4\pi^2}{k_i^2} \frac{f_{ji}}{\Delta E} g(k_j, k_i).$$

A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

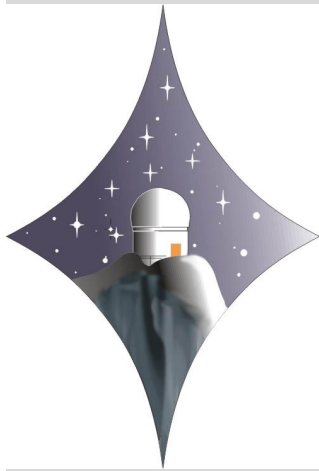
Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies



- Similar for photoionization (cross section $a(E_k)$)

$$\sigma_{\text{ion}}(i) = \frac{2}{k_i^2 \alpha \sqrt{3}} \int_0^{\frac{1}{2}k_i^2 - I} \frac{a(E_k) g(k_j, k_i)\, dE_k}{I + E_k}$$

- Plane waves (Born) gives Bethe

$$g = \frac{\sqrt{3}}{\pi} \log\left(\frac{k_i + k_j}{|k_i - k_j|}\right).$$

- Seaton and van Regemorter use g as fit parameter
- Only good when f_{ij} large
- Do not use if possible

A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

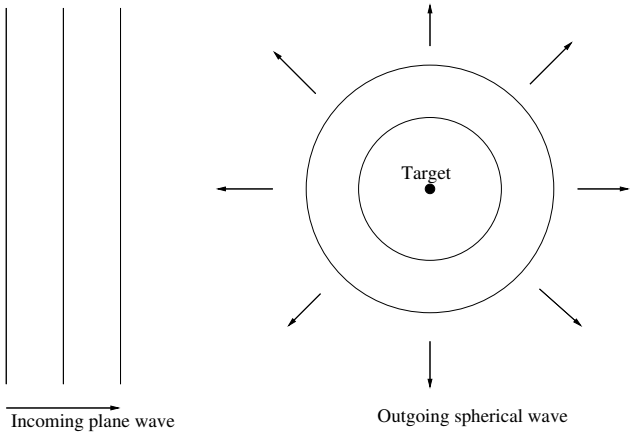
Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies

Partial Wave Theory

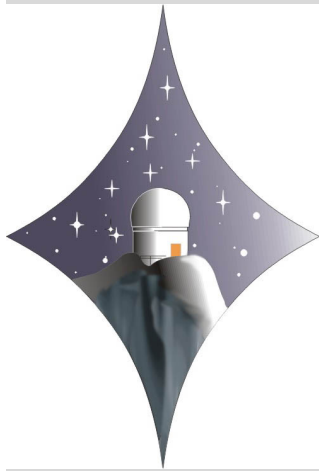


- Convenient to use outgoing *and* incoming spherical wave functions – problem is more symmetric
- waves look like

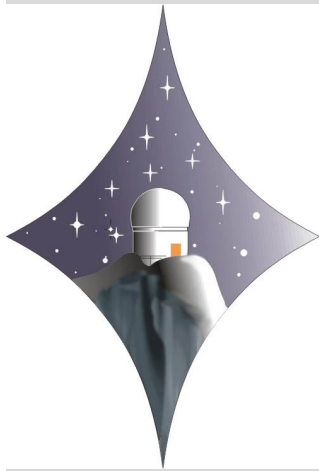
$$\phi_{\pm}(klm|\mathbf{r}) = k^{-1/2}\, Y_{lm}(\hat{\mathbf{r}})\, \frac{e^{\pm(kr-\frac{1}{2}l\pi)}}{r}.$$

- normalize (gives S matrix)

$$\Psi_S(al_2m_2|\mathbf{r_1},\mathbf{r_2}) \underset{r_2\to\infty}{\sim} \psi(a|\mathbf{r_1})\phi_-(k_a l_2 m_2|\mathbf{r_2}) - \sum_{a'l_2'm_2'} \psi(a'|\mathbf{r_1})\phi_+(k_{a'} l_2' m_2'|\mathbf{r_2}) S(a'l_2'm_2', al_2m_2) \quad (2)$$



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies



- then

$$f(a'\hat{\mathbf{k}}_{a'}, a\hat{\mathbf{k}}_{\mathbf{a}}) = \frac{2\pi i}{(k_a k_{a'})^{\frac{1}{2}}} \sum_{\substack{l_2' m_2' \\ l_2 m_2}} Y^*_{l_2 m_2}(\hat{\mathbf{k}}_{\mathbf{a}}) Y_{l_2' m_2'} \times (\hat{\mathbf{k}}_{\mathbf{a}}') i^{l_2 - l_2'} T(a' l_2' m_2', a l_2 m_2) \tag{3}$$

and $T(\alpha', \alpha) = \delta(\alpha', \alpha) - S(\alpha', \alpha)$ is the transmission matrix.

A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

General case

- Couple l_1, l_2, include spin and generalize
- Cross section is

$$Q(\alpha_i L_i S_i \rightarrow \alpha_j L_j S_j) = \frac{\pi}{k_i^2} \sum_{\substack{LS\pi \\ l_i l_j}} \frac{(2L+1)(2S+1)}{2(2L_i+1)(2S_i+1)} \left| T_{ji}^{LS\pi} \right|^2$$

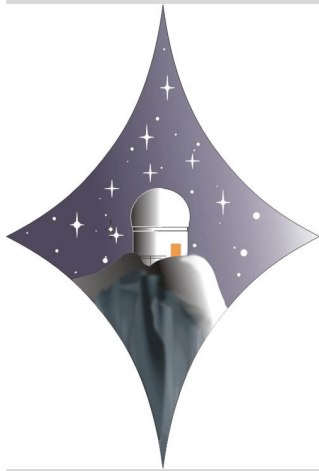
- collision strength is

$$\Omega(i,j) = \frac{(2L_i+1)(2S_i+1)}{\pi} k_i^2 Q$$

- convolve with Maxwellian

$$q_{ij} = n_e \frac{8.631 \times 10^{-6}}{w_i T^{1/2}} \Upsilon_{ij}.$$

- $\Upsilon_{ij} = \int_0^\infty \Omega(x) e^{-x} dx \qquad (x = E/kT)$ varies slowly



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

The K matrix

- computers don't like complex numbers
- so use

$$\phi_{\binom{c}{s}}(klm|\mathbf{r}) = k^{-1/2} Y_{lm}(\hat{\mathbf{r}}) \frac{1}{r} \begin{pmatrix} \cos \\ \sin \end{pmatrix} (kr - \frac{1}{2} l\pi)$$

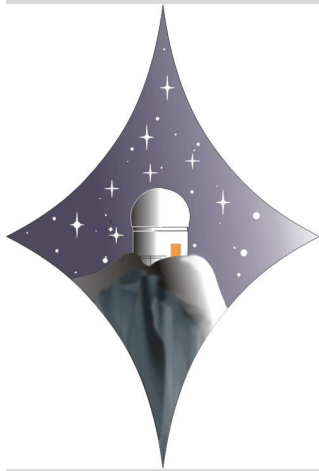
- K given by

$$\Psi_K \sim \Phi_S(\alpha) + \sum_{\alpha'} K(\alpha', \alpha) \Phi_C(\alpha).$$

- $2i\Phi_s \sim \Phi_+ - \Phi_-$ and $2\Phi_c \sim \Phi_+ + \Phi_-$ so

$$S = \frac{1 + iK}{1 - iK}$$

- With only one channel $K = \tan\delta$, the phase shift.



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

Accuracy of calculation

- Depends on target
- More levels (should be better)

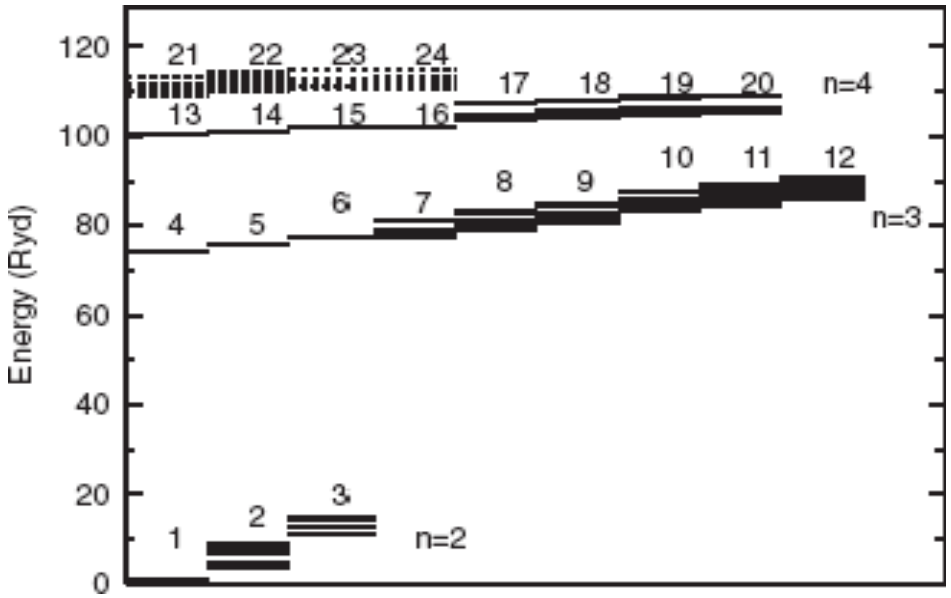
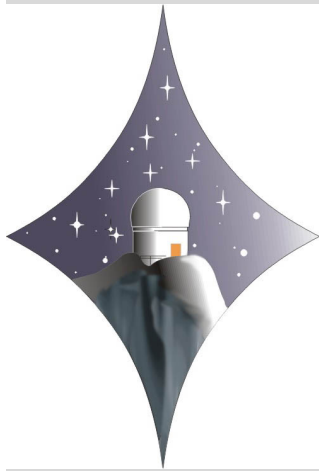


Figure: Target energies for Fe^{21+} (Badnell, Griffin and Mitnik, 2001)

- Agreement between observed and calculated energies
- Agreement between length and velocity f-values
- Agreement with other f-values



A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies

R-Matrix method for Hydrogen

- seek solutions for $r \leq a$ (R-matrix boundary). R-matrix box.
- a is finite so this is a bound state problem
- Equations solved once for each value of LS.

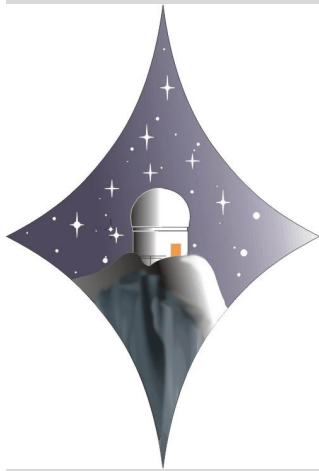
Radial Schrödinger equation for H is

$$(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \frac{2}{r} - E)F_E(r) = 0$$

with boundary condition

$$F'_E(a) = 0.$$

Solutions only for a discrete set of energies $E = e_k$ written as $f_k(r)$.



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

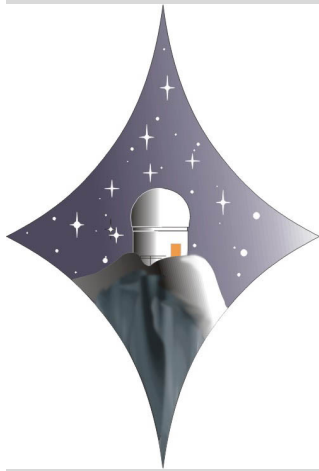


Table: Eigenvalues and functions for H, $l = 0$ (Yan & Seaton, 1985)

k	e_k	$f_k(a)$
1	−1.007362	0.136186
2	−0.232335	−0.719054
3	1.093783	0.688598
4	3.335493	−0.661618
5	6.400272	0.650858
6	10.272967	−0.645343

- f_k used to expand $F_E(r)$

$$F_E(r) = \sum_{k=1}^{\infty} f_k(r) A_{kE}$$

- some more algebra shows

$$F_E(a) = R(E) F'_E(a)$$

- R-matrix is

$$R(E) = \sum_{k=1}^{\infty} f_k(a)(e_k - E)^{-1} f_k(a).$$

- If we know f_k and e_k we can calculate F_E at all energies.

A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies

Matching at $r = a$: Bound states

- look for vector X so that at $r = a$

$$\begin{aligned} F &= PX \\ F' &= P'X \end{aligned}$$

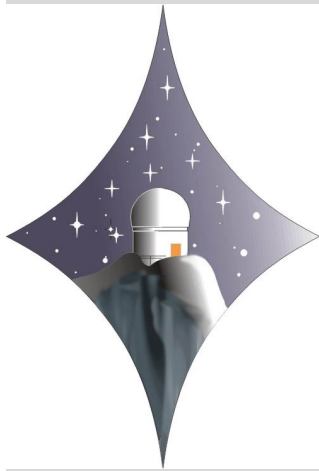
- $F = RF'$ so

$$PX = RP'X$$

- non-trivial solutions only when

$$\det[P - RP'] = 0.$$

- R comes from inner region, P from outer.
- calculate determinant on a fixed energy mesh, scan for roots with X have *physical* wavefunctions and energies from $r = 0$ to $r = \infty$.



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

Matching at $r = a$: Free states

For all channels open

$$P = S + CK$$

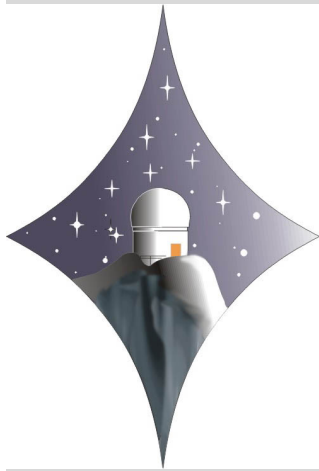
S and C are the sine and cosine-like Coulomb functions.

$$F = RF' \qquad \text{at } r = a$$

which gives immediately

$$K = (C - RC')^{-1}(S - RS').$$

The same can be done when some channels are closed, the principle is the same.



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

Summary

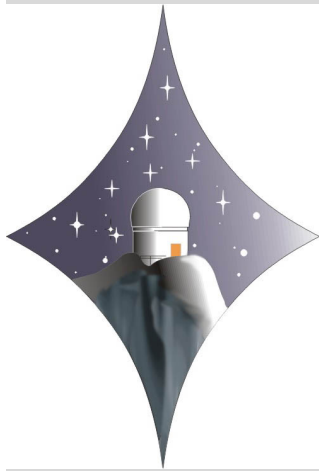
- Diagonalisation of H gives R at any energy.
- Matching to the Coulomb functions at $r = a$ gives K or bound states.
- K is enough for collisional data.
- radiative need

$$(\Psi|\mathbf{r}|\Psi') = (\Psi|\mathbf{r}|\Psi')_I + (\Psi|\mathbf{r}|\Psi')_O$$

- inner integrals are sums of

$$(u|\mathbf{r}|u')$$

  pre-calculated and stored.
- outer region Ψ are Coulomb functions and calculated rapidly



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

Some examples

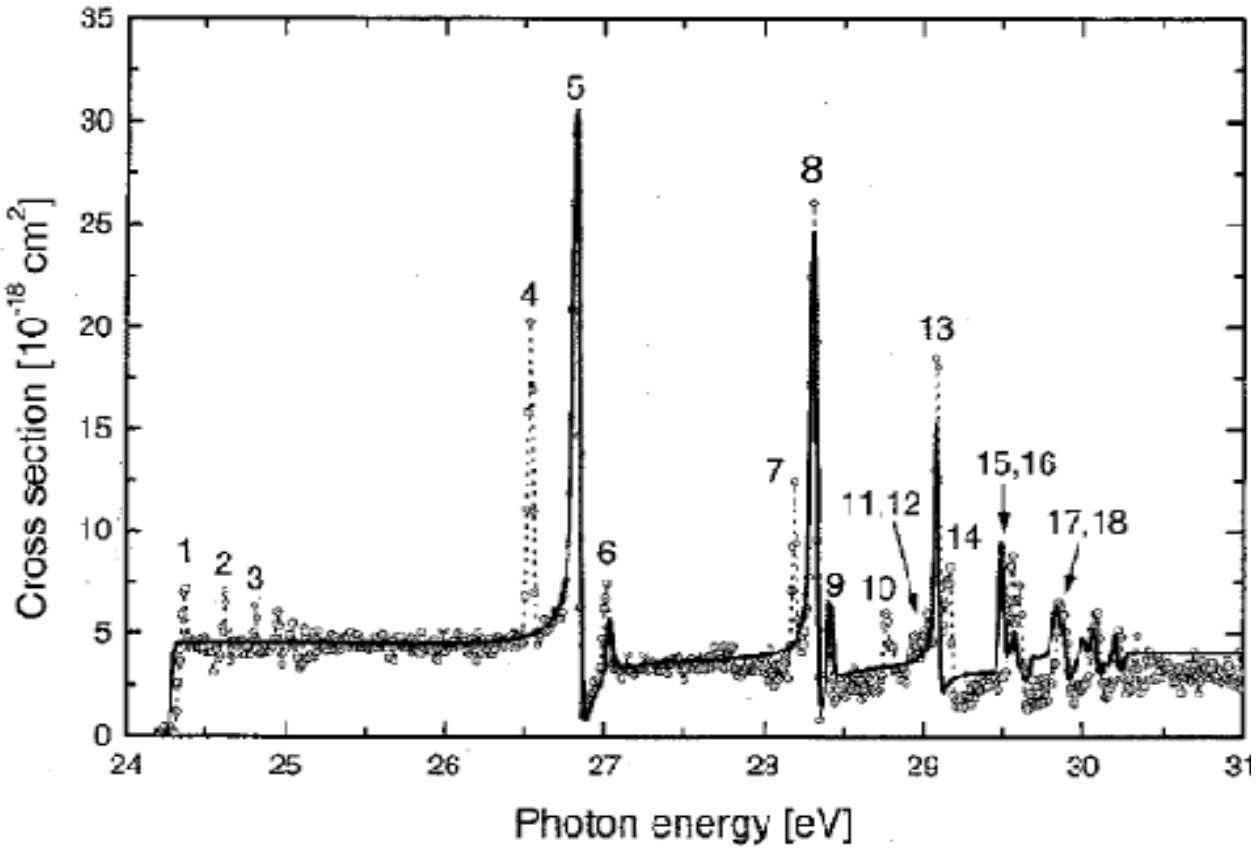
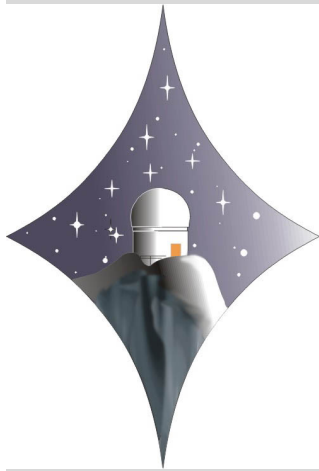
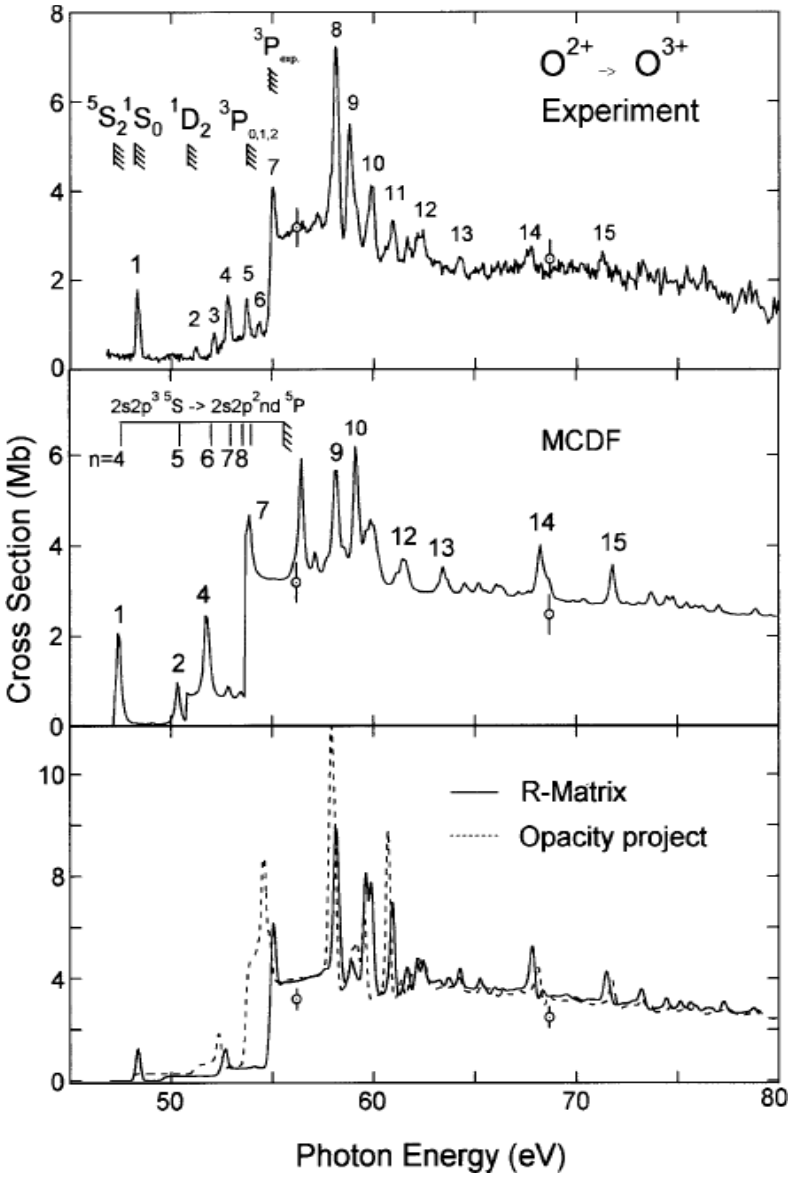


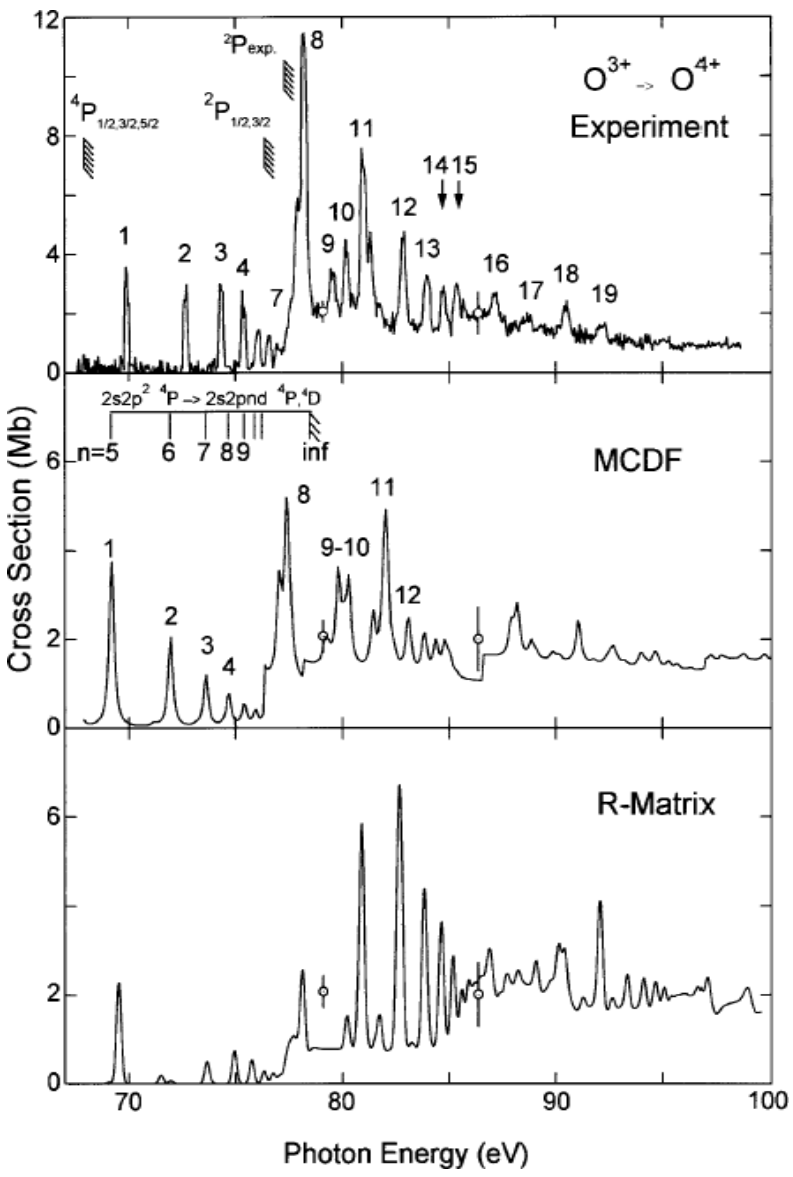
Figure: Low energy photoionzation of C^+. (Kjeldsen et al, 1999. The solid curve is from Nahar (1995)

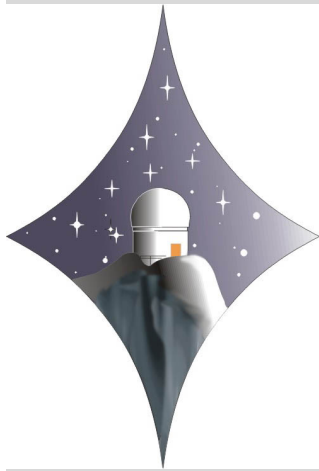


A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

Some examples (Champeaux et al, 2003)







A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies

Dielectronic recombination

- Resonances in photoionization is dielectronic recombination
- Can also combine f-values and background cross sections

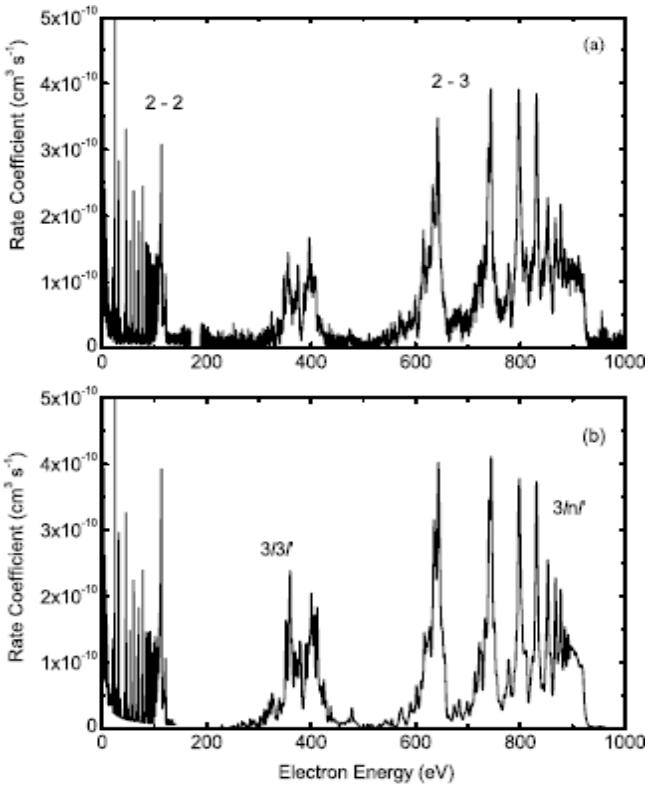
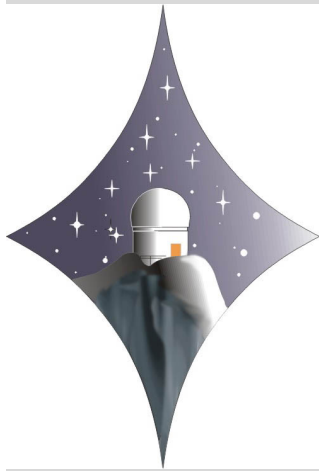


Fig. 1. Fe^{18+} to Fe^{17+} total DR rate coefficients due to $2 \rightarrow 2$ and $2 \rightarrow 3$ core excitations: **a)** TSR experiment (Savin et al. 1999, 2002a); **b)** the present MCBP calculations with the RR contribution added, which is responsible for the upward curve of the background with decreasing energy.

Figure: Zatsarinny et al (2003)



A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies

Relativistic Effects

- Full relativistic - DARC (Norrington and Grant)
- BP R-Matrix (Berrington et al)
- Breit-Pauli - DW packages (various)
- ICFT - Algebraic transformation (Badnell)

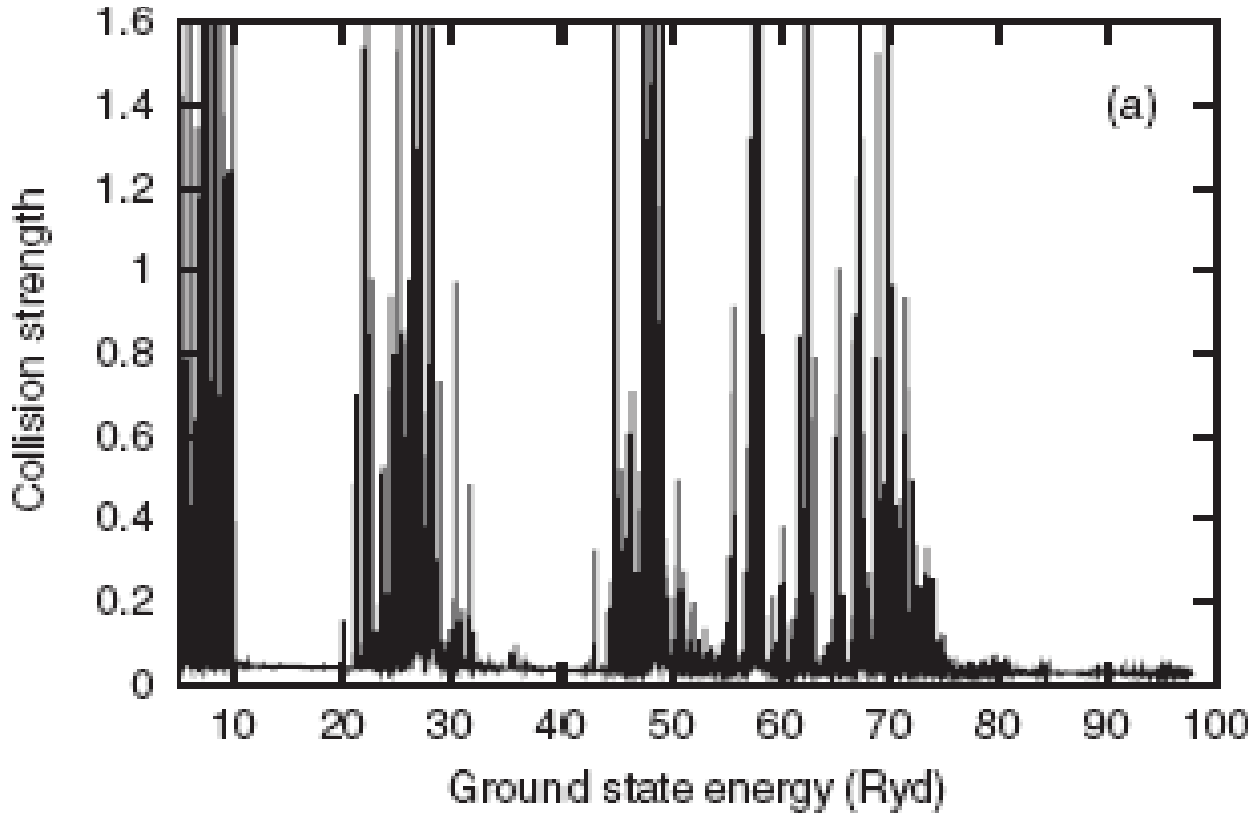
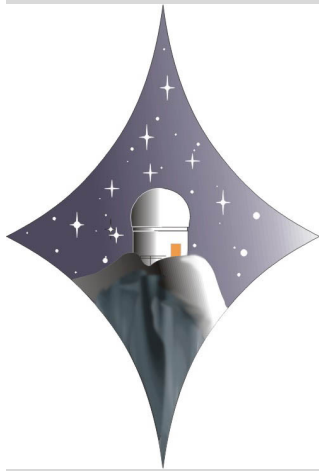


Figure: Badnell & Griffin, 2001



A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies

Intermediate energies

- at low energies – close coupling
- at high energies – Born
- at intermediate energies - CCC, RMPS

There's nothing new

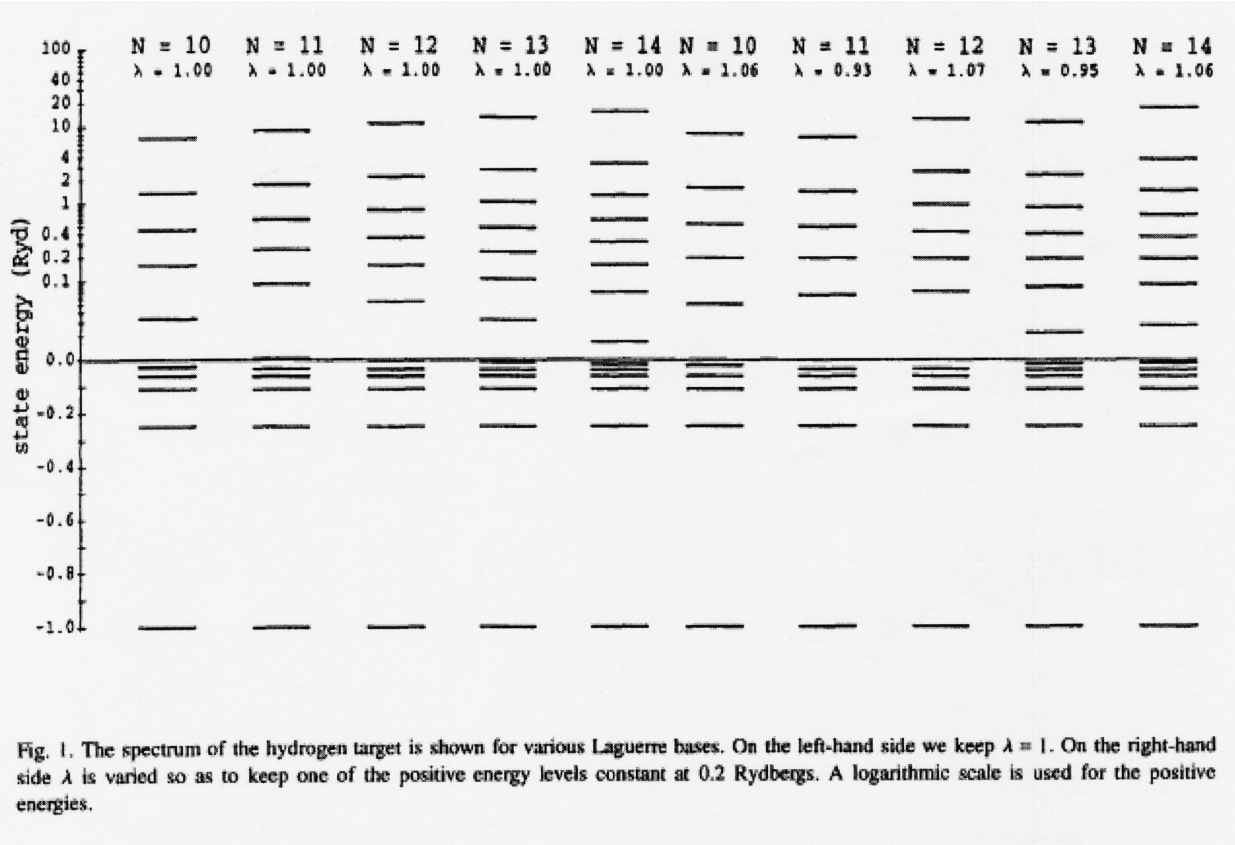
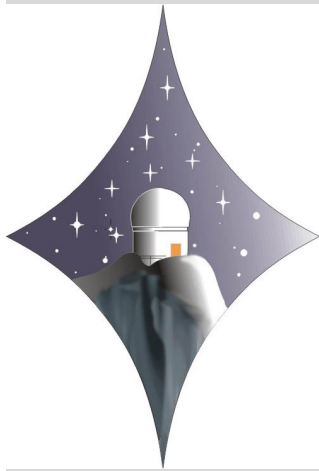


Fig. 1. The spectrum of the hydrogen target is shown for various Laguerre bases. On the left-hand side we keep $\lambda = 1$. On the right-hand side λ is varied so as to keep one of the positive energy levels constant at 0.2 Rydbergs. A logarithmic scale is used for the positive energies.

Figure: Bray and Stelbovics, 1995



A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

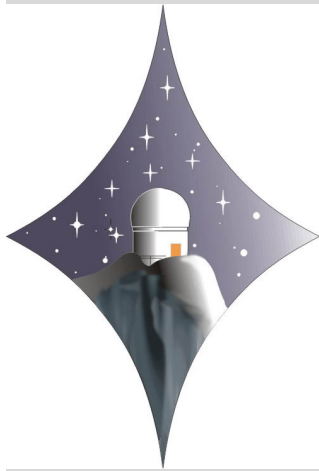
Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies



Convergent close coupling (CCC) and R-matrix with pseudostates (RPMS) differ in detail but both solve the problem in the same way. RPMS has an advantage compared to CCC since, as in the normal R-matrix method, the diagonalization of the Hamiltonian is done once and then cross sections at a large number of energies are obtained by matching the external functions to those from the inner region. This allows the resonances to be delineated which can only be done at great expense with the CCC method.

A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies

Intermediate energy calculations for H

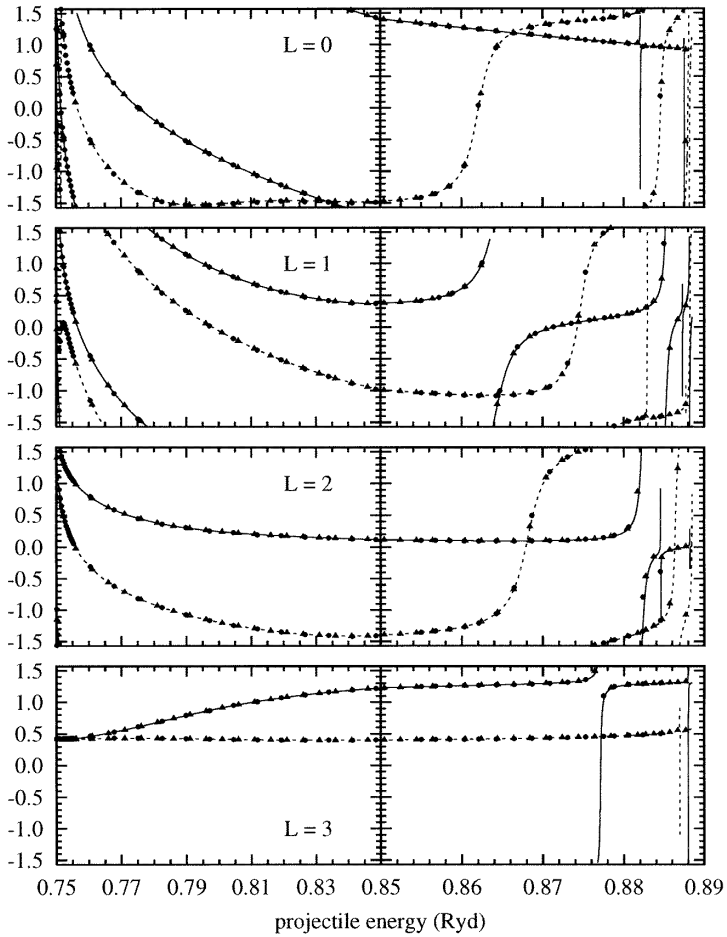
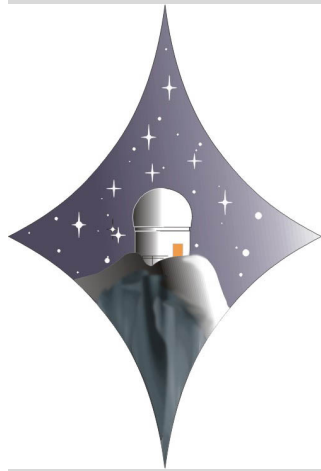


Figure: Bartschat et al, 1996



A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies

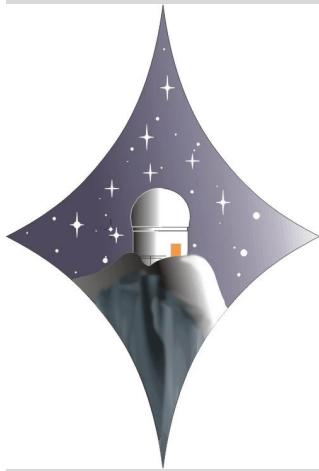
Summary

Radiative data

- quantum defect good for 1 electron systems
- CI calculations (much) better
- MCDF best for oscillator strengths
- There are good and bad calculations
- Photoionization from R-matrix method

Collisional data

- Bethe only if nothing else
- Born only very high energies
- Distorted wave not good for low z
- R-matrix good for low temperatures
- CCC and RMPS best



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies

Addendum: Determination of possible terms

Note that for a closed sub-shell, only a ^{1}S term is possible since $M_L = \sum_i m_{l_i} = 0$, $M_S = \sum_i m_{s_i} = 0$. For non-equivalent electrons, the exclusion principle is automatically satisfied, so that we can simply use the addition rules for angular momenta

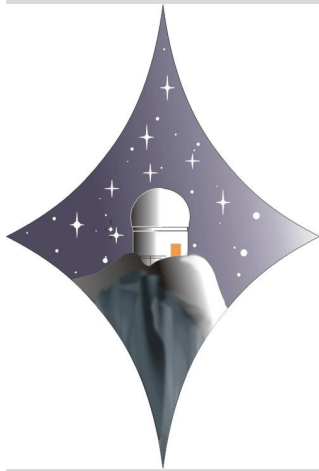
$$J = |J_1 - J_2|, \ldots, |J_1 + J_2|$$

for L and S separately. Consider two electrons with l_1, l_2. Then

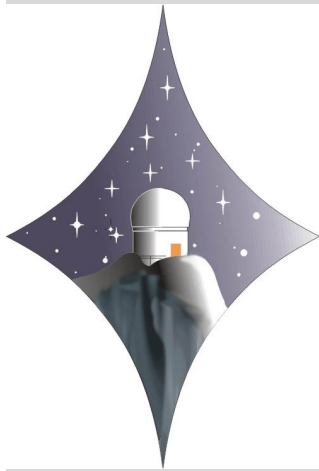
$$L = |l_1 - l_2| \ldots |l_1 + l_2|$$

and since $s_1 = s_2 = \frac{1}{2}$, $S = 0$ or 1. E.g. for $np\,n'p$, $l_1 = l_2 = 1$ and $L = 0$,1, or 2. Thus the possible terms are

$$^{1,3}\mathrm{S}, ^{1,3}\mathrm{P}, ^{1,3}\mathrm{D}.$$



A brief overview
Introduction
Hydrogen wavefunctions
The Quantum Defect Method
Many electron systems
Scattering theory
The close-coupling expansion
R-Matrix method
Intermediate energies



If $l_1 = 1$ and $l_2 = 2$, $(np\,n'd)$, on the other hand, $L = 1, 2, 3$ and the possible terms are

$$^{1,3}\mathrm{P}, ^{1,3}\mathrm{D}, ^{1,3}\mathrm{F}.$$

To work out the terms for three electrons, we start from the known two electron terms and then systematically add the third electron, using (65) once more. For example, consider $np\,n'p\,n''d$. The first two electrons give the terms listed in (66). The d electron has $l = 2, s = \frac{1}{2}$. If we add this to the ^{1}S term $(L' = S' = 0)$, we find $L = 2, S = \frac{1}{2}$, a ^{2}D term.

A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

Scattering theory

The close-coupling expansion

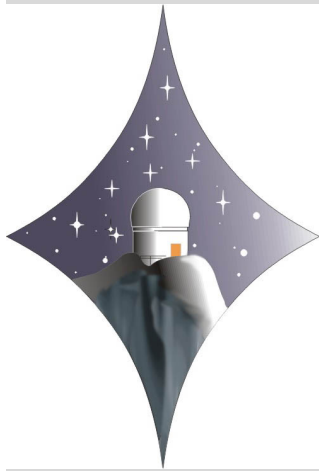
R-Matrix method

Intermediate energies

In the same way, adding the $n''d$ electron to

^{1}P	gives	^{2}P, ^{2}D, ^{2}F
^{1}D	gives	^{2}S, ^{2}P, ^{2}D, ^{2}F, ^{2}G
^{3}S	gives	^{2,4}D
^{3}P	gives	^{2,4}P, ^{2,4}D, ^{2,4}F
^{3}D	gives	^{2,4}S, ^{2,4}P,^{2,4}D, ^{2,4}F, ^{2,4}G

The process can be continued but it is obvious that the number of possible terms grows very rapidly.



A brief overview

Introduction

Hydrogen wavefunctions

The Quantum Defect Method

Many electron systems

Scattering theory

The close-coupling expansion

R-Matrix method

Intermediate energies