

Overview of Atomic Structure and Collision Theory

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Atomic Structure Methods

It is deceptively simple to write down the structure problem to be solved

$$\Psi = \sum_{\nu} a_{\nu} \psi_{\nu} . \quad (1)$$

The total wavefunction for the atom Ψ is expanded in terms of a complete set of (antisymmetric) basis states ψ_{ν} (an N -product of one-electron orbitals) with expansion coefficients a_{ν} .

Spherically symmetric problem \rightarrow (θ, ϕ) problem solved. Use standard angular algebra methods and packages are used, mostly based on Racah algebra but also Condon and Shortley (Slater-states).

Only require to determine radial dependence of wavefunction.

- Hartree/Dirac-Fock: coupled-set of radial equations result from formally varying radial orbitals to give stationary value of an energy functional — self-consistent solution: MCHF (Froese), HFR (Cowan), MCDF (Grant) etc. (Expansion coefficients may also be determined this way, MCHF.)
- Configuration Interaction (CI): radial equations (usually uncoupled) contain variational parameters (e.g. "model potentials") which are varied (numerically) to minimize a computed energy functional: AS/SS, CIV3, HULLAC
- As CI but using a self-consistent model potential: AS, HULLAC, FAC.

All approaches then, usually, construct and diagonalize the Hamiltonian to give the final e-states and e-energies.

Basis expansion is slow to converge in general. A plethora of basis functions are used: spectroscopic, psuedo (Laguerre), B-splines etc.

Pros & Cons: problems with converging HF for excited states. Local vs global minimum, flexible enough variational parameters.

Scattering codes can use only the simplest HF methods, in general: unique, orthogonal...

Hamiltonian

♣ Schrödinger equation based (AS, CIV3, MCHF):

- Non-relativistic: kinetic, nuclear & electrostatic operators.
- Breit-Pauli: as above, plus one-body fine-structure (spin-orbit), and non-fine-structure (Mass-Velocity & Darwin).
Fine structure mixes terms, non-fine-structure can be added to NR above.
- Breit-Pauli: as above, plus two-body fine-structure (spin-spin, spin-orbit, spin-other-orbit).
- Breit-Pauli: as above, plus two-body non-fine-structure (orbit-orbit, contact-spin-spin, Darwin).

♣ Kappa-averaged Dirac equation based (\pm small component): radial functions still depend only on nl , not nlj . Then using above Breit-Pauli operators. (HFR one-body only, AS.)

♣ Dirac equation based, large and small component.

- Dirac-Coulomb (HULLAC, FAC)
- + (Generalized) Breit +QED (GRASP, Sampson/LANL)

Others: Sapirstein & Johnson, Desclaux, Chen...

Coupling schemes: LS, LSJ, jK, jj (unitary transformations).

What matters more are good quantum numbers...

Atomic Structure Data

Bound-Bound

- Energy levels, ("All")
- E_k and M_k radiative rates ("Most")

Bound-Free

- Autoionization rates, DR (AS, HULLAC, FAC, MCDF(Chen) ...)
- Photoionization cross sections, RR (ditto)

Free-Free

- Infinite and finite energy Plane-wave Born (AS, Cowan)

And More...

- Hyperfine
- Stark-mixing, DR
- ...

Complex (Heavy) Species

- Unresolved Transition Array (UTA) Spectral shape — Bauche-Arnault, Bauche & Klapisch
- Configuration-average (CA) collisions — Cowan driven.

Both neglect configuration interaction.

Atomic Collision Methods

Time-dependent methods solve the full Schrödinger equation — TDCC.

Time-independent methods expand the antisymmetric total wavefunction for the target-plus-colliding particle Ψ in terms of a known complete basis of target states ψ_ν .

$$\Psi = \mathcal{A} \sum_{\nu} \psi_{\nu} \phi . \quad (2)$$

The expansion coefficients ϕ representing the colliding particle (projectile) are then to be freely determined by a variational of the scattering matrix leading to the continuum Hartree/Dirac-Fock equations.

Coupled-channel methods

Resonances arise naturally when the scattering energy of an open-channel coincides with that of a closed-channel.

Traditional close-coupling approximation truncates the expansion to a low-lying set of closely-coupled atomic states — neglects ionization loss.

Pseudo-state expansions attempt to approximate the sum/integral over a wide range of energies and work towards practical numerical convergence — RMPS, CCC.

Complete basis expansions can be used over a limited energy range and volume (particle in a box) — B-spline R-matrix, Intermediate Energy R-matrix.

Distorted-wave methods

DW methods solve (elastic) uncoupled continuum Schrödinger/Dirac equations and treat the (inelastic) coupling as a perturbation — can keep problem small, a series of 2x2 calculations: AS/HULLAC/FAC/LANL & UCL(historic)

Resonances are often neglected from electron-impact excitation, but not recombination — DR. Use of the IPIRDW approximation (Independent Processes Isolated Resonance using DW): AS/HULLAC/FAC

Simple 'DW': Coulomb or plane-wave Born for EIE & EII: ATOM or AS/Cowan

Heavy species: Baseline PWB → uplift to 'proper' DW.

R-matrix

Probably the most successful method/code suite for electron-impact excitation and photoionization (no so much for electron-ionization).

A close-coupling method which is very efficient at mapping-out resonances, compared to CCC, UCL-IMPACT (historic) etc. (But not compared to IPIRDW...)

Need to solve the coupled integro-differential scattering equations at tens, if not hundreds, of thousands of energies and for ~ 100 angular momentum symmetries.

Key Idea

Divide scattering region into two: an inner region that just encompasses the atom/ion (wavefunctions $\lesssim 10^{-3}$, say, outside) and where the scattering potentials are complicated (e.g. short-range); and an outer region where we only have an asymptotic Coulomb potential and, maybe, dipole and quadrupole coupling potentials (with analytic coefficients). Let the dividing boundary radius be r_0 .

The inner region is a finite volume and we can expand our (to be determined) continuum wavefunction in terms of a simple orthogonal basis of states $u_i(r)$, say, with a fixed (outer) boundary condition given by the logarithmic derivative:

$$\left. \frac{d}{dr} \log(u_i(r)) \right|_{r=r_0} = \left. \frac{u_i'(r)}{u_i(r)} \right|_{r=r_0} = b \quad (3)$$

where b is usually taken to be zero (it must be a constant).

This leads to a set of discrete positive energy solutions k_i^2 , say (particle in a box).

The inner region solution at $r = r_0$ for any scattering energy k^2 is completely characterized by the R -matrix:

$$R \equiv \sum_{i=1}^{\infty} \frac{[u_i(r_0)]^2}{k_i^2 - k^2}. \quad (4)$$

The scattering matrix (hence, cross section) is determined by matching the outer region solution to the inner region one at r_0 .

For example, for s-wave ($l = 0$) scattering off a neutral atom

$$K = \frac{-\sin(kr_0) + R(k \cos(kr_0) - b \sin(kr_0))}{\cos(kr_0) + R(k \sin(kr_0) + b \cos(kr_0))}. \quad (5)$$

Here, K is the reactance matrix, which is simply related to the S -matrix.

A more detailed exposition, based on Burke & Robb (1975), is available.

Web Links

<http://amdpp.phys.strath.ac.uk/>

<http://amdpp.phys.strath.ac.uk/tamoc/>

<http://amdpp.phys.strath.ac.uk/autos/>

http://amdpp.phys.strath.ac.uk/UK_APAP/codes.html