Configurations and superconfigurations models in Atomic Physics

X-ray radiation in hot plasmas

J. Bauche and C. Bauche-Arnoult

Laboratoire Aimé Cotton, UPR 3321, Campus d’Orsay, 91405 ORSAY

Cross talks in the physics of many-body systems, Paris, December 2006
TWO DIFFERENT APPROACHES

STATISTICAL MECHANICS

few details

some refinements are needed

FLUCTUATIONS

PHENOMENONS

QUANTUM MECHANICS

many details

some « globalization » is needed

STATISTICS
Outline

I. Introduction

II. Statics (structures)

III. Dynamical equilibrium \( \frac{dN_i}{dt} = 0 \)

IV. Dynamics \( \frac{dN_i}{dt} \neq 0 \)

V. Conclusion
I. INTRODUCTION

Basic theoretical *ab-initio* methods

Central field (radial potential)

Hartree-Fock method

Average Atom

Tensor Operators

Second Quantization

Statistical distributions
Central field

In Slater’s approach, an atom is a sphere, centered at which is the center of symmetry of the system.

The simplest form of the Hamiltonian

\[
H = - \sum_{i=1,N} \frac{\vec{p}^2_i}{2m} - \sum_{i=1,N} \frac{Ze^2_i}{r_i} + \sum_{i<j=1,N} \frac{e^2}{r_{ij}} + \sum_{i=1,N} \xi(r_i)(\vec{s}_i \cdot \vec{l}_i)
\]

has also spherical symmetry.

\[
H_0 = - \sum_{i=1,N} \frac{\vec{p}^2_i}{2m} + \sum_{i=1,N} V(r_i)
\]

is the zeroth-order Hamiltonian.

\[
H_r = - \sum_{i=1,N} V(r_i) - \sum_{i=1,N} \frac{Ze^2_i}{r_i} + \sum_{i<j=1,N} \frac{e^2}{r_{ij}} + \sum_{i=1,N} \xi(r_i)(\vec{s}_i \cdot \vec{l}_i)
\]

is the residual Hamiltonian.
Central field (cont’d)

Zeroth-order solutions:

the configurational states, which gather into degenerate electronic configurations. These states are made of angular and spin functions, and of radial functions.

Higher-order solutions:

the states obtained by diagonalizing the H matrix
- for one configuration (this is a calculation of intermediate coupling)
- for several configurations (this is a calculation of configuration interaction).

An approximate $ab$-$initio$ $V(r)$ radial potential is generally obtained through the variational optimization of an expansion in terms of Slater basis functions $r^n e^{-\alpha r}$.

The central-field model can be chosen to be relativistic
The tensor-operator methods have been invented by Gill and fully explained, and extended by Brian R. Judd. They compute the angular and spin parts of the configurational states, computation of the corresponding matrix elements of the

For very complicated cases, it is convenient to use the graphical methods developed by A. P. Jucys et al.
Second-Quantization formalism

The Second-Quantization formalism has been adapted in Physics by Brian R. Judd. In his version, the well-known annihilation operators do not relate to photons, or to nucleons or electrons.

This formalism is extremely efficient for the calculation of quantities, e.g., moments of statistical distributions, subspaces, or averages, or correlation factors.
II. STATICS

Statistics of configuration states and levels

An electronic configuration is denoted \((nl)^N (n'l')^N' (n''l'')^N'' \ldots\), i.e.,
a suite of open subshells \((nl)^N\). Each of its quantum states corresponds
to a pair of quantum numbers \((J, M_J)\) which are, in \(\hbar\) units, the values
of the total angular momentum and of its projection
on the z axis, respectively. The degeneracy of each \(J\) level is equal
to \(2J+1\).

It is remarkable that the number of \((\alpha J M_J)\) states of the
configuration, for example, is the well-known combinatorial factor,
whereas no simple formula has yet been found for the
number of \(J\) levels. However, the statistical distribution of
the \(J\) values is related to the derivative vs \(M_J\) of that of the \(M_J\) values,
which can be expressed as a Gram-Charlier distribution, whose moments
are computed \textit{exactly}. 

\[
\frac{\sqrt{2}}{\pi} \sqrt{\frac{N}{\pi}} \left( \begin{array}{c} \frac{1}{2} \\ \frac{N+1}{2} \end{array} \right) \frac{(2J+1)}{(2J+2)}
\]
The Gram-Charlier distribution function of $M_J$ (denoted $M$) in the $(l)^N$ configuration reads

$$D (M) = g \left( \frac{2\pi v}{\sqrt{\pi}} \right)^{1/2} \exp \left(- \frac{M^2}{2v}\right) \left[ 1 + \left( \alpha_4 - 3 \right) \left( 3 - \frac{6M^2}{v} + \frac{M^4}{v^2} \right)/24 + \ldots \right]$$

with the distribution moments $\mu_n (M) = \Sigma_i M_i^n / g$

$$\mu_2 \text{ (the variance } v) = N(4l - N + 2) \left( 4l^2 + 4l + 3 \right) / (4l + 1)$$

$$\mu_4 = N(4l - N + 2) \left[ N(4l - N + 2) x(1) + y(1) \right]$$

(where $x(1)$ and $y(1)$ are polynomials in 1)

and the kurtosis coefficient $\alpha_4 = \mu_4 / (\mu_2)^2$. 
Configuration levels

Configuration $4f^6$ de Pu I

Energie (cm$^{-1}$)

0 20000 40000 60000 80000 100000
J distribution of the levels of configurations

Example: 4f $^5$5d
Transition arrays

A transition array is the ensemble of the radiative processes which link two configurations.
Transition array

C'

C

λ
Lanthanum spectrum
The Unresolved Transition Array (UTA) model

In most arrays, the linewidths and the spectral deconvoluted lines are large enough for the line profiles to coalesce into a continuous band. That band can be simulated as a Gaussian (or skewed-Gaussian) feature, using the analytical expansion of the strength-weighted two (or three) lowest-order moments of the line wavenumbers.
<table>
<thead>
<tr>
<th>Transition array</th>
<th>Number</th>
<th>of lines</th>
<th>Exact</th>
<th>Relative error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p^3 - p^2s$</td>
<td>37</td>
<td>35</td>
<td></td>
<td>+5.5</td>
</tr>
<tr>
<td>$d^9 - d^8p$</td>
<td>59</td>
<td>60</td>
<td></td>
<td>-1.7</td>
</tr>
<tr>
<td>$d^8 - d^7f$</td>
<td>728</td>
<td>721</td>
<td></td>
<td>+1.0</td>
</tr>
<tr>
<td>$d^8p - d^8d'$</td>
<td>1574</td>
<td>1554</td>
<td></td>
<td>+1.3</td>
</tr>
<tr>
<td>$d^4 - d^3p$</td>
<td>1741</td>
<td>1718</td>
<td></td>
<td>+1.3</td>
</tr>
<tr>
<td>$f^3s^2 - f^3sp$</td>
<td>7429</td>
<td>7402</td>
<td></td>
<td>+0.4</td>
</tr>
<tr>
<td>$f^{13}d^2s - f^{13}dsp$</td>
<td>16027</td>
<td>15821</td>
<td></td>
<td>+1.3</td>
</tr>
<tr>
<td>$d^7f - d^6fp$</td>
<td>162289</td>
<td>160887</td>
<td></td>
<td>+0.9</td>
</tr>
<tr>
<td>$f^8 - f^7d$</td>
<td>279112</td>
<td>277827</td>
<td></td>
<td>+0.5</td>
</tr>
<tr>
<td>$d^6f - d^5f^2$</td>
<td>293376</td>
<td>291521</td>
<td></td>
<td>+0.6</td>
</tr>
</tbody>
</table>
Statistics of strengths in a transition array

Porter and Thomas have proved that the radiative array of the lines nearly obey a Poisson distribution (the strength to $a^2$).

This agrees with the fact that most (allowed) line array are very weak.
Amplitude distribution in Fe$^{4+}$ 3d$^4$ - 3d$^3$4p
Emissive zones
Configuration interaction effects between UTAs

It may happen that a configuration is linked radially to other ones, which are mixed by the residual Hamiltonian $H_r$ and whose energies are perturbed very little (to the second order of perturbation theory), but the strengths are perturbed to the first-order. Therefore, it is possible to predict the qualitative (and quantitative) changes in the UTAs without diagonalizing $H_r$. 
Configuration-interaction effects

Pr XXII  \( 4p^6 \, 4d^2 - (4p^5 \, 4d^3 + 4p^6 \, 4d \, 4f) \)
The Spin-Orbit-Split-Array (SOSA) model

It may happen that the spin-orbit interactions are so large that the UTA Gaussian feature is split into two or three smaller ones, called *sub-arrays*. Other specific global formulas can be used, in pure j-j coupling.
The $3d^84s - 3d^84p$ array

Kr X

Mo XVI

Pr XXXIII
The Resolved Transition Array (RTA) model

For computing the monochromatic absorption, a smooth curve like the Gaussian functions of the UTA model ought to be replaced by a line-by-line model, because the gaps between the lines are essential data. For achieving an RTA model, one uses the same energy variance and total strength as for the relevant UTA. The individual-line characteristics are picked at random in the following joint triple distribution of the upper and lower level energies \( E \) and \( E' \) and of the line amplitudes \( a \):

\[
D(E, E', a) = \mathcal{N} \exp\left(-\frac{E^2}{2\nu} - \frac{E'^2}{2\nu'} - \lambda a^2\right)
\]

where \( \nu \) and \( \nu' \) are the energy variances of the configurations, and \( \lambda \) is a correlation factor.
Correlation between energies and strengths
The propensity law

In most $C_1 - C_2$ transition arrays, the higher (lower) levels of $C_1$ are more strongly linked to the higher (lower) levels of $C_2$. 
The more intense lines are closer to the center of the array.

Exact line-by-line calculation

Statistical calculation, without correlation
RTA model: the Iron absorption spectrum (T=20 eV)

\[ \rho = 10^{-4} \text{ g/cc} \]

\[ \rho = 10^{-3} \text{ g/cc} \]

\[ \rho = 10^{-2} \text{ g/cc} \]
The Local Thermodynamical Equilibrium (LTE)

Four simple laws, from *Statistical Mechanics*, are enough for calculating the populations of all the levels of all the ions.

1) Planck’s law \( \text{ (the radiation spectral distribution)} \)

2) Maxwell’s law \( \text{ (the free-particle kinetic-energy distribution)} \)

3) Boltzmann’s law \( \text{ (the populations of the } J \text{ levels)} \)

4) Saha’s law \( \text{ (the populations of the ions)} \)
The Local Thermodynamical Equilibrium (LTE) (cont’d)

In the LTE plasma conditions, the population of each $\alpha J$ level

$$N(\alpha J) = (2J + 1) N \exp \left[ -\Delta E(\alpha J) / kT_e \right]$$

where $N$ is a calibration factor and $\Delta E(\alpha J)$ is the energy of level referred to the ground level of the relevant ion. Additional properties can be deduced.

However, when too many levels are involved, it is more practical to achieve the calculations by using configurations, or even superconfigurations. Codes like STA and SCO have been written for that purpose.
Definition of superconfigurations

A superconfiguration is the totality of all the configurations of the core electrons possess the same ensemble of principal quantum numbers. For example,

\[(3)^2\] represents all the two-electron configurations with

\[3s^2, 3s3p, 3s3d, 3p^2, 3p3d, 3d^2\]
Superconfigurations in Xe (Fe-like)

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Configurations</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3)^16</td>
<td>6</td>
</tr>
<tr>
<td>(3)^15 (4)^1</td>
<td>36</td>
</tr>
<tr>
<td>(3)^15 (5)^1</td>
<td>45</td>
</tr>
<tr>
<td>(3)^15 (6)^1</td>
<td>54</td>
</tr>
<tr>
<td>(3)^15 (7)^1</td>
<td>63</td>
</tr>
<tr>
<td>(3)^15 (8)^1</td>
<td>72</td>
</tr>
<tr>
<td>(3)^14 (5)^2</td>
<td>180</td>
</tr>
<tr>
<td>(3)^14 (5)^1 (6)^1</td>
<td>360</td>
</tr>
<tr>
<td>(3)^14 (6)^2</td>
<td>252</td>
</tr>
</tbody>
</table>

2436 configurations

5 700 000 levels

(n)^N : N electrons in the n shell.
e.g. (3)^15 (4)^1 : (3s 3p 3d)^15 (4s 4p 4d 4f)^1
Non-LTE cases

Practically, LTE situations are very rarely found. Planck’s law is rarely obeyed, due to the escape of photons from the medium. In those NLTE cases, one has to study the competition between the atomic processes.

The balance equation is used. A Collisional-Radiative model of homogeneous linear equations is obtained.
NLTE: balance equation

\[ \frac{dN_i}{dt} = \sum_{j \neq i \, P} N_j R_{ji}^P - N_i \sum_{j \neq i \, P} R_{ij}^P = 0 \]
NLTE codes for levels, configurations, and/or superconfigurations

Pairs of atomic processes:
- spontaneous emission
- photoionization
- collisional excitation
- collisional ionization
- autoionization
- radiative absorption
- radiative recombination
- collisional de-excitation
- 3-body recombination
- resonant electron capture

NLTE codes

for levels
HULLAC, FAC are very accurate NLTE codes.

for configurations
In ATOMIC, the CR system is solved for configurations, adapted rates

for superconfigurations
In AVERROES, the CR system is solved for SCs, as in each SC, the reduced configuration population follows a decreasing-exponential law vs energy, for temperatures...
For superconfigurations (cont’d)

In MOST/AVERROES, the CR system is solved for SC assuming that, in each SC, the reduced configuration population follow a decreasing-exponential law vs energy, for temperature specific to the different SCs. The CR system can be split into systems of the same size, one for the reduced populations and one for the $1/T(\text{SC})$ values.

For levels, configurations, and/or superconfigurations

In SCRAM/HYBRID, the CR system is solved for lowly-excited configurations, and highly-excited SCs, with...

In SCROLL, an iteration/convergence procedure is used. At the beginning, the CR system contains many SCs. Further depending on the results of the comparisons between successive iterations, some SCs may be discarded, and others may be split into other levels, configurations, and/or superconfigurations, with adapted rates, at each iteration.
Configuration temperatures

$T_e = 20 \text{ eV}$

Collisional-radiative calculations in Fe IV, V, VI (4668 levels)

Log (state populations)

Energies of $3d^34p$ states

$n_e (\text{cm}^{-3})$

$10^{19}$

$10^{18}$

$10^{17}$

$10^{16}$

$10^{15}$

$10^{14}$

240.0 260.0 280.0 300.0 320.0 340.0 360.0
superconfiguration temperatures in Xe (Cu-like)

\[ T_e = 450 \text{ eV} \]
\[ T_1 = 183 \text{ eV} \]
\[ T_2 = 300 \text{ eV} \]
\[ T_3 = 165 \text{ eV} \]
\[ T_4 = 178 \text{ eV} \]
Ionic excitation temperature in Xe (Cu-I)

- $T_c = 450$ eV
- $T_1 = 183$ eV
- $T_2 = 300$ eV
- $T_3 = 165$ eV
- $T_4 = 178$ eV
Ionic excitation temperatures in Gold

$T_0 = 2500 \text{ eV} \quad n_0 = 10^{22} \text{ cm}^{-3}$
<Z> values for Gold  \( (N_e=1.10^{21} \text{ cm}^{-3}) \)
(NLTE-4 Workshop data base)
IV. DYNAMICS

The balance equation written above only holds for the stationary cases, i.e., in the assumption that no ions escape from the plasma. It is much more complicated, but necessary, to study the dynamic cases. In the genuine physical situations, the plasma exchanges ions with its environment (this is hydrodynamics), and photons (this is radiative transfer and radiative power loss).
V. CONCLUSION

Work is in progress in many laboratories. A new scientific journal, entitled *High Energy Density Physics*, has been created recently by Dick Lee (Livermore) and Steve Rose (Oxford). This proves that many new methods and results are still expected.

Finding the best compromise between accuracy (of the completeness (of the plasma description), and time reduction (computing times) is a challenge.

For that purpose, global methods are recommended. They have the advantage of putting some phenomenons into evidence. Instead of when one only produces millions of numerical results, « One cannot see the wood for the trees! ».
Pr XXII \[ 4p^6 \ 4d^2 - (4p^5 \ 4d^3 + 4p^6 \ 4d \ 4f) \]
Emissive zones
THE TRANSFER EQUATION

\[
\frac{dN(C_i)}{dt} = \sum_j R(C_j' \rightarrow C_i) \cdot g(C_j') \cdot n_{SC'} \exp \left[ -\frac{\Delta E(C_j')}{kT(SC')} \right]
\]

2nd correlation

\[
= g(C_i) [\alpha + \beta \Delta E(C_i)] \cdot n_{SC'} \exp \left[ -\rho \frac{\Delta E(C_i)}{kT(SC')} \right]
\]

1st correlation

where \(\Delta E(C_i) = E(C_i) - E_{av}(SC)\).

\(n_{SC'}\) is the population of the "average state" of \(SC'\).
Total radiative power loss of the $(3)^N$ superconfigurations (Iron ions)
Relative configuration-interaction contribution to the total RPL of the $(3)^N$ superconfigurations (Iron ions)
Hartree-Fock methods

Essentially, a Hartree-Fock calculation consists in minimizing the total energy of a configurational state of given angular and spin parts, through a variational optimization of the electronic radial functions.

In general, for the computed state, the results are better than those of any central field. But, in principle, the obtained radial quantities are not valid for the other levels of the same configuration, in contrast with those of the central-field approach. Configuration-mixing can be accounted for by assuming that to be optimized is a linear combination of the states of configurations. The corresponding code is a MultiConfiguration Hartree-Fock (MCHF) code, or Dirac-Fock (MCDF) code.
Ionic excitation temperatures in Au$^{52+}$ (Co-like)

$T_e = 2500\ eV\quad n_e = 10^{22}\ cm^{-3}$

$T(\text{ion}) = 2675\ eV$

$T(\text{ion}) = 427\ eV$

6 processes + spontaneous emission

6 processes

Superconfiguration energy (eV)