Atomic Data Needs for X-ray Astronomy. 22 June 2000
http://heasarc.gsfc.nasa.gov/docs/heasarc/atomic/
M. A. Bautista, T. R. Kallman, and A. K. Pradhan, eds.

Theoretical Calculations of Atomic Data for Spectroscopy

Manuel A. Bautista

Laboratory for High Energy Astrophysics

NASA Goddard Space Flight Center

Greenbelt, MD 20771, USA

Abstract.
Several different approximations and techniques have been developed for the calculation of atomic structure, ionization, and excitation of atoms and ions. These techniques have been used to compute large amounts of spectroscopic data of various levels of accuracy. This paper presents a review of these theoretical methods to help non-experts in atomic physics to better understand the qualities and limitations of various data sources and assess how reliable are spectral models based on those data.

1. Introduction

Spectroscopic data for atoms and ions fall into the category of fundamental scientific research and this by itself may be good justification for experimental and theoretical work. The data are also essential to the analysis of spectra of laboratory and astronomical plasmas. These applications have been as important motivation as, if not greater than, the fundamental physics For several decades, theoretical atomic physicists have devoted great effort to the development of methods and computation of vast amounts of data, particularly that needed for the study of optical spectra. On the other hand, the progress of the atomic data sets for X-ray spectroscopy has been much slower, due in part to the scarcity of high quality X-ray spectra to motivate the work. At present, the new generation of observatories (like *Chandra* and *XMM*) and the incoming facilities with the *Constellation-X* program are starting to provide high resolution, high signal-to-noise spectra for which the need of improved atomic data is not just granted but urgent. But the production of high quality atomic data for X-ray spectroscopy is far from simple or routine. The high energy conditions of the emitting plasmas demand the study of large numbers of energy levels as well as inner-shell and Auger processes, Thus, current theoretical methods and computational tools encounter severe difficulties in producing high accuracy data.

The present review of theoretical atomic physics is aimed at astronomers and spectroscopists in general who need to understand the limitations of atomic data. In that sense, the present paper tries to give a general, but relatively simple, overview of the most commonly used approximations and methods for the production of spectroscopic data. The review pays particular attention to the the calculation of atomic structure and the spectral processes of photoionization and electron impact excitation. Other processes like collisional ionization and proton impact excitation, although relevant, are not discussed in much detail due to lack of space. For discussions on electron-ion recombination see papers by Nahar and Savin in this volume. Also, the present review emphasizes inner-shell processes that are most relevant to X-ray spectroscopy.

From the point of view of the kinds of atomic data needed for the analysis of spectra there are two general atomic physics problems to be solved:

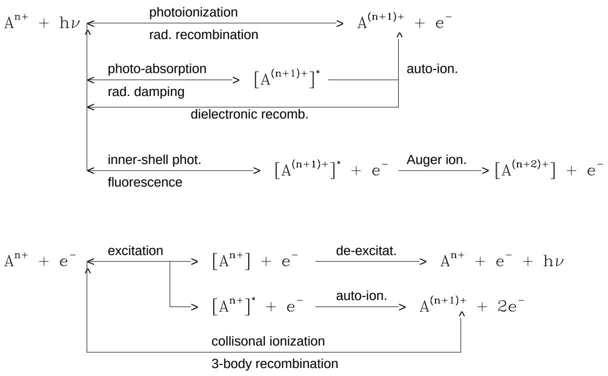

Figure 1. Physical processes after photon-ion and electron-ion scattering. The brackets indicate excited states of the ion and brackets and asterisc indicate autoionizing states.

1) Atomic structure
- Energy Levels
- Radiative transition rates
- Autoionization rates

2) Scattering
- ion + photon
- ion + charged particle

The atomic structure problem is concerned with the computation of energy levels and rates of spontaneous transition rates among levels of the same ion (transition rates or A-values), and from autoionizing levels of one ion to levels of the next ionized species (autoionization rates). The scattering problem, relevant to the formation of spectra of warm and hot plasmas, has to do with all different processes that can occur after a collision of an ion with a photon or with a charged particle. The most important physical processes that occur after ion scattering are illustrated in Figure 1.

2. Atomic Structure Calculations

From the point of view of quantum mechanics the physical representation of ions and spectral processes comes down to the fundamental problem of solving the Schrödinger equation

$$H\Psi_i = E_i\Psi_i. \tag{1}$$

Here, i represents the set of quantum numbers necessary to describe the system, Ψ_i are the wavefunctions of the system, E_i are the eigenvalues, and H is the Hamiltonian which, for a non-relativistic system, can be written as

$$H = \sum_{i=1}^{N} \frac{p_i}{2m_e} - \sum_{i=1}^{N} \frac{Ze^2}{r_i} + \sum_{i\neq j} \frac{e^2}{|r_i - r_j|}, \tag{2}$$

where the first term is the sum of the kinetic energies of all electrons, the second term is the potential energy due to Coulomb attraction of all electrons by the nucleus, the third term is the energy due to electrostatic repulsion between the electrons, and N is the total number of electrons in the system. The previous equation neglects the spin of the electron, which can be considered separately in non-relativistic systems.

The presence of the two-electron operators $1/|r_i - r_j|$ makes it impossible to obtain exact solutions to the Schrödinger equation for the N-electron system. On the other hand, the two-electron operator should never be neglected as it is often comparable in magnitude to the Coulomb attraction term or one-electron operator. One can show

$$\frac{two - electron\ term}{one - electron\ term} \equiv \xi \simeq \frac{1}{2}\frac{N(N-1)}{ZN}. \quad (3)$$

For a neutral ion ($Z = N$), $1/4 \leq \xi \leq 1/2$.

Approximate methods for solving Equation (1) replace the two-electron terms by approximate one-electron potentials to give an effective Hamiltonian of the form

$$H^{eff} = \sum_i^N H_i^{eff} = -\sum_{i=1}^N \left[\frac{1}{2}\frac{p_i^2}{m_e} + \frac{Ze^2}{r_i} - V_i^{eff}(r_i)\right]. \quad (4)$$

The exact eigenfunctions of H^{eff} can now be constructed from products of single-electron eigenfunctions of H_i^{eff}. Since H commutes with angular momentum and spin operators (L^2, L_z, S^2, S_z) the eigenfunctions of H^{eff} are required to be eigenfunctions of these operators as well.

For highly ionized ions ($Z \gg N$), the inter-electronic repulsions are only small perturbations relative to the much stronger nuclear central potential. Then, it is a good approximation to choose V_i^{eff} as a *central field potential.* If this can be achieved the orbital wavefunction may be written explicitly as products of spherical harmonics, spin functions, and radial functions. The advantage of using central field orbitals cannot be overestimated. The effect is to reduce the computational problem from solving N coupled integro-partial-differential equations (one for each orbital) in four variables to N coupled integro-differential equations in a single radial variable.

In general V^{eff} does not need to be of central field type, but the advantages of a central potential are so great that essentially all methods for atomic structure calculations use spherically averaged potentials even for neutral and open-shell systems. There are several techniques regularly used in the atomic structure calculations. The most important are: use of model potentials, methods based on the Hartree-Fock theory, semiempirical methods, perturbation methods, and the R-matrix method in the close coupling formalism. These methods, with the exception of the R-matrix, are discussed below followed by a discussion of two particularly important physical effects, i.e. configuration interaction and relativistic effects. The R-matrix method will be described in Section 3.5.

2.1. Model potentials in atomic structure

Alkali atoms and ions are good systems for testing model potentials since, by having a single valence electron, their analysis leads to a single equation for the one-electron wavefunction. For these ions one would expect the potential for large r to approach

$$V^{eff}(r) = -\frac{(Z - N_c)}{r}, \quad (5)$$

where N_c is the number of core electrons. The solution of the Schrödinger equation based on this potential is discussed by Bates and Damgaard (1949). In spite of the simplicity of this potential it gives accurate oscillator strengths in many cases, but it is not always reliable (Bromander et al. 1978).

A large variety of model potentials have been constructed from the assumptions that they behave as shown in Equation (5) for $r > R$, for some suitable R, while for r approaching 0 the potential could be infinite, equal to a finite boundary value, or even zero. For a review of model potentials in atomic structure see Hibbert (1982).

A generally applicable potential is the modified Thomas-Fermi potential by Eissner and Nussbaumer (1969). This potential is implemented in the widely used computer program SUPERSTRUCTURE (Eissner, Jones, and Nussbaumer 1974). This program uses a Thomas-Fermi-Dirac type of central potential to generate one-electron orbitals.

This potential differs from that in Equation (5) not only in the added sophistication of the model, but also in that this one depends on the angular momentum of the valence electrons. SUPERSTRUCTURE is quite efficient and can provide relatively accurate results ($\sim 1\%$ for energy levels and $\sim 10\%$ for oscillator strengths). Recently the code has been extended to calculate autoionization and dielectronic recombiantion data (AUTOLSJ by Bely-Dubau 1982 and AUTOSTRUCTURE by Badnell 1985, unpublished) has extended the code to calculate autoionization rates and dielectronic recombination.

2.2. Atomic structure calculations base on the Hartree-Fock Formalism

In contrast to the local central-field potentials, the Hartree-Fock (HF) method entails the computation of the one-electron orbitals in the non-local potential (direct and exchange) generated from electronic orbitals in a self-consistent manner using the variational principle. More extensive discussion of the HF method can be found in Hartree (1957), Slater (1960), Froese Fischer (1977), Cohen and McEachran (1980).

Early HF calculations indicated that in going from the ground state of beryllium $1s^22s^2\ {}^1S$ to the first excited states $1s^22s2p\ {}^{1,3}P^o$, the $1s$ orbital remains almost unchanged. This led Fock (1933) to realize that accurate wavefunctions could be found by varying only valence orbitals while keeping the orbitals for the core fixed. This approach is known as the *frozen core* (FC) approximation.

In spite of the success of the FC approximation, this is not always directly applicable, such as in the case of configurations containing equivalent electrons. The simplest example of such configurations is the ground state of helium $1s^2\ {}^1S$, which has two equivalent electrons, both described by a single radial function $P_{1s}(r)$. Yet, if one identifies one of the electron as "core" and the other as "valence" they require different radial functions. Evidently, these two $1s$-orbitals cannot be made orthogonal. The use of nonorthogonal orbitals to solve the atomic structure problem leads to equations much more complex than otherwise. Calculations with such nonorthogonal orbitals have been carried out only for a few systems (e.g. Pratt 1956; Froese 1966; Jucys 1967).

The FC approximation yields goods results for simple systems, but for the mayority of cases it is necessary to include electronic configuration interactions like in the multiconfiguration Hartree-Fock (MCHF) or in the superposition of configurations (SOC) methods. For example, for boron-like cores a possible two-configuration core wave function is

$$\Psi({}^1S) = c_1\Psi_1(1s^22s^2\ {}^1S) + c_2\Psi_2(1s^22p^2\ {}^1S). \tag{6}$$

Clementi and Veillard (1965) showed that including $\Phi(1s^22p^2\ {}^1S)$ accounts for most of the correlation energy error for all values of Z.

The MCHF (e.g. Froese Fischer 1977) method computes orthonormal orbitals self-consistently in an iterative fashion for every choice of the $\{c_i\}$ coefficients. Then, these coefficients are varied and the radial wavefunctions are recomputed until sufficient degree of convergence is achieved. This makes the method potentially very accurate, but computationally lengthy.

Based on the MCHF technique, Hibbert (1975) developed the SOC method in which analytic radial functions depending on variational parameters are used. Core wave functions of the kind shown in Equation (7) are used and the $\{c_i\}$ coefficients are determined for a given choice of the radial wavefunction parameters. Then, the radial wavefunctions are changed and the coefficients determined again until the description of the atom converges satisfactorily. The SOC method is somewhat more efficient than the MCHF technique and is able to provide similarly accurate results. The main implementation of the SOC method is in the computer program CIV3 (Hibbert 1975).

Another approach used to improve calculations of atomic structure arises from the realization that a single valence electron may polarize the spherically symmetric core, including a dipole moment at the nucleus of the form α/r^2, where α is the dipole polarizability of the core (Hartree 1957). This gives rise to an additional attractive field with a long-range r dependence which is experienced by the valence electron, and at large distances may be represented by a "polarization potential"

$$V_{pol} = -\alpha/2r^4. \tag{7}$$

This potential is singular at $r = 0$, but it can be modified to avoid this singularity as (Biermann and Trefftz 1953)

$$V_{pol} = -(\alpha/2r^4)[1 - exp(-x^p)], \quad x = r/\rho\ . \tag{8}$$

The use of a V_{pol} in the orbital equations for valence electrons can be formally justified (Caves and Dalgarno 1972), and it has been shown (e.g. Cohen and McEachran 1980, and references therein) to provide a very satisfactory description of simple spectra. However, the method has the disadvantage that the choice of the parameters p and ρ in Equation (9) remains completely *ad hoc*.

2.3. Semiempirical methods

Semiempirical methods try to compute the atomic structure of ions by solving simplified forms of the HF equations. One of the first examples of this approach is the Hartree-Fock-Slater (HFS) scheme, which consists in replacing the two-electron non-local exchange terms of the Hamiltonian by the statistical potential function

$$V_{xs}(r) = -\frac{3}{2}\left(\frac{24}{\pi}\rho\right)^{1/3}, \tag{9}$$

where ρ is the local electron density $\rho(r)$ of the atom.

Later, Cowan (1967) modified the HFS approach to write the total potential of the ion as

$$V^i(r) = -2Z/r + V_e(r) + V_{xs}(r), \tag{10}$$

where V_e is the potential energy for the density $\rho - \rho_i$ of electrons other than i and V_{xs} is an exchange term of the form

$$V_{xs} = -k_1 f(r)\left[\frac{\rho'}{\rho' + k_2/(n-l)}\right]\left(\frac{\rho'}{\rho}\right)\left(\frac{24}{\pi}\rho\right)^{1/3}, \tag{11}$$

where k_1 and k_2 are constants, ρ' is the electron density less the densities of the electron i and of the electron with which it is paired, and

$$f(r) = \begin{cases} 1 & r \geq r_0 \\ 1 + k(1 - r/r_0) & r < r_0 \end{cases} \tag{12}$$

for suitable k and r_0.

This definition for the atomic potential is mostly empirically motivated and requires preconceived wave functions with which to construct the electron density functions ρ and ρ'. Once these functions are created the atomic structure equations are solved in an iterative fashion. Then, the accuracy of the results is assessed upon the agreement between obtained energy levels and oscillator strengths with a given sample of experimental values. The method has the advantage of being quite efficient, but it requires a lot of care in the construction of the initial electron density distribution. Further, it is difficult to estimate the accuracy of any given calculation except by the observed agreement of a limited sample of data with experimental values.

The Cowan code has been widely used by many researchers like Kurucz (e.g. Kurucz 1988; Kurucz and Peytremann 1975), who computed millions of energy levels and oscillators strengths for most ions of astrophysical interest.

2.4. Perturbation treatments

Perhaps the best known perturbation treatment is the Z-expansion method which was first introduced by Hylleraas (1930). The main idea behind this method is that one can rewrite the N-electron atom Hamiltonian of Equation (2) in terms of units of length of Z atomic units (au) and unit of energy of Z^2 au (thus different units for each N-electron ion) to obtain

$$H = \left[\frac{1}{2}\sum_i^N \frac{p^2}{m_e} - \sum_i^N \frac{1}{r}\right] + Z^{-1}\left[\sum_{i\neq i} \frac{1}{|r_i - r_j|}\right]. \tag{13}$$

Then, for highly ionized systems ($Z \gg N$) one can divide this Hamiltonian as indicated by the brackets into a one-electron zero order Hamiltonian (H_0) and a two-electron perturbation (H_1) with the expansion parameter Z^{-1}. Perturbation theory leads to the expansion for the energy and wavefunction of the form

$$E = E_0 Z^2 + E_1 Z + E_2 + E_3 Z^{-1} + \ldots \tag{14}$$

$$\Psi = \Psi_0 Z^{3/2} + \Psi_1 Z^{1/2} + \Psi_2 Z^{-1/2} + ... \tag{15}$$

Here, H_0 is the sum of hydrogenic Hamiltonians, so Ψ_0 is a linear combination of Slater determinants of hydrogenic orbitals. Subsequent orders of the Hamiltonian and wavefunctions are found as in standard perturbation theory.

The Z-expansion method is conceptually simple, but computationally lengthy when trying to go beyond the first perturbation term. One advantage of the method is that a single calculation provides results for a whole isoelectronic sequence, but accuracy is normally restricted to highly ionized ions. Another problem occurs in cases of strong configuration interaction (see Section 2.5) where states are labeled by the single configuration with the largest mixing coefficient, thus zero order mixing does not represent the physical state being considered.

Several extensions of the Z-expansion method have been developed (see Cohen 1988, Crossley 1969, and references therein) and a lot of data for astrophysical applications has been published in recent years by Vainshtein, Safronova, and collaborators (e.g. Vainshtein and Safronova 1980; Safronova et al. 1998).

2.5. Additional considerations

Configuration interaction Configuration interaction (CI) can be seen as a way to correct for Hartree's single-electron orbital approximation that pictures each electron moving individually in the field of the nucleus screened by the other electrons. Each electron is described by a single wavefunction and the whole atom is described by the Slater determinant of these wavefunction (e.g. Slater 1960). This model admits the familiar configuration description of, for example, the ground state of Be $1s^2 2s^2 (^1S)$. This kind of description is often not very accurate. Much better wavefunctions may be obtained from linear combinations of single configuration wavefunctions of the same total angular momentum and spin symmetry (Condon and Shortley 1935). This approach is named CI.

Going back to the case of the ground state of Be, a good CI description may be

$$\Psi(^1S) = \alpha\Psi(1s^2 2s^2\ ^1S) + \beta\Psi(1s^2 2p^2\ ^1S), \tag{16}$$

where α and β are the so-called mixing coefficients.

Such CI representation has important effects on atomic quantities like oscillator strengths. For example, in the transition probability of the resonant transition $1s^2 2s^2(^1S) - 1s^2 2s2p(^1P^o)$. In the single configuration model the transition probability is determined by the matrix element $< 2s|r|2p >$. On the other hand, in the two-configuration description of the ground ^1S state, the matrix element becomes $(\alpha \pm \beta) < 2s|r|2p >$. Depending on the relative signs of the mixing coefficients and the $\pm$ sign, the transition may be strengthened or weakened, but which way the value will go is generally impossible to know without a full solution of the atomic structure problem.

CI is very important in the representation of the majority of atomic systems and is a standard capability of codes like SUPERSTRUCTURE, CIV3, Cowan's code, and Froese Fischer's MCHF code.

Relativistic Effects So far we have neglected relativistic effects in atomic structure calculations and we have considered oscillator strengths for dipole allowed transitions under LS coupling. In order to consider forbidden transitions it is necessary to use jj (or at least intermediate) coupling, and this requires some treatment of relativistic effects. For heavy atoms and ions relativistic effects are important even for allowed transitions. There are two ways of treating relativistic effects: by the addition of Breit-Pauli operators to non-relativistic equations, or by the fully relativistic Dirac formalism. The Breit-Pauli operators are seven and each one accounts for a specific physical effect (Bethe and Salpeter 1957). These operators are: (1) the mass operator which gives the correction due to the relativistic variation of mass with velocity; (2) the Darwin term which is characteristic of the Dirac theory but has no obvious physical interpretation; (3) the spin-orbit coupling term which arises from the interaction of spin and orbital magnetic moments of each electron; (4) the spin-other-orbit term which is due to the interaction between the spin of one electron with the orbital magnetic moment of another electron; (5) and (6) are spin-spin coupling terms that describe the interactions between the spin magnetic moments of pairs of electrons; (7) the orbit-orbit coupling term which accounts for the interactions between the orbital magnetic moments of pairs of electrons.

The expectation value of the orbit-orbit coupling term cannot be calculated accurately in the one-electron approximation. Moreover, experience suggests that this term is rather small for all ions of interest to the present discussion (Ufford and Callen 1958; Cohen and McEachran 1980). The mass and Darwin terms contribute to the overall energy shift, but do not break LS coupling. The spin-spin, orbit-orbit, and spin-other-orbit operators serve to split energy terms into fine structure levels.

Most current codes for atomic structure calculations such as SUPERSTRUCTURE and CIV3 use the Breit-Pauli approximation to account for relativistic effects. A more precise treatment of relativistic effects using the Dirac formalism has been implemented in the computer package GRASP (Dyall et al. 1989).

3. Scattering Calculations

In considering the problems of photoionization and excitation or ionization by electron impact it is customary to think of the residual ion as the "target" or "core" with N electrons and the incoming/outgoing (electron impact/photoionization) as "free electron". Thus, the wavefunctions of the $(N+1)$-electron system can be expanded in terms of products of wavefunctions of the core (ϕ_i) and those of the electron (θ_i), i.e.

$$\Psi = \sum_i \phi_i(x_1, ..., x_N)\theta_i(x_{N+1}). \tag{17}$$

Substitution of (18) in Equation (2) yields the system of coupled equations

$$-(\nabla^2 + k_i^2)\theta_i(x) + \sum_{i'} V_{ii'}\theta_i(x) = 0 \tag{18}$$

where

$$V_{ii'}(x) = -\frac{2Z}{r_1}\delta_{ii'} + \int \phi^*(x_1, ..., x_N) \times \sum_{n=1}^{N} \frac{2}{r_{N+1,n}}\phi(x_1, ..., x_N)dx_1...dx_N \tag{19}$$

and k_i^2 is defined by

$$E = E_i(N) + k_i^2. \tag{20}$$

It is important to notice that these equations have to be solved for every value of the energy (k^2) and of the total angular momentum (L) of the $(N+1)$-electron system. This last condition motivates the so-called *partial waves expansion* in which all states of definite angular momentum of the free electron are considered separately. Furthermore, the calculated collision strength is divided into partial waves as

$$\Omega = \sum_{l=0}^{\infty} \Omega_l \tag{21}$$

There are several methods to solve the scattering problem and calculate the cross sections necessary for practical applications. Below is a discussion of the most widely used methods ordered according to their level of sophistication, starting with the simplest method. This discussion is followed by a study of several physical effects that affect the cross sections. The techniques are: the central field approximation, used in photoionization calculations; the Gaunt factor and the Coulomb-Born approximation, used for electron impact excitation; and the Distorted Wave and the R-matrix methods, used for both photoionization and electron impact excitation and ionization, as well as atomic structure.

3.1. The central field approximation

This is the simplest approximation used to solve the multi-electron problem. As discussed above, in the context of atomic structure calculations, it is assumed that inter-electronic couplings are small and can be treated as small perturbations with respect to an effective central field potential that includes the attraction by the nucleus less the screening by the core electrons. A further substantial simplification of the problem results by treating *subshells* of equivalent electrons (having the same values of n and l, but different values of m and s) by means of a single radial function. This has the effect of reducing the number of coupled radial equations to only one for each subshell.

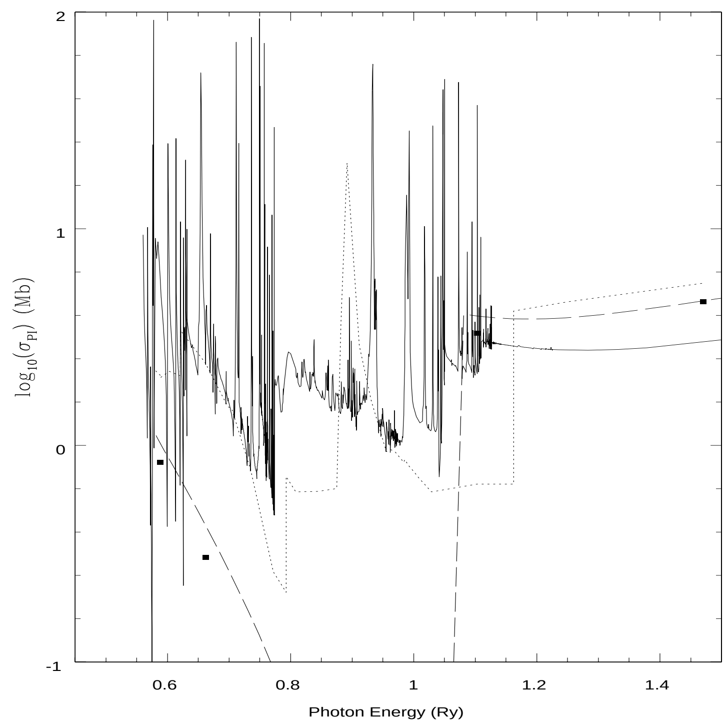

Figure 2. Photoionization cross section of the ground state $3d^6 4s^2\ ^5D$ of Fe I. The full curve represents the R-matrix results of Bautista and Pradhan (1995); the dotted curve shows the results of Kelly and Ron (1972) and Kelly (1972) using the many-body perturbation method; the dashed curve and the square dot represent the central-field results of Verner et al. (1993) and Reilman and Manson (1979) respectively.

Central field type calculations of photoionization cross sections have been carried out by Reilman and Manson (1979), who adopted Hartree-Slater wave functions (Herman and Skillman 1963), and Verner et al. (1993), using the Dirac-Slater potential (Slater 1960; Band et al. 1979). These cross sections are reasonable accurate at high photon energies, but often give poor results near the threshold, particularly where CI is strong. For example, in the photoionization of Fe I the central field cross section from the threshold to the $3d$ subshell is underestimated by more than three orders of magnitude, as seen in Figure 2 (Bautista and Pradhan 1995). Similar errors of up to orders of magnitude are found in Fe II through Fe V (Bautista and Pradhan 1998).

Other problems with central field cross sections are that they neglect resonances and, because only degenerate subshells of equivalent electrons rather than individual energy levels are considered, the utility of these cross sections in detailed spectral modeling is limited.

3.2. The Gaunt factor

Burgess, Seaton, and Van Regemorter (Burgess 1961; Seaton 1962, Van Regemorter 1962) suggested an approximate formula to obtain near threshold collision strengths for optically allowed transitions. The formula is based on the Kramers approximation and the Gaunt factor, g, and is usually accurate within a factor of a few. Later, the formula was modified to replace g, which is a varying function with energy, by an empirical parameter $\bar{g} \sim 0.2$. The formula is

$$\Omega(i,i') = \frac{8\pi}{3\sqrt{(3)}} S(i,i')\bar{g}, \tag{22}$$

where $S(i, i')$ is the line strength, which relates to the absorption oscillator strength as $g_{i'} f_{i'i} = (2/3)(E_{i'} - E_i)S(i, i')$

At high energies $\bar{g}$ increases logarithmically and the collision strength takes the form (Seaton 1962)

$$\Omega(i.i') = \frac{4}{3} S(i, i') \ln[4k^2/(r_0 \Delta E)^2], \tag{23}$$

where $\Delta E = E_{i'} - E_i$, and r_0 is the distance of closest approach given by

$$\frac{2z}{r_0} - \frac{l(l+1)}{r_o^2} + k^2 = 0. \tag{24}$$

3.3. The Coulomb-Born approximation

In the Coulomb-Born (CB) approximation $V_{ii'}$ is replaced by its asymptotic form at large r, $2z/r$, where $z = Z - N + 1$. In doing this the solutions to the scattering problem are known analytically. The CB approximation is best for highly charged ions and transitions not affected by channel coupling and large partial waves (e.g. Seaton 1975; Van Regemorter 1960).

3.4. The Distorted Wave approximation

The Distorted Wave (DW) method assumes the coupling between different target states to be weak ($V_{ii'} = 0$, for $i \neq i'$ in Equation 19). Then, the system of coupled equations is reduced to

$$\{-(\nabla^2 + k_i^2) + V_{ii}\}\theta_i = 0. \tag{25}$$

Some of the most refined forms of the method were developed by Saraph, Seaton, and Shemming (1969) and Eissner and Seaton (1972) including exchange, which is important in many cases, like in intercombination transitions. In addition, *correlation functions*, χ_i, which are wavefunctions of the $(N+1)$-electron system, were introduced to modify the wavefunctions as

$$\Psi = \sum_i \phi_i(x_1, ..., x_N)\theta_i(x_{N+1}) + \sum_{j=1} c_j \chi_j(x_1, ..., x_{N+1}), \tag{26}$$

where the coefficients c_j are determined variationally. This form of expansion of the wavefunction is known as the close-coupling (CC) expansion (Seaton 1953).

The DW method usually gives accurate collision strengths in the absence of resonances for systems more than a few times ionized (see paper by Bhatia in this volume). Hershkowitz and Seaton (1973) showed that the DW method could also provide information about bound states of the $(N+1)$-electron system, and hence obtain resonance structures. However, for detailed calculations of cross sections including resonances it is usually preferred to use the R-matrix method.

3.5. The R-matrix method

The R-matrix method is the most sophisticated of the techniques discussed here and is also the most accurate. The method takes into account nearly all of the physical effects that contribute to cross sections for astrophysical applications and is applicable to all kinds of ions, from neutral to highly ionized species. Of course, with the increased complexity of the calculations the R-matrix method can be computationally very intensive.

The R-matrix theory starts by dividing the configuration space by a sphere of radius a centered on the target nucleus. In the internal region, $r < a$, where r is the relative coordinate of the free electron, electron exchange and correlation between the scattered electron and the target are important. Thus a CC expansion like that in Equation (27) is adopted for the system. In the external region, $r > a$, electron exchange between the free electron and the target can be neglected if a is large enough to contain the charge distribution of the target. Then the scattered electron moves in the long-range multipole potentials of the target ion. The internal and external regions are linked by the R-matrix on the boundary, $r = a$.

Following the theory from Burke et al. (1971), and Burke and Robb (1975), the total wavefunction Ψ in the inner region for any energy E can be written in terms of the basis states set $\{\psi_k\}$ as

$$\Psi = \sum_k A_{Ek}\psi_k \tag{27}$$

where the ψ_k functions are energy independent and are expanded as shown in Equation (27), and the energy dependence is carried through the A_{Ek} coefficients.

Then, the R matrix is defined as

$$R_{ij}(E) = \frac{1}{2a}\sum_k \frac{w_{ik}(a)w_{jk}(a)}{E_k - E}, \tag{28}$$

where

$$\frac{1}{r}w_{ik}(r) =< \chi_i|\psi_k > \tag{29}$$

This R matrix is the basic solution of the electron-scattering problem as it allows one to determine the atomic structure of the $(N+1)$ system, the collision strengths, and photoionization cross sections. The R matrix, the amplitude of the wavefunctions at the $r = a$ boundary, and the poles E_k are obtained from the eigenvalues and eigenvectors of the Hamiltonian matrix. Further, quantitative results for physical parameters of interest are obtained by matching the solutions with those in the outer region which are known analytically.

One important point to note is that in the R-matrix method the solution inner region is obtained only once, then cross sections for any number of energy points are readily available. Furthermore, although the basic computations in this method are lengthly, it turns out to be a very efficient technique as it provides results for large numbers of points which allow complex resonance structures in the cross sections to be delineated.

The R-matrix method has been implemented in the RMATRX package of codes (Berrington, Eissner, and Norrington 1995) which has been widely used by several groups like the Opacity Project, that carried out extensive atomic structure and photoionization calculations of astrophysically important ions, and the Iron Project, and the RmaX Project (see papers by Pradhan and Berrington in this volume).

3.6. Important physical effects

There are several specific physical effects that should be taken into account when calculating or evaluating cross sections for photoionization or collisional excitation/ionization. These are: target CI, resonances, convergence of the wavefunction expansion, convergence of partial waves expansion, relativistic effects, and radiation damping.

Configuration interaction The first requirement in any scattering calculation is a good representation of the target, i.e. accurate wavefunctions for the target ion. Such representation usually requires the inclusion of CI in the atomic structure model, which as we saw in Section 2.5.1 affects the calculated energy levels and oscillator strengths of the ion. Furthermore, comparisons between calculated and experimental energies and oscillator strengths of the target are important indicators of the quality of the target representation and the overall accuracy of the obtained cross sections.

Resonances Resonances are an important part of collisional excitation/ionization and photoionization cross sections. Physically, resonances occur when the incoming particle (electron or photon) with just the right kinetic energy gets trapped into an autoionizing state[1] of the $(N+1)$-electron system. Then, as the electron remains trapped for a time before autoionization occurs, the time delay yields a phase shift in the wavefunction that manifests itself in sharp peaks or throughs in the cross sections (resonances).

Resonances appear as Rydberg series converging onto the various excitation thresholds of the target. In complex ions with many levels close in energy the series of resonances often overlap and interference

[1] Autoionizing states are compound states of the (electron+ion) system located above the ionization potential. These states result from the excitation of two or more electrons of the system or by excitation of inner-shell electrons.

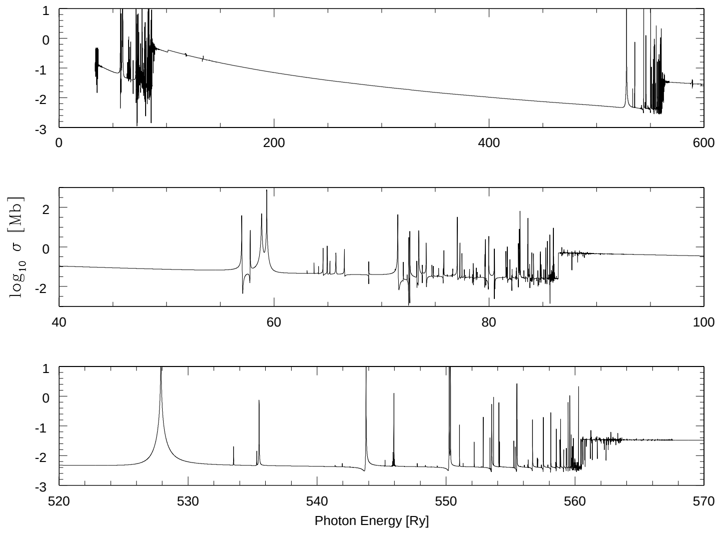

Figure 3. Photoionization cross section of the Fe XV $2p^6 3s^2(^1S)$ ground state from the R-matrix calculation of Bautista (2000a). The top panel shows the full cross sections and the lower panels present close-ups of the cross section around the L- and K-inner shell thresholds.

effects can occur which makes the resonances inseparable from the background cross section. An example of this is the photoionization cross section of the ground state of Fe I (Figure 2). The R-matrix cross section (Bautista and Pradhan 1995) given by the solid line is over three orders of magnitude greater than the central field results without resonances. Similar discrepancies with respect to central field photoionization cross section are found for all iron ions up to Fe V (Bautista and Pradhan 1998). Like in the case of photoionization near the inner $3d$ subshell of Fe I, resonances are a general phenomenon near inner-shell ionization thresholds. Figure 3 shows the photoionization cross section of Fe XV from the first ionization threshold to just above the K-shell threshold (Bautista 2000a). Complex resonances structures are seen converging onto both L and K-shell thresholds. The anhancement of the cross section due to resonances near the L-shell threshold was first pointed out by Hanque and Pradhan (1999) These resonance can change the appearance of the thresholds from sharp edges to more complex and continuous transitions. The resonances also enhance the photoionization rates. For example, assuming a power law continuum of the kind $F \propto E^{-\alpha}$ for E from 500 to 700 Ry, the resonances near the K-shell threshold of Fe XV enhance the ionization rate of this ion by factors of 1.7 for $\alpha = 1$, 1.8 for $\alpha = 2$, and 2.9 for $\alpha = 3$.

Resonances in the collision strengths are known to enhance the excitation rates by up to several factors in the case of valence electron excitation. In the case of inner-shell excitation, Bautista (2000b) carried out R-matrix calculations for Fe XVI and compared the results with earlier DW results. In the region free of resonances the agreement is generally very good, but huge numbers of near threshold narrow resonances are found from the R-matrix calculation (see Figure 4). These resonances enhance the effective collision strengths by up to three order of magnitude, as shown in Table 1.

Convergence of the partial waves expansion It is an standard approach to expand the collision strengths in partial waves from 0 to infinity from every possible value of the angular momentum of the free electron. Clearly, infinite expansion terms cannot be computed in practice and one takes only the lowest dominant partial waves and extrapolate through infinity. The convergence of the partial waves expansion is usually rapid for forbidden transitions, but it can be quite slow for allowed transitions. Also, the number of partial waves needed for convergence increases with increasing energy of the free electron. Thus, the convergence of the partial waves expansion becomes a difficult practical problem, and a possible source

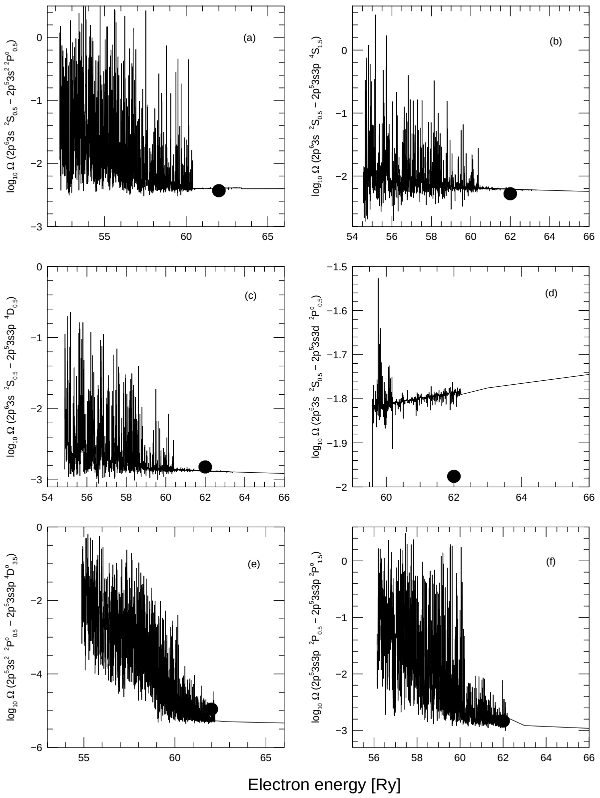

Figure 4. Comparison between R-matrix collision strengths from Bautista (2000b) and distorted wave results by Phillips et al. (1997).

of error in the collision strengths for highly ionized systems for which very high collision energies need to be considered (e.g. Burke and Seaton 1986; Chidichimo 1988, 1989; Eissner et al. 1999)

Convergence of the close coupling expansion The general form of the CC expansion for the radial wavefunction Ψ in terms of a N-electron target basis χ_i and the scattering electron function θ_i is

$$\Psi = \sum_i^{\infty} \chi_i \theta_i + \int_\epsilon \chi_\epsilon \theta_\epsilon . \qquad (30)$$

In the DW and the standard R-matrix approach, however, the integral term that accounts for the target continuum is neglected or replaced by a discrete sum over bound correlation functions (Equation 27) and the sum over the infinite number of target states is truncated to a small number of strongly coupled states. This approximation is usually good when considering valence electron excitations among the lowest energy levels of the ion. However, for excitations to highly excited levels and inner-shell excitations the convergence of the CC expansion must be looked at in great detail. For example, Sawey and Berrington (1993) showed that in order to obtain accurate collision strengths for the $n = 4$ levels

Table 1. Comparison between effective collision strengths from Bautista (2000b) and the DW results of Phillips et al. (1997). The results are given for temperatures of 5.10^4, 10^5 and 10^6 K. The last column indicates the maximum factor of enhancement over the DW results.

Lower level	Upper Level	$\Upsilon(5.10^4\mathrm{K})$	$\Upsilon(10^5\mathrm{K})$	$\Upsilon(10^6\mathrm{K})$	Phillips et al.	max. ratio
$2p^6 3s\ ^2S_{0.5}$	$2p^5 3s^2\ ^2P^o_{1.5}$	4.02(-2)	4.37(-2)	1.99(-2)	3.70(-3)	12
	$2p^5 3s^2\ ^2P^o_{0.5}$	2.01(-2)	2.18(-2)	9.96(-3)	1.96(-3)	11
	$2p^5 3s3p\ ^4D_{2.5}$	4.10(-2)	3.43(-2)	1.24(-2)	2.10(-4)	236
	$2p^5 3s3p\ ^4D_{3.5}$	2.92(-2)	2.36(-2)	5.36(-3)	1.10(-5)	2660
	$2p^5 3s3p\ ^4P_{2.5}$	2.17(-2)	1.87(-2)	6.76(-3)	6.60(-5)	380
	$2p^5 3s3p\ ^2D_{2.5}$	1.18(-1)	9.92(-2)	2.74(-2)	1.21(-3)	105
$2p^5 3s3p\ ^4S_{1.5}$	$2p^5 3s3p\ ^4P_{1.5}$	3.05(-1)	3.46(-1)	1.22(-1)	5.38(-3)	64
$2p^5 3s3p\ ^4D_{2.5}$	$2p^5 3s3p\ ^2D_{1.5}$	5.93(-2)	5.66(-2)	1.79(-2)	2.03(-4)	292
$2p^5 3s3p\ ^4D_{0.5}$	$2p^5 3s3p\ ^4D_{3.5}$	5.41(-1)	4.61(-1)	1.24(-1)	3.40(-3)	159
$2p^5 3s3p\ ^4D_{3.5}$	$2p^5 3s3p\ ^2P_{0.5}$	1.69(-2)	1.52(-2)	6.83(-3)	6.12(-4)	30
$2p^5 3s3p\ ^4D_{1.5}$	$2p^5 3s3p\ ^2D_{1.5}$	5.23(-2)	4.95(-2)	1.57(-2)	3.24(-4)	161
$2p^5 3s3p\ ^4P_{2.5}$	$2p^5 3s3p\ ^2P_{1.5}$	1.05(-1)	9.25(-2)	3.84(-2)	3.22(-3)	38
	$2p^5 3s3p\ ^2D_{1.5}$	4.84(-2)	4.15(-2)	1.31(-2)	1.47(-4)	329
$2p^5 3s3p\ ^4P_{1.5}$	$2p^5 3s3p\ ^2D_{1.5}$	4.02(-2)	3.47(-2)	1.18(-2)	2.82(-4)	143
$2p^5 3s3p\ ^4P_{0.5}$	$2p^5 3s3d\ ^4F^o_{4.5}$	1.04(-2)	9.27(-3)	3.03(-3)	7.00(-5)	162
	$2p^5 3s3p\ ^2D_{2.5}$	1.47(-1)	1.14(-1)	3.11(-2)	9.72(-4)	224
	$2p^5 3s3p\ ^2P_{0.5}$	2.19(-1)	1.93(-1)	5.23(-2)	1.43(-3)	154
$2p^5 3s3p\ ^2P_{1.5}$	$2p^5 3s3p\ ^2D_{2.5}$	3.46(-1)	2.80(-1)	7.80(-2)	2.98(-3)	161
	$2p^5 3s3p\ ^2P_{1.5}$	6.01(-1)	5.40(-1)	1.51(-1)	1.85(-3)	325

of He I one must include target states in the CC expansion up to at least $n = 5$. Otherwise, if the CC expansion is too small the obtained collision strengths tend to be severely overestimated.

The use of pseudo-orbitals to accelerate the convergence of CC expansions was first introduced by Burke, Gallagher, and Geltman (1969). Recant developments are the convergent close-coupling (CCC) and R-matrix with pseudo-states (RMPS) methods (see the review by Gorczyca et al. in this volume).

Relativistic effects If relativistic corrections are small, one can carry out the scattering calculation in LS coupling and then perform an algebraic transformation of the K (reactance) matrices to fine structure (Saraph 1972, Luo and Pradhan 1990).

As the relativistic effects become significant one must allow for the fine structure splitting of the target by using the so-called term-coupling-coefficients (TCCs) to diagonalize the Hamiltonian with the inclusion of relativistic corrections.

For more complete and proper treatament of relativistic effects it is necessary to use either the Breit-Pauli or the Dirac formulations. The Breit-Pauli operators have been implemented into the RMATRX package of codes by the Iron Project (Hummer et al. 1993). One limitation with relativistic calculations is that by splitting the structure of the core into fine structure the size of the computation often exceeds the capacity of modern vectorized supercomputers. Perhaps, this problem may be solved in the near future with the use of massively parallel computers.

Radiation damping Radiation damping of resonances can be an important effect for highly charged ions. When the radiative de-excitation rates of autoionizing states are comparable to the autoionization rates the resonances associated with these states become damped. In the case of photoionization damping of resonances occurs because as the target is photo-excited to an autoionizing state radiative de-excitation competes with autoionization. In collisional excitation damping of resonances indicates a competition between dielectronic recombination and autoionization.

Radiation damping in electron-ion scattering were studied by Pradhan (1981, 1983a, 1983b) using the branching ratios between autoionization and radiative rates and more recently by Zhang and Pradhan (1995) employing the detailed Bell and Seaton (1985) theory of dielectronic recombination. Radiation damping was found to be important in reducing the strength of resonances in boron-like Fe XXII and helium-like Fe XXV. As expected, radiation damping increases with the principal quantum number n within a give Rydberg series of resonances. This is because autoionization rates typically decrease as n^{-3} while radiative rates remain approximately constant.

Robicheaux et al. (1995) and Gorczyca and Badnell (1996) have studied radiation damping in photoionization cross sections. However, in practical applications of photoionization and and scattering the overall radiation damping effect may be not so great in most cases. This is because while the higher n resonances can be highly damped, the lower resonances in the series, which are usually dominant, are not affected significantly, except in highly charged ions (Pradhan and Zhang 1997; Robicheaux 1998).

4. Conclusions

A number of methods for atomic structure and electron-ion scattering calculations have been developed, which are able to provide atomic data for spectroscopic applications. These methods vary in complexity and accuracy of the results in such a way that one must often decide between promptly available and highly accurate data to fulfill current spectroscopic needs. In the case of X-ray spectroscopy most of the atomic data currently available have been produced using some of the simplest techniques described here, while improved data such as that from the IRON Project (see review by Pradhan) is slowly been calculated. In some cases, new more elaborate calculations will help in refining the spectral models, while in other cases the new atomic data could vastly change the previous results leading to dramatic changes in the spectral models. Therefore, it is of prime importance to researchers trying to analyze and/or model spectra to have at least some basic understanding of the quality of the data bing used.

References

Band, I.M., Kharitonov, Y.I., and Trzhaskovskaya, M.B. 1979, Atom. Data Nucl. Data Tables 23, 443.

Bates, D.R. and Damgaard, A. 1949, Philo. Trans R. Soc. Londo, Ser. A 242, 101.

Bautista, M.A. 2000a, J. Phys. B: Atom., Mol. & Optic. Physics , (submitted).

— 2000b, J. Phys. B: Atom., Mol. & Optic. Physics 33, 71.

Bautista, M.A. and Pradhan A.K. 1995, J. Phys. B: Atom., Mol. & Optic. Physics 28, L173.

— 1998, Astrophys. J. 492, 650

Bell, R.H. and Seaton, M.J. 1985, J. Phys. B: Atom., Mol. & Optic. Physics 18, 1589.

Bely-Dubau, F., Fuacher, P., Dubau, J., Gabriel, A.H. 1982, MNRAS 198, 239.

Berrington, K.A., Eissner, W.B., and Norrington, P.H. 1995, Comput. Phys. Commun. 92, 290.

Bethe, H.A. and Salpeter, E.E. 1957, "Quantum Mechanics of One- and Two-electron Atoms." Springer-Verlag, Berlin and New York.

Biermann, L. and Trefftz, E. 1953, Z. Astrophys. 30, 275.

Bromander, J., Durić, N., Erman, P., and Larsson, M. 1978, Phys. Scr. 17, 119.

Burgess, A. 1961, Mem. Soc. Roy. Sci. Liege 4, 299.

Burke, P.G., Gallagher, D.F., and Geltman, S. 1969, J. Phys. B: Atom., Mol. & Optic. Physics 2, 1142.

Burke, P.G., Hibbert, A., and Robb, W.D. 1971, J. Phys. B: Atom., Mol. & Optic. Physics 4, 153.

Burke, P.G., and Robb, W.D., 1975, Adv. Atom. Mol. Phys.. 11, 143.

Burke, V.M. and Seaton M.J. 1986, J. Phys. B: Atom., Mol. & Optic. Physics 19, L527.

Caves, T.C. and Dalgarno, A. 1972, J. Quantum Spectrosc. Radiat. Transfer 12, 1539.

Chidichimo, M.C. 1988, Phys. Rev. A 37, 4097.

— 1989, Phys. Rev. A 38, 6107.

Clementi, E. and Veillard, A. 1965, J. Chem. Phys. 44, 3050.

Cohen, M. 1988, Adv. Atom. Mol. Phys. 25, 195.

Cohen, M. and McEachran, R.P. 1980, Adv. Atom. Mol. Phys. 16, 1.

Condon, E.U. and Shortley, G.H. 1935, "The Theory of Atomic Spectra." Cambridge Univ. Press, London and New York.

Cowan R.D. 1967, Phys. Rev. 163, 54.

Crossley, R.J.S. 1969, Adv. Atom. Mol. Phys. 5, 237.

Dyall, K.G., Grant, I.P., Johnson, C.T., Parpia, F.A., and Plummer, E.P. 1989, Comput. Phys. Commun. 55, 425,

Eissner, W., Galavís, M.E., Mendoza, C., and Zeippen, C.J. 1999, Atron. and Astrophys. Suppl. Ser. 136, 394.

Eissner, W. and Nussbaumer, H. 1969, J. Phys. B: Atom., Mol. & Optic. Physics 2, 1028.

Eissner, W., Jones, M., and Nussbaumer, H. 1974, Comput. Phys. Commun. 8 271.

Eissner, W. and Seaton, M.J. 1972, J. Phys. B: Atom., Mol. & Optic. Physics 5, 2187.

Fock, V. 1933, Z. Phys. 81, 195.

Froese, C. 1966, Phys. Rev. 150, 1.

Froese Fischer, C. 1977 "The Hartree-Fock Method for Atoms." Wiley, New York.

Gorczyca, T.W. and Badnell, N.R. 1996, J. Phys. B: Atom., Mol. & Optic. Physics 29, L283.

Hanque, N. and Pradhan, A.K. 1999, Phys. Rev. A 60, R4221.

Hartree, D.R. 1957, "The Calculation of Atomic Structures." Wiley, New York.

Hershkowitz, M.D. and Seaton, M.J. 1973, J. Phys. B: Atom., Mol. & Optic. Physics 6, 1176.

Herman, F. and Skillman, S. 1963, "Atomic Structure Calculations." Englewood Cliffs, NJ: Prentice-Hall.

Hibbert. A. 1975, Comput. Phys. Commun. 9, 141.

— 1982, Adv. in Atom. and Mol. Phys. 18, 309.

Hylleras, E.A. 1930, Z. Physik 65, 209.

Jucys, A.P. 1967, Int. J. Quantum Chem. 1, 311.

Kelly H.P. 1972, Phys. Rev. A 6, 1048.

Kelly, H.P. and Ron, A. 1972, Phys. Rev. A 5, 168.

Kurucz, R.L. 1988, Trans. IAU, XXB, M. McNally, ed., Dorfrecht: Kluwer, pp. 168.

Kurucz, R.L. and Peytremann, E. 1975, SAO Special Report 362.

Luo, D. and Pradhan, A.K. 1990, Phys. Rev. A 41, 165.

Phillips K.J.H., Greer C.J., Bhatia A.K., Coffey I.H., Barnsley R., and Keenan F.P. 1997, Astron. & Astrophys. 324, 381.

Pradhan, A.K. 1981, Phys. Rev. Letters 47, 79.

— 1983a,b, Phys. Rev. A 28, 2113; 2128.

Pradhan, A.K. and Zhang, H.L. 1997, J. Phys. B: Atom., Mol. & Optic. Physics 30, L571.

Pratt, G.W. 1956, Phys. Rev. 102, 1303.

Reilman, R.F. and Manson S.T. 1979, Astrophys. J. Supp. Ser. 40, 815.

Robicheaux, F. 1998, J. Phys. B: Atom., Mol. & Optic. Physics 31, L109.

Robicheaux, F., Gorczyca, T.W., Pindzola, M.S., and Badnell, N.R. 1995, Phys. Rev. A 52, 1319.

Safronova, U.I., Shlyaptseva, A.S., Cornille, M., and Dubau, J. 1998, Physica Scripta 57, 395.

Saraph, H.E. 1972, Comput. Phys. Commun. 3, 256.

Saraph H.E., Seaton, M.J. and Shemming, J. 1969, Phil. Trans. Roy. Soc. London, Ser. A 264, 77.

Sawey, P.M.J. and Berrington, K.A. 1993, Atom. Data Nucl. Data Tables 55, 81.

Seaton, M.J. 1953, Proc. Roy. Soc. Lond. Ser. A 218, 400.

— 1962, in "Atomic and Molecular Processes." (D.R. Bates, ed.), p.374, Academic Press, New York.

— 1975, Adv. Atom. Mol. Phys. 11, 83.

Slater, J.C. 1960, "Quantum Theory of Atomic Structure." McGraw-Hill, New York.

Ufford, C.W. and Callen, H.B. 1958, Phys. Rev. 110, 1352.

Vainshtein, L.A. and Safronova, U.I. 1980, Atom. Data and Nucl. Data Tables 25, 311.

Van Regemorter, H. 1960, Mon. Notic. Roy. Astron. Soc. 121, 213.

—, 1962, Astrophys. J. 136, 906.

Verner, D.A., Yakovlev, D.G., Brand, I.M., and Trzhaskovskaya, M.B., 1993, At. Data. Nucl. Data Tables 55, 233.

Zhang, H.L. and Pradhan, A.K. 1995, J. Phys. B: Atom., Mol. & Optic. Physics 28, L285.