

# PRACTICAL ATOMIC PHYSICS

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(September 2, 2000)

## Abstract

This lecture note describes how to calculate (a) relativistic wave functions for neutral atoms and atomic ions, (b) atomic energy levels, (c) bound-bound transition probabilities, (c) bound-bound plane-wave Born excitation cross sections by electron impact, (d) bound-bound distorted wave Born excitation cross sections by electron impact, (e) bound-free photoionization cross sections, and (f) bound-free ionization cross sections by electron impact. These atomic data are obtained from the multiconfiguration Dirac-Fock (MCDF) wave functions described in (a).

## I. INTRODUCTION

Many decades after the Schrödinger equation was discovered in 1925, we still have difficulty in calculating “exact” wave functions for many-electron atoms. For all practical purposes, “exact” or “almost exact” wave functions are available only for hydrogen-like and helium-like systems. “Almost exact” solutions to the electron-impact ionization of the hydrogen atom have been available only in the last few years [1–3].

However, atomic physics data, particularly collision data, are needed in solving many problems in other branches of physics, chemistry, and engineering. These “practical” applications require “practical” solutions, majority of which involve neutral atoms and ions with far more than two electrons.

The objective of this series of lectures is to describe methods to obtain such “practical” solutions using “practical” wave functions. Relativistic wave functions are needed to handle heavy atoms (roughly Kr and heavier), particularly to handle intermediate coupling in heavy atoms, highly excited states of light atoms, and highly charged ions.

These lectures will be based on the use of a set of Fortran codes developed from the early 1970s primarily by Jean-Paul Desclaux of Grenoble, France [4] with help from Paul Indelicato of Paris and myself at various stages of the code development and usage. Theoretical details will be kept to the minimum.

The codes described in this note have been frozen in their contents around 1992. This is why these codes are labeled DF92, MJ92, PH92, and DW92. The backbone of the code package is the Dirac-Fock wave function code, DF92. Other codes use the wave functions generated by DF92. The functions of these codes are:

DF92: calculate single- and multi-configuration Dirac-Fock wave functions;

MJ92: integrate angular functions and produce appropriate Slater coefficients;

PH92: calculate bound-bound and bound-free photoexcitation and photoionization cross sections; bound-bound Plane-wave Born excitation cross sections by electron impact;

DW92: calculate bound-bound and bound-free distorted-wave Born excitation and ionization cross sections by electron impact.

In addition, a theoretical model called the BEB (binary-encounter-Bethe) model has been developed [5] to use simple data from DF92 to calculate total cross sections for the ionization of atoms and ions by electron impact. The BEB model is simple, analytic, and requires no special computer codes. Spreadsheet programs on a PC, such as Lotus123 and MS Excel is sufficient.

It is customary to use atomic units in atomic and molecular calculations. In atomic units, the electron rest mass  $m$ , Planck’s constant divided by  $2\pi = \hbar$ , the electronic charge  $e$ , and the Bohr radius  $a_0$  are set to unity. All the physical quantities associated with the ground state of the hydrogen atom, except for the total energy, become unity in atomic units. The total energy of the hydrogen atom is  $-0.5$  a.u., i.e., 1 a.u. of energy is 27.2 eV. The atomic unit of energy is called hartree, while the total energy of the hydrogen atom with the *infinite mass* nucleus is called a rydberg ( $= 0.5$  hartree). The speed of light  $c$  in a.u. becomes  $1/\alpha \approx 137$ , where  $\alpha = e^2/\hbar c$  is the fine-structure constant. Atomic units are used throughout this note. However, symbols representing appropriate dimensions will be retained in expressions for collision cross sections because cross sections are expressed in many different units, viz.,  $\text{cm}^2$ ,  $\text{Å}^2$ , barns, megabarns,  $\pi a_0^2$ ,  $\text{Å}^2/\text{eV}$ ,  $\pi a_0^2/\text{hartree-steradian}$ ,

etc. Some fundamental constants associated with atomic units are listed in Table I.

The audience of this lecture is assumed to be familiar with the basic nonrelativistic quantum theory for atomic structure and collision. A brief summary of the required atomic structure theory is described in Sec. II, collision theory in Sec. III, the BEB model in Sec. IV, the DF92 code in Sec. V, MJ92 in Sec. VI, PH92 in Sec. VII, and DW92 in Sec. VIII. Input data formats are described Sec. IX.

## II. OUTLINE OF ATOMIC STRUCTURE THEORY

All computer codes described in this lecture note use relativistic Hartree-Fock (often called Dirac-Fock) wave functions. Relativistic theories for both wave functions and collision cross sections have their origin in nonrelativistic theories. The fundamental difference is that nonrelativistic theories use LS coupling while relativistic theories use jj coupling. Since the users of this note are much more familiar with nonrelativistic notations than relativistic ones, I shall outline underlying theories for atomic structure and collision in nonrelativistic notations first, and then point out changes necessary to switch to relativistic notations.

### A. Hartree-Fock Wave Functions

For many-electron atoms, the only practical wave functions suitable for various applications are Hartree-Fock (HF) wave functions. Hartree-Fock wave functions are the best wave functions based on the independent particle model, i.e., there is a wave function for each electron, and the one-electron function does not contain any variable referring to other electrons. These wave functions for individual electrons are called *orbitals*. Each orbital for a bound electron in an atom carries four quantum numbers, the principal quantum number  $n$ , the angular momentum  $l$ , the projection  $m_l$  of the angular momentum  $l$ , and the projection  $m_s$  of the spin angular momentum  $s$ . The spin angular momentum for all individual electrons is  $1/2$ , and hence not explicitly included in the quantum number set.

For a many-electron atom, the one-electron quantum numbers  $l$ ,  $m_l$ ,  $s = 1/2$ , and  $m_s$  are combined to determine the total orbital angular momentum  $\mathbf{L}$ , the total spin  $\mathbf{S}$ , the total angular momentum  $\mathbf{J}$ , and matching projections  $M_L$ ,  $M_S$ , and  $M_J$ .

A one-electron orbital used in the Hartree-Fock wave function has the form:

$$\psi_{nlm_l}(r, \theta, \varphi) = r^{-1}P_{nl}(r)Y_{lm_l}(\theta, \varphi), \quad (1)$$

where  $r^{-1}P_{nl}(r)$  is the one-electron radial wave function, and  $Y_{lm_l}(\theta, \varphi)$  are the spherical harmonics. These one-electron functions satisfy the usual orthonormality conditions.

Since the Schrödinger equation does not explicitly contain spin-dependent operators, the spin eigenfunctions are often omitted in the definition of the one-electron orbital, Eq. (1). When necessary, the two-component spinors are used,  $\hat{\alpha}$  for spin up and  $\hat{\beta}$  for spin down:

$$\hat{\alpha} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \hat{\beta} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (2)$$

When one of these spinors are multiplied to Eq. (1), the resulting one-electron function with spin projection is called a spin-orbital.

The total wave function  $\Psi_{LSM_LM_S}$  is built by constructing one or more Slater determinants from the one-electron orbitals. The Slater determinants are weighted by Clebsch-Gordan coefficients to represent appropriate  $L$ ,  $S$ ,  $M_L$ , and  $M_S$ . When the resulting  $L$  and  $S$  are unique, a Hartree-Fock wave function consists of one Slater determinant. Closed-shell atoms, alkali atoms, and halogen atoms are examples of the single-determinant case.

A simple list of occupied one-electron orbitals, such as  $1s^2$  for the helium atom, is called a configuration. For example,  $1s^2 2s^2 2p^2$  is the configuration for the ground state of the carbon atom. In this case however, one must also specify  $L$  and  $S$  because two  $2p$  electrons can be coupled to have different  $L$  and  $S$ :  $^3P$ ,  $^1D$ , and  $^1S$ . The superscript on the left is the spin multiplicity,  $2S + 1$ , and the capital letters denote  $L$ . The letters A, B, C, D, E, and J and their lower case letters are not used for the orbital angular momentum, though S/s(=0) and L/l(=8) are used. When coupling more than two electrons, e.g.,  $3d^3$ ,  $\mathbf{L}$  and  $\mathbf{S}$  are not sufficient to give unique total angular quantum numbers. For such cases, a seniority number must be assigned. For the cases of our interest, however, seniority can be ignored. Instead, we must specify whether an atomic level is the second, third, or fourth level with the same  $L$ ,  $S$ ,  $J$ , and parity, usually starting from the lowest level in energy.

A total wave function consists of Slater determinants weighted by appropriate Clebsch-Gordan coefficients. Each Slater determinant is normalized to unity, and the total wave function is also normalized to unity. This normalization process also alters the coefficients in front of each Slater determinant.

The Hartree-Fock equation is obtained by applying the variational principle to the expectation value for the total energy. The expression for the total energy can be reduced to a combination of one-electron integrals involving a pair of  $P_{nl}$ 's and two-electron integrals involving two to four different  $P_{nl}$ 's.

The spherical harmonics are analytically integrated, and appear as a numerical constant in front of each one-electron and two-electron radial integral. This constant, which includes the Clebsch-Gordan coefficient to represent appropriate  $L$  and  $S$ , the normalization constants, and the results of integrating the spherical harmonics over  $\theta$  and  $\varphi$ , are known as the Slater coefficients. Tables of Slater coefficients are available for simple cases [6]. For complicated cases computer codes are available both in LS and jj couplings. The function of the MJ92 code to be described later is to calculate these Slater coefficients not only for energy levels, but also for various matrix elements to be calculated for collision cross sections.

When the integration over the angular variables and summation over the spin are performed, the total energy of an atom is expressed in terms of radial integrals and the Slater coefficients:

$$E = \sum_i \sum_{a,b} I(ab) \langle P_a(r_i) | \hat{h}_i | P_b(r_i) \rangle + \sum_{i,j} \sum_{a,b,c,d} \sum_k R^k(abcd) \langle P_a(r_i) P_b(r_j) | \frac{r_{<}^k}{r_{>}^{k+1}} | P_c(r_i) P_d(r_j) \rangle, \quad (3)$$

where subscripts  $i$  and  $j$  refer to individual electrons,  $a$ ,  $b$ ,  $c$  and  $d$  stand for sets of one-electron quantum numbers,  $r_{<} = \min(r_i, r_j)$ ,  $r_{>} = \max(r_i, r_j)$ ,  $I(ab)$  and  $R^k(abcd)$  are the Slater coefficients, and  $\hat{h}_i$  is the radial part of the one-electron Schrödinger Hamiltonian

$$\hat{h}_i = -\frac{1}{2} \frac{d^2}{dr_i^2} + \frac{l(l+1)}{2r_i^2} - \frac{Z}{r_i}, \quad (4)$$

with the nuclear charge  $Z$ .

The variational principle  $\delta E = 0$  is applied to Eq. (3) along with the orthonormality conditions for the radial functions to obtain an integro-differential equation for the radial functions  $P_{nl}$ , which is called the Hartree-Fock equation:

$$\left\{ \frac{d^2}{dr^2} + \frac{2}{r} [Z - Y_{nl}(r)] - \frac{l(l+1)}{r^2} - \epsilon_{nl,nl} \right\} P_{nl}(r) = \frac{2}{r} X_{nl}(r) + \sum_{n'} \epsilon_{nl,n'l} P_{n'l}(r), \quad (5)$$

where the ‘‘effective screening’’ term  $Y_a(r)$  is

$$Y_a(r) = \sum_{b,k} A^k(ab) Y_{bb}^k(r), \quad (6)$$

while the ‘‘exchange’’ term  $X_a(r)$  is

$$X_a(r) = \sum_{b \neq a, k} B^k(ab) Y_{ab}^k(r) P_b(r), \quad (7)$$

with appropriate Slater coefficients  $A^k(ab)$  and  $B^k(ab)$ . The function  $Y_{ab}^k(r)$  is defined by

$$Y_{ab}^k(r) = r \int_0^\infty U^k(r, s) P_a(s) P_b(s) ds \quad (8)$$

where the function  $U^k(r, s)$  is given by

$$U^k(r, s) = \frac{s^k}{r^{k+1}} \quad \text{for } r \geq s \quad (9)$$

$$= \frac{r^k}{s^{k+1}} \quad \text{for } r < s. \quad (10)$$

The exchange term includes  $P_a$  itself in the integrand, which makes the Hartree-Fock equation an inhomogeneous equation in  $P_a$ . The orthonormality conditions for the radial functions are combined with the variational principle by introducing Lagrange multipliers  $\epsilon$ . There is a diagonal  $\epsilon_{aa}$  for each radial function  $P_a$ , and off-diagonal Lagrange multipliers  $\epsilon_{ab}$  to insure the orthogonality between two radial functions  $P_a$  and  $P_b$  with the same orbital angular momentum  $l$ . Equation (5) must be solved as coupled, inhomogeneous, integro-differential equations. Typically, about 90% of the computational time for a Hartree-Fock equation is spent to satisfy the exchange term and the off-diagonal Lagrange multipliers on the right-hand side (RHS) of Eq. (5).

Equation (5) without the RHS is homogenous in  $P_a$  and it is known as the Hartree equation. There are as many Hartree or Hartree-Fock equations as the total number of distinct radial functions  $P_a$ . These equations for individual  $P$ 's must be solved simultaneously. The Hartree equation looks very much like the Schrödinger equation for the hydrogen atom. In this case, the diagonal Lagrange multiplier  $\epsilon_{aa}$  plays the role of an energy eigenvalue, and it is often used as an approximate binding energy of the electrons represented by the radial function. This approximation is known as Koopmans' theorem. However, the correct way to calculate the binding energy of an atomic electron is to take the difference between the total energy of the atom with and without the electron in question.

Normally, a radial function  $P_{nl}$  is assigned for all  $m_l$  for a given  $l$ . This is called a restricted Hartree-Fock wave function. However, in some condensed matter and chemistry

applications, radial functions are assumed to be different depending on the spin projection. Such a radial function is called an unrestricted Hartree-Fock wave function.

The standard method to solve the Hartree-Fock equation is to start with a set of approximate radial functions—often from the Thomas-Fermi model or hydrogenic functions with screened nuclear charges—and solve the inhomogeneous, coupled second-order integro-differential equations. More detailed discussions of the Hartree-Fock method are found in a book by Slater [7] and a monograph by Fischer, Brage and Jönsson [8].

## B. Electron Correlation

Since the independent particle model is not an exact theory for many-electron systems, often the Hartree-Fock wave functions are not accurate enough to reproduce atomic properties. The difference between the predictions of the non-relativistic Hartree-Fock wave functions (or equivalent independent particle model) and the “exact results minus relativistic corrections” are called *electron correlation effects*. The reader is warned, however, that this is a very loose definition, which was sufficient 50 years ago when powerful computers and relativistic wave functions were not available. We now know much more about relativistic effects, such as quantum electrodynamic (QED) corrections. Dirac-Fock wave functions for all atoms in the periodic table can easily be calculated in minutes now with powerful PC’s. The modern definition of the “electron correlation effects” should be the difference between the “best” predictions using the independent particle model—which includes the Dirac-Fock wave functions with QED corrections—and the “exact” results, usually meaning the “best” experimental results.

There are several ways to account for the electron correlation effects. One obvious approach is to introduce an empirical or *ab initio* effective potential. A core polarization potential is often used to account for the electron correlation involving core electrons. An effective potential with several empirical parameters may replace the RHS of the Hartree-Fock equation, Eq. (5), to make the equation homogeneous and eliminate the time-consuming exchange term. The Slater approximation (also known as the Kohn-Sham or Herman-Skillman approximation) replaces the exchange term with the integral  $Y_{nl}(r)$  [Eq. (6)] multiplied by a scaled coefficient [see Sec. II B 1].

The exchange term is often referred to as a “nonlocal” potential because it is not a simple function of  $r$  as the “effective screening” term, which is called a “local” potential. The Hartree equation that contains only local potentials can be solved rapidly with modern computers. Moreover, because of its hydrogen-like solutions, one can generate a complete set of eigenfunctions, which can serve as a convenient starting point for a perturbation series. This is a method of choice if electron correlation contributions from the continuum states are important.

A more traditional approach known as the configuration interaction (CI) method is to add configurations that include excited states. For instance, the ground state of He can be described by two configurations,  $1s^2 + 2p^2$ . This method allows more flexibility in the wave function. Physically, one can interpret the multi-configuration wave function mentioned above as an indication that the two electrons in He are in the  $1s^2$  configuration and the  $2p^2$  configuration simultaneously. The relative ratio of the two configurations is determined

again by applying the variational principle. Since the CI method is popular and its physical interpretation is intuitive, we explain the method in more detail in Sec. II B 2.

### 1. Slater Approximation

To avoid the difficulties associated with the exchange term Eq. (7) in the Hartree-Fock equation, Slater [7] proposed an approximation [see Appendix 22 of his book] to simplify the exchange term. Wave functions based on Slater's approximation is known as the Hartree-Slater wave functions. There are some variations, such as the Herman-Skillman wave functions [9]. Later, Kohn and Sham [10] derived a slightly different expression for the exchange term using a variational method.

The exchange term in the Slater approximation is given by:

$$\frac{2}{r}X_{nl}(r) = -\gamma\frac{3}{2}\left[\frac{24}{\pi}\rho(r)\right]^{1/3}, \quad (11)$$

where  $\rho(r)$  is the total charge density

$$\rho(r) = \sum_{nl}N_{nl}P_{nl}(r)^2, \quad (12)$$

with the electron occupation number  $N_{nl}$  of the  $nl$  orbital.

The constant  $\gamma = 1$  in the original Slater approximation, while  $\gamma = 2/3$  in the Kohn-Sham approximation. In many applications, including the popular Cowan code for atomic structure [11],  $\gamma$  is taken as an adjustable parameter. Note that all these approximations are efforts to simplify the exchange term, Eq. (7) in the Hartree-Fock equation. As a result, these approximations will lead to solutions that are not Hartree-Fock wave functions any more, and usually lead to results inferior than the genuine Hartree-Fock solutions.

Regardless of what is used for  $\gamma$ , the Slater approximation and its variants simplify the exchange term into a local potential, which makes the Hartree-Fock equation into a Schrödinger equation for a hydrogen-like system with an effective local potential. This in turn makes it possible to generate a complete set of one-electron orbitals covering both the discrete and continuous spectrum to be used in many-body perturbation theories.

The Kohn-Sham approximation is often used in solid-state physics and quantum chemistry applications as the starting point to introduce more electron correlation, commonly known as the density functional theory. However, to introduce many-body correlation beyond the Hartree-Fock method, the charge density function  $\rho(r)$  must be derived from wave functions superior than Hartree-Fock wave functions.

### 2. Configuration Mixing

The additional configurations—known as the correlation configurations—must have the same total angular quantum numbers,  $L$  and  $S$  or  $J$  and the parity as those of the main configuration, which are configurations normally occupied by the atomic state in question. Extra configurations with different angular quantum numbers or parity do not have any interaction with the occupied configurations. In principle, there are no limits to how many

configurations one can mix as long as a computer code/computer can handle them. In practice, however, introducing too many configurations may lead to numerical instability and redundancy problems.

Note that “solving” the Hartree-Fock equations means to determine radial functions  $P_a$  for all quantum number sets  $a$ , whether they are for actually occupied orbitals or correlation orbitals. Two main methods to obtain such solutions are either to solve  $P_a$  as pure numerical functions or by expanding  $P_a$  in terms of known analytic functions (e.g., Slater-type functions or Gaussian functions) or numerical functions (e.g., splines). The former is known as the numerical Hartree-Fock wave functions, while the latter is known as the basis-set Hartree-Fock wave functions.

Both methods have their advantages and disadvantages, which we shall not discuss in detail here. At present, most atomic wave functions are of the numerical type, while most molecular wave functions are of the basis-set type. The numerical Hartree-Fock wave functions are usually more accurate than the basis-set Hartree-Fock wave functions, but the former are more prone to numerical convergence problems when a large number of configurations are used. The basis-set wave functions have no convergence problems but the computation takes much longer, and the results depend on the choice of basis sets used, i.e., there is no unique solution for a given atomic state, even when the same number of configurations are used.

We shall illustrate the fine points of the configuration mixing method by an example. For the ground state of Be, we use:

$$\Psi(\text{Be}) = a\psi(1s^22s^2) + b\psi(1s^22p^2), \quad (13)$$

where  $a$  and  $b$  are “configuration mixing coefficients” to be determined by applying the variational principle to the total energy expression, which will naturally involve  $a$  and  $b$ . We also have an additional choice in selecting the individual orbitals  $\psi(1s^22s^2)$  and  $\psi(1s^22p^2)$ .

One choice is to calculate them separately by solving the Hartree-Fock equations for each of them. Then,  $a$  and  $b$  are solved by the variational principle while keeping the radial functions  $P_{2s}$  and  $P_{2p}$  frozen. This is known as the “CI” wave functions (not to be confused with the CI *method*, which is another name often used for the configuration mixing method).

Another choice is to let the variational procedure determine both the mixing coefficients and the radial functions. In practice a set of trial radial functions are kept frozen while the mixing coefficients  $a$  and  $b$  are determined. Then, new  $Y^k$  functions are calculated with the new mixing coefficients and the Hartree-Fock equations are now solved for the radial functions while the mixing coefficients are kept frozen. This process is repeated until the mixing coefficients and the radial functions have satisfied the convergence criteria for both. This type of wave functions are called the “multi-configuration” Hartree-Fock (MCHF) wave functions. Obviously, MCHF wave functions are more compact, flexible and superior wave functions than CI wave functions, but MCHF wave functions will not converge well if too many correlation configurations are introduced.

Radial functions obtained in this manner are called “relaxed” radial functions, in contrast to the “frozen” radial functions mentioned earlier. The *relaxed* radial functions peak at the same place the radial functions in the main configuration peak. In the above example, the “relaxed” 2p radial function obtained through the MCHF procedure will peak near where the 2s orbital peaks, while the peak position of the “frozen” 2p radial function will not

change as a result of the configuration maxing procedure.

Another example of the “relaxed” and “frozen” radial functions is the *term-dependent* solutions. The excited configuration, 2s2p, of Be can form either  $^3\text{P}$  or  $^1\text{P}$  states because of the two spin angular momenta involved. One can calculate radial functions 2s and 2p either for the specific total spin state, or for an average of the triplet and singlet spin states, and then calculate the total energy for a specific total spin while keeping the radial functions frozen.

The total spin specific radial functions are called “term-dependent” radial functions, while the spin-independent radial functions are called “configuration average” radial functions. The term-dependent 2p radial functions for the triplet and singlet states of Be are very different. For better results, term-dependent radial functions should be used, though it takes longer to calculate term-dependent radial functions.

### 3. Dirac-Fock Equation

The Dirac-Fock method is a relativistic version of the Hartree-Fock method described so far. The one-electron Schrödinger Hamiltonian, Eq. (4) is replaced by the one-electron Dirac Hamiltonian (in atomic units):

$$h_D = \boldsymbol{\alpha} \cdot \mathbf{p}c + c^2(\beta_D - 1) - Z/r, \quad (14)$$

with  $4 \times 4$  matrix operators  $\boldsymbol{\alpha}$  and  $\beta_D$  defined by

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma}_P \\ \boldsymbol{\sigma}_P & 0 \end{pmatrix} \quad \beta_D = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \quad (15)$$

in terms of the usual  $2 \times 2$  Pauli spinor  $\boldsymbol{\sigma}_P$ , and the  $2 \times 2$  unit matrix  $I$ .

The one-electron Dirac wave function associated with  $h_D$  is given by

$$\psi_{n\kappa m}(r, \theta, \varphi) = \frac{1}{r} \begin{pmatrix} P_{n\kappa}(r)\chi_{\kappa m}(\theta, \varphi) \\ iQ_{n\kappa}(r)\chi_{-\kappa m}(\theta, \varphi) \end{pmatrix}, \quad (16)$$

where  $P_{n\kappa}$  and  $Q_{n\kappa}$  are the radial functions for the large and small components, respectively,  $\kappa$  is the Dirac quantum number that combines  $l$  and  $j$ , and the two-component spinor  $\chi_{\kappa m}$  combines the usual spherical harmonics  $Y_{lm_l}(\theta, \varphi)$  with the two-component spinors  $\hat{\alpha}$  and  $\hat{\beta}$  defined earlier, Eq. (2).

The Dirac quantum number  $\kappa$  is defined by (see Table II):

$$\kappa = \begin{cases} -l - 1 & \text{if } j = l + 1/2, \\ +l & \text{if } j = l - 1/2, \end{cases} \quad (17)$$

$$j = |\kappa| - 1/2. \quad (18)$$

The relativistic correction to the Coulomb repulsion between two bound electrons,  $e^2/r_{jk}$ , is known as the Breit operator,  $H_B$ :

$$H_B = \sum_{j,k>j} \left[ \frac{\boldsymbol{\alpha}_j \cdot \boldsymbol{\alpha}_k}{r_{jk}} \cos(\omega_{jk} r_{jk}) + \frac{(\boldsymbol{\alpha} \cdot \nabla)_j (\boldsymbol{\alpha} \cdot \nabla)_k \cos(\omega_{jk} r_{jk}) - 1}{r_{jk} \omega_{jk}^2} \right], \quad (19)$$

where  $\omega = (\epsilon_j - \epsilon_k)/c$  is the frequency of the virtual photon exchanged between the interacting electrons in the framework of QED. The variable  $\omega$  is rigorously defined only when the unperturbed system is assumed to be a collection of non-interacting electrons, which is not the case for many-electron atoms.

The Breit operator with  $\omega \neq 0$  is called the *frequency-dependent* Breit operator, while its  $\omega = 0$  limit is called the *zero-frequency* Breit operator. The frequency-dependent Breit operator becomes ill-defined in multiconfiguration Dirac-Fock (MCDF) calculations, and hence is not recommended in a routine application of the MCDF method.

There are still unresolved fundamental questions about the use of the Breit operator as part of the unperturbed Hamiltonian for a many-electron system, so that the radial functions are fully influenced by the Breit operator. Hence for routine applications, it is safer to use the Dirac-Coulomb Hamiltonian  $H_{DC}$  (often called the “no virtual  $e^+e^-$  pair Hamiltonian”) which is given by

$$H_{DC} = \sum_j \left[ h_D(j) + \sum_{k>j} e^2 / r_{jk} \right], \quad (20)$$

and use  $H_B$  in the first-order perturbation after the radial functions have been determined by using  $H_{DC}$ .

As in the case of the nonrelativistic Hartree-Fock method, Slater determinants are built with the Dirac orbitals  $\psi_{n\kappa m}$  to get the proper total  $\mathbf{J}$  using jj-coupling. The expression for the total energy is derived by sandwiching  $H_{DC}$  with the eigenfunction of  $\mathbf{J}$ , the spin-angular parts [ $\chi$  in Eq. (16)] are integrated analytically, and the variational principle is applied to the total energy expression in terms of radial functions.

The Hartree-Fock equation consists of a set of second-order differential equation for each radial function  $P_{nl}$ . The matching Dirac-Fock equation consists of a pair of coupled first-order differential equations for the large component and the small component radial functions  $P_{n\kappa}$  and  $Q_{n\kappa}$  for each Dirac orbital  $\psi_{n\kappa}$ . There are as many pairs as the total number of distinct radial functions. It is customary, as is done in the Hartree-Fock method, to assume all one-electron functions with the same  $n$  and  $\kappa$  but with different  $m = m_j$  share the same radial functions.

After the application of the variational principle, one gets the following Dirac-Fock equation:

$$\begin{aligned} \left[ \begin{array}{cc} \frac{d}{dr} + \frac{\kappa_A}{r} - \frac{\epsilon_{AA}}{c} & \frac{V_A(r)}{c} - 2c \\ -\frac{V_A(r)}{c} & \frac{d}{dr} - \frac{\kappa_A}{r} - \frac{\epsilon_{AA}}{c} \end{array} \right] \begin{pmatrix} P_A(r) \\ Q_A(r) \end{pmatrix} = \\ \sum_{\kappa_B = \kappa_A} \frac{\epsilon_{A,B}}{c} \begin{pmatrix} Q_B(r) \\ -P_B(r) \end{pmatrix} + \begin{pmatrix} X_{Q_A}(r) \\ X_{P_A}(r) \end{pmatrix}, \end{aligned} \quad (21)$$

where, in analogy to the Hartree-Fock equation (5),  $A$  and  $B$  represent the one-electron quantum number set  $n\kappa$ ,  $V_A(r)$  is the “screened nuclear charge” term equivalent to  $(2/r)[Z - Y_A(r)]$  in Eq. (5),  $\epsilon_{A,B}$  are the Lagrange multipliers, the  $X_{P,Q}(r)$  are the exchange terms equivalent to  $(2/r)X_{nl}(r)$ . Both  $V_A(r)$  and  $X_{P,Q}(r)$  contain relativistic Slater coefficients resulting from the integration of spin-angular functions and the Clebsch-Gordan coefficients to make the total wave function an eigenfunction of  $J^2$ .

As is common in Hartree-Fock calculations, Dirac-Fock wave functions can also be classified into the configuration average, or term-specific wave functions, except that the relativistic configuration average is  $(2J + 1)$ -weighted whereas the nonrelativistic configuration average is  $(2S + 1)(2L + 1)$ -weighted. The total  $J$  for a relativistically closed shell (e.g.,  $2p_{1/2}^2$ ,  $3d_{5/2}^6$ ) is 0, and the corresponding wave function is a single determinant. Similarly, alkali- and halogen-like configurations can be represented by a single Slater determinant of relativistic one-electron orbitals.

Conversion between  $J$  and  $LS$  is not unique when the number of open-shell electrons is three or more. Even in a simpler case such as  $2s2p$ , the matching relativistic configurations are  $2s2p_{1/2}$  and  $2s2p_{3/2}$ , resulting in one  $J = 2$  level, two  $J = 1$  levels, and one  $J = 0$  level. The  $J = 2, 0$  levels and one of the two  $J = 1$  levels belong to the  $^3P$  term, while the other  $J = 1$  level belongs to the  $^1P$  term. Since  $LS$  labels are not used in the  $jj$ -coupling, the two  $J = 1$  levels are usually identified as the “first” and “second”  $J = 1$  levels, starting from the lowest one.

The  $2s2p$  nonrelativistic configuration is a good example that a matching relativistic representation requires a larger number of relativistic configurations. The nonrelativistic  $2p^2$  configuration for the ground state of carbon is another example: the equivalent relativistic configuration consists of three— $2p_{1/2}^2$ ,  $2p_{1/2}2p_{3/2}$ , and  $2p_{3/2}^2$ . The  $2p_{1/2}$  and  $2p_{3/2}$  orbitals are not equivalent any more, and hence the  $2p_{1/2}2p_{3/2}$  relativistic configuration may have all possible  $J$  values, viz.,  $J = 1$  and  $2$ , while  $2p_{1/2}^2$  can only have  $J = 0$  because it is a relativistically closed shell.

### III. OUTLINE OF COLLISION THEORY

#### A. General Comments

Atomic collision theory takes diverse formats depending on the type of incident particles. For photon-atom collisions, one can get accurate results if accurate target wave functions are available. In other words, the accuracy of photoexcitation or photoionization cross sections is entirely dependent on the ability to calculate good target wave functions.

Theories for electron-atom collisions are divided into two classes according to the treatment of the interaction between the incident electron and the bound electrons in the target. Most theories treat the interaction as a perturbation to the total Hamiltonian of the target (without the incident electron). The other type of theories treat this interaction on the same level as the interaction among the bound electrons and with the nucleus. A typical example of the perturbative theories is the plane-wave Born approximation (PWBA), while the R-matrix method is a typical strong-coupling theory.

In general, strong-coupling theories are suitable for slow incident electrons, while perturbative theories provide reliable answers for fast incident electrons. It is rare for a collision theory to be valid at both low and high incident energies. The only exception is the binary-encounter-dipole (BED)/BEB model for electron-impact ionization of atoms and molecules. The BED/BEB model is outlined in Sec. VIII.

Theories for atom-atom and ion-atom collisions are the most difficult ones, even if accurate wave functions are known for the projectile and the target, because the nature of the interaction between the colliding particles strongly depends on the relative velocity of the

colliding particles. For slow collisions, the two particles form a transient diatomic molecule, and this is one of the most difficult class of collision problems to solve. In this section, discussions will be limited to the theory of photon-atom and electron-atom collisions, not only because these cross sections are needed most in many applications, but also because the atom-atom and ion-atom collisions must be treated case by case.

## B. Photon-Atom Collisions

The interaction of an atom with radiation is introduced by adding the vector potential  $\mathbf{A}$  to the kinetic energy operator  $\mathbf{p}$  in the Hamiltonian, i.e.,  $\mathbf{p}^2$  is replaced by  $[\mathbf{p} - (e/c)\mathbf{A}]^2$ . Then,  $\mathbf{p} \cdot \mathbf{A}$  is treated as the perturbation. The resulting transition matrix element contains  $\mathbf{p}$  as the operator, which is known as the velocity form. The momentum operator is then replaced by  $\mathbf{r}$  using the commutation relation [12]

$$[\mathbf{r}, H] = \frac{i\hbar}{m}\mathbf{p}, \quad (22)$$

where  $H$  is the usual Hamiltonian

$$H = \sum_j \left[ \frac{p_j^2}{2m} + V(\mathbf{r}_j) + \sum_{k>j} \frac{e^2}{r_{jk}} \right], \quad (23)$$

where the summation is over all electrons in the target.

The transition probability for going from an upper level  $n$  to a lower level  $n'$  by emitting a photon is called Einstein's  $A$  coefficient:

$$A_{nn'} = \frac{4e^2\omega^3}{3\hbar c^3} |\langle \Psi_n | \sum_j \mathbf{r}_j | \Psi_{n'} \rangle|^2, \quad (24)$$

where the angular frequency  $\omega = (E_n - E_{n'})/\hbar$  with the total energies  $E$ . This is called the dipole or  $E1$  transition matrix element in the length form. Einstein's  $A$  coefficient (dimension =  $\text{s}^{-1}$ ) is the total number of photons emitted per second. Alternatively, the dipole oscillator strength  $f_{n'n}$  is used for photoabsorption:

$$\begin{aligned} f_{n'n} &= \frac{2m\omega g_n}{3\hbar g_{n'}} |\langle \Psi_n | \sum_j \mathbf{r}_j | \Psi_{n'} \rangle|^2 \\ &= \frac{mc^3 g_n}{2e^2\omega^2 g_{n'}} A_{nn'}, \end{aligned} \quad (25)$$

where  $g$  is the multiplicity of the respective state. The above definition of oscillator strength applies only to the dipole transition. The dipole oscillator strength is often called the  $f$ -value, and it is dimensionless.

A very useful sum rule, the Thomas-Kuhn-Reich (TKR) sum rule for the  $f$ -value is known:

$$\sum_n f_{n'n} = N, \quad (26)$$

where  $N$  is the total number of electrons in an atom. The summation must include all transitions from a given state, including all transitions to the continuum and inner-shell

excitations. The TKR sum rule is satisfied only for the entire atom, but not for each orbital. Since the proof of the sum rule uses the nonrelativistic Hamiltonian, Eq. (23), it does not hold for heavy atoms.

When the photon energy is high, non-dipole transitions become significant. Multipole transition probabilities are calculated by expanding the photon field into multipole electromagnetic field. The magnetic dipole transition is called the  $M1$  transition, the electric quadrupole transition the  $E2$  transition, the magnetic quadrupole transition the  $M2$  transition, and so on. Each multipole transition has a different set of selection rules. Rigorous selection rules are in terms of  $\Delta J$  and parity. The selection rules based on spin quantum numbers are approximate and often violated in heavy atoms where spin-orbit interaction is significant. Selection rules for the  $E1$ ,  $M1$ , and  $E2$  transitions are listed in Table III. The PH92 code will calculate  $En$  and  $Mn$  transitions for all  $n$ , provided that wave functions satisfy the selection rules.

When wave functions from local potentials are used, the length and velocity forms of the f-value and hence transition probability agree exactly. Results from Hartree-Fock wave functions will not, because they are computed with non-local potentials. The difference between the length and velocity forms of the f-value *is not* an indication of the accuracy of the f-value. Numerical convergence of the f-value as the wave functions are improved is the only sure way of assuring accuracy.

### C. Electron-Atom Collisions

When the incident electron energy  $T$  is only a few times the excitation/ionization threshold, the incoming electron and the target atom form a transient compound state, or an excited negative ion, and a successful collision theory at such low values of  $T$  must take the correlation between the incident and target electrons into account. This is why most electron-atom collision theories are not reliable at low  $T$ .

At high  $T \gtrsim 10B$ , where  $B$  is the binding energy of the target electron, first-order perturbation theory such as the plane-wave Born approximation becomes reliable, provided that good target wave functions are used. The user must keep in mind that approximations for the collision theory and approximations for the target wave functions are not related. The approximations used for the incident, scattered, and ejected electrons determine the reliability of the collision theory part. It is important to use as accurate target wave functions as possible before attempting to use “fancy” collision theories.

For modeling applications, a large number of various types of cross sections are needed. In such cases, it is important to find “practical” solutions of as uniform quality as possible, rather than a mixture of a few very accurate results and poor quality results for the remainder. In many cases, it is very difficult to calculate accurate target wave functions for highly excited states. The “practical” solutions for such cases reduce to single-configuration target wave functions used with the plane-wave Born or distorted-wave Born approximations for the collision part.

Electron-atom collision cross sections can be divided into three basic categories: (a) elastic scattering, (b) excitations, and (c) ionization. For ions in a plasma environment, (d) recombination becomes also a significant collision process. Unlike photon-atom collisions,

there is no selection rules in electron-atom collisions, though spin-forbidden and dipole-forbidden transitions tend to be weaker than spin-allowed and dipole-allowed transitions. This lecture note covers only discrete excitations and ionization.

The plane-wave Born approximation (PWBA) uses plane waves for the incident and scattered electron. The target wave functions should be as accurate as practical. Bethe [13] worked out details of the PWBA in the early days of quantum mechanics. Although he applied the PWBA mostly to the hydrogen atom, most of his conclusions are also valid for many-electron atoms and molecules [14].

First, he showed that the essence of the PWBA is given in its form factor, known as the generalized oscillator strength (GOS), which is a function of the momentum transfer from the incident electron to a target electron but independent of  $T$ . The GOS is uniquely determined from the initial and final state wave functions of the target. Hence, once the GOS for a transition is calculated, the PWBA cross section for that transition can be deduced from the GOS for all  $T$ . Of course, the quality of a GOS will depend on the quality of the target wave functions used, but this is the simplest and easiest collision cross section to calculate. For modeling purposes, Hartree-Fock or slightly better wave functions will produce “useful” cross sections at high  $T$ , beyond the cross section peak.

Bethe showed further that the asymptotic form (i.e., high  $T$ ) of the PWB cross sections for excitation and ionization, which is usually called the Bethe cross section, is given by

$$\sigma_{\text{Bethe}} = \frac{4\pi a_0^2}{T/R} \left[ M_n^2 \ln \left( \frac{T}{R} \right) + C_n \right], \quad (27)$$

where  $a_0$  is the Bohr radius,  $R$  is the rydberg energy, the dipole quantity  $M_n^2$  for excitation is

$$M_n^2 = f_{0n}/(E/R) \quad (28)$$

with the dipole oscillator strength for excitation to state  $n$  from the initial state 0, excitation energy  $E$ , and  $C_n$ , which is also a constant characteristic of the excitation but independent of  $T$ . For a dipole-forbidden transition  $M_n^2$  vanishes.

*The logarithmic dependence of the asymptotic cross section of a dipole-allowed transition is valid for all inelastic collisions of charged particles (electrons, protons, ions, pions, etc.) with atoms, molecules, and their ions. Similarly, the lack of the logarithmic term in the asymptotic cross section for a dipole-forbidden transition is also valid for all incident charged particles and targets.* Classical collision theories do not lead to this logarithmic dependence, and their asymptotic cross sections for dipole-allowed transitions tend to be too low at high  $T$ . Ionization cross sections always contain both dipole-allowed and dipole-forbidden transitions and hence the logarithmic dependence is always observed in asymptotic ionization cross sections.

Another important conclusion about the PWBA is that the same formula such as Eq. (27) applies to heavy ions simply by using  $T = \frac{1}{2}mv^2$  where  $v$  is the *speed* of the ion. For example, a proton with 2 MeV in kinetic energy has the speed of an electron with about 1 keV in kinetic energy. Hence, if the electron-impact excitation or ionization cross section of He at  $T = 1$  keV is known, the same value will represent the cross section for a 2 MeV proton on He. Note that this type of scaling is valid only when the heavy ions are moving

fast. A slow positive incident ion has additional interactions that an equal-speed electron does not have, such as charge transfer and formation of a transient molecule with the target.

The validity of the PWB cross sections at low  $T$  can be extended by altering the denominator  $T/R$  on the RHS of Eq. (27) as is shown in the next section on the BEB model. The general form of the Bethe cross section is valid not only for the integrated excitation and ionization cross sections, but also for the singly differential (=energy distribution of secondary electrons) and the doubly differential (=energy and angular distributions of secondary electrons) cross sections by replacing the constants  $M_n^2$  and  $C_n$  with appropriate *functions*.

When the target is an ion, the incident electron is subject to a long-range Coulomb attraction, and plane waves should not be used. An obvious alternative is to use the continuum Coulomb function with a bare or screened nuclear charge which is a constant. This is known as the Coulomb-wave Born approximation (CWBA). For a many-electron target, even for a neutral target, the screened nuclear charge seen by the incident electron is a function of the distance from the nucleus. Hence, another alternative, though more laborious, is to use an  $r$ -dependent screened charge calculated from the charge density of the target. This is known as the distorted-wave Born approximation (DWBA). In the DWBA, the incident and scattered electron is represented by partial waves expanded in terms of the angular momentum  $l$ , i.e., there is no closed analytic expression for the radial part of the continuum functions. The angular part consists of spherical harmonics as in the bound-state wave functions.

The PH92 code calculates transition probabilities and electron-impact PWB cross sections between bound states using bound-state wave functions generated by the DF92 code. The DW92 code calculates electron-impact DWB excitation cross sections between bound states using the wave functions from the DF92 code. The computer time required for the DWB cross sections are almost two orders of magnitude longer than the PWB cross sections for the same excitation. Moreover, the total number of partial waves that can be used in DWB cross sections are limited to  $l \lesssim 50$  because higher  $l$  requires handling numbers smaller than  $10^{-308}$  for orbitals near the origin, which is the limit of the “real” numbers most computers can handle. When this limit is reached, usually PWB cross sections become valid and can replace DWB cross sections for higher  $T$ .

#### IV. OUTLINE OF THE BED/BEB MODEL

As was mentioned in the beginning of this lecture series, “almost exact” solutions to the electron-impact ionization of the hydrogen atom were obtained only in the last decade, 70 years after the discovery of quantum mechanics. The difficulty is rooted in handling correlation of two electrons in the continuum, while accounting for the indistinguishability of the two electrons. The conventional ionization theory expands the incident, scattered, and ejected electron wave functions in partial waves, requiring in principle three independent sets of infinitely many partial waves. This type of expansion cannot be carried out for fast incident or ejected electrons because the required computer resources in cpu time, storage, random memory, and the limits on the exponent range of real numbers cannot be met in any foreseeable future. Fortunately, the PWBA—which does not expand continuum functions—is valid at high  $T$ . Unfortunately, however, most applications require ionization cross sections for slow incident electrons.

In 1994, Kim and Rudd [5] developed a theory that does not depend on partial wave expansion. They combined modified Mott cross section for the collision of two free electrons and the asymptotic Born cross section, Eq. (27) in the singly differential form, which is referred to as the binary-encounter-dipole (BED) model. The BED model requires the knowledge of continuum dipole oscillator strength,  $df/dE$ , for each orbital in the target. However, for many atoms and most molecules,  $df/dE$  is unknown. For such cases, Kim and Rudd adopted a model  $df/dE$  that has the shape of the  $df/dE$  for the hydrogen atom, and obtained a simple, analytic expression for the integrated ionization cross section per orbital. This simplified cross section is called the binary-encounter-Bethe (BEB) cross section. The BEB cross section per orbital requires only three orbital constants, the binding energy  $B$ , the kinetic energy  $U = \langle \mathbf{p}^2/2m \rangle$ , and the electron occupation number  $N$ :

$$\sigma_{\text{BEB}} = \frac{S}{t + u + 1} \left[ \frac{1}{2} \ln t \left( 1 - \frac{1}{t^2} \right) + 1 - \frac{1}{t} - \frac{\ln t}{t + 1} \right], \quad (29)$$

where  $S = 4\pi a_0^2 N(R/B)^2$ ,  $t = T/B$ , and  $u = U/B$ . Energies expressed in terms of the ionization threshold  $B$  is said to be in the threshold unit. The first logarithmic term on the RHS of Eq. (29) comes from the leading term of the Bethe cross section, Eq. (27), the last logarithmic term represents the interference between the direct and exchange (because electrons are fermions) scattering, and the middle term,  $1 - 1/t$ , originates from the direct (=Rutherford scattering) and exchange collisions.

The only *ad hoc* expression in the BED/BEB model is the denominator,  $t + u + 1$  on the RHS of Eq. (29). Note that the Bethe cross section, Eq. (27), has only  $t$  ( $= T/B$ ) in the denominator. Originally, the  $T$  in the Bethe cross section—and in all rigorous collision theories—came from normalizing the cross section to the incoming electron flux per unit area perpendicular to the incident beam direction, i.e., divide the transition rate by  $v^2$  where  $v$  is the speed of the incident electron.

However, Burgess proposed to modify it with the argument that the effective kinetic energy of the incident electron seen by the target bound electron is  $T + U$  plus potential energy of the bound electron. Accordingly,  $T$  was replaced by  $T + U + B$ , or  $t + u + 1$  in the threshold unit. Another way to look at Eq. (29) is to consider the expression in the square brackets on the RHS as the basic cross section in an independent particle model, and the Burgess denominator  $t + u + 1$  as the scaling factor to represent the correlation between the two colliding electrons. In this way, the Burgess denominator must be adapted to different types of targets—e.g., neutral atoms versus ions, inner versus valence shells—while the basic cross section is unchanged as long as an independent particle model, such as the Hartree-Fock method, is used to describe the target.

The BEB model is very successful in reproducing known ionization cross sections for large and small molecules from threshold to several keV in  $T$  [15]. Until the BEB model was developed, existing methods for estimating molecular ionization cross sections were either empirical or additivity rules with limited applicability. The BED/BEB model has also successfully been applied to small atoms [16], and applications to large, heavy atoms and their ions are being developed now.

## V. DESCRIPTION OF DF92

The DF92 code calculates bound-state Dirac-Fock wave functions. The wave function generated may be an eigenfunction of  $J^2$  or the configuration average, i.e.,  $2J + 1$ -weighted average of total energies of all possible  $J$  that can be constructed from the occupied electrons. Also, the wave function generated may be a single configuration wave function or multiconfiguration wave function.

The type of wave function to be generated is determined by the input. The basic input data includes: (a) a title line to identify the input data, (b) electron configurations, i.e., electron occupation numbers for each orbital, (c) Slater integrals to specify  $J^2$  eigenfunction, (d) nuclear charge, and (e) the total number of bound electrons. The last two numbers should be the same for a neutral atom. The relativistic configurations include the principal quantum number  $n$ , orbital angular momentum  $l$ , and  $j$  quantum number. The row marked “Input” in Table II shows the  $lj$  combination to be used in the input data for all computer codes described in this lecture note.

The DF92 code internally generates the appropriate total energy expressions for configuration average wave functions. To generate an eigenfunction of a specific  $J^2$ , appropriate Slater integrals, which are generated from the MJ92 code described in Sec. VI, must be provided in the input data. The configuration average is the correct  $J^2$  eigenfunction for a relativistically closed-shell configuration, alkali-like configuration, and halogen-like configuration. When the configurations used in an MCDF calculation can lead to more than one eigenfunctions of the same  $J^2$ , as in the case of  $2s2p^*+2s2p$ , which leads to either  $^3P_1$  or  $^1P_1$ , the input data must specify the order of the eigenfunction, e.g., the first or second  $J = 1$  eigenfunction counting from the lowest.

Accounting for electron correlation, i.e., the many-body effect beyond the Hartree-Fock method, remains to be the most difficult challenge for both relativistic and nonrelativistic atomic structure theories. The MCHF and MCDF methods can easily account for the leading correlation terms, which are configurations within the Coulomb complex. The Coulomb complex consists of all combinations of one-electron orbitals that have the same energy in the hydrogenic limit and the same total parity.

For example, the ground state of Mg is  $3s^2$ . The Coulomb complex consists of  $3s^2$ ,  $3p^2$ , and  $3d^2$  in the nonrelativistic notation, or  $3s^2$ ,  $3p^{*2}$ ,  $3p^2$ ,  $3d^{*2}$ , and  $3d^2$  in the relativistic notation. For highly charged ions, the relativistic Coulomb complex reduces to  $3s^2$  and  $3p^{*2}$  because not only  $n$  but also  $j$  must be the same to be the same energy in the Dirac theory for the hydrogen atom [17]. For neutral and lightly charged ions, however, the nonrelativistic Coulomb complex should be used even in relativistic calculations.

For the calculation of excitation energies, i.e., the energy difference between two levels, the user should try to include as many correlation configurations as possible, though it is difficult to obtain convergence if too many configurations are introduced. An important concept is to “balance” the correlation in the initial and final states. “Unbalanced” calculations will lead to unreliable results. When an accurate binding energy of an orbital is desired, the user should take the difference in the total energies of the initial state and the final state with one electron removed from the orbital.

Many atomic energy levels are often known to 6–8 significant figures from experiments. Theoretical calculations of energy levels can compete with the best experiments only in

one-electron and two-electron atoms. However, isoelectronic trends are well reproduced by relativistic theories, and hence it is advantageous to study systematics in energy levels along isoelectronic series [18].

In the case of transition probabilities, best theories can compete with the best experiments, particularly for the transitions from the ground state to low-lying excited states. Although occasionally experimental transition probabilities with an accuracy of  $\pm 1\%$  for strong, dipole and spin allowed transitions are reported in the literature, an experimental accuracy of  $\pm 10\%$  is common, and this is the accuracy theory can achieve.

When many transition probabilities are needed, such as in plasma modeling, consistency among the same kind of data are as important as accuracy. To maintain consistency, wave functions of similar quality should be used throughout. For this purpose, “configuration average” wave functions are recommended because they are easy to generate, i.e., without convergence difficulties. Then, the configuration average radial functions are kept frozen and used in the CI mode to generate eigenfunctions of  $J^2$  as needed. Another advantage of using configuration average wave functions is that they are all automatically orthogonal to each other, an important requirement when many levels of similar energies are involved. Schmidt orthogonalization alone will produce mostly useless wave functions. Orbitals in a many-electron wave function must be orthogonalized through Lagrange multipliers and the SCF procedure.

All SCF codes for atomic wave functions require trial radial functions at the start. The DF92 code has options to generate trial radial functions using the Thomas-Fermi method or hydrogenic functions with screened charges. It can also read an external input for radial functions. For instance, configuration average orbitals can be generated first, saved as binary files, and then used as the input for an MCDF or CI calculation for a given  $J$ .

For deep inner shells, quantum electrodynamic (QED) corrections are substantial. The DF92 code estimates these corrections automatically. The ionization energies of inner-shell electrons become reliable only when these QED corrections are included. In addition, the DF92 code uses an extended nucleus: a uniform charge distribution for light nuclei and a Fermi distribution for heavy nuclei. An option for using a point nucleus is also available.

Aside from the total energy, the standard output from the DF92 code lists the convergence data for each cycle of iteration, the orbital and kinetic energies of each orbital, expectation values of  $\langle r^n \rangle$ , configuration weights for a multiconfiguration or CI wave function, and a list of various terms contributing to the total energy. The radial functions and the total charge density are tabulated and “punched” as an option. The input format for the DF92 code and sample input data are listed in Sec. IX.

## VI. DESCRIPTION OF MJ92

The MJ92 code is an all-purpose code for integrating the angular part of expressions for total energies,  $En$  and  $Mn$  transition probabilities, photoionization, PWB cross sections for discrete excitations by electron impact, and DWB cross sections for excitations and ionization by electron impact. The integrated results are generically called Slater coefficients.

The DF92 code assumes that the wave functions are linear combinations of Slater determinants each with definite parity,  $J$ , and  $M_J$ . Expectation values and matrix elements between the DF wave functions generated by DF92 must be calculated using the same phase

convention used for both the wave functions and matrix elements. Therefore, it is crucial that the user generates the necessary Slater coefficients using the same phase convention in handling Clebsch-Gordan coefficients. Countless mistakes were made in the history of atomic structure calculations because mixed phase conventions were used. One should never use formulas from two different books on angular momentum coupling, unless it is proven beyond any doubt that the books use the same phase convention.

For convenience, the input configurations for the MJ92 code are in nonrelativistic notation, e.g.,  $2p^2$ . Then the code generates all relativistic counterparts,  $2p^{*2}$ ,  $2p^{*}2p$ , and  $2p^2$ , and evaluates appropriate matrix elements between relativistic configurations. The output identifies the angular coefficients and matching radial integrals. These output data are placed in a file, which can be read by the DF92, PH92, and DW92 codes, or if the list is short, they can be incorporated directly into the input file for the DF92, PH92, and DW92 codes.

For an isoelectronic sequence, the same output file from the MJ92 code can be used by ions with different nuclear charges. Also, an output file from the MJ92 code may contain Slater coefficients for many different energy states or transitions. Different cases are distinguished by the first four characters on the first line of an output data set. A general input convention for all codes described in this lecture note is that the start of an input data set is identified by an asterisk "\*" in the first column, and a 3-digit number. The first four characters of all input lines are often used as identifiers. The MJ92 code also generates generic input data for the DF92 code listing the appropriate relativistic configurations to be used. The ordering of the configurations listed in this generic input data must be kept to make the phase conventions used by the DF92 and MJ92 codes consistent. The input format and sample input data for the MJ92 code are listed in Sec. IX.

## VII. DESCRIPTION OF PH92

The PH92 code calculates  $En$  and  $Mn$  transition probabilities for discrete transitions. The code also generates appropriate continuum partial waves for photoionization and calculates photoionization cross sections. The partial waves, however, are calculated in the field of frozen core orbitals, though the electron exchange interaction is treated correctly. This is known as the continuum Dirac-Fock wave functions. Since this is not a correlated continuum wave function, the results for photon energies near the ionization threshold are unreliable.

The PH92 code can also calculate plane-wave Born cross sections for discrete excitations by electron impact. As is shown in Sec. IX, the keyword in the input data identifies which type of cross section is calculated.

To use the PH92 code, appropriate Slater coefficients must be generated using the MJ92 code and Dirac-Fock wave functions using the DF92 code. As was mentioned in the theory section, the accuracy of the  $En$  and  $Mn$  transition probabilities is determined by the accuracy of the Dirac-Fock wave functions used. The accuracy of the Born cross sections, however, is governed by the approximation used in the Born approximation in addition to the accuracy of the Dirac-Fock wave functions used. The PWB cross sections are reliable only at high incident electron energies  $T$  beyond the cross section peak.

Also, the shape of the PWB cross sections near the threshold for discrete excitations of ion targets is wrong. The PWB cross section starts from zero, while the correct cross section starts from a finite value. The distorted-wave Born (DWB) cross section described in the next section has the correct shape near the threshold.

For neutral targets, both the PWB and DWB cross sections have the correct shape, i.e., start from zero. The PWBA overestimates the cross section between the threshold and the peak by as much as 50%. For a quick estimate, the Burgess denominator mentioned in Sec. IV may be used to scale the PWB cross sections at low  $T$ . The DWB cross sections should not be scaled by the Burgess denominator because the DWB cross sections become too low when scaled by the Burgess denominator. The input format and sample input data for the PH92 code are listed in Sec. IX.

### VIII. DESCRIPTION OF DW92

The DWB cross sections take almost two orders of magnitude more cpu time than the PWB cross sections to calculate. Therefore, DWB cross sections should be used only for the discrete excitations of ion targets by electron-impact. For the excitations of neutral targets, PWB cross sections scaled by the Burgess denominator are recommended. Besides, the DWB cross sections can be calculated only for low  $T$  because of the limitations in partial wave expansions mentioned earlier.

For ionization, DWB cross sections take several orders of magnitude longer in cpu time than the BEB model described in Sec. IV. For ionization, the correct shape near the threshold is given by both the DWBA and the BEB model, and the BEB cross sections are more reliable than the DWB cross sections at low  $T$ .

The DW92 code generates continuum partial waves for the incident, scattered, and ejected electrons. The partial waves are generated in the field of frozen core orbitals with proper electron exchange interaction, as is also done in the PH92 code. As in the case of bound-state orbitals, continuum partial waves can be made  $J$ -specific (=term dependent) or in the configuration average because it is certain that either the initial or the final state contains open-shell configurations. Since the continuum partial waves are not true SCF wave functions—core orbitals are frozen during the SCF process—it is not worth elaborating on term-dependent partial waves. This is the reason that configuration average partial waves are the default. The term-dependent partial waves are seldom needed, and the results from them are not necessarily more reliable.

Computational difficulties limit the use of the DWBA to low  $T$ , about 5 times the threshold energy in  $T$ . For higher  $T$ , either the Coulomb-wave Born approximation or the PWBA should be used. Since the largest differences between the DWBA and PWBA results are found in partial waves with low  $l < 5$ , the user can combine DWB partial wave cross sections for low  $l$  and PWB partial wave cross sections for high  $l$ .

Convergence in the DWB cross sections must be confirmed by calculating partial wave cross sections for high  $l$ . Since the PWB cross sections from the PH92 code are calculated without partial wave expansions, the DWB cross sections can be combined with the PWB cross sections from the PH92 code after subtracting the low  $l$  partial wave cross sections included in the DWB cross sections. For this purpose, the DW92 code provides options to calculate the CWB and PWB cross sections in partial wave expansion. Small differences may

persist between the DWB cross sections from the DW92 code and the PWB cross sections from the PH92 code because the latter does not include the exchange contribution, which is significant for low  $l$  partial waves. The input format and sample input data for the DW92 code are listed in Sec. IX.

### Exercises

To familiarize with the DF92, MJ92, PH92, and DW92, the user should try the following set of exercises.

**Exercise 1.** Calculate Hartree-Fock wave functions for Be:  $1s^2 2s^2 \ ^1S$  and  $1s^2 2p^2 \ ^1S$  separately. Then, calculate the total energy of the ground state of Be by using (a)  $1s^2 2s^2$  only, and (b)  $1s^2[a2s^2+b2p^2]$  keeping the radial functions frozen.

**Exercise 2.** Repeat step (b) above by relaxing radial functions, i.e., use the MCDF option. Compare the total energies and  $\langle r \rangle$  of the 2s and 2p radial functions.

**Exercise 3.** Calculate the total energies for Be  $2s2p \ ^3P$  and  $2s2p \ ^1P$  states using term-dependent and configuration average radial functions. Compare total energies and  $\langle r \rangle$ .

**Exercise 4.** Calculate  $E1$  transition probabilities for the  $2s2p \ ^3P \rightarrow 2s^2 \ ^1S$  and  $2s2p \ ^1P \rightarrow 2s^2 \ ^1S$  transitions for Be. Try the same transitions for  $\text{Xe}^{50+}$  and compare the ratios of the triplet and singlet transitions.

**Exercise 5.** Calculate the PWB excitation cross sections for the  $2s^2 \ ^1S \rightarrow 2s2p \ ^3P$  and  $^1P$  excitations for Be and  $\text{Xe}^{50+}$ .

**Exercise 6.** Calculate the same transitions in Ex. 5 using the DWBA.

**Exercise 7.** Calculate the BEB cross section for the ionization of He and compare to the experimental data by Shah et al., J. Phys. B **21**, 2751 (1988). The kinetic energy of the 1s orbital of He can be obtained by calculating the Dirac-Fock wave function of He.

## IX. INPUT FORMAT FOR MJ92, DF92, PH92 AND DW92

### A. Introduction

The MJ92 code calculates angular coefficients for the total energy expression (including the Breit operator), and the DF92 code solves multiconfiguration Dirac-Fock (MCDF) equations. The MJ92 code also calculates the Slater coefficients for arbitrary  $En$  and  $Mn$  transition probabilities, PWB cross sections, and DWB cross sections. Although the MJ92 code can handle angular momentum coupling and integration for several other processes, such as the hyperfine interaction, Auger transitions, and parity nonconservation, we shall not cover such topics in this lecture note. The features in MJ92 and PH92 for these extra processes have been omitted in the following description of the input format.

For each set of input data, variables to be read are listed either in upper or lower case with the following conventions:

- Variables listed in upper case must be given a value.
- For variables listed in lower case default values are automatically assigned if no value is given as input.
- Default values are given in parentheses after the definition of the variables.
- Lines beginning with a  $\#$  in the first column are treated as comments.

All input data are read in free format using the **STR...** set of subroutines. The conventions used are the following :

- Input stream may include an arbitrary number of data sets, one for each case to be calculated. A data set consists of a certain number of files each file being divided into an arbitrary number of records.
- A file is defined as an arbitrary number of input lines followed by a line with **END** as its first 3 characters.
- A record is defined as an arbitrary number of input data. A record may extend over an arbitrary number of lines and more than one record may be on the same line. The colon “:” after at least one blank may be used to interrupt data list of a record and let the program assign default values to the rest of the data in the record.
- An input line is a set of 72 characters followed by a carriage return.
- The first 4 characters of each input line are considered as an identifier that can be used to identify a set of input data.
- An input value is defined as a string of characters *without blanks*.
- Strings are separated by at least one blank.
- An input value and its optional identifier (see below) must be on the same line.

For convenience each input value can be labeled with an identifier followed by the character “=”. Both the identifier and the character “=” are considered as comments and are thus ignored (*These are not list-directed input!*). Valid input data are: strings of characters (case insensitive), integers or real numbers.

In all codes, atomic states are defined as a superposition of electronic configurations each of which is defined as a list of orbitals with their electron occupation numbers. These configurations are given, only in the case of the MJ92 code, in LS coupling and the program will generate all jj configurations arising from a given LS configuration. The rest of the codes use jj coupling for input data.

Note that:

- The configurations given as input data in LS coupling use 1s, 2s, 2p and so on as labels.
- The jj configurations generated by the MJ92 use 1s, 2s, 2p\*, 2p and so on as labels. The \* denotes  $j = l - \frac{1}{2}$ , while no \* stands for  $j = l + \frac{1}{2}$ .
- When a certain number of orbitals are common to all configurations, they can be given only once at the beginning as a record with CORE in the first 4 columns. Also if some or all of these core orbitals make up a rare gas configuration, it is sufficient to give the symbol of the rare gas to generate the full set of orbitals. Valid symbols are: NE, AR, KR, XE and RN.

As an example input for silicon will read:

In LS coupling	In jj coupling
CORE NE 3S2 :	CORE NE 3S2 :
C 1 3P2 :	C 1 3P*2 :
END	C 2 3P2 :
	END

The structure of input data are the same for all programs and include:

- The first input line associated with Fortran unit number 5. This line contains information to be given only once and includes the following parameters:

**idebug:** Minimum output if = 0, and long output otherwise. (0)

**iread:** Fortran unit number to read the next sets of input data. (5)

**iwri:** Fortran unit number for standard (printed) output. (6)

**ipun:** Fortran unit number to save formatted (=ascii) output. (7)

**iba:** Fortran unit number for Slater coefficients. (8)

**ibb:** Fortran unit number to read wave functions in binary form. (9)

**ibc:** Fortran unit number to write wave functions in binary form. (9)

**nblipa:** Number of output lines per page. (57)

**npow** Power of 10 by which the speed of light is to be multiplied. (0)

- The second input line contains the following item:  
**ttot:** If positive, overall cpu time for the job in seconds. (0.)
- Specific data for each case to be calculated.
- A line with two asterisks as the first two characters indicating the end of the input data for the case(s) to be calculated.

## B. Input Format for MJ92

### Files Used

- Initial input file (initially Fortran unit number 5)
- Optionally a second input file (defined by IREAD as the unit number)
- Standard output file (defined by IWRI)
- One or two files to save results (defined by IPUN and IBA which may be the same)
- Two scratch files (defined by IBB and IBC)

### Input Data Provided Only Once at the Beginning

#### 1. 1st set

**idebug:** Minimum output if = 0, and long output otherwise. (0)

**iread:** Fortran unit number to read the next sets of input data. (5)

**iwri:** Fortran unit number for standard (printed) output. (6)

**ipun:** Fortran unit number to save formatted (=ascii) output. (7)

**iba:** Fortran unit number for Slater coefficients. (8)

**ibb:** Fortran unit number to read wave functions in binary form. (9)

**ibc:** Fortran unit number to write wave functions in binary form. (9)

**nblipa:** Number of output lines per page. (57)

#### 2. 2nd set

**ttot:** If positive, overall cpu time for the job in seconds. (0.)

The following data sets may be in different files depending on the values of **IREAD**, **IBA** read in the 1st and 2nd sets above.

### Input Data for Each Case to Be Calculated

#### 3. 1st set

**ITITLE:** Title line with one asterisk as its first character and a maximum of 79 characters.  
The rest of the input on this line is ignored.

#### 4. 2nd set

This option is not used in MJ92. A colon “:” is required.

#### 5. 3rd set

**KEYWORD** : Keyword for the type of expectation values to calculate. Options are:

ENERGY for the total energy

EXCITATION for the DWB cross section for electron-impact excitation

IONIZATION for the DWB cross section for electron-impact ionization

ELECTRIC for electric multipole transition

MAGNETIC for magnetic multipole transition

BORN for the PWB cross section for electron-impact excitation

Only the first 4 characters are meaningful

**ipun1**: File unit number to save Slater coefficients. (8)

For photoionization, the required Slater coefficients are identical to those for  $En$  and  $Mn$  discrete transitions by photon, because the only difference is in radial functions. The required Slater coefficients for photoionization can be generated by using the ELECTRIC or MAGNETIC option, and rename the final-state orbitals. Also, note that the role of the initial and final states switches. The sample input data for the PH92 code show examples of properly labeled Slater coefficients for photoionization.

#### 6. 4th set

*Only for ELECTRIC or MAGNETIC options:*

**MULTPOL** : Multipolarity. For instance, MULTPOL=1 means dipole, MULTPOL=2 means quadrupole.

#### 7. 5th set

**JJTOT** : Twice the value of the total angular momentum  $J$ .

**mjjtot** : Twice the projection  $M = J_z$  of the total angular momentum  $J$ . (JJTOT)

### 8. 6th set

**LIST:** List of configurations in LS coupling.

A line with **END** as the first 3 characters.

Note that:

- The **configurations must be in LS coupling**. The MJ92 code will automatically generate all matching jj configurations.

### 9. 7th set

*Only for EXCITATION or IONIZATION option:*

**LABEL:** Label for partial waves, only the first 3 characters will be used.

**LADONE:** Angular coefficients that have already been generated for orbital angular momentum  $l$  up to and including LADONE. If nothing was done earlier, a negative number. This option is used when the generation of Slater coefficients takes long on a slow computer.

**LQMAX:** Maximum value of the orbital angular momentum  $l$  for the expansion in partial waves.

The MJ92 code will generate matching  $j$  and  $\kappa$  values corresponding to the  $l$  in the above input data.

### 10. 8th set

*For EXCITATION and IONIZATION options:* The 5th, 6th and the 7th sets above are for the initial state and must be repeated for the final state. For the DWB cross sections, Set 7 is associated with the incident electron while Set 8 is associated with the scattered electron.

*For ELECTRIC and MAGNETIC option:* The 4th, 5th, and the 6th sets above are for the initial state and must be repeated for the final state. *For BORN*, only the 5th and 6th sets above must be repeated for the final state.

### 11. 9th set

*Only for IONIZATION option:* LABEL, LQDONE and LQMAX with the same definitions as Set 7 for the ejected electron.

### 12. 10th set

*For ENERGY, EXCITATION or IONIZATION option:* Indicate whether to include or not the Breit operator (for EXCITATION and IONIZATION options, only the magnetic part of the Breit operator will be included). Must be Y or N.

### 13. 11th set

*Only for EXCITATION or IONIZATION option:* If Y, the Dirac-Fock equation for partial waves is reduced to the configuration average only. If N, then extra angular coefficients are generated. Must be Y or N.

### **End of Input Data**

Two asterisks as the first 2 characters. This indicates the end of all input data.

## C. Input Format for DF92

### Files Used

- Initial input file (Fortran unit 5)
- Optionally a second input file (defined by IREAD as the unit number)
- Optionally a third input file (defined by IBA)
- Standard output file (defined by IWRI)
- One file to save formatted (=ascii) results (defined by IPUN)
- One file to read radial functions in binary form (defined by IBB)
- One file to write radial functions in binary form (defined by IBC, may be the same as IBB)
- One scratch file when the Breit operator is included in the SCF process (defined internally as IBE)

### Input Data Provided Only Once at the Beginning

#### 1. 1st set

**idebug:** Minimum output if = 0, and long output otherwise. (0)

**iread:** Fortran unit number to read the next sets of input data. (5)

**iwri:** Fortran unit number for standard (printed) output. (6)

**ipun:** Fortran unit number to save formatted (=ascii) output. (7)

**iba:** Fortran unit number for Slater coefficients. (8)

**ibb:** Fortran unit number to read wave functions in binary form. (9)

**ibc:** Fortran unit number to write wave functions in binary form. (9)

**nblipa:** Number of output lines per page. (57)

**npow:** Power of 10 by which the speed of light is multiplied to emulate the nonrelativistic limit  $c \rightarrow \infty$ .

#### 2. 2nd set

**ttot:** If positive overall cpu time for the job in seconds. (0.)

The following data sets may be in different files depending on the values of **IREAD**, **IBA** given in the 1st set above.

### Input Data for Each Case to Be Calculated

### 3. 1st set

**ITITLE:** Title line with one asterisk as its first character and a maximum of 79 characters.

**Unlike the MJ92 code,** the 3-digit number in columns 2–4 are used to identify matching Slater coefficients in Fortran unit IBA, if IBA is defined in the 1st set above.

### 4. 2nd set

**LIST:** List of configurations in jj coupling.

A line with **END** as the first 3 characters.

Note that:

- **Unlike in MJ92, configurations must be in jj coupling.**

### 5. 3rd set

**NEIGV :** The order of the eigenvalue for which convergence is to be achieved. If positive it will be the NEIGV-th eigenvalue (the first being the lowest). If negative it will be the eigenvalue having the  $|\text{NEIGV}|$ -th configuration as its largest component.

**ICMUL :** Initial configuration mixing coefficients are read (described as the 18th set) as input data if ICMUL  $\neq 0$ . Furthermore if ICMUL  $< 0$ , the weights are frozen to their initial values during all the SCF process. ICMUL =  $-2$  generates configuration average wave functions.

**iprfrg :** If IPRFRG  $\neq 0$ , energy expression is written in the printed output. (0)

**lamrq:** If LAMRQ  $> 0$ , initial estimates of the off-diagonal Lagrange multipliers (ODLM) are calculated using the Rayleigh quotient method. (0)

**cofrg:** Multiply initial ODLM's (if any) by the value of COFRG. (To be read only if LAMRQ is positive.) (1.)

### 6. 4th set

**NZ:** Atomic number.

**NEL:** Number of bound electrons. NZ  $>$  NEL for a positive ion.

**NORBSC:** Orbitals to be made self-consistent. If NORBSC = 0, all orbitals are made self consistent. If  $< 0$ , all orbitals are frozen. If  $> 0$ , some orbitals (list to be given as the 9th set) are frozen.

**iorth:** If IORTH  $\neq 0$ , orbitals are Schmidt orthogonalized at the beginning and before each diagonalization of the total energy matrix. (0)

- ndep:** Default option for the trial radial functions to start the SCF process. (1)  
 NDEP = 1, generate trial functions from the Thomas-Fermi potential.  
 = 2, generate from a local potential (to be provided as input).  
 = 3, hydrogenic.  
 = 4, read from an input file in ascii format.  
 = 5, read from a binary file.  
 > 6, restart from a job terminated by time control.
- nlec:** Record number to read initial radial functions from a binary file. (0)
- nec:** Record number to write the calculated radial functions in a binary file. (0)
- ifcwf:** Convergence acceleration factors are kept fixed if IFCWF  $\neq$  0. (0)
- nes :** Number of trials to adjust one-electron energies while solving the Dirac equation. (40)
- infini:** Not used in this version. (0)
- inexwf:** Defines the next radial function to be made self consistent. If = 0, the code will choose the orbital that shows the largest variation between successive iterations. Otherwise all functions are solved sequentially. (0)
- idr1:** If  $\neq$  0, radial mesh points are defined using the data from an input binary file. Otherwise, the input data set in the 7th set are used. (0)
- iprfgr:** If IPRFGR  $\neq$  0, extra Slater integrals for the total energy expression are printed only. (0)
- idfbeg:** If IDFBEG = 0, deferred correction is used from the beginning of the SCF process. Otherwise, it is used only after the accuracy of the radial functions is better than 0.01. (0)

## 7. 5th set

- NSTEP :** Number of diagonalization cycles in the SCF process. If = 0, input is replaced by 1 for a single (5 for a multi) configuration calculation.

## 8. 6th set

*Only if NSTEP > 0:* ISCPAR(J,N) J=1 to 3, AZPRY(1,N), AZPRY(2,N), ACCF(1,N), ACCF(2,N), N=1 to NSTEP.

- ISCPAR(1,.) :** Exchange potential is included only if  $\neq$  0. Furthermore, Schmidt orthogonalization is used if  $<$  0. (1)

- ISCPAR(2,.) :** If = 0, omit off-diagonal Lagrange multipliers. (1)

**ISCPAR(3,.)** : Number of iterations divided by number of orbitals. (30)

**AZPRY(1,.)** : Nuclear charge. (=NZ)

**AZPRY(2,.)** : Accuracy to be satisfied by the radial functions. ( $10^{*(NSTEP-6-N)}$ )

**ACCF(1,.)** : Mixing coefficient of the eigenvectors between successive iterations. (1.)

**ACCF(2,.)** : Fraction of electron exchange to be included. (1.)

#### 9. 7th set

Option to modify radial mesh and accuracy criteria. Must be **Y** or **N**. *Only if option is Y:*

**H:** Mesh step size in the variable  $t$  defined as  $t = \ln(r/r_1) + ar$ . (0.05)

**DR(1):** First tabulation point multiplied by the nuclear charge NZ. (0.01)

**AMESH:** Mesh step size in the linear region, i.e. value of  $a$  in the above definition of  $t$ . (0.01)

**TESTE:** Relative accuracy to be obtained for one-electron energies. (0.000005)

**RAP:** Defines the accuracy to which the small component must be matched when solving the Dirac equation. (100.)

#### 10. 8th set

Option to modify nuclear parameters. Must be **Y** or **N**. If option is **N**, standard atomic masses are used with a uniform nuclear charge distribution and a radius given in NUCPOT for  $Z \leq 45$ . For  $Z > 45$ , Fermi distribution is used. *Only if option is Y:*

**A:** Atomic mass (used to calculate reduced mass of all particles including electrons).

**FERC:** Nuclear radius in fermi. (0.)

**FERT:** Thickness parameter for the Fermi charge distribution of the nucleus. (0.)

**NUC:** Index of the nuclear radius (1 if FERC=0, and  $\max(\text{NUC}, 41)$  otherwise).

For the nucleus a point charge is used when  $\text{FERC} \leq 0$  and a finite one when  $\text{FERC} > 0$ . For a finite charge distribution, a uniform charge inside a sphere of radius FERC is used if  $\text{FERT} \leq 0$  and otherwise a Fermi distribution written as:

$$Ct / (1. + \exp((r - \text{FERC}) * (4 \ln 3) / \text{FERT})),$$

$Ct$  being a normalization constant.

#### 11. 9th set

*Only if NORBSC > 0:* Labels of the frozen orbitals and a line with **END** as the first 3 characters.

## 12. 10th set

Option to modify the default options for some of the orbitals. Must be **Y** or **N**.

*Only if option is Y, for each orbital to be modified:*

**LABEL:** Label of the orbital to be modified.

**IDOI:** Type of initial orbital (see definition of NDEP in Set 6).

**ZH:** Only if IDOI=3, screening of the nuclear charge for hydrogenic initial orbital. A positive number reduces the effective nuclear charge.

**INDSOL(1):** Method for solving the Dirac equation. (1=normal case; 3=when frozen orbitals are involved; 4=for correlation orbitals; 5 for using B-splines, **this method may be tricky to use.**) (1)

**indsol(2):** If  $\geq 0$ , use deferred correction. If = 0, use the solution of previous iteration to calculate deferred correction. (0)

**indsol(3):** If = 0, enforce number of nodes on radial functions. (0)

**indsol(4):** If  $\neq 0$ , use the Schmidt orthogonalization before solving the Dirac equation. (0)

**indsol(5):** If  $\neq 0$ , use the Rayleigh quotient to obtain an estimate of the one-electron eigenvalue. If = 0, use previous value. (0)

**indsol(6):** If = 0, use full exchange. If not, reduce exchange by the coefficient given in the 6th set, **ACCF(2,N)**. (0)

**iormax:** Maximum number of tabulation points. (Maximum value allowed by array dimensions. This is controlled by maxpts in length.def.)

**scew:** Initial value of the mixing coefficient of the orbital between two successive iterations. (0.3)

**K:** Flag to distinguish between electron (0) and muon ( $\neq 0$ ).

A line with **END** as the first 3 characters.

## 13. 11th set

Option to modify method for computing off-diagonal Lagrange multipliers. Must be **Y** or **N**. *Only if option is Y:*

**TESTEP:** Criteria to switch from the difference method to the sum method. (0.001)

For each Lagrange multiplier:

**LABOI(1), LABOI(2):** Labels of the orbitals involved in the Lagrange multiplier.

**N:** Selection of the method to compute Lagrange multiplier. (-1)

N < -1: The difference method.

N = -1: The difference or sum method depending on the occupation numbers.

N = 0: Omit Lagrange multiplier.

N = 1: The sum method.

N > 1: The Rayleigh quotient.

Example:

0.001

6D\* 5D\* 2

5D\* 6D\* 0 (or try 2)

END

A line with **END** as the first 3 characters.

#### 14. 12th set

*Only if NDEP=2:*

**K:** Number of tabulation points for the local potential to use.

**VN(I) I=1 to K:** Local potential multiplied by  $r$  (i.e.,  $r * V(r)$ ) with the format 5(1PD14.7).

#### 15. 13th set

*Only if IDOI=4:*

**K:** Number of tabulation points for the orbital to read.

**AP(I) I=1 to 10:** Coefficients for series expansion of the large component radial function near the origin.

**AQ(I) I=1 to 10:** Coefficients for series expansion of the small component radial function near the origin.

**P(I) I=1 to K:** Large component radial function.

**Q(I) I=1 to K:** Small component radial function.

with the format 5(1PD14.7) for AP, AQ, P, and Q.

#### 16. 14th set

Only if absolute value of  $ICMUL=1$ , for each configuration for which the weights are to be read:

**I:** Configuration index.

**CW:** Initial coefficient of the configuration.

Note that some of the weights may already have been read from a binary file.

#### 17. 15th set

Only if the Fortran unit to read the Slater coefficients was defined to be the same as the rest of the input data. For each line:

**A:** Angular coefficient.

**IC, JC:** Configuration indexes.

**K:** Multipolarity.

**LABEL(I) I=1 to 4:** Labels of the orbitals associated with this radial integral.

A line with **END** as the first 3 characters.

#### 18. 16th set

**NBREIT:** Option for the Breit operator.

If  $< 0$ , the Breit operator is omitted.

If  $= 0$ , the Breit operator is calculated in the first-order perturbation.

If  $> 0$ , The magnetic part of the Breit operator is included in the SCF process at the zero-frequency limit.

**NRET:** If  $\neq 0$ , full retardation correction in the Coulomb and Lorentz gauges are calculated.

\*\*\*\* This will almost double CPU time. Furthermore must be used only for single configuration calculations. Otherwise meaningless results may be produced. \*\*\*\*

**ibe:** Fortran unit number to write magnetic integrals when they are used in the SCF process, i.e., when  $NBREIT > 0$ . (IBC+2)

### 19. 17th set

Only if the Fortran unit to read the Slater coefficients was defined to be the same as the rest of the input data. For each line:

**A:** Angular coefficient for the magnetic interaction.

**B:** Angular coefficient for the retardation interaction.

**IC, JC:** Configuration indexes.

**K:** Multipolarity.

**LABEL(I) I=1 to 4:** Labels of the orbitals associated with this radial integral.

**NEN:** If  $\geq 0$ , the integration of both radial variables is from 0 to  $\infty$ . If  $< 0$ , the integration over  $r_2$  is from 0 to  $r_1$ .

A line with **END** as the first 3 characters.

### 20. 18th set

**ilams:** Distance from the origin to integrate charge density for self-energy screening, in 1/100 Compton wavelength. (30)

### 21. 19th set

**input(1):** If  $\neq 0$ , Coulomb or Breit integrals are calculated.

**input(2):** If  $\neq 0$ , one-electron integrals are calculated.

**input(3):** If  $\neq 0$ , expectation values of  $\langle r^n \rangle$  are calculated.

**input(4):** If  $\neq 0$ , one-electron radial functions are tabulated in the standard output file.

**input(5):** If  $\neq 0$ , the total charge density is written to Fortran unit IPUN in the ascii format. Furthermore if  $> 0$ , the total charge density is also listed in the standard output file.

**input(6):** Number of radial functions to be written on Fortran unit IPUN.

**input(7):** If  $\neq 0$ , the series expansion coefficients of the radial functions near the origin are tabulated.

## 22. 20th set

Only if  $INPUT(1) \neq 0$ :

**LABELI(I) I=1 to 4:** Label of the orbitals associated with the integral.

**K:** Multipolarity.

**NEM:** If = 0, the Coulomb integral, and Breit integral otherwise. Furthermore if < 0, integration over the variable S is from 0 to R only. The integrals are defined as:  
 $\int F(R) * UK(R, S) * G(S) dR dS$  with

$$\begin{array}{ll} F = P1 * P2 + Q1 * Q2 & G = P3 * P4 + Q3 * Q4 \text{ if NEM} = 0 \\ F = P1 * Q2 & G = P3 * Q4 \text{ if NEM} \neq 0 \end{array}$$

A line with **END** as the first 3 characters.

## 23. 21st set

Only if  $INPUT(2) \neq 0$ :

**LABELI(I) I=1,2:** Label of the orbitals associated with the requested integral.

**IALL:** If  $\neq 0$ , all one-electron integrals are calculated starting from the one defined by the first label.

A line with **END** as the first 3 characters.

## 24. 22nd set

Only if  $INPUT(3) \neq 0$ :

**LABELI(I) I=1,2:** Label of the orbitals associated with the requested integral.

**K:** Power of  $r$ .

**NEM:** Integral is:

$$\begin{array}{ll} (P1 * P2 + Q1 * Q2)r^K & \text{if NEM} = 0 \\ (P1 * Q2 + P2 * Q1)r^K & \text{if NEM} \neq 0 \end{array}$$

**IALL:** If > 0, (< 0) all integrals (only the diagonal ones) are calculated starting from the one defined by the first label.

A line with **END** as the first 3 characters.

25. 23rd set

*Only if INPUT(6)  $\neq$  0:*

**LABELI(I) I = 1 to INPUT(6):** Label of the orbitals to be written on Fortran unit  
IPUN in the ascii format.

**End of Input Data**

Two asterisks as the first 2 characters.

## D. Input Format for PH92

### Files Used

- Initial input file (initially Fortran unit number 5)
- Optionally a second input file (defined by IREAD as the unit number)
- Optionally a third input file (defined by IBA as the unit number)
- Standard output file (defined by IWRI)
- One file to read wave functions in binary form (defined by IBB)

### Input Data Provided Only Once at the Beginning

#### 1. 1st set

**idebug:** Minimum output if = 0, and long output otherwise. If IDEBUG > 9, and IOUTPR in the 10th set is Y, last 1000 values of the continuum wave functions are printed. (0)

**iread:** Fortran unit number to read the next sets of input data. (5)

**iwri:** Fortran unit number for standard (printed) output. (6)

**ipun:** Not used. (7)

**iba:** Fortran unit number for Slater coefficients. (8)

**ibb:** Fortran unit number to read wave functions in binary form. (9)

**ibc:** Not used. (9)

**nblipa:** Number of output lines per page. (57)

#### 2. 2nd set

**ttot:** If positive, overall cpu time for the job in seconds. (0.)

The following data sets may be in different files depending on the values of **IREAD**, **IBA** read in the 1st and 2nd sets above.

### Input Data for Each Case to Be Calculated

#### 3. 1st set

**ITITLE:** Title line with one asterisk as its first character and a maximum of 79 characters. The 3-digit number in columns 2–4 is used to match the Slater coefficients in the Fortran unit IBA.

#### 4. 2nd set

**KEYWORD** : Keyword for the type of expectation values to calculate. Options are:

GENERAL for off-diagonal mean values of  $\langle i | r | j \rangle$ .

ELECTRIC for electric multipole transition

MAGNETIC for magnetic multipole transition

BORN for the PWB cross section for electron-impact excitation

PHOTOIONIZATION for photoionization

Only the first 4 characters are meaningful

#### 5. 3rd set

**LIST**: List of initial-state configurations in jj coupling (e.g., upper state for the  $En$  and  $Mn$  transitions, lower state for the Born excitation cross sections).

A line with **END** as the first 3 characters.

#### 6. 4th set

**NRECI**: Record number to read the initial-state orbitals from a binary file.

#### 7. 5th set

**LIST**: List of final-state configurations in jj coupling (e.g., lower state for the  $En$  and  $Mn$  transitions, upper state for the Born excitation cross sections).

A line with **END** as the first 3 characters.

#### 8. 6th set

**NRECF**: Record number to read the final-state orbitals from a binary file.

*Only for PHOTOIONIZATION, the 7th through the 17th set.*

#### 9. 7th set

**LABEL**: Label for ejected electron partial waves, only the first 3 characters will be used.

#### 10. 8th set

**EVFREE**: Ejected photoelectron energy in eV.

**11. 9th set**

**AUGER:** Should be N to compute photoionization cross section.

**12. 10th set**

**IOUTPR:** If Y, tabulate partial waves.

*Only if IOUTPR is Y:*

**IPSTEP:** Tabulate every IPSTEP points. (20)

**13. 11th set**

**MODFREE:** If Y, modify the methods for the partial waves.

*Only if MODFREE is Y:*

**IOPTLA:** If Y, include off-diagonal Lagrange multipliers. (Y)

**IOPEXD:** If Y, include exchange interaction between bound and free electrons. (Y)

**IORTH:** If Y, Schmidt orthogonalize before solving the Dirac-Fock equation. (Y)

**14. 12th set**

**SCFCRIT:** If Y, convergence acceleration is used.

*Only if SCFCRIT is Y:*

**COFSTO:** Initial value of mixing between two iterations (kept frozen if no convergence acceleration). (0.9)

**CTEST:** SCF accuracy to be satisfied. ( $10^{-5}$ )

**ITERMA:** Maximum number of SCF iterations. (600)

**15. 13th set**

**WKB:** If Y, modify parameters used in the normalization of the asymptotic Dirac-Fock solution using the WKB approximation.

*Only if WKB is Y:*

**CTNOR:** Accuracy for partial wave normalization. ( $3 \times 10^{-6}$ )

**MAXNOR:** Maximum number of extensions (by 240 points) to reach the asymptotic form of partial waves. (100)

16. 14th set

**NBFREE:** Number of continuum partial waves.

17. 15th set

**KFREE(I), I=1 to NBFREE:**  $\kappa$  quantum number of partial waves.

18. 16th set

**ITITLE:** Title line with one asterisk as its first character and a maximum of 79 characters. The 3-digit number in columns 2–4 is used to match the Slater coefficients in the Fortran unit IBA.

19. 17th set

*For each transition matrix element, a line with (=output from MJ92, the first four characters must be PHOT):*

**A:** Angular coefficient.

**IC, JC:** Configuration indexes.

**K:** Multipolarity.

**LABELI, LABELF:** Labels of orbitals for the matrix element.

A line with **END** as the first 3 characters.

**Only for ELECTRIC and MAGNETIC:**

20. 7th set

**EVI:** Energy of the initial (=upper) state in eV.

**EVF:** Energy of the final (=lower) state in eV.

21. 8th set

**JJI:**  $2 \times J$  of the initial state.

**JJF:**  $2 \times J$  of the final state.

22. **9th set**

**IPO**L: Multipolarity of the transition.

23. **10th set**

**ITITLE**: Title line with one asterisk as its first character and a maximum of 79 characters. The 3-digit number in columns 2–4 is used to match the Slater coefficients in the Fortran unit IBA.

24. **11th set**

*For each transition matrix element, a line with (=output from MJ92, the first four characters must be “ En ” for ELECTRIC and “ Mn ” for MAGNETIC multipole transitions):*

**A**: Angular coefficient.

**IC, JC**: Configuration indexes.

**K**: Multipolarity.

**LABELI, LABELF**: Labels of orbitals for the matrix element.

A line with **END** as the first 3 characters.

**Only for BORN**:

25. **7th set**

**JJI**:  $2 \times J$  of the initial (=lower) state.

**JJF**:  $2 \times J$  of the final (=upper) state.

26. **8th set**

**EEXC**: Excitation energy in eV. **Colon (:)** required after **EEXC**.

27. **9th set**

**TEV**: List of incident energy in eV. The code accepts a total of 100 incident energies separated by a blank. Be careful not to use columns 1–4.

## 28. 10th set

**ITITLE:** Title line with one asterisk as its first character and a maximum of 79 characters.  
The 3-digit number in columns 2–4 is used to match the Slater coefficients in the Fortran unit IBA.

## 29. 11th set

*For each transition matrix element, a line with (=output from MJ92, the first four characters must be BORN):*

**A:** Angular coefficient.

**IC, JC:** Configuration indexes.

**K:** Multipolarity.

**LABELI, LABELF:** Labels of orbitals for the matrix element.

A line with **END** as the first 3 characters.

### **End of Input Data**

Two asterisks as the first 2 characters. This indicates the end of all input data.

## E. Input format for DW92

### Files Used

- Initial input file (initially Fortran unit number 5)
- Optionally a second input file (defined by IREAD as the unit number)
- Optionally a third input file (defined by IBA as the unit number)
- Standard output file (defined by IWRI)
- One file to read wave functions in binary form
- Three scratch files (Fortran units IBC=IBB, IBC+1, IBC+2)

### Input Data Provided Only Once at the Beginning

#### 1. 1st set

**idebug:** Minimum output if = 0, and long output otherwise. If IDBUG > 9, and IOUTPR in the 10th set is Y, last 1000 values of the continuum wave functions are printed. (0)

**iread:** Fortran unit number to read the next sets of input data. (5)

**iwri:** Fortran unit number for standard (printed) output. (6)

**ipun:** Not used. (7)

**iba:** Fortran unit number for Slater coefficients. (8)

**ibb:** Fortran unit number to read wave functions in binary form. (9)

**nblipa:** Number of output lines per page. (57)

**npow:** Power of ten by which to multiply the speed of light. (0)

#### 2. 2nd set

**ttot:** If positive, overall cpu time for the job in seconds. (0.)

The following data sets may be in different files depending on the values of **IREAD**, **IBA** read in the 1st and 2nd sets above.

**DW92 calculates cross section for one incident energy. New input data must be submitted for each incident energy.**

### 3. 3rd set

**ITITLE:** Title line with one asterisk as its first character and a maximum of 79 characters. The 3-digit number in columns 2–4 is used to match the Slater coefficients in the Fortran unit IBA.

### 4. 4th set

Debugging output requests:

**IDEBUG1:** If  $\neq 0$ , stop execution after generating free waves. (0)

**IDEBUG2:** If  $\neq 0$ , stop execution after interpolation between the initial and final state radial meshes. (0)

**IDEBUG3:** If  $\neq 0$ , stop execution after calculating matrix elements. (0)

**IDEBUG4:** If  $\neq 0$ , print cross section matrix elements. (0)

**IDEBUG5:** If  $\neq 0$ , maximum output during the calculation of partial waves. (0)

### 5. 5th set

**KEYWORD :** Keyword for the type of cross section to calculate. Options are:

EXCITATION for discrete excitations by electron impact.

IONIZATION for ionization by electron impact.

Only the first 4 characters are meaningful

### 6. 6th set

**LIST:** List of initial-state configurations in jj coupling.

A line with **END** as the first 3 characters.

### 7. 7th set

**NRECI:** Record number to read the initial-state orbitals from a binary file.

**JTARG:**  $2 \times J$  of the target.

**LABEL:** Label for the partial waves. Only the first 3 characters will be used.

**ENFEV:** Energy of the free electron in eV.

## 8. 8th set

**IOUTPR:** If Y, tabulate partial waves.

*Only if IOUTPR is Y:*

**IPSTEP:** Tabulate every IPSTEP points. (20)

## 9. 9th set

TYPE of partial waves to be calculated:

**DW:** Distorted waves.

**CW:** Coulomb waves.

**PW:** Plane waves.

*If TYPE=CW, then read:*

**ZEFF:** Effective nuclear charge.

**The following 10th through 12th sets are only for DW:**

## 10. 10th set

**MODFREE:** If Y, modify the methods for the partial waves.

*Only if MODFREE is Y:*

**IOPTLA:** If Y, include off-diagonal Lagrange multipliers. (Y)

**IOPEXD:** If Y, include exchange interaction between bound and free electrons. (Y)

**IORTH:** If Y, Schmidt orthogonalize before solving the Dirac-Fock equation. (Y)

## 11. 11th set

**SCFCRIT:** If Y, convergence acceleration is used.

*Only if SCFCRIT is Y:*

**COFSTO:** Initial value of mixing between two iterations (kept frozen if no convergence acceleration). (0.9)

**CTEST:** SCF accuracy to be satisfied. ( $10^{-5}$ )

**ITERMA:** Maximum number of SCF iterations. (600)

## 12. 12th set

**WKB:** If Y, modify parameters used in the normalization of the asymptotic Dirac-Fock solution using the WKB approximation.

*Only if WKB is Y:*

**CTNOR:** Accuracy for partial wave normalization. ( $3 \times 10^{-6}$ )

**MAXNOR:** Maximum number of extensions (by 240 points) to reach the asymptotic form of partial waves. (100)

## 13. 13th set

**LQMIN:** The highest  $l$  value of the partial waves for which calculation has been completed already.

**LQMAX:** Maximum  $l$  value of the partial waves to be calculated. **Warning: most computers cannot handle LQMAX > 50 because of the smallest real number allowed ( $10^{-308}$ ).**

## 14. 14th set

*For IONIZATION only:*

**LABEL:** Label for the scattered electron partial waves.

**ENFEV:** Scattered electron energy in eV.

**For EXCITATION (IONIZATION), the sets 3 and 6 through 14 are for the incident electron (incident and scattered electron), and the same sets must be repeated for the scattered (ejected) electron.**

## 15. 15th set

**ITITLE:** Title line with one asterisk as its first character and a maximum of 79 characters. The 3-digit number in columns 2–4 is used to match the Slater coefficients in the Fortran unit IBA.

## 16. 16th set

**BREIT:** If Y, Breit operator is included. (Appropriate Slater coefficients from MJ92 must be available.)

**CONFAV:** If Y, configuration average is used. If N, term-dependent partial waves are generated and used. In the latter case, appropriate Slater coefficients from MJ92 must be available.

### **End of Input Data**

Two asterisks as the first 2 characters. This indicates the end of all input data.

Since the calculation of DWB cross sections involves a large number of partial waves and hence Slater integrals, the Slater integrals are to be read from a file separate from the input data listed above. The Slater coefficients generated by the MJ92 code should be identified as the Fortran unit 8. Then, the DW92 code reads the Slater coefficients and use them in the calculation of the DWB cross sections.

## F. Samples of Input Data for MJ92

```
:
:
*881 Be-like, 2s2+2p2, total energy
:
ENERGY :
JT=0 :
CORE (1S)2 :
C 1 (2S)2 :
C 2 (2P)2 :
END
Y :
*882 Be-like, 2s2p+2p3d, J=1 total energy
:
ENERGY :
JT=2 :
CORE (1S)2 :
C 1 (2S)1 (2P)1 :
C 2 (2P)1 (3D)1 :
END
Y :
*883 Be-like, 2s2p+2p3d -> 2s2+2p2, E1
:
ELECTRIC :
MULTPOL=1
# upper state configurations first
JT=2 :
CORE (1S)2 :
C 1 (2S)1 (2P)1 :
C 2 (2P)1 (3D)1 :
END
JT=0 :
CORE (1S)2 :
C 1 (2S)2 :
C 2 (2P)2 :
END
*884 Be-like, 2s2p+2p3d <- 2s2+2p2, Born
:
BORN :
# initial state configurations first
JT=0 :
CORE (1S)2 :
C 1 (2S)2 :
C 2 (2P)2 :
```

```

END
      JT=2 :
CORE (1S)2 :
C 1 (2S)1 (2P)1 :
C 2 (2P)1 (3D)1 :
END
*885 Be-like, 2s2p+2p3d <- 2s2+2p2, DW
      :
      EXCITATION :
      0 :
C 1 (1S)2 (2S)2 :
C 2 (1S)2 (2P)2 :
END
LABEL IN -1 20 :
      2 :
C 1 (1S)2 (2S)1 (2P)1 :
C 2 (1S)2 (2P)1 (3D)1 :
END
LABEL OUT -1 20 :
# N=no Breit; Y=configuration average
      N Y :
**

```

### G. Samples of Input Data for DF92, PH92, and DW92

```

      0 5 6 7 8 :
      :
*881 C++, 2s2+2p2, ground state, MCDF
C 1 (1S)2 (2S)2 :
C 2 (1S)2 (2P*)2 :
C 3 (1S)2 (2P)2 :
END
      NEIGV=1 ICMUL=0 IPRFGR=0 :
      NZ=6 NOE=4 NORBSC=0
      IORTH=0 NDEP=0 NLEC=0 NEC=1 :
      NSTEP=0
      N :
      N :
      N :
      N :
      NBRE=0 NRET=0 :
      :
      :
*882 C++, 2s2p+2p3d, 2nd J=1 MCDF
C 1 (1S)2 (2S)1 (2P*)1 :

```

```

C 2 (1S)2 (2S)1 (2P)1      :
C 3 (1S)2 (2P*)1 (3D*)1   :
C 4 (1S)2 (2P)1 (3D*)1   :
C 5 (1S)2 (2P)1 (3D)1     :
END
NEIGV=2  ICMUL=0  IPRFGR=0  :
NZ=6  NOE=4  NORBSC=0
IORTH=0  NDEP=0  NLEC=0  NEC=2  :
NSTEP=0
N  :
N  :
N  :
N  :
NBRE=0  NRET=0  :
:
:
**
0 5 6 7 8  :
:
# *881 Be-like, 2s2p+2p3d -> 2s2+2p2, E1
ELECTRIC  :
C 1 (1S)2 (2S)1 (2P*)1     :
C 2 (1S)2 (2S)1 (2P)1     :
C 3 (1S)2 (2P*)1 (3D*)1   :
C 4 (1S)2 (2P)1 (3D*)1   :
C 5 (1S)2 (2P)1 (3D)1     :
END
NRECI=2
C 6 (1S)2 (2S)2             :
C 7 (1S)2 (2P*)2           :
C 8 (1S)2 (2P)2            :
END
NRECF=1
EVI=0.
EVF=12.69
JJI=2
JJF=0
IPOL=1
*881 Be-like, 2s2p+2p3d <- 2s2+2p2, Born
BORN  :
C 1 (1S)2 (2S)2           :
C 2 (1S)2 (2P*)2         :
C 3 (1S)2 (2P)2          :
END
NRECI=1

```

```

C 4 (1S)2 (2S)1 (2P*)1 :
C 5 (1S)2 (2S)1 (2P)1 :
C 6 (1S)2 (2P*)1 (3D*)1 :
C 7 (1S)2 (2P)1 (3D*)1 :
C 8 (1S)2 (2P)1 (3D)1 :
END
      NRECF=2
      JJI=0
      JJF=2
      EEXC=12.69 :
      TEV=13. 14. 15. 17. 20. 25. 30. 40. 50. :
**
      0 5 6 7 8 :
      :
*881 C++, 2s2p+2p3d <- 2s2+2p2, DW, T=15 eV
      EXCITATION :
C 1 (1S)2 (2S)2 :
C 2 (1S)2 (2P*)2 :
C 3 (1S)2 (2P)2 :
END
      FILE=1 JINI=0 LABL=IN ENGY=15. TABUL=N TYPE=DW
      LGEXOR=N SCF=N WKB=N :
      0 20 :
*882 C++, 2s2p+2p3d <- 2s2+2p2, DW, T'=15-12.69=3.31 eV
C 4 (1S)2 (2S)1 (2P*)1 :
C 5 (1S)2 (2S)1 (2P)1 :
C 6 (1S)2 (2P*)1 (3D*)1 :
C 7 (1S)2 (2P)1 (3D*)1 :
C 8 (1S)2 (2P)1 (3D)1 :
END
      FILE=2 JFIN=2 LABL=OUT ENGY=3.31 TABUL=N TYPE=DW
      LGEXOR=N SCF=N WKB=N :
      0 20 :
*883 C++, 2s2p+2p3d <- 2s2+2p2, DW, lmax=20
# N=no Breit; Y=config. ave.
      N Y :
**

```

## ACKNOWLEDGMENTS

The computer codes described in this lecture note were developed primarily by J. P. Desclaux with modifications by myself and P. Indelicato. This lecture series was arranged with the financial support from the Korea Atomic Energy Research Institute and the Asia-Pacific Center for Theoretical Physics.

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TABLES

TABLE I. Fundamental constants associated with atomic units.\*

electron mass $m$	$9.109\,381\,88\,(72) \times 10^{-31}$ kg
electron charge $e$	$-1.602\,176\,462\,(63) \times 10^{-19}$ C
Planck's constant/ $2\pi$ $\hbar$	$1.054\,571\,596\,(82) \times 10^{-34}$ Js
speed of light $c$	299 792 458 m/s (exact)
inverse fine-structure constant $1/\alpha = \hbar c/e^2$	137.035 999 76 (50)
Bohr radius $a_0 = \hbar/mc^2$	0.529 177 2083 (19) Å
rydberg constant $R_\infty = \frac{1}{2}mc^2\alpha^2$	109 737.315 685 49 (83) cm <sup>-1</sup>
	13.605 691 72 (53) eV
electron volt $e/C$ in joules	8065.544 77 (32) cm <sup>-1</sup>

\* From P. J. Mohr and B. H. Taylor, *J. Phys. Chem. Ref. Data* **28**, 1713 (1999). This reference contains the latest list of recommended fundamental constants.

TABLE II. Dirac quantum number  $\kappa$ .

$\kappa$	-1	1	-2	2	-3	3	-4	4	-5
$l$ and $j$	s <sub>1/2</sub>	p <sub>1/2</sub>	p <sub>3/2</sub>	d <sub>3/2</sub>	d <sub>5/2</sub>	f <sub>5/2</sub>	f <sub>7/2</sub>	g <sub>7/2</sub>	g <sub>9/2</sub>
Input	s	p*	p	d*	d	f*	f	g*	g

TABLE III. Selection rules for  $E1$ ,  $M1$ , and  $E2$  transitions.\*

	E1	M1	E2
(1)	$\Delta J = 0, \pm 1$ (No $0 \leftrightarrow 0$ )	$\Delta J = 0, \pm 1$ (No $0 \leftrightarrow 0$ )	$\Delta J = 0, \pm 1, \pm 2$ (No $0 \leftrightarrow 0, \frac{1}{2} \leftrightarrow \frac{1}{2}, 0 \leftrightarrow 1$ )
(2)	$\Delta M = 0, \pm 1$	$\Delta M = 0, \pm 1$	$\Delta M = 0, \pm 1, \pm 2$
(3)	Parity change	No parity change	No parity change
(4)	One electron jump	No electron jump	One or no electron jump
(5)	$\Delta \ell = \pm 1$ $\Delta S = 0$	$\Delta \ell = 0, \Delta n = 0$ $\Delta S = 0$	$\Delta \ell = 0, \pm 2$ $\Delta S = 0$
(6)	$\Delta L = 0, \pm 1$ (No $0 \leftrightarrow 0$ )	$\Delta L = 0$	$\Delta L = 0, \pm 1, \pm 2$ (No $0 \leftrightarrow 0, 0 \leftrightarrow 1$ )

\* From R. H. Garstang, *Forbidden Transitions in Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press, New York, 1962), p. 4.