

PRACTICAL ATOMIC STRUCTURE AND COLLISION THEORY

Yong-Ki Kim

Quantum Optics Laboratory

*Korea Atomic Energy Research Institute, Taejon 305-353, Korea
and*

Atomic Physics Division

National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8422 U.S.A.

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Abstract

This lecture note outlines atomic structure and collision theories needed to use a comprehensive computer code to calculate (a) relativistic wave functions for neutral atoms and atomic ions, (b) atomic energy levels, (c) bound-bound transition probabilities, and (d) bound-bound plane-wave Born excitation cross sections by electron impact. This computer code is for a Windows based PC, and uses multiconfiguration Dirac-Fock method. The code is called MCDF2002, and its usage will be covered in this course. A simple yet powerful method to calculate excitation and total ionization cross sections for atoms by using the atomic data from this code will be described.

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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 decade [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 involving neutral atoms and their 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 krypton and heavier), particularly to handle intermediate coupling in medium and 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 (JPD) of Grenoble, France [4] with the help from Paul Indelicato (PI) of the Univ. of Paris and myself (YKK) at various stages of the code development and usage.

A. History of Wave Function Code Development

Initially, codes for different products were packaged separately, though they shared many common subroutines because the computers in the 1970s and 1980s had severe limitations in the random memory size, disc space, and CPU speed. It was uneconomical to combine them into one gigantic code because such a code will get low priority in running on mainframe computers, which were the only kind that could run such codes. Over the years, various versions of these codes ran on mainframes provided by IBM, CDC, Cray, DEC, etc.

In the mid-1990s there was a revolution in the computing power of desktop computers, known genetically as personal computers (PCs). High-power PCs available at the time of this writing (Summer 2002) can run faster than the first-generation Crays with much larger random memory and many gigabytes of disc space that were never available to individual users of mainframes in the 1980s and the early 1990s.

To take advantage of this unprecedented computing power of PCs, many components of the codes were rewritten in Fortran 90 and have been integrated into one code. This integrated code will be introduced and detailed description and practice on realistic problems will be provided later.

The older version had the following components in the early 1990s. These codes were labeled DF92, MJ92, PH92, and DW92 in my earlier lectures. The backbone of the code package was the Dirac-Fock wave function code, DF92. However, to specify the quantum numbers (basically the total angular momentum \mathbf{J} and one-electron configurations), MJ92 was first used to generate appropriate input data for DF92.

PH92 used the wave functions from DF92 and calculated photon-atom interaction cross sections such as electromagnetic transition probabilities (Einstein’s A coefficients), photoionization cross sections, and plane-wave Born cross sections for electron-impact excitation. The

angular parts of the interaction matrix elements were integrated analytically in MJ92 and provided as input data for PH92.

DW92 generated continuum wave functions and used bound-state wave functions from DF92 to calculate electron-impact excitation and ionization cross sections for atoms and their ions in the first-order Born approximation. The continuum waves were generated as partial waves (i.e., separate radial functions for each orbital angular momentum). Partial waves of plane waves, Coulomb waves, and distorted waves were calculated in the potential of the bound electrons in the target atom. Again, the angular parts were integrated analytically in MJ92 and provided as input data for DW92.

B. New Developments

To alleviate the inconvenience of going back and forth on these component codes, JPD and PI began to integrate some components into one comprehensive package. This integration effort is still in progress. As of August 2002, DF92 has been integrated with parts of MJ92 and PH92. The new code, to be referred to as MCDF2002 hereafter, can calculate sophisticated relativistic wave functions, calculate electric and magnetic multipole transition probabilities, and plane-wave Born cross sections for electron-impact excitations. The required angular coefficients are calculated internally and passed on to successive steps until the final results are obtained.

In addition, a theoretical model called the BEB (binary-encounter-Bethe) model has been developed [5] to use orbital data from MCDF2002 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.

The goal of these lectures is to demonstrate how to take advantage of the capability of the MCDF2002 code and generate atomic structure and collision data useful for practical applications. More orthodox theories for electron-atom collision cross sections are either unreliable—if a theory is easy to use—or too complicated, require immense computational investments, or have very limited applicability—if a theory is reliable. The collision theories presented in this lecture series are more intuitive than rigorous, simple to use, and generate reliable results.

C. Units

It is customary to use atomic units (a.u.) in atomic and molecular calculations. In atomic units, the electron mass m_e , $\hbar = \text{Planck's constant divided by } 2\pi$, and the electronic charge e are set to unity. All physical quantities associated with the ground state of the hydrogen atom, except for the total energy, become unity in atomic units.

The unit of length in atomic units is called the bohr and denoted by $a_0 = \hbar^2/m_e e^2$. This is the distance between the nucleus and the $1s$ electron in the hydrogen atom. The unit of energy in atomic units is called the hartree, which is the Coulomb repulsion between two electrons at a distance of a_0 : $1 \text{ hartree} = e^2/a_0$. The total energy of the hydrogen atom is -0.5 a.u. , i.e., 1 a.u. of energy is 27.2 eV .

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., cm^2 , \AA^2 , barns, megabarns, πa_0^2 , $\text{\AA}^2/\text{eV}$, $\pi a_0^2/\text{hartree-steradian}$, 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 usually found in standard textbooks for beginning graduate students. Nonrelativistic and relativistic energy levels and wave functions of one-electron atoms are outlined in Sec. II. Nonrelativistic atomic structure theories for more complex atoms are presented in Sec. III, while their relativistic counterparts and quantum electrodynamic effects, commonly known as the Lamb shift, are described in Sec. IV. Interaction of photons with atoms are presented in Sec. V, while interaction of electrons with atoms are outlined in Sec. VI. Electron-impact ionization of molecules are briefly described in Sec. VII. The MCDF2002 code and its usage are discussed in Sec. VIII, and the input format and sample input data are listed in the Appendix.

II. HYDROGEN ATOM: NONRELATIVISTIC AND RELATIVISTIC SOLUTIONS

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 the LS coupling while relativistic theories use the jj coupling. Since the users of this note are more familiar with nonrelativistic notations than relativistic ones, underlying theories for atomic structure and collision are presented in nonrelativistic notations first, and then necessary changes to switch to relativistic notations are pointed out.

A. Bound and Continuum Solutions of Hydrogen Atom, Nonrelativistic

The nonrelativistic bound and continuum wave functions of the hydrogen atom and hydrogenic ions with nuclear charge Z , principal quantum number n , orbital angular momentum l , azimuthal quantum number m , wave number k (momentum $\mathbf{p} = \mathbf{k}\hbar$), electron energy E , radial variable r , polar angle θ , and azimuthal angle φ are obtained by solving the Schödinger equation [6]:

$$H\psi(r, \theta, \varphi) = \left(\frac{p^2}{2m} - \frac{Ze^2}{r} \right) \psi(r, \theta, \varphi) \quad (1)$$

$$= E_n \psi_{nlm}(r, \theta, \varphi) \quad \text{for bound states with} \quad (2)$$

$$E_n = -\frac{Z^2}{2n^2}. \quad (3)$$

The total energy E_n depends only on the principal quantum number, i.e., the hydrogenic energy levels are degenerate in quantum numbers l and m , though the matching eigenfunctions are not degenerate.

The eigenfunctions are

$$\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm}(\theta, \varphi), \quad (4)$$

$$\psi_{klm}(r, \theta, \varphi) = R_{kl}(r)Y_{lm}(\theta, \varphi), \quad (5)$$

where the Y_{lm} are the spherical harmonics. It is more convenient to express the radial function R_{nl} in terms of $P_{nl}(r) \equiv rR_{nl}(r)$, which is the actual quantity calculated in all wave function codes, both relativistic and nonrelativistic. The radial functions are expressed in terms of confluent hypergeometric functions $F(a, b; z)$:

$$P_{nl}(r) = \frac{1}{(2l+1)!} \sqrt{\frac{(n+l)!}{2n(n-l-1)!}} \left(\frac{2Z}{n}\right)^{\frac{3}{2}} r e^{-\frac{Zr}{n}} \left(\frac{2Zr}{n}\right)^l F\left(-n+l+1, 2l+2; \frac{2Zr}{n}\right), \quad (6)$$

$$P_{kl}(r) = \frac{2\sqrt{kZ}}{\sqrt{1-e^{-2\pi Z/k}}} \prod_{s=1}^l \sqrt{s^2 + \left(\frac{Z}{k}\right)^2} \frac{(2kr)^l}{(2l+1)!} r e^{-ikr} F\left(\frac{iZ}{k} + l + 1, 2l + 2; 2ikr\right). \quad (7)$$

When a or b is a negative integer, $F(a, b; z)$ becomes a polynomial. Hence, the bound-state radial functions P_{nl} are polynomials that vanish as $r \rightarrow \infty$ while the continuum radial functions P_{kl} are oscillating functions that do not vanish as $r \rightarrow \infty$. The continuum radial function shown in Eq. (7) corresponds to a stationary wave—not incoming or outgoing wave—and for an attractive potential, i.e., an electron bound to a nucleus. Note that the radial functions are degenerate in m because of the spherical symmetry built into the Schrödinger equation, Eq. (1).

For a one-electron atom, the total energy E of the atom is the same as the energy of the electron even when the electron is in the continuum. However, for a non-hydrogenic atom, the total energy of the atom is very different from the kinetic energy of one valence electron in the continuum because the total energy includes energies of all remaining bound electrons. Since most applications of interest to us involve non-hydrogenic atoms, we will denote the kinetic energy of the continuum electron by $w = (k\hbar)^2/2m_e$. Only in hydrogenic atoms $E = w$.

Continuum wave functions cannot be normalized to unity in the same way as bound-state wave functions. Instead, it is normalized either to the momentum interval or to the energy interval. The normalization for continuum radial functions is performed by requiring

$$\int_0^\infty r^2 dr R_{Tl}(r) \int_{T-\Delta T}^{T+\Delta T} R_{T'l}(r) dT' = 1, \quad (8)$$

where T can be either k or w . The conversion between a k -normalized radial function and a w -normalized radial function is performed using the relation

$$R_{wl} = \left(\frac{dw}{dk}\right)^{-1/2} R_{kl}. \quad (9)$$

Since $dw/dk = k$ in a.u.,

$$R_{wl} = (k)^{-1/2} R_{kl}, \quad (10)$$

$$P_{wl}(r) = \frac{2\sqrt{Z}}{\sqrt{1-e^{-2\pi Z/k}}} \prod_{s=1}^l \sqrt{s^2 + \left(\frac{Z}{k}\right)^2} \frac{(2kr)^l}{(2l+1)!} r e^{-ikr} F\left(\frac{iZ}{k} + l + 1, 2l + 2; 2ikr\right). \quad (11)$$

Most experimental cross sections that involve continuum electrons correspond to energy-normalized quantity, i.e., cross section is expressed per continuum electron (or photon in photoionization) energy interval, while theoretical calculations tend to be performed with momentum-normalized continuum wave functions.

B. Bound Solutions of the Hydrogen Atom, Relativistic

The relativistic bound wave functions of the hydrogen atom and hydrogenic ions are obtained by solving the Dirac equation [6]. However, unlike the solution of the Schrödinger equation, Dirac combined the orbital angular momentum \mathbf{l} and the spin angular momentum \mathbf{s} into one angular quantum number κ , which is a scalar number.

With the Dirac Hamiltonian, the Dirac equation and matching eigenfunctions are given by:

$$H\psi(r, \theta, \varphi) = \left(\boldsymbol{\alpha} \cdot \mathbf{p}c + \beta_D m_e c^2 - \frac{Ze^2}{r} \right) \psi(r, \theta, \varphi) \quad (12)$$

$$= E_{n\kappa} \psi_{n\kappa m}(r, \theta, \varphi), \quad (13)$$

where $\boldsymbol{\alpha}$ is a 4×4 vector matrix, β_D is a 4×4 scalar matrix defined by:

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma}_P \\ \boldsymbol{\sigma}_P & 0 \end{pmatrix} \quad \beta_D = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \quad (14)$$

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

The Dirac quantum number κ is the eigenvalue of the operator

$$K = \beta_D (\boldsymbol{\sigma}' \cdot \mathbf{l} + 1), \quad (15)$$

where

$$\boldsymbol{\sigma}' = \begin{pmatrix} \boldsymbol{\sigma}_P & 0 \\ 0 & \boldsymbol{\sigma}_P \end{pmatrix}. \quad (16)$$

The κ quantum number is the eigenvalue of the K operator in the sense that the following equation is satisfied:

$$K\psi_{n\kappa m} = -\kappa\psi_{n\kappa m}, \quad (17)$$

for the Dirac eigenfunction $\psi_{n\kappa m}$ defined below. The κ quantum number is related to j and spin as follows (see Table II):

$$\kappa = \begin{cases} -l - 1 & \text{if } j = l + 1/2, \\ +l & \text{if } j = l - 1/2, \end{cases} \quad (18)$$

$$j = |\kappa| - 1/2. \quad (19)$$

Note that κ is not an angular momentum, and hence does not follow the usual rules for adding angular momentum vectors.

The one-electron, bound-state solution to the Dirac equation (12) is given by

$$\psi_{n\kappa m}(r, \theta, \varphi) = \frac{1}{r} \begin{pmatrix} P_{n\kappa}(r)\chi_{\kappa m}(\theta, \varphi) \\ iQ_{n\kappa}(r)\chi_{-\kappa m}(\theta, \varphi) \end{pmatrix}, \quad (20)$$

where $P_{n\kappa}$ and $Q_{n\kappa}$ are the radial functions for the large and small components, respectively.

The two-component spinor $\chi_{\kappa m}$ combines the usual spherical harmonics $Y_{lm_l}(\theta, \varphi)$ with the two-component spinors ϕ_{m_s} using a Clebsch-Gordan coefficients $C(j_1 j_2 j; m_1 m_2 m)$:

$$\chi_{\kappa m}(\theta, \varphi) = \sum_{m_s=\pm 1/2} C(l \frac{1}{2} j; m_l m_s m) Y_{lm_l}(\theta, \varphi) \phi_{m_s} \quad (21)$$

where

$$\phi_{1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \phi_{-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (22)$$

With the wave function defined by Eq. (20), the large and small component radial functions $P_{n\kappa}$ and $Q_{n\kappa}$ satisfy a coupled first order differential equation

$$\frac{d}{dr} \begin{pmatrix} P_{n\kappa}(r) \\ Q_{n\kappa}(r) \end{pmatrix} = \begin{bmatrix} -\frac{\kappa}{r} & \frac{1}{\hbar c} \left(E_{n\kappa} + \frac{Ze^2}{r} + m_e c^2 \right) \\ -\frac{1}{\hbar c} \left(E_{n\kappa} + \frac{Ze^2}{r} - m_e c^2 \right) & \frac{\kappa}{r} \end{bmatrix} \begin{pmatrix} P_{n\kappa}(r) \\ Q_{n\kappa}(r) \end{pmatrix}, \quad (23)$$

with the eigenenergy $E_{n\kappa}$ given by

$$E_{n\kappa} = \frac{m_e c^2}{\left[1 + \left(\frac{\alpha Z}{n - |\kappa| + \sqrt{\kappa^2 - (\alpha Z)^2}} \right)^2 \right]^{1/2}}. \quad (24)$$

Note that the relativistic eigenenergies for the hydrogenic atoms are degenerate only for m , but not for the Dirac quantum number κ . For instance, the energy for the $2p_{1/2}$ ($\kappa = 1$) and $2p_{3/2}$ ($\kappa = -2$) levels are no longer degenerate, though they are degenerate in the nonrelativistic solution.

The relativistic, large and small component radial functions are again given in terms of the confluent hypergeometric functions:

$$P_{n\kappa}(r) = \frac{\sqrt{\Gamma(2\gamma + n' + 1)}}{\Gamma(2\gamma + 1)\sqrt{n'!}} \sqrt{\frac{1+W}{4N(N-\kappa)}} \left(\frac{2Z}{N}\right)^{3/2} r e^{-\frac{Zr}{N}} \left(\frac{2Zr}{N}\right)^{\gamma-1} \times \\ \times \left[-n' F\left(-n' + 1, 2\gamma + 1; \frac{2Zr}{N}\right) + (N - \kappa) F\left(-n', 2\gamma + 1; \frac{2Zr}{N}\right) \right], \quad (25)$$

$$Q_{n\kappa}(r) = -\frac{\sqrt{\Gamma(2\gamma + n' + 1)}}{\Gamma(2\gamma + 1)\sqrt{n'!}} \sqrt{\frac{1-W}{4N(N-\kappa)}} \left(\frac{2Z}{N}\right)^{3/2} r e^{-\frac{Zr}{N}} \left(\frac{2Zr}{N}\right)^{\gamma-1} \times \\ \times \left[n' F\left(-n' + 1, 2\gamma + 1; \frac{2Zr}{N}\right) + (N - \kappa) F\left(-n', 2\gamma + 1; \frac{2Zr}{N}\right) \right], \quad (26)$$

where α is the fine-structure constant and

$$\gamma = \sqrt{\kappa^2 - (\alpha Z)^2}, \quad (27)$$

$$W = E_{n\kappa}/m_e c^2 = \frac{1}{\sqrt{1 + \left(\frac{\alpha Z}{n - |\kappa| + \sqrt{\kappa^2 - (\alpha Z)^2}}\right)^2}}, \quad (28)$$

$$n' = n - |\kappa|, \quad (29)$$

$$N = \sqrt{n^2 - 2n' \left(|\kappa| - \sqrt{\kappa^2 - (\alpha Z)^2} \right)}. \quad (30)$$

III. NONRELATIVISTIC ATOMIC STRUCTURE THEORY FOR COMPLEX ATOMS

An alert graduate student should have noticed, almost 80 years after the Schrödinger equation was discovered, that hardly any textbook on quantum mechanics has a chapter on how to calculate “exact” wave functions for He, which has only one more electron than H. The Dirac equation, Eq. (12), was discovered in 1928. Again, there is hardly any current or old textbook on advanced quantum mechanics that has a chapter on how to extend the Dirac equation to two-electron atoms.

Researchers who are interested in applying quantum mechanics to problems on the earth (i.e., not astrophysics) have to deal with the world made of mostly non-hydrogenic atoms. This necessity drove physicists to invent numerous approximations to be applied to non-hydrogenic atoms. Methods which survived the test of time and turned out to be useful—either yielded very accurate results, or applied to a wide class of non-hydrogenic atoms—are discussed in this section.

A. Hylleraas Wave Functions for Helium

As early as 1929, Hartree and Hylleraas proposed totally different “quantum” jumps from the Schrödinger equation for H to calculate wave functions for He. Hartree proposed the self-consistent-field (SCF) method, while Hylleraas introduced the distance between the two electrons $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ into the solution of the Schrödinger equation for a two-electron atom:

$$H\Psi(1, 2) = \left[\sum_{i=1,2} \left(\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \frac{e^2}{r_{12}} \right] \Psi(1, 2). \quad (31)$$

Both the SCF and the Hylleraas method apply the variational principle to the total energy expression obtained by using their own wave function formats. However, the Hylleraas method produces far more accurate wave functions than the SCF method—after introducing various combinations of the r_{12} and also the angle between the two electrons ϑ_{12} . At present, the most accurate wave functions for He are of the Hylleraas type. Aside from various relativistic corrections, the best Hylleraas-type wave functions for low-lying bound states of two-electron atoms may be considered “exact” nonrelativistic solutions of the Schrödinger

equation, Eq. (31), in numerical accuracy, though such solutions lack the beauty of analytic functions for H presented in Sec. II.

It is very difficult, however, to extend the Hylleraas-type wave functions to more complex atoms not only because the integration limits of the r_{ij} and ϑ_{ij} variables for different (i, j) pairs are *dependent* on each other, but also because the number of interelectronic variables increases rapidly as the square of the number of bound electrons. In the past, there were efforts to use the Hylleraas variables for atoms as large as neon, but the Hylleraas-type wave functions that produce results far more accurate than Hartree’s SCF method are still limited to He and Li.

B. Hartree-Fock Method for Complex Atoms

The basic difficulty in finding the “exact” solution to the Schrödinger equation for He, Eq. (31), is the fact that the equation involves six independent variables, three for each bound electron. Unlike the hydrogen atom, for instance, there is no *a priori* justification for using spherical harmonics for the angular part of each electron. An intuitive approach will be to keep only the one-electron operators in the unperturbed Hamiltonian, and then take $1/r_{12}$ as a perturbation. Then the unperturbed solution is a simple product of hydrogenic functions, and it is easy to calculate the energy correction due to the perturbation, $1/r_{12}$, using the hydrogenic product function as the zeroth order wave function.

Unfortunately, $1/r_{12}$ is not a small perturbation to the other terms in the Hamiltonian, and this approach eventually required more than 20th order of perturbation to reproduce the well-known nonrelativistic total energy of He.

Although Hartree’s original paper in 1929 did not include spin nor based on the variational principle, within a few years his SCF method was improved to include spin—the Fock in Hartree-Fock is the spin part—and its theoretical foundation was reformulated by applying the variational principle to the total energy expression derived from the product-type wave function arranged in the form of a Slater determinant. The Hartree-Fock method is now used not only in atomic/molecular structure theory but also in condensed matter theory and the nuclear shell model.

The Hartree-Fock method is often referred to as the independent particle model. It is the best theoretical model as long as the total wave function consists of products of one-electron functions. A Hylleraas-type wave function is not an independent-particle model solution, and this is the reason that even a simple Hylleraas-type wave function with only a few terms involving the r_{12} or ϑ_{12} variables leads to a much better total energy than the more advanced form (to be discussed later) of the Hartree-Fock wave functions for He.

For atoms heavier than He, however, the only practical wave functions suitable for various applications are Hartree-Fock (HF) wave functions. The wave functions for individual electrons used in a HF wave function are called *orbitals*. Each orbital for a bound electron in an atom carries four quantum numbers, the principal quantum number n , the angular momentum \mathbf{l} , its projection m_l , and the projection m_s of the spin angular momentum \mathbf{s} . The spin angular momentum for all electrons is $1/2$, and hence not explicitly included in the quantum number set.

For a many-electron atom, the one-electron orbital angular momentum \mathbf{l} , its projection m_l , spin angular momentum $\mathbf{s} = 1/2$, and its projection m_s are combined to determine

the total orbital angular momentum \mathbf{L} , the total spin \mathbf{S} , the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$, and matching projections M_L , M_S , and M_J .

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

$$\psi_{nlm_l}(r, \theta, \varphi) = r^{-1} P_{nl}(r) Y_{lm_l}(\theta, \varphi), \quad (32)$$

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. (32). When necessary, the two-component spinors are used, $\hat{\alpha}$ for spin up and $\hat{\beta}$ for spin down:

$$\hat{\alpha} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \hat{\beta} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (33)$$

When one of these spinors are multiplied to Eq. (32), the resulting one-electron function with spin projection is called a spin-orbital.

The total wave function $\Psi_{LSM_L M_S}$ 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 list of occupied one-electron orbitals, such as $1s^2$ for He, is called a configuration. For example, $1s^2 2s^2 2p^2$ is the configuration for the ground state of C. 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 θ and φ , are known as the Slater coefficients. Tables of Slater coefficients are available for simple cases [7]. For

complicated cases computer codes are available both in the LS and jj couplings. These Slater coefficients not only for energy levels but also for some collision cross sections are now calculated by the MCDF2002 code and passed on to subsequent internal steps of the code.

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:

$$E = \sum_i \sum_{a,b} I(ab) \langle P_a(r_i) | \hat{h}_i | P_b(r_i) \rangle + \sum_{i,j} \sum_{a,b,c,d} \sum_k R^k(abcd) \langle P_a(r_i) P_b(r_j) | \frac{r_{<}^k}{r_{>}^{k+1}} | P_c(r_i) P_d(r_j) \rangle, \quad (34)$$

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

$$\hat{h}_i = -\frac{1}{2} \frac{d^2}{dr_i^2} + \frac{l(l+1)}{2r_i^2} - \frac{Z}{r_i}, \quad (35)$$

with the nuclear charge Z .

The variational principle $\delta E = 0$ is applied to Eq. (34) along with the orthonormality conditions for the radial functions to obtain a set of coupled integro-differential equations for the radial functions P_{nl} , which is called the Hartree-Fock equation:

$$\left\{ \frac{d^2}{dr^2} + \frac{2}{r} [Z - Y_{nl}(r)] - \frac{l(l+1)}{r^2} - \epsilon_{nl,nl} \right\} P_{nl}(r) = \frac{2}{r} X_{nl}(r) + \sum_{n'} \epsilon_{nl,n'l} P_{n'l}(r), \quad (36)$$

where the “effective screening” term $Y_a(r)$ is

$$Y_a(r) = \sum_{b,k} A^k(ab) Y_{bb}^k(r), \quad (37)$$

while the “exchange” term $X_a(r)$ is

$$X_a(r) = \sum_{b \neq a, k} B^k(ab) Y_{ab}^k(r) P_b(r), \quad (38)$$

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

$$Y_{ab}^k(r) = r \int_0^\infty U^k(r, s) P_a(s) P_b(s) ds \quad (39)$$

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

$$U^k(r, s) = \frac{s^k}{r^{k+1}} \quad \text{for } r \geq s \quad (40)$$

$$= \frac{r^k}{s^{k+1}} \quad \text{for } r < s. \quad (41)$$

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 ϵ . There is a diagonal ϵ_{aa} for each radial function P_a , and off-diagonal Lagrange multipliers ϵ_{ab} to insure the orthogonality between two radial functions P_a and P_b with the same orbital angular momentum l . Equation (36) must be solved as a set of coupled inhomogeneous integro-differential equations for all distinct radial functions. 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. (36).

Equation (36) 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 ϵ_{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 the Koopmans theorem. However, the correct way to calculate the binding energy of an atomic electron is to take the difference between the total energies of the atom with and without the electron in question.

Normally, a radial function $P_{nl}(r)$ 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 [8] and a monograph by Fischer, Brage and Jönsson [9].

C. 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. (36), 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. (37)] multiplied by a scaled coefficient [see Sec. III C 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 which are not normally occupied. 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 multiconfiguration wave function for He mentioned above as an indication that the two electrons in He are partly in the $1s^2$ configuration and the rest in the $2p^2$ configuration. The 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. III C 2.

1. Slater Approximation

To avoid the difficulties associated with the exchange term Eq. (38) in the Hartree-Fock equation, Slater [8] 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 [10]. Later, Kohn and Sham [11] derived a slightly different expression for the exchange term using a variational method.

The exchange term in the Slater approximation is given by:

$$\frac{2}{r}X_{nl}(r) = -\gamma\frac{3}{2}\left[\frac{24}{\pi}\rho(r)\right]^{1/3}, \quad (42)$$

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

$$\rho(r) = \sum_{nl}N_{nl}P_{nl}(r)^2, \quad (43)$$

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 [12], γ is taken as an adjustable parameter. Note that all these approximations are designed to simplify the exchange term, Eq. (38) 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 worse than the genuine Hartree-Fock solutions.

Regardless of what is used for γ , the Slater approximation and its variants transform the exchange term into a simpler, 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 better 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 the configurations normally occupied in the atomic state in question. Extra configurations with different angular quantum numbers or parity do not have any interaction with the occupied configurations and hence do not affect the total energy. 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 equation 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 orbitals (STOs) or Gaussian-type orbitals (GTOs)] or numerical functions (e.g., splines). The former is known as a numerical Hartree-Fock wave function, while the latter is known as a basis-set Hartree-Fock wave function.

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. Numerical Hartree-Fock wave functions are usually more accurate than basis-set Hartree-Fock wave functions, but the former are more prone to numerical convergence problems when a large number of configurations are used. Basis-set wave functions have no convergence problems but their computation takes much longer, and the results depend on the choice of the 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:

$$\Psi(\text{Be}) = a\psi(1s^2 2s^2) + b\psi(1s^2 2p^2), \quad (44)$$

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 configuration functions $\psi(1s^2 2s^2)$ and $\psi(1s^2 2p^2)$.

One choice is to calculate them separately by solving the Hartree-Fock equations for each of them. Then the mixing coefficients a and b are solved by the variational principle

while keeping the radial functions P_{1s} , 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 new 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 set for each. This type of wave functions are called the “multiconfiguration” Hartree-Fock (MCHF) wave functions. In principle, 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 mixing procedure.

Another example of the “relaxed” and “frozen” radial functions is the *term-dependent* solutions. The excited configuration, $2s2p$, of Be can form either 3P or 1P terms 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 radial functions dependent on the total angular quantum numbers L and S are called “term-dependent” radial functions, while the radial functions independent of L and S 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.

IV. RELATIVISTIC ATOMIC STRUCTURE THEORY FOR COMPLEX ATOMS

As was mentioned earlier, the Dirac theory has not been extended even to He in a rigorous manner. Again, the difficulty is in generalizing the 4-component Dirac theory to a two-electron system, because a rigorous extension requires a 16-component ($= 4^2$) relativistic equation.

Furthermore, the existence of the negative energy band (which is approximately $2m_e c^2$ below the ground level for hydrogen) brings a conceptual difficulty, commonly referred to as the Brown-Ravenhall “disease.” For a “relativistic” He, one electron can be high above in the positive energy continuum and the other electron may be deep in the negative energy continuum, while the total energy of the atom may be the same as the energy of a “normal” helium atom in the ground state with both electrons in the $1s$ configuration. In fact, there

will be an infinite number of such combination, implying that the ground state of helium is unstable because an electron in the positive continuum must fly away eventually.

Since helium atoms in the ground state as we know are stable, we must postulate again, as Dirac did when he first proposed his theory, that the negative energy band is full and atomic electrons cannot go there. However, the mathematical solution of the Dirac equation must include the small component that represents the negative energy band. Therefore, any extension of the Dirac theory to many-electron atoms must explicitly or implicitly forbid any electron to fall into the negative energy band. This type of negative energy band should not be confused with the negative energy levels of “normal” bound electrons which are slightly below the positive energy band, as are all nonrelativistic solutions of the Schrödinger equation for bound electrons.

Also quantum electrodynamics allows for the creation of an arbitrary number of electron-positron pairs without changing the net charge of an atom, i.e., the number of electrons in an atom is not conserved. Again, this implies that a relativistic Hamiltonian may have to include an infinite number of electron-positron pairs to be “correct” though totally impractical.

Because of these conceptual difficulties peculiar to relativistic theory known as the quantum electrodynamics, there is no “exact” or “correct” relativistic Hamiltonian that provides a total energy expression to apply the variational principle and to obtain a relativistic counterpart of the Hartree-Fock equation. A relativistic atomic structure theory necessarily must adopt an approximate or model Hamiltonian from the start. In contrast, there is no ambiguity in the nonrelativistic Hamiltonian to be used for a many-electron atom.

A. Dirac-Fock Method

The Dirac-Fock method is a relativistic version of the Hartree-Fock method described so far. The one-electron Schrödinger Hamiltonian, Eq. (1), is replaced by the one-electron Dirac Hamiltonian, Eq. (12), after subtracting the rest mass energy of the electron, $m_e c^2$, to match the nonrelativistic energy eigenvalues which do not include rest mass energy of the electron:

$$h_D = \boldsymbol{\alpha} \cdot \mathbf{p}c + m_e c^2(\beta_D - 1) - Ze^2/r, \quad (45)$$

where $\boldsymbol{\alpha}$ and β_D have already been defined in Sec. II B. The one-electron Dirac orbitals to be used in the Dirac-Fock method have the same form as those defined for the hydrogenic atoms in Sec. II B.

For a many-electron atom, we must add the nonrelativistic Coulomb repulsion e^2/r_{ij} as well as the relativistic corrections to the Coulomb repulsion, which is known as the Breit operator, H_B :

$$H_B = \sum_{j,k>j} \left[\frac{\boldsymbol{\alpha}_j \cdot \boldsymbol{\alpha}_k}{r_{jk}} \cos(\omega_{jk} r_{jk}) + \frac{(\boldsymbol{\alpha} \cdot \nabla)_j (\boldsymbol{\alpha} \cdot \nabla)_k \cos(\omega_{jk} r_{jk}) - 1}{r_{jk} \omega_{jk}^2} \right], \quad (46)$$

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 ω 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 modified by the Breit operator. 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

$$H_{DC} = \sum_j \left[h_D(j) + \sum_{k>j} e^2/r_{jk} \right], \quad (47)$$

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 the jj coupling. The expression for the total energy is derived by sandwiching H_{DC} with the eigenfunction of \mathbf{J} , the spin-angular parts [χ in Eq. (20)] are integrated analytically, and the variational principle is applied to the total energy expression in terms of the 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 also consists of a set of coupled equations, but the HF equation for each P_{nl} is now replaced by a pair of coupled first-order differential equations for the large and small component radial functions $P_{n\kappa}$ and $Q_{n\kappa}$ for each Dirac orbital $\psi_{n\kappa m}$ with distinct n and κ . 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 κ 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:

$$\begin{aligned} \left[\begin{array}{cc} \frac{d}{dr} + \frac{\kappa_A}{r} - \frac{\epsilon_{AA}}{c} & \frac{V_A(r)}{c} - 2C \\ -\frac{V_A(r)}{c} & \frac{d}{dr} - \frac{\kappa_A}{r} - \frac{\epsilon_{AA}}{c} \end{array} \right] \begin{pmatrix} P_A(r) \\ Q_A(r) \end{pmatrix} = \\ \sum_{\kappa_B=\kappa_A} \frac{\epsilon_{A,B}}{c} \begin{pmatrix} Q_B(r) \\ -P_B(r) \end{pmatrix} + \begin{pmatrix} X_{Q_A}(r) \\ X_{P_A}(r) \end{pmatrix}, \end{aligned} \quad (48)$$

where, in analogy to the Hartree-Fock equation (36), 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. (36), $\epsilon_{A,B}$ 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 total wave function for the atom 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 the jj and LS couplings 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 C is another example: the equivalent relativistic configurations consist 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.

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 have the same energy in the Dirac theory for the hydrogen atom [13]. 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 both relativistic and nonrelativistic theories, and hence it is advantageous to study systematics in energy levels along isoelectronic sequences [14]. The charge expansion theory discussed later in Sec. V C is precisely the kind of theory designed to study atomic properties along isoelectronic sequences.

B. Quantum Electrodynamic (QED) Corrections

The term “QED” corrections imply corrections to the quantities calculated from the solutions of the Dirac equation, i.e., physical effects not included in the Dirac Hamiltonian. However, one of the largest energy corrections to be added to the solutions of nonrelativistic atomic structure theory is the effect of using a finite size, or extended nucleus. In all popular nonrelativistic wave function codes for atoms, a nuclei is assumed to be a point nucleus. In contrast, all relativistic wave function codes for atoms use an extended nucleus. For instance, the MCDF2002 code uses uniform spherical charge for the nuclei of light atoms, and Fermi distribution for heavy atoms. There is even an input option to use non-standard nuclear charge distribution or a point nucleus.

Since an extended nucleus “dilutes” the nuclear charge density and relativistic effects are the strongest near the nucleus, the use of extended nuclei results in less binding (or higher) total energy. The difference in the total energies calculated with a point nucleus and with an extended nucleus is much larger than any QED corrections discussed below. Since physically observable energies correspond to differences in calculated total energies, the effect of the nuclear size almost cancels out as long as the same nuclear model is used in all calculations. Some researchers treat this nuclear-size correction as one of the relativistic corrections or QED corrections.

The corrections to the total energy from the use of a finite-size nucleus instead of a point nucleus could be calculated even with the Schrödinger equation by replacing Ze^2/r in Eq. (1) with an appropriate local potential that includes a finite-size nucleus. Therefore, QED corrections in the following discussion refer only to the physical effects not included in the conventional Dirac theory, mostly involving interactions with virtual photons and virtual electron-positron pairs.

For deep inner shells, quantum electrodynamic (QED) corrections, which are commonly referred to as the Lamb shift, are substantial. The MCDF2002 code estimates these corrections automatically. The ionization energies of inner-shell electrons become reliable only when these QED corrections are included.

There are numerous corrections that contribute to the Lamb shift. Among them, the most important one is the self energy correction, which is a positive energy shift (i.e., reduces the binding energy) from the exchange of virtual photons between a bound electron and the nucleus. The second most important QED correction is the vacuum polarization, which is a positive or negative shift from the interaction of a bound electron with virtual electron-positron pairs it creates in the vicinity of a strong nuclear field. Beyond these two, many smaller QED corrections compete with each other. All QED effects are amplified as the nuclear charge increases.

For light atoms these corrections can be classified according to the powers of $Z\alpha$ and α . Fewer powers of $Z\alpha$ and α mean more significant corrections. For heavy atoms for which $Z\alpha$ is not very small compared to unity, conventional perturbation expansion in powers of $Z\alpha$ fails, and non-perturbative treatment is necessary. Exact non-perturbative solutions are known only for a few kinds of QED corrections and only for one-electron systems. As in the case of the solutions of the Schrödinger equation and Dirac equation for He, no “exact” solutions of QED corrections are known for He and heavier atoms.

In the MCDF2002 code, QED corrections for many-electron atoms are estimated using

two different models. The first model is based on an old QED (meaning before the Feynman diagrams were known) argument proposed by Welton [15]. The second model is based on the ratio of the charge densities near the nucleus: the charge densities calculated from the exact solutions of the hydrogenic Dirac equation with a point nucleus and those calculated from the SCF solutions with an extended nucleus. Then, hydrogenic QED corrections are scaled according to these ratios for each bound electron.

These two methods produce corrections slightly different in magnitudes, but when the differences in total energies are taken, they lead to comparable transition energies. Again, a user should use total energies based on a given method, never mixing results from different models for the nucleus and for the QED corrections.

V. INTERACTION OF PHOTONS WITH ATOMS

A. Electric and Magnetic Multipole Transitions

The discussions in this section are limited to the interaction of an atom with one photon. 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 a 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 [6]

$$[\mathbf{r}, H] = \frac{i\hbar}{m_e}\mathbf{p}, \quad (49)$$

where H is the usual Hamiltonian

$$H = \sum_j \left[\frac{p_j^2}{2m_e} + V(\mathbf{r}_j) + \sum_{k>j} \frac{e^2}{r_{jk}} \right], \quad (50)$$

and 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:

$$A_{nn'} = \frac{4e^2\omega^3}{3\hbar c^3} |\langle \Psi_n | \sum_j \mathbf{r}_j | \Psi_{n'} \rangle|^2, \quad (51)$$

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 = sec^{-1}) is the total number of photons emitted per second. Alternatively, the dipole oscillator strength $f_{n'n}$ is used for photoabsorption:

$$\begin{aligned} f_{n'n} &= \frac{2m\omega g_n}{3\hbar g_{n'}} |\langle \Psi_n | \sum_j \mathbf{r}_j | \Psi_{n'} \rangle|^2 \\ &= \frac{mc^3 g_n}{2e^2 \omega^2 g_{n'}} A_{nn'}, \end{aligned} \quad (52)$$

where g is the multiplicity of the respective state. The above definition of the 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:

$$\sum_n f_{n'n} = N, \quad (53)$$

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. (50), 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.

When wave functions from a local potential are used, the length and velocity forms of the f -value and hence its matching length and velocity forms of the transition probability agree exactly. Results from Hartree-Fock wave functions will not agree, 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 way to assure accuracy.

When the MCDF2002 code is used to calculate electromagnetic transition probabilities, appropriate Slater coefficients are generated internally to calculate the Dirac-Fock wave functions specified in the input data and the requested types of transition probabilities. The accuracy of the En and Mn transition probabilities is determined by the accuracy of the Dirac-Fock wave functions used.

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 \mathbf{J} 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.

B. Selection Rules for Electromagnetic Transitions

Each multipole transition has a different set of selection rules. Rigorous selection rules are in terms of ΔJ 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, and those for the $M2$, $E3$, and $M3$ transitions in Table IV. The MCDF2002 code will calculate En and Mn transitions for all n , provided that wave functions satisfy the selection rules. The selection rules arise from the fact that the total angular momentum and the parity of the combined system of an atom and a photon it emits must be conserved before and after the emission.

The strict selection rules listed in Tables III and IV arise from the $3j$ symbol:

$$\begin{pmatrix} J & \nu & J' \\ M & \mu & M' \end{pmatrix}, \quad (54)$$

where J , M and J' , M' are the angular quantum numbers and their projections of the initial and final target states, and ν and μ are the angular quantum number and its projection of the multipole expansion of the electromagnetic radiation. $\nu = 1$ is dipole, $\nu = 2$ is quadrupole, $\nu = 3$ is octupole, and so forth.

In addition the combined parity of the target plus the electromagnetic field must be conserved. This leads to the selection rules on parity listed in the Tables. The parity of electric multipole moment is $(-1)^\nu$ and the parity of magnetic multipole moment is $-(-1)^\nu$.

C. Charge-Expansion of Atomic Properties

Many atomic properties exhibit systematic trends along an isoelectronic sequence. Such systematic trends provide an important tool not only to verify both experimental and theoretical results but also to fill gaps in existing data along isoelectronic sequences. The Z dependence of nonrelativistic total energies, for instance, has a simple form:

$$E = E_0 Z^2 + E_1 Z + E_0 + E_{-1}/Z + \dots, \quad (55)$$

where the expansion coefficients E_λ are constants that are independent of Z but depend on the quantum numbers that identify a nonrelativistic term, such as L , S and any additional quantum numbers. For instance, the hydrogenic total energy is $E_n(Z) = -\frac{Z^2}{2n^2} \times \frac{1}{2}m_e c^2 \alpha^2$, where $\frac{1}{2}m_e c^2 \alpha^2$ is the rydberg energy [Eq. (2)]. This is the first term in the Z -expansion of the total energy of hydrogenic ions.

In principle, exact expressions for the E_λ in Eq. (55) for all orders can be calculated using hydrogenic wave functions. In practice, summations over all hydrogenic eigenstates including the continuum must be carried out for E_0 and all expansion coefficients associated with negative powers of Z , a task which has been carried out only to E_{-1} for ions with a few bound electrons.

Hartree-Fock solutions contain the correct E_2 but account only for part of other expansion coefficients. When all configurations in a Coulomb complex—meaning those with degenerate total energy in the hydrogenic limit—are included in an MCHF calculation, then

such solutions contain the correct E_2 and E_1 , but only parts of E_0 and parts of the coefficients for negative powers of Z .

Comparisons of theoretical and experimental data on atomic properties, not only transition energies but also transition probabilities, fine-structure splittings, etc., along an isoelectronic sequence readily reveal any faulty data [14]. This type of comparisons have been used extensively in the production of atomic data for fusion applications in the past because many members of an isoelectronic sequence of an impurity atom appear in a fusion plasma.

The nonrelativistic form of the Z -expansion formula, Eq. (55), is modified when relativity is introduced as can readily be seen by expanding the relativistic hydrogenic energy, Eq. (24). Relativity adds powers of $Z\alpha$ in the nonrelativistic expansion coefficients in Eq. (55), i.e., the Z -expansion coefficients for all atomic properties are not free of Z any more but includes terms dependent on powers of $Z\alpha$ [13].

For highly charged ions where the jj coupling is expected to be valid, a relativistic Coulomb complex now will contain only those configurations that have degenerate total energies in the Dirac theory. Hence, $2p_{3/2}$ is no longer part of the relativistic Coulomb complex for $n = 2$ and $j = 1/2$. Similarly, the relativistic Coulomb complex for $n = 3$ and $j = 3/2$ consists of $3p_{3/2}$ and $3d_{3/2}$ but not $3d_{5/2}$.

A common practice in selecting correlation configurations in an MCDF calculation is to include all configurations that belong to a relativistic Coulomb complex for highly charged ions. For neutral atoms and ions with low net charges, however, all configurations that belong to a more expanded nonrelativistic Coulomb complex should be included because the jj coupling is invalid for such cases.

D. Differences in Hartree-Fock and Dirac-Fock Calculations

Notable relativistic effects manifested as the differences between the results from the Hartree-Fock method and the Dirac-Fock methods are listed below.

(a) *Orbital size* $\langle r \rangle$. The solutions of the hydrogenic Dirac equation leads to smaller values of the orbital size $\langle r \rangle$ for all quantum numbers than those calculated from the corresponding solutions of the hydrogenic Schrödinger equation. However, the values of $\langle r \rangle$ from the Dirac-Fock orbitals of heavy, neutral atoms such as Hg may be larger than those from the corresponding Hartree-Fock orbitals. This is interpreted as the result of inner bound electrons shielding the nuclear charge more effectively, and hence subjecting the outer electrons to a weaker nuclear field.

(b) *Orbital binding energy* ϵ . The solutions of the hydrogenic Dirac equation leads to stronger orbital binding energy ϵ , i.e., more negative values for all quantum numbers than those calculated from the corresponding solutions of the hydrogenic Schrödinger equation. However, the values of ϵ from the Dirac-Fock orbitals of heavy, neutral atoms such as Hg may be higher (i.e., less negative) than those from the corresponding Hartree-Fock orbitals. Again, this is interpreted as the result of more screening of the nuclear field by the inner bound electrons.

(c) *f-values*. The definition of the dipole oscillator strength, or f -values, includes the transition energy, which increases much faster than the predictions from the Hartree-Fock calculations along an isoelectronic sequence. In fact, the nonrelativistic f -value for a given

transition in a one-electron ion should remain constant along an entire isoelectronic sequence because $\langle r \rangle^2$ scales as Z^{-2} while the transition energy scales as Z^2 . The relativistic corrections add $(Z\alpha)^4$ and higher powers to the transition energies.

(d) *Intercombination lines.* Dipole-allowed but spin-forbidden $E1$ transitions (e.g., $1s2p\ ^3P_1 \rightarrow 1s^2\ ^1S$ transition of He) are known as intercombination lines and they are weak in light atoms because the LS coupling is valid for light atoms (see Table III). However, spin becomes less effective as a quantum number in an atom dominated by the jj coupling, such as highly charged heavy ions, or heavy neutral atoms. For instance, the $5p^56s\ ^3P_1 \rightarrow 5p^6\ ^1S$ transition of Xe is stronger than the $5p^56s\ ^1P_1 \rightarrow 5p^6\ ^1S$ transition because the LS coupling no longer holds for neutral Xe.

E. Nonrelativistic Limit of Dirac-Fock Wave Functions and Nonrelativistic Offsets

Although hydrogenic relativistic solutions readily reduce to the correct nonrelativistic solutions in the limit $c \rightarrow \infty$, some Dirac-Fock wave functions do not reduce to the correct nonrelativistic Hartree-Fock wave functions. When the outermost electron is removed from the configuration used for a Dirac-Fock wave function and the resulting “core” configuration leads to more than one nonrelativistic LS terms, the relativistic potentials [V and X in Eq. (48)] for orbital pairs split by the spin-orbit interaction, such as $2p^*$ and $2p$, are different even in the nonrelativistic limit.

A typical example is F, whose ground state has the relativistic configuration $2s^22p^*2p^3\ ^2P$ ($1s^2$ is omitted for brevity). The nonrelativistic configuration for F^+ is $2s^22p^4$, and this configuration generates 3P , 1D , and 1S terms in the LS coupling. Hence, when we calculate the nonrelativistic limit of the Dirac-Fock wave function for the ground state of F by letting $c \rightarrow \infty$ (an option available in the MCDF2002 code), the $2p^*$ and $2p$ radial functions will not be the same in the nonrelativistic limit. When the configuration average is taken in the Dirac-Fock calculation, then the Dirac-Fock wave functions reduce to the correct nonrelativistic limit because the relativistic potentials used in an average configuration calculation becomes the same for the orbital pairs split by the spin-orbit interaction. Again in the example of F, the $2p^*$ and $2p$ orbitals reduce to the same nonrelativistic limit if we specify configuration average (EAL option in the input data for the MCDF2002 code). In this case, the MCDF2002 code mixes two relativistic configurations $(1/3)[2s^22p^*2p^4\ ^2P_{1/2}] + (2/3)[2s^22p^*2p^3\ ^2P_{3/2}]$.

The failure of Dirac-Fock solutions to reduce to the correct Hartree-Fock solutions cause subtle problems in calculating fine-structure splitting and transition probabilities for intercombination lines.

For those cases for which Dirac-Fock wave functions have incorrect nonrelativistic limits, also incorrect fine-structure splitting is produced. For F, the “nonrelativistic” total energies obtained from the Dirac-Fock solutions with $2s^22p^*2p^3\ ^2P_{3/2}$ and $2s^22p^*2p^4\ ^2P_{1/2}$ are not the same. This difference is referred to as the “nonrelativistic offset” in total energy. The magnitude of the nonrelativistic offset is of the order of the fine-structure splitting in a neutral atom, and changes very slowly as a function of the nuclear charge Z in an isoelectronic sequence. Note that the fine-structure splitting should be zero in the nonrelativistic limit: in the case of F, the nonrelativistic total energies of the $^2P_{3/2}$ and $^2P_{1/2}$ levels should be the same. Therefore, it is very important to subtract the nonrelativistic offset (including its

sign) in the transition energy from the relativistic results for the fine-structure splitting of neutral atoms and their ions with low net charge. Nonrelativistic offset in transition energies become an insignificant part of the fine-structure splittings of highly charged ions because the splittings become very large.

Similar nonrelativistic offset appears in the calculation of transition probabilities for the transitions that is allowed relativistically but forbidden nonrelativistically, such as the intercombination lines which are transitions between spin-forbidden levels. For example, the $2s2p\ ^3P_1 \rightarrow 2s^2\ ^1S_0$ transition in C^{2+} is forbidden in the LS coupling, while it is a weakly allowed relativistic $E1$ transition. The transition matrix element calculated from the Dirac-Fock wave functions with the configurations listed above vanishes when the nonrelativistic limit is taken by letting $c \rightarrow \infty$ as expected, because the “core” configuration for the upper and lower levels, $1s^22s$, leads to a unique LS term, 2S . On the other hand, when correlation orbitals are introduced to improve the wave functions, e.g., $2s2p + 2p3d\ ^3P_1$ ($1s^2$ is omitted for brevity) for the upper level and $2s^2 + 2p^2 + 3d^2\ ^1S_0$ for the lower level, then the transition matrix element does not vanish even in the nonrelativistic limit. This residual amount is the nonrelativistic offset in transition matrix element (before it is squared to calculate the transition probability). As was done in the case of the fine-structure splitting, this nonrelativistic offset in transition matrix element is of the order of the correct transition matrix element in neutral atoms. Hence, to obtain reliable transition probabilities for weak transitions in neutral atoms and their ions with low net charges, this nonrelativistic offset must be subtracted from the relativistic transition matrix element calculated with the correct speed of light c .

The subtraction of nonrelativistic offsets for fine-structure splitting and transition probability helps only if the desired quantity vanishes in the nonrelativistic limit. For instance, this type of subtraction should not be used for $E2$ transitions, which are weak but allowed both in relativistic and nonrelativistic formulations. The MCDF2002 code provides options to subtract nonrelativistic offsets for transition probabilities.

VI. INTERACTION OF ELECTRONS WITH ATOMS

Although atoms can interact with all kinds of charged particles, such as positrons, protons, and atomic ions, electron-atom interaction is involved in most cases because energetic incident particles including photons will generate secondary electrons through ionization. Some of these secondary electrons will have enough kinetic energies to undergo additional scattering with the other atoms and by-products such as atomic ions.

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 sum of the Hamiltonian of the target and that of the free incident electron. This type of theories are called the weak-coupling theories. The other type of theories treat this interaction on the same level as the interaction among the bound electrons and the electrons with the nucleus of the target

atom. This type of theories are called strong-coupling theories. A typical example of the weak-coupling theory is the first-order Born approximation, while the R-matrix method is a typical strong-coupling theory.

In general, strong-coupling theories are suitable for slow incident electrons, while weak-coupling theories provide reliable results 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. VI D.

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 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.

A. First-Order Born Approximation

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. We 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 [16] 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 [17]. The accuracy of the Born cross sections is governed by the approximation used in the Born approximation in addition to the accuracy of the wave functions used. The PWB cross sections are reliable only at high incident electron energies T beyond the cross section peak.

First, Bethe 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/Dirac-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

$$\sigma_{\text{Bethe}} = \frac{4\pi a_0^2}{T/R} \left[M_n^2 \ln \left(\frac{T}{R} \right) + C_n \right], \quad (56)$$

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

$$M_n^2 = f_{0n}/(E/R) \quad (57)$$

with the dipole oscillator strength f_{0n} 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. 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. (56) applies to incident heavy ions simply by using $T = \frac{1}{2}m_e v^2$ where v is the *speed* of the ion while still keeping the electron mass m_e . 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 be very close to 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. (56) 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* of the energy and angle of the ejected electron.

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 Born approximation (CBA). 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 plane-wave, Coulomb, and the distorted-wave partial waves all have the same form as Eq. (5); only their radial parts, P_{kl} or P_{wl} , are different.

The MCDF2002 code calculates electron-impact PWB cross sections between bound states using bound-state wave functions generated by another component of the MCDF2002 code. The old DW92 code (see Sec. VIC) calculates electron-impact DWB excitation cross sections between bound states using the wave functions from the old DF92 code. The DW92 code will eventually be integrated into the MCDF2002 code. However, the angular momentum algebra needed for the DWB calculation must also be integrated into the MCDF2002 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. As T is increased partial continuum waves with higher l are needed. Unfortunately, the total number of partial waves that can be used in DWB cross sections are limited to $l \lesssim 50$ because higher l requires radial functions near the nucleus to be smaller than 10^{-308} , which is the limit of the double precision “real” numbers most Fortran compilers can handle. When this limit is reached, usually PWB cross sections become valid and can replace DWB cross sections for higher T .

The shape of the PWB cross sections near the threshold for discrete excitations of ion targets is wrong. A PWB cross section always starts from zero, while the correct excitation cross section for a target ion starts from a finite value. The Coulomb Born (CB) and distorted-wave Born (DWB) cross sections have the correct shape near the threshold.

For neutral targets, the PWB, CB, and DWB cross sections all have the correct shape, i.e., start from zero. The PWBA overestimates the cross sections between the threshold and the peak by as much as 50%. For a reliable estimate, the scaling method discussed next in Sec. VIB may be used to scale the PWB cross sections at low T . A similar scaling method has also been developed to scale CB excitation cross sections of singly charged ions. The

input format and sample input data to calculate PWB excitation cross sections with the MCDF2002 code are listed in the Appendix.

B. Scaling of Born Excitation Cross Sections

Recently a simple yet powerful scaling method, to be referred to as the BE scaling [18], was found to transform PWB cross sections for electron-impact excitations of neutral atoms into reliable results from the threshold to high incident energy T , where the PWBA is expected to be valid. The BE scaling works only for dipole- and spin-allowed excitations.

The standard form of a PWB excitation cross section is

$$\sigma_{PWB} = \frac{4\pi a_0^2 R}{T} F_{PWB}(T), \quad (58)$$

where R is the rydberg energy, and F is the collision strength. In the BE scaling, the T in the denominator on the RHS of Eq. (58) is replaced by $T + B + E$, i.e.,

$$\sigma_{BE}(T) = \sigma_{PWB}(T) \frac{T}{T + B + E}, \quad (59)$$

where B is the binding energy of the electron being excited, and E is the excitation energy. Equation (59) amounts to shifting the incident energy by a constant that characterizes the excitation. The BE scaling is very effective for excitations from the ground state to low-lying excited states of light as well as heavy atoms.

Since the accuracy of any theoretical collision cross section strongly depends on the accuracy of wave functions used, the BE scaling is also affected by the wave functions used for the original PWB excitation cross sections. When a more accurate f -value is known than the theoretical f -value calculated from the wave functions used for the PWB cross section of interest, then the BE-scaled cross section can be scaled once more using the ratio of the accurate f -value and the “inaccurate” f -value. This is referred to as the f -scaling:

$$\sigma_{BEf}(T) = \sigma_{BE}(T) \frac{f_{accurate}}{f_{inaccurate}}. \quad (60)$$

Note that the f -scaling is fundamentally different from earlier efforts to find an approximate excitation cross section using only the excitation energy and the f -value, such as the Gaunt factor method popular in plasma and astrophysical applications. The Gaunt factor and similar methods “invented” a collision strength F in Eq. (58), while the BE and f -scaling retains the F from the Born approximation without change.

As was mentioned earlier, the cross section shape at the threshold for the excitation of an ion starts with a finite value, unlike the excitation of a neutral atom, whose cross section at the threshold starts from zero. To preserve the correct shape of cross sections for the excitation of ions, CB or DWB cross sections must be used for the excitation of ions.

A simpler scaling for the CB excitation cross sections, to be referred to as the E scaling, was found to work well for electron-impact excitations of singly charged atomic ions [19]. The E scaling is applied to a CB excitation cross section:

$$\sigma_E = \sigma_{CB}(T) \frac{T}{T + E}. \quad (61)$$

Again, the E scaling can only be used for the dipole- and spin-allowed excitations of singly charged ions. As in the case of the BE scaling for neutral atoms, the E-scaled cross section can further be improved by applying the f -scaling, if a more accurate f -value is available:

$$\sigma_{Ef}(T) = \sigma_E(T) \frac{f_{\text{accurate}}}{f_{\text{inaccurate}}}. \quad (62)$$

Numerous examples of the BE/BE f /E/E f scalings are presented in [18] and [19]. Since PWB and CB excitation cross sections are the simplest ones to calculate, these scaling methods offer not only tremendous savings in computational efforts, but also unprecedented accuracy in estimating contributions to autoionization by the excitation of inner-shell electrons to unoccupied bound states. The BE-scaled autoionization cross section of aluminum has resolved a long standing “mystery” of large discrepancies in the total ionization cross section between experiment and existing theories [21].

C. Description of DW92

This description of the old DW92 code is included here in anticipation of its integration into the MCDF2002 code in the future. At present, the DW92 code still needs the Slater coefficients generated by the old MJ92 code although the DW92 code can use the radial functions generated by the MCDF2002 code.

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, the scaled PWB cross sections described in Sec. VI B 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. VI D.

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 or without proper electron exchange interaction. 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 CBA 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 use the PWB cross sections for the rest.

Since the PWB cross sections from the MCDF2002 code are calculated without partial wave expansions, the DWB cross sections can be combined with the PWB cross sections from the MCDF2002 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 CB and PWB cross sections in partial wave expansion. The DWB cross sections without the electron exchange converge to the PWB cross sections at high incident electron energies T as expected.

D. Binary-Encounter-Dipole (BED) and Binary-Encounter-Bethe (BEB) Models

As was mentioned in the beginning of this lecture series, “almost exact” solutions to the electron-impact ionization of H 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. Most existing ionization theories expand 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 number of required partial waves increases rapidly and overwhelms computer resources in cpu time, disc storage, and random memory. Moreover, the limits on the exponent range of real numbers cannot be corrected easily. Fortunately, the PWBA—which does not expand continuum functions into partial waves—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. (56), in the form of singly differential cross section in ejected electron energy. 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 :

$$\sigma_{\text{BEB}} = \frac{S}{t + u + 1} \left[\frac{1}{2} \ln t \left(1 - \frac{1}{t^2} \right) + 1 - \frac{1}{t} - \frac{\ln t}{t + 1} \right], \quad (63)$$

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. (63) comes from the leading term of the Bethe cross section, Eq. (56), 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 total ionization cross section of an atom or molecule is obtained by summing the orbital cross section given by Eq. (63) over all occupied orbitals.

The only *ad hoc* expression in the BED/BEB model is the denominator, $t + u + 1$ on the RHS of Eq. (63). Note that the Bethe cross section, Eq. (56), 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 $T + U$ 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. (63) 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 may 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 has been very successful in reproducing known ionization cross sections for large and small molecules from threshold to several keV in T [20]. Until the BEB model was developed, existing methods for estimating molecular ionization cross sections were either empirical or used additivity rules with limited applicability. Application of the BEB model to molecules is discussed in Sec. VII. The BED/BEB model has also successfully been applied to small atoms [22,21,23], and application to large, heavy atoms and their ions is in progress now. The BEB model is an example of a “practical” theory that can produce reliable and useful atomic and molecular data from a simple generic formula that embodies essential physics.

VII. ELECTRON-IMPACT IONIZATION OF MOLECULES

Although the BED/BEB models have been developed originally to be applied to atoms, the BEB model generated total ionization cross sections for molecules of all kinds in excellent agreement with available experiments, from the ionization thresholds to several keV in incident electron energies with an accuracy of $\pm 10\%$ or better at the peak [20]. When reliable continuum oscillator strength, df/dE , was available, as is the case for H_2 , the BED model generated energy differential ionization cross sections again in good agreement with available experiment.

The basic molecular orbital constants to be used with the BEB model, B , U , and N in Eq. (63), can easily be obtained from public domain quantum chemistry code such as GAMESS [24]. Note that U cannot be obtained from B using the virial theorem because the virial theorem is for the ratio of the total potential energy and the total kinetic energy but not for individual orbitals.

The following modifications were necessary to make the BEB model work for a variety of molecules, such as H_2 and SF_6 .

(a) When a molecular orbital is dominated by an atomic orbital with the principal quantum number $n \geq 3$, the denominator $t + u + 1$ in Eq. (63) is replaced by $t + (u + 1)/n$. The dominant atomic orbital is determined from the Mulliken population analysis. If the analysis indicates more than 50% contribution from such an atomic orbital, then the modified

denominator is used. This is necessary because the kinetic energies of atomic orbitals with high principal quantum numbers increase rapidly, reducing the cross section too much.

(b) For a singly charged molecular ion, $t+u+1$ in the denominator of Eq. (63) is replaced by $t + (u + 1)/2$ if the dominant atomic orbitals have principal quantum numbers $n \leq 2$, and by $t + (u + 1)/(2n)$ if the dominant atomic orbitals have principal quantum numbers $n \geq 3$. This is necessary because the ionization cross sections of molecular ions rise from the threshold faster than the cross sections for neutral molecules.

In principle, ionization of a molecule is a much more complex process than ionization of atoms. First of all, atoms have distinct and well-spaced thresholds for the excitation and ionization of electrons from different orbitals. In contrast, molecules have numerous rotational and vibrational excitations between electronic excitations and ionization of electrons from different molecular orbitals. Secondly, electron occupation numbers of molecular orbitals are low compared to atomic orbitals. For instance, a π molecular orbital can hold 4 electrons while a p atomic orbital can contain 6 electrons. As a result, the total number of molecular orbitals in a molecule is much larger than the total number of atomic orbitals in an atom, and the ionization thresholds for these molecular orbitals are closer to each other than the thresholds for atomic orbitals. These differences tend to blur sharp onsets of new channels of ionization and average out features from different molecular orbitals more efficiently than in an atom. As a result, the BEB model, which depicts only the main features of electron-impact ionization, turns out to be very successful in reproducing total ionization cross sections of molecules better than any other theory for ionization of molecules.

Since theoretical values of the lowest ionization energy of a neutral molecule is notoriously unreliable compared to experimental values, the lowest B value should be taken from experiment if available. Other molecular constants needed in Eq. (63) can be obtained from Hartree-Fock wave functions or better quality wave functions.

The BEB model has one serious flaw. As is the case for all binary-encounter type collision theories, the model assumes that a bound electron is ionized when it receives an energy transfer from the incident electron that is equal to or higher than its binding energy. This may be true most of the time for atoms but many molecules may simply dissociate into two neutral fragments without producing an ion. The BEB model cannot account for such neutral dissociation. Hence, the BEB model overestimates an ionization cross section if the molecule has strong tendency to dissociate, particularly when the energy transfer is slightly higher than the ionization energy. In general, 2/3 or more of the ionization involves energy transfers less than twice the binding energy of the electron being ionized regardless of the incident electron energy T .

The BEB model produced total ionization cross sections in excellent agreement with available experiments for the ionization of hydrocarbon radicals, while the BEB model produced ionization cross sections almost twice the observed results for radicals containing fluorine atoms, such as CF_x , $x = 1-3$. Although the existing experimental data still require independent verification, there is a high possibility that the radicals containing F atoms readily dissociate into neutral fragments with high probability.

The BEB model can provide valuable estimates for total ionization cross sections of molecules, radicals, and molecular ions which are difficult to prepare and measure their cross sections. The NIST public website [20] provides relevant references, tables of ionization cross sections, molecular orbital constants to be used with Eq. (63), and comparisons to available

theoretical and experimental data for over 80 molecules, radicals, and molecular ions. The website also provides on-line calculation of ionization cross sections by simply typing in the incident electron energy.

VIII. MCDF2002 CODE AND ITS USAGE

The MCDF2002 code calculates bound-state Dirac-Fock wave functions. The wave function generated may be an eigenfunction of \mathbf{J} 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) nuclear charge, and (d) the total number of bound electrons. The last two numbers should be the same for a neutral atom. The corresponding relativistic configurations are generated internally. The row marked "Input" in Table II shows the *lo* combination to be used in the input data for all computer codes described in this lecture note.

The MCDF2002 code internally generates the appropriate total energy expressions for configuration average wave functions. To calculate an eigenfunction of a specific J , appropriate Slater integrals are also generated internally by the MCDF2002 code. The configuration average is the correct J 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 , 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.

All SCF codes for atomic wave functions require trial radial functions at the start. The MCDF2002 code has options to generate trial radial functions using the Thomas-Fermi method or hydrogenic functions with screened charges. It can also read previously calculated radial functions stored as binary files. 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 .

Aside from the total energy, the standard output from the MCDF2002 code lists the convergence data for each cycle of iteration, the orbital and kinetic energies of each orbital, expectation values $\langle r^n \rangle$, 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 stored as binary files for subsequent applications as an option.

Exercises

Exercise 1. Show that the relativistic energy, Eq. (24), reduces to the nonrelativistic energy, Eq. (3) in the nonrelativistic limit.

Exercise 2. Show that the relativistic large component $P_{n\kappa}$ for the $1s_{1/2}$, $2p_{1/2}$ and $2p_{3/2}$ levels reduce to the nonrelativistic P_{1s} and P_{2p} functions in the nonrelativistic limit. Hint: take the limit $c \rightarrow \infty$, or $\alpha \rightarrow 0$. In atomic units, $\alpha = 1/c$.

Exercise 3. Calculate the energy difference in eV between the $2p_{1/2}$ and $2p_{3/2}$ levels for U^{91+} .

To familiarize with the MCDF2002 code, the user should try the following set of exercises. For brevity, nonrelativistic configurations are given. Matching relativistic configurations will be generated automatically by the MCDF2002 code.

Exercise 4. Calculate Dirac-Fock wave functions for Be: $1s^2 2s^2 \ ^1S_0$ and $1s^2 2p^2 \ ^1S_0$ separately.

Exercise 5. Calculate the ground-state wave function of Be using $1s^2 2s^2 + 1s^2 2p^2$, i.e., as an MCDF wave function. Compare the total energies and $\langle r \rangle$ of the $2s$, $2p^*$, and $2p$ radial functions from Ex. 4 and Ex. 5.

Exercise 6. Calculate the total energies for Be $2s2p \ ^3P_1$ and $2s2p \ ^1P_1$ states using term-dependent and configuration average radial functions. Compare the total energies and $\langle r \rangle$.

Exercise 7. Calculate $E1$ transition probabilities for the $2s2p \ ^3P_1 \rightarrow 2s^2 \ ^1S_0$ and $2s2p \ ^1P_1 \rightarrow 2s^2 \ ^1S_0$ transitions for Be. Try the same transitions for Xe^{50+} and compare the ratios of the triplet and singlet transitions.

Exercise 8. Calculate the PWB cross sections for the $2s^2 \ ^1S_0 \rightarrow 2s2p \ ^3P_1$ and 1P_1 excitations for Be and Xe^{50+} .

Exercise 9. Calculate the PWB cross section for the $1s^2 \ 2s \ ^2S_{1/2} \rightarrow 1s^2 2p \ ^2P_{1/2,3/2}$ excitation of Li. Apply the BE scaling to the PWB cross section and compare to unscaled PWB cross section. Compare both cross sections to the experimental data by Leep and Gallagher [Phys. Rev. A **10**, 1082 (1974)].

Exercise 10. 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.

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TABLES

TABLE I. Fundamental constants associated with atomic units.

electron mass m_e	9.109 381 88 (72) $\times 10^{-31}$ kg
	510.998 902 (21) keV
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 $a_0 = \hbar/m_e e^2$	0.529 177 2083 (19) Å
rydberg constant $R_\infty = \frac{1}{2}m_e c^2 \alpha^2$	109 737.315 685 49 (83) cm^{-1}
	13.605 691 72 (53) eV
electron volt	8065.544 77 (32) cm^{-1}

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 κ .

κ	-1	1	-2	2	-3	3	-4	4	-5
l and j	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$	$f_{5/2}$	$f_{7/2}$	$g_{7/2}$	$g_{9/2}$
Input	s	p*	p	d*	d	f*	f	g*	g

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

Rules (1)–(3) are strict, rules (4) and (5) apply only to the LS coupling, and rule (6) to intermediate coupling.

	E1	M1	E2
(1)	$\Delta J = 0, \pm 1$ (No $J = 0 \leftrightarrow 0$)	$\Delta J = 0, \pm 1$ (No $J = 0 \leftrightarrow 0$)	$\Delta J = 0, \pm 1, \pm 2$ (No $J = 0 \leftrightarrow 0, \frac{1}{2} \leftrightarrow \frac{1}{2}, 0 \leftrightarrow 1$)
(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)	$\Delta l = \pm 1$ If $\Delta S = 0$	$\Delta l = 0, \Delta n = 0$ If $\Delta S = 0$	$\Delta l = 0, \pm 2$ If $\Delta S = 0$
(6)	$\Delta L = 0, \pm 1$ (No $L = 0 \leftrightarrow 0$) If $\Delta S = \pm 1,$ $\Delta L = 0, \pm 1, \pm 2$	$\Delta L = 0$ If $\Delta S = \pm 1,$ $\Delta L = 0, \pm 1, \pm 2$	$\Delta L = 0, \pm 1, \pm 2$ (No $L = 0 \leftrightarrow 0, 0 \leftrightarrow 1$) If $\Delta S = \pm 1,$ $\Delta L = 0, \pm 1, \pm 2, \pm 3$ (No $L = 0 \leftrightarrow 0$)

TABLE IV. Selection rules for $M2$, $E3$, and $M3$ transitions.

Rules (1)–(3) are strict, rules (4) and (5) apply only to the LS coupling, and rule (6) to intermediate coupling.

	M2	E3	M3
(1)	$\Delta J = 0, \pm 1, \pm 2$ (No $J = 0 \leftrightarrow 0, \frac{1}{2} \leftrightarrow \frac{1}{2},$ $0 \leftrightarrow 1$)	$\Delta J = 0, \pm 1, \pm 2, \pm 3$ (No $J = 0 \leftrightarrow 0, \frac{1}{2} \leftrightarrow \frac{1}{2},$ $0 \leftrightarrow 1, \frac{1}{2} \leftrightarrow \frac{3}{2},$ $0 \leftrightarrow 2, 1 \leftrightarrow 1$)	$\Delta J = 0, \pm 1, \pm 2, \pm 3$ (No $J = 0 \leftrightarrow 0, \frac{1}{2} \leftrightarrow \frac{1}{2},$ $0 \leftrightarrow 1, \frac{1}{2} \leftrightarrow \frac{3}{2},$ $0 \leftrightarrow 2, 1 \leftrightarrow 1$)
(2)	$\Delta M = 0, \pm 1, \pm 2$	$\Delta M = 0, \pm 1, \pm 2, \pm 3$	$\Delta M = 0, \pm 1, \pm 2, \pm 3$
(3)	Parity change	Parity change	No parity change
(4)	One electron jump	One electron jump	One or no electron jump
(5)	$\Delta l = \pm 1$ If $\Delta S = 0,$	$\Delta l = \pm 1, \pm 3$ If $\Delta S = 0,$	$\Delta l = 0, \pm 2$ If $\Delta S = 0,$
(6)	$\Delta L = 0, \pm 1, \pm 2$ (No $L = 0 \leftrightarrow 0, 0 \leftrightarrow 1$)	$\Delta L = 0, \pm 1, \pm 2, \pm 3$ (No $L = 0 \leftrightarrow 0, 0 \leftrightarrow 1,$ $0 \leftrightarrow 2, 1 \leftrightarrow 1$)	$\Delta L = 0, \pm 1, \pm 2, \pm 3$ (No $L = 0 \leftrightarrow 0, 0 \leftrightarrow 1,$ $0 \leftrightarrow 2, 1 \leftrightarrow 1$)
	If $\Delta S = \pm 1,$ $\Delta L = 0, \pm 1$ (No $L = 0 \leftrightarrow 0$)	If $\Delta S = \pm 1,$ $\Delta L = 0, \pm 1, \pm 2,$ $\pm 3, \pm 4$ (No $L = 0 \leftrightarrow 0, 0 \leftrightarrow 1$)	If $\Delta S = \pm 1,$ $\Delta L = 0, \pm 1, \pm 2$ (No $L = 0 \leftrightarrow 0$)

* Prepared by Y.-K. Kim (Jan. 2001). General selection rules for electromagnetic multipole transitions in J. D. Jackson, *Classical Electrodynamics* (John Wiley & Sons, New York, 1962), p. 549; also in I. I. Sobel'man, *Introduction to the Theory of Atomic Spectra* (Pergamon Press, Oxford, 1972), p. 327. Selection rules for E1, M1, and E2 transitions in R. H. Garstang, *Forbidden Transitions in Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press, New York, 1962), p. 4; $\Delta S = \pm 1$ selection rules for magnetic multipole transitions in M. Mizushima, Phys. Rev. **134**, A883 (1964).

APPENDIX A: INPUT DATA FOR MCDF2002

APPENDIX: Contents

INTRODUCTION

This package calculates a number of atomic quantities, taking fully into account relativistic effects. In the current version, the code is able to:

- build the eigenstates of the total angular momentum J^2 ,
- calculate the angular coefficients for energy expression (including Gaunt, Breit and higher order retardation),
- solve the multiconfiguration Dirac-Fock equations including various contributions self-consistently (Coulomb, Breit, vacuum polarization),
- include, besides electrons, several exotic particles, including bosons,
- correct the total energy for QED contributions,
- compute
 - radiative transition probabilities,
 - hyperfine structure constants,
 - Landé factor,
 - Born electron impact excitation cross section,
 - Stark effect,
 - parity non-conserving amplitude,
 - magnetic part of the $g - 2$ correction for antiprotons,
 - scalar product of wave functions.

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 and underlined 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 **FIN_..** and **REC_..** sets 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 is composed of a certain number of files each of them 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 character “:” 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 (*It is not list-directed inputs!*).

Valid input data are : strings of characters (case insensitive), integers or real numbers.

The atomic states are defined as a superposition of electronic configurations each of which is defined as a list of orbitals with their occupation numbers. These configurations are given, as input data, in LS coupling and the program will generate all the jj configurations arising from a given LS configuration.

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 program use 1s, 2s, 2p*, 2p and so on as labels. The * denotes $j=l-1/2$, while no * stands for the $j=l+1/2$.
- 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.
- orbitals of identical labels can be distinguished using an extra number. For example 2p1] will be treated by the code as different from 2p, while 2p0] and 2p are equivalent. Orbitals with $j=l-1/2$ will be noted 2p1]* for example. If l is too large to use a letter

(the letters valid in the code are: s, p, d, f, g, h, i, k, l, m, n, o, q, r, t, u, v, w, x, y, z for $l=0$ to $l=20$) one can give the orbital in the form $xxSyy/$ or $xxSyy[n$ if one needs an extra label to distinguish orbitals with same quantum numbers. xx is the principal quantum number and yy the l value. S must be $+$ in ls coupling. For example $40+39/$ is an orbital with $n=40$ and $l=39$. $40+39[1/$ or $40+39[1]$ are also valid orbital labels.

As an example input for silicon will read:

```
core   Ne  3s2  :
cf 1   3p2  :
end
```

FILES USED

The first file used by the program is one that defines Fortran unit numbers for inputs and output and the generic names for all other files needed by the program. This file **must be named mdfgme.dat**.

Other file names are labeled according to the following convention : for each Fortran file with number nn , the associated name will be the generic name appended with $.fnn$. As an example assume that the given generic name was **testmcdgme**, then the input file associated with Fortran unit number 5 **must be named testmcdfgme.f05**, and **testmcdfgme.f06** will be the name of the output file associated with Fortan unit number 6 and so on. Input data to be provided in the **mdfgme.dat** file

APPENDIX C: FORTRAN FILE NUMBERS: *ITEM 0*

iread: fortran file number to read the next sets of input data. (5)

iwri: fortran file number for standard outputs. (6)

ipun: fortran file number to save formatted outputs. (7)

iba: fortran file number for the energy expression. (8)

ibb: fortran file number to read wave functions in binary form. (9)

ibc: fortran file number to write wave functions in binary form. (9)

nblipa: number of output lines per page. (75)

APPENDIX D: GENERIC NAME OF THE FILES: *ITEM 0*

NAME: a string of 36 characters or less.

As was pointed out above this string will be appended with $.fnn$ for various files used, where the two digits nn is the Fortran unit number. Furthermore, for the energy expression, each case to be run is associated with one or two specific file(s) depending

upon the fact that one or two state(s) is (are) involved. The name is then obtained from the generic name by using for the 6 rightmost characters the 3 identification characters of the case under consideration (see the definition of the title line below) followed by `_01` for the first state and `_02` for the second state if any. For the given example of input data the file(s) for the energy expression will be given the name(s) `testmcdfgmeABC_01.f08` and `testmcdfgmeABC_02.f08` if "ABC" are the 3 characters used to identify the case being runned (see 3.1.1).

APPENDIX E: TOTAL CPU TIME: *ITEM 0*

ttot: maximum overall running time for the job in seconds, will be ignored if a value lower or equal to zero is given. (*0*)

Input data to be provided in the second input file This second input data file (with name `testmcdfgme.f05` within the present illustration) includes data for each case to be runned. The data for each case are divided into three subsets: the first one deals with the data independant of the states (initial and final when two are involved). The second set defines the configuration(s) involved while the third set includes data specific to each state and thus must be given twice when two states are involved.

APPENDIX F: DATA COMMON TO BOTH STATES

1. Title: *Item 4*

ITITLE: title line with one asterisk as its first character and a maximum of 79 characters, the first 3 are taken as the identification of the case being run (they are used to build the name of the energy expression file, as described above).

2. Optional outputs: *Item 5*

For debugging purpose, names of programs in which extra output is requested, followed by a keyword describing the amount of debugging requested (min med max). (*none*) Any subroutine or function name is valid provided debug options have been implanted. For the pesent version of the code, examples of routines including this option are:

scfmdf : more extensive output during the self-consistent field process.

hdimdf : more extensive output during the diagonalization of the energy matrix.

sdispl : more extensive output during solution of the inhomogeneous Dirac equation by a spline + projector method.

maelam : more extensive output during evaluation of one-electron operator angular coefficients (no relaxation of orbital or diagonal cases)

menoam : more extensive output during evaluation of one-electron operator angular coefficients (relaxation cases-orbital in initial and final states are not assumed to be orthogonal)

tranam : more extensive output during evaluation of one-electron operator (off-diagonal case)

operam : more extensive output during evaluation of one-electron operator (diagonal case).

coevam : more extensive output during actual calculation of angular integrals.

emngme : more extensive output during transition probabilities evaluation.

hfsgme : more extensive output during hyperfine matrix elements evaluation.

pncgme : more extensive output during parity-non conserving amplitudes evaluation.

alloc : keep track of the dynamic allocation of arrays in the program (note that there is no subroutine or function with that name)

podmdf : Shows direct potential contributions for Coulomb (in max. only)

poemdf : Shows exchange potential contributions for Coulomb (in max. only)

3. Speed of light: *Item 6*

MOD_LIGHTSPEED : must be *y* or *n* . If *y* speed of light is multiplied by **cmux**

Only if **mod_lightspeed** is *y*:

CMUX : factor to multiply speed of light.

4. Atomic number: *Item 7*

NZ: atomic number.

5. Type of calculation and energy expression: *Item 8*

KEYWORD : keyword for expectation value of the energy to optimize, options available are:

mdf for full multiconfiguration.

eal for extended average energy level.

rci for relativistic interaction of configuration.

Only if KEYWORD is mdf or rci

DO_ENERGY : option to compute or not expectation value of the total energy. Must be *y* or *n*. If option is **n** the energy expectation value is assumed to have been already computed and saved in a file.

KEEP_ENER : option to keep or not the file with the expectation value of the total energy. Must be *y* or *n*.

BINARY_ENER : the file with the expectation value of the total energy will be in binary form if this option is **y** and in formatted form otherwise.

DO_SCF : option to perform or not the self-consistent field process. Must be *y* or *n*.

Only if KEYWORD is rci

MODRCI : option to define how RCI Dirac-wave functions will be generated, must be *y* or *n*. If **n** hydrogen-like, Thomas-Fermi or wave function read on file are to be used. If **y** the code will solve the Dirac-Fock equation using BSpline for each orbital symmetry given in a list and use the complete set thus generated in the RCI process. This complete set will be orthogonalized to all wave functions generated by other methods. Positive continuum orbitals will be used.

6. Breit interaction: *Item 9*

KEYWORD : option for Breit interaction.

neglect to omit Breit interaction.

average to include Breit interaction at the average level only.

full to include exact contribution of the Breit interaction.

Only if KEYWORD is not neglect

MAG_SCF : must be *y* or *n* : **y** if magnetic part of the Breit interaction is to be included in the self-consistent process. If **n** it will be added as a first order correction after self-consistency has been reached.

Only if MAG_SCF is y

RET_SCF : must be *y* or *n* : **y** if retardation part of the Breit interaction is to be included in the self-consistent process. If **n** it will be added as a first order correction after self-consistency has been reached.

Only if either MAG_SCF or RET_SCF is n

DIAG_AFTERSCF : must be *y* or *n* : **y** if a diagonalization with the complete (magnetic + retardation) Breit interaction is to be done after self-consistency has been reached.

KEEP_SCFCOEFF : must be *y* or *n* : **y** to keep the configuration weights as given by the SCF process, **n** to use those from the above diagonalization for forthcoming calculations.

7. Vacuum polarization: *Item 10*

VACPOL_SCF : option to include or not vacuum polarization in the self-consistent process. Must be *y* or *n* . If **y** , Uëhling potential is included in the Dirac-Equation. This include diagrams with several vacuum-polarization loop The one with two-loop enter at the same order as the Källén and Sabry contribution.

8. Calculation to be done: *Item 11*

KEYWORD : keyword for the type of calculation:

energy for a single mcdF calculation of the energy of a set of configurations

lande for a single mcdF calculation of the energy of a set of configurations followed by the calculation of the Landé factor.

electric for mcdF calculations of the energy of two sets of configurations and computation of the electric transtion rate between them.

magnetic for mcdF calculations of the energy of two sets of configurations and computation of the magnetic transtion rate between them.

radiative for mcdF calculations of the energy of two sets of configurations followed by the calculation of all the allowed electric and magnetic transtion rates between them.

born for mcdF calculations of the energy of two sets of configurations and computation of the electron impact Born cross section between them.

hyperfine for hyperfine matrix element calculations.

pncamplitude for parity non-conserving amplitude.

stark for Stark matrix elements.

scalar for Scalar product of two wavefunctions to test Orthogonality.

gm2pbar to calculate the Magnetic part of the $g - 2$ correction for antiprotons. The electric part which is only diagonal is calculated directly during the mcdF phase.

2photon Two-photon transition proability and spectral distribution (still **very** experimental).

Only if KEYWORD is electric, magnetic or hyperfine:

MULPOL : operator multipole value. Can be any positive integer for **electric and magnetic** or 1 (magnetic dipole) or 2 (electric quadrupole) for **hyperfine** structure.

Only if KEYWORD is hyperfine

inuc : nuclear spin ($\times 2$). The code will calculate the matrix element for all possible values of $F = J + I$

GNUC : nuclear magnetic moment in nuclear magneton for $mulpol=1$ or nuclear quadrupole moment (in barns) for $mulpol=2$

DIAG : Must be **y** if matrix element is diagonal or **n** if an off-diagonal matrix element is computed. *Note that if one choose **y** then only one state must be given.*

*Only if KEYWORD is **2photon***

IPOL1 : a two character string to provide type of transition and multipole value like *E1* or *M2* for the first photon

IPOL2 : a two character string to provide type of transition and multipole value like *E1* or *M2* for the second photon

9. Transition energy: *Item 12*

The following data are only needed when the above option is **electric** , **magnetic** , **born** or **2photon** and will define the value of the transition energy used to compute the transition probability optionally corrected to recover the non-relativistic limit.

USE_MCDFENER : must be *y* or *n*. If **y** the program will use computed energies to define the transition energy. Otherwise an energy value has to be provided.

*The following two input data are to be given only if USE_MCDFENER=*n**

ETRANS : Transition energy in unit defined by next data keyword

KEYWORD : unit of energy for transition energy ETRANS

cm for cm^{-1} .

ev for eV.

au for a.u.

mh for MHz.

SUB_OFFSET : must be *y* or *n*. If **y** a matrix element provided as the next item is subtracted from the total transition matrix element. This is useful when a non-relativistic offset has to be removed from the matrix element obtained in a relativistic calculation.

*Only if SUB_OFFSET=*y**

ACINF : Matrix element to be subtracted from the total transition matrix element.

10. Overlaps between initial and final states: *Item 13*

This input data is only needed for calculations involving two states.

OPT_RELAX : must be *y* or *n*. If **y** the program take into account lack of orthogonality between the orbitals of the initial and final states. Do not use OPT_RELAX=*n* if you have optimized initial and final wave function independently.

11. Retardation in Lorentz gauge: *Item 14*

RET_LORENTZ : must be *y* or *n*. If **y** full retardation correction in Coulomb and Lorentz gauges are calculated.

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

12. Vacuum polarization due to electrons: *Item 15*

OPT_QEDEL : option to calculate vacuum polarization induced by bound electrons. *y* or *n*. If **y** compute this contribution or do not compute if **n**.

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

13. Option to modify tabulation mesh: *Item 16*

This option allows to modify the mesh grid onto which the wave functions are tabulated

MOD_MESH : must be *y* or *n*. If **n** standard options will be used.

Only if MOD_MESH is y:

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

r(1) : first tabulation point multiplied by the nuclear charge NZ and the mass of the heaviest particle. (0.01)

amesh : mesh step in the linear region, i.e. value of a in the above definition of t . (0.01)

14. Option to include a non-electron particle: *Item 17*

EXOTIC_PART : must be *y* or *n*. If **y** one exotic particle will be present. This particle will be designed by an @ in the label as in, e.g., (1s@)]. In that case, there must obviously be one and only one such label in each configuration.

Only if EXOTIC_PART is y:

KEYWORD : exotic particle name:

muon for a muon (spin 1/2 lepton)

pbar for an antiproton (spin 1/2 baryon)

pion for a pion (spin 0 meson)

kaon for a kaon (spin 0 meson)

sigma for a sigma (spin 1/2 baryon)

tstf for a test particle of mass 1 (as the electron) and spin 1/2

tstb for a test particle of mass 1 (as the electron) and spin 0
The last two are used for debugging purposes.

15. Option to modify nuclear parameters: *Item 18*

This option allows to modify the parameters of the nucleus.

MOD_NUC : must be *y* or *n*. If option is **n** calculation is done using standard atomic masses and with a uniform nuclear charge distribution with radius as given in NUCPOT for $Z \leq 45$. For $Z > 45$, Fermi distribution is used.

Only if MOD_NUC is y:

A : atomic mass (used to calculate reduced mass of all particles including electrons). If $A < 0$ the internal value is used. If $A > 400$ A is set to infinity, but internal RMS radius and isotope number are used.

ferc : RMS nuclear radius in Fermi. (internal value for most abundant isotope)

fert : thickness parameter for the Fermi charge distribution of the protons.
(0. for $Z \leq 45$, 2.3 Fm for $Z > 45$)

nuc : index of the nuclear radius (1 if $FERC=0$. and $\max(NUC,41)$ otherwise)

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

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

Ct being a normalization constant.

APPENDIX G: DEFINITION OF THE STATES

1. Number of electrons: *Item 19*

NBELI: number of electrons in initial state

Only if this case involves two states

NBELF: number of electrons in final state

2. List of configurations: *Item 20*

As stated previously the configurations are define in terms of LS configurations and the program will generate internally all the associated jj configurations. Furthermore the list of configurations may be given explicitly or generated internally as all double and single excitations starting from a "reference" configuration.

DEF_CONFIG : a keyword to define how the list of configurations should be handled.
Two keywords are valid data:

given if the configurations are given explicitly.

build if the configurations have to be build from a reference configuration.

*If DEF_CONFIG was assigned the keyword **given***

LIST of configurations, each set followed by “:”.

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

*If DEF_CONFIG was assigned the keyword **build***

DEFINITION of the reference configuration, followed by “:”.

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

LABORB_DEB label of the lowest orbital used to build excitations.

LABORB_FIN label of the highest orbital used to build excitations.

SINGLE_EXCIT option (must be *y* or *n*) to include or not single excitations. IF **y** single and double excitations will be included while if **n** only double excitations will be considered.

Note: as stated in the introduction the definition of the configuration(s) can begin with a record identified by **CORE** to define all the orbitals common to all configurations for the first and second state if any.

2 states: *If the case under consideration involves two states, the above input data have to be repeated for the second state without the **CORE** definition, if any, since from above it is assumed to be shared by the two states*

3. Total angular momenta: *Item 21*

JJTOT : twice the value of the total angular momentum *J*.

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

2 states: *If the case under consideration involves two states, the above data are for the first state and must also be given for the second state*

4. Negative continuum: *Item 22*

IFLAGP : must be *y* or *n* : **n** if negative continuum *must be excluded* by using projection operators when using method=5 (BSpline) to solve the inhomogeneous Dirac-Fock equation for correlation orbitals, **y** otherwise. **n** should be used when the energy is the aim of the calculation, **y** when one-electron operators are the aim (transition rate, hyperfine structure, or pnc amplitude).

5. Particle finite size: *Item 23*

To be given only if the calculation involves a non-electron particle and if this particle is either an antiproton, a pion or a kaon.

IPFSSC : must be y or n : Correction due to particle size is treated self-consistently if y and in perturbation otherwise. It is important to use y if $g - 2$ correction for antiproton is to be evaluated for $j = 1/2$ states

APPENDIX H: DATA FOR EACH STATE

1. *Item 24*

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. If = 0 convergence towards the LSJ level defined by the next input data.

LSJLEVEL : to be given only if NEIGV = 0 and as XL#n where X=2S+1 (S being the spin value), L the total angular momentum and n its energy ordering (n=1 being the lowest).

ICMUL : initial mixing coefficients between the configurations are read (see *Item 33*) as input data if ICMUL is not zero. If some wave functions are read from file, the mixing coefficients corresponding to the configurations already calculated are read too. *note that the configurations have to be given in the same order* Furthermore if $\text{ICMUL} < 0$, the weights are frozen to their initial values during all the SCF process. (0) If $\text{ICMUL} \geq 3$ *Item 34* consist of two values: a replacement threshold and a replacement value. After first diagonalization all mixing coefficient with value lower than threshold are replaced. Signs are kept.

iprfgr : energy expression is written on the standard output if IPRFGR is not 0. (0)

2. *Item 25*

norbsc : define orbitals to be made self-consistent. If equal to 0 all orbitals are made self consistent. If < 0 all orbitals are frozen. If > 0 some orbitals (list to be given as *Item 29*) are frozen.

ndep : default option for initial orbitals. (1)

< 2 calculated with the Thomas Fermi potential.

$= 2$ hydrogenic.

$= 3$ read from a binary file.

$= 4$ internal use only! Use BSpline basis to generate RCI orbitals

nlec : record number to read initial orbitals from a binary file. (0)

nec : record number to write orbitals on a binary file. (0)

ifcwf : convergence acceleration factors are kept fixed if IFCWF is not 0. (0)

nes : number of trials to adjust one-electron energies when solving the Dirac equation. (40)

iprfgr : after self consistency has been achieved, radial integrals for the energy are printed only if IPRFGR is not 0. (0)

idfbeg : deferred correction is used from the beginning of the SCF process if IDFBEG=0. Otherwise it is used only after the accuracy in the wavefunctions is better than 0.01. (0)

3. Item 26

NSTEP : number of cycles in the SCF process. If lower than 1 input is replaced by (1) for a single (5) for a multi) configuration calculation.

4. Item 27

Only if NSTEP is greater than 0: ISCPAR(J,N) J=1 to 3, AZPRY(1,N), AZPRY(2,N), ACCF(1,N) ACCF(2,N) ACCF(3,N) N=1 to NSTEP.

ISCPAR(1,.) : exchange potential is included only if not 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 reached for the radial functions. (10**(NSTEP-6-N))

ACCF(1,.) : mixing coefficient of the eigenvectors between 2 iterations. (1)

ACCF(2,.) : fraction of Coulomb electron exchange to be included. (1)

ACCF(3,.) : fraction of the Breit contribution to the electron exchange to be included (usefull only when Breit is included in the SCF). (1)

5. Item 28

Option to use regularization when computing magnetic integrals must be *y* or *n*.

Option to modify accuracy criteria must be *y* or *n*.

Only if option is y:

teste : relative accuracy to be obtained for one-electron energies. (0.000005)

rap : defines the accuracy to which the small component has to be matched when solving the Dirac equation. (100.)

6. Item 29

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

7. Item 30

Option to modify the standard 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 for which modifications are requested.

IDOI : define the type of initial orbital (see definition of NDEP in *Item 25*)

ZH : only if IDOI=2, screening of the nuclear charge for hydrogenic initial orbital.

numfil : only if IDOI=3: record number in file *ibb* to use to read this orbital. if *numfil* ≤ 0 , set to the same value as *nlec*.

indsol(1) : select method of solving the Dirac equation. (1=normal case; 3=when frozen orbitals are involved; 4=for correlation orbitals; 5 for using spline package **this method may be tricky to use, be sure to know what you are doing**). Projection operators to exclude negative-energy continuum are included or not depending on the switch from *Item 22*.

indsol(2) : if ≥ 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 of radial functions. If 2 check the sign of the slope at origin for method 5. (0)

indsol(4) : if not 0 use Schmidt orthogonalization before solving the Dirac equation. (0)

indsol(5) : if not 0, use 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 *Item 26*, **ACCF(2,N)**. (0)

icho5 : (**Only if indsol(1)=5**) Choose one of the bound solutions of the spline method. If (0) use the lower one, else use the icho5-th one or the first available below if there are not enough solutions

scew : initial value of the mixing coefficient of the orbital between two iterations. (0.3)

a line with **end** as the first 3 characters.

8. *Item 31*

Option to modify method of computing off-diagonal Lagrange multipliers. Must be *y* or *n*.
Only if option is y:

TESTEP : criteria to switch from difference method to 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: difference method.

N = -1: difference or sum method upon occupation numbers.

N = 0: do not compute Lagrange multiplier.

N = 1: sum method.

N > 1: Rayleigh quotient.

a line with **end** as the first 3 characters.

9. *Item 32*

Only if KEYWORD in 4th set is rci

BSPLINE Number of BSpline in the basis set for **rci** calculation.

KSPLINE number of collocation points for the BSplines

Only if modrci=y

Labels of the lower *n* orbital for which one starts to use BSpline basis to provide the radial wave function (one for each symmetry) and a line with **end** as the first 3 characters.

10. Item 33

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

I : configuration index.

CW : initial coefficient of the configuration.

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

11. Item 34

Only if ICMUL= 3

CWTHRES : replacement threshold for mixing coefficients: After first diagonalization, all coefficient lower than CWTHRES are replaced.

CWREP : replacement value for mixing coefficients. The sign from the diagonalization are kept.

12. Item 35

input(1) : if not 0 Coulomb or Breit integrals are calculated.

input(2) : if not 0 one-electron integrals are calculated.

input(3) : if not 0 expectation values of r^{**n} are calculated.

input(4) : if not 0 one-electron radial wavefunctions are tabulated.

input(5) : if not 0 total density is written to file with Fortran number IPUN. Furthermore if > 0 total density is also written to the standard output file.

input(6) : number of radial wavefunctions to be written on file with Fortran number ipun.

input(7) : if not 0 coefficients of the series expansions near the origin are tabulated.

input(8) : if not 0 direct potential is printed for all orbitals.

13. Item 36

Only if INPUT(1) is not 0:

LABELI(I) I=1 to 4: label of the orbitals involved in the integral.

K: power of the multipole

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

$$\begin{array}{ll} F = P1 * P2 + Q1 * Q2 & G = P3 * P4 + Q3 * Q4 \text{ if NEM=0} \\ F = P1 * Q2 & G = P3 * Q4 \text{ if NEM not 0} \end{array}$$

a line with **end** as the first 3 characters.

14. Item 37

Only if INPUT(2) is not 0:

LABELI(I) I=1,2: label of the orbitals involved in the integral.

IALL: if not 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.

15. Item 38

Only if INPUT(3) is not 0:

LABELI(I) I=1,2: label of the orbitals involved in the integral.

K: power of r.

NEM: integral is:

$$\begin{array}{ll} (P1 * P2 + Q1 * Q2)r^K & \text{if NEM=0} \\ (P1 * Q2 + P2 * Q1)r^K & \text{if NEM not 0} \end{array}$$

IALL: if greater than 0 (lower than 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.

16. Item 39

Only if INPUT(6) is not 0:

LABELI(I) I= 1 to INPUT(6): label of the orbitals to be written on file ipun.

17. Specific data for Born cross section: *Item 40*

To be given only for electron impact Born excitation cross section

Input to include the scaling as described by Y.K. Kim, Phys. Rev. A 64, 032713 (2001). The scaled value is given by $[T/(T + B + E)] * unscaled$ where T is the incident energy, B the binding energy and E the excitation energy.

bind_en : binding energy (must be positive otherwise the scaling is ignored). If positive, unit for bind_en is defined by next data keyword

keyword : unit of energy for binding energy bind_en (to be given only if the previous input data is a positive number).

cm for cm^{-1} .

ev for eV.

au for a.u.

mh for MHz.

q1: first value for the grid to integrate over momentum transfer. (0.0001)

hqm: mesh for the grid to integrate over momentum transfer. (0.04)

INCIDENT ENERGIES: values for the electron incident energy (in **eV**)

Next case(s) to be run. For each of them repeat input data 3.1.1 to 3.3.17 as needed.

18. End of input data: *Item 41*

Two asterisks as the first 2 characters.

APPENDIX I: SUBROUTINES READING INPUT DATA

Items	read by subroutine
1 to 3	ini_at1
4	ini_at2
5 to 17	in1_mcdfgme
18	nucpot_par
19 to 23	in2_mcdfgme
24 to 34	i2mhdf
35 to 39	uwfrdf
40	borgme
41	ini_at2

SELECTED EXAMPLES OF INPUT DATA

APPENDIX J: TEST CASE FOR ENERGY CALCULATION WITH BSPLINE SOLUTION FOR CORRELATION ORBITAL

Test case for energy calculation only, use spline method for correlation orbital, with projection operator and both full Breit interaction and vacuum-polarization self-consistent

mdfgme.dat input file

```
:  
testhe-like  
0.
```

testhe-like.f05 input file

```
*801  he-like 1s2    z=54  
      scfmdf max  els2am max hdimdf max :  
      mod_lightspeed=n  
      nz=54  
      mdf do_ener=y keep_ener=n binary_ener=y do_scf=y  
      Breit=full mag_scf=y ret_scf=y  
      vacpol_scf=y  
      energy  
      ret_Lorentz=y  
      opt_qedel=y :  
      mod_mesh=n  
      exotic=n  
      mod_nuc=n  
      nbel=2  
      def_config=given  
c 1 1s2 : end  
      jjt=0  mjt=0  
      negative_continuum=y  
      neigv=1  icmul=0  iprfgr=1  
      norbsc=00 ndep=0  nlec=0  nec=1 :  
      nstep=0  
      lregul=n modtest=n  
      modsolv_orb=n  
      mod_odlm=n  
# data for uwfrdf  
:  
*802  he-like 1s2+2s2    z=54  
      scfmdf max  els2am max hdimdf max :  
      mod_lightspeed=n  
      nz=54  
      mdf do_ener=y keep_ener=n binary_ener=y do_scf=y
```

```

Breit=full mag_scf=y ret_scf=y
vacpol_scf=y
energy
ret_Lorentz=y
opt_qedel=y :
mod_mesh=n
exotic=n
mod_nuc=n
nbel=2
def_config=given
c 1 1s2 : c 2 2s2 : end
  jjt=0 mjt=0
  negative_continuum=y
# check threshold for mixing coefficients
  neigv=1 icmul=3 iprfgr=1
# read 1s wavefunction from previous case
  norbsc=00 ndep=3 nlec=1 nec=0 0 0 1 :
  nstep=0
  lregul=n modtest=n
  modsolv_orb=y
  2s 1 5 0 1 :
end
  mod_odlm=n
# threshold and replacement values for mixing coefficients
  cwthresh=1.E-3 cwrep=1.5E-3
# data for uwfrdf
  :
**

```

APPENDIX K: TEST CASE FOR ENERGY CALCULATION FOLLOWED BY TRANSITION RATE EVALUATION

mdfgme.dat input file

```

:
testprob
0.

```

testprob.f05 input file

```

*tm1 he-like 1s2s->1s2 M1 z=54
:
mod_lightspeed=n
nz=54
mdf do_ener=y keep_ener=n binary_ener=y do_scf=y

```

```

Breit=full mag_scf=y ret_scf=y
vacpol_scf=y
magnetic ipol=1
use_mcdfener=n eexp=30127.3 eV sub_offset=n
opt_relax=y
ret_Lorentz=y
opt_qedel=y :
mod_mesh=n
exotic=n
mod_nuc=n
nbeli=2 nbelf=2
def_config=given
c 1 (1s1])1 (2s1])1 : end c 1 (1s2])2 : end
jjti=2 mjti=2
jjtf=0 mjtf=0
negative_continuum=n
# initial state parameters
neigv=1 icmul=0 iprfgr=0
norbsc=00 ndep=0 nlec=0 nec=1 :
nstep=0
lregul=n modtest=n
modsolv_orb=n
mod_odlm=n
# data for uwfrdf
:
#final state parameters
neigv=1 icmul=0 iprfgr=0
norbsc=00 ndep=0 nlec=0 nec=2 :
nstep=0
lregul=n modtest=n
modsolv_orb=n
mod_odlm=n
# data for uwfrdf
:
**

```

APPENDIX L: TEST CASE FOR ENERGY CALCULATION FOLLOWED BY HYPERFINE MATRIX ELEMENT CALCULATION. CASE WITH DIAGONAL AND NON DIAGONAL MATRIX ELEMENTS APPEARS IN THE SAME FILE.

mdfgme.dat input file

```

:
testhfs
0.

```

testhfs.f05 input file

```
*805    diagonal hydrogenlike Bi 1s HFS
      :
      mod_lightspeed=n
      nz=83
      mdf do_ener=y keep_ener=n binary_ener=y do_scf=y
      Breit=full mag_scf=y ret_scf=y
      vacpol_scf=y
      hyperfine ipol=1 inuc=9 gnuc=4.1106 diagonal=y
      ret_Lorentz=y
      opt_qedel=y :
      mod_mesh=y
      hx=0.025 :
      exotic=n
      mod_nuc=y
      A=209 rms=5.518 ferc=2.0566022 nuc=101
      nbeli=1
      def_config=given
c 1 (1s2])1          : end
      jjtf=1  mjtj=1
      negative_continuum=n
# initial state parameters
      neigv=1  icmul=0  iprfgr=0
      norbsc=00 ndep=0  nlec=0  nec=1  :
      nstep=0
      lregul=n  modtest=n
      modsolv_orb=n
      mod_odlm=n
# data for uwfrdf
      :
*807    Non-diagonal gold he-like 1s2p 3P1-3P0
      maelam max operam max hfs gme max :
      mod_lightspeed=n
      nz=79
      mdf do_ener=y keep_ener=n binary_ener=y do_scf=y
      Breit=full mag_scf=y ret_scf=y
      vacpol_scf=y
      hyperfine ipol=1 inuc=3 gnuc=0.14486 diagonal=n
      opt_relax=n
      ret_Lorentz=y
      opt_qedel=y :
      mod_mesh=n
      exotic=n
      mod_nuc=n
      nbeli=2 nbelf=2
```

```

    def_config=given
c 1 (1s1])1 (2p1])1 :                               : end c 1 (1s1])1
(2p1])1 :                                           : end
    jjti=2  mjtj=2
    jjtf=0  mjtf=0
    negative_continuum=n
# initial state parameters
    neigv=1  icmul=0  iprfgr=0
    norbsc=00  ndep=0  nlec=0  nec=1  :
    nstep=0
    lregul=n  modtest=n
    modsolv_orb=n
    mod_odlm=n
# data for uwfrdf
    :
# final state parameters
    neigv=1  icmul=0  iprfgr=0
    norbsc=00  ndep=0  nlec=0  nec=2  :
    nstep=0
    lregul=n  modtest=n
    modsolv_orb=n
    mod_odlm=n
# data for uwfrdf
    :
**

```

APPENDIX M: TEST CASE FOR ENERGY CALCULATION ON A PIONIC AND AN ANTIPROTONIC ATOM

mdfgme.dat input file

```

:
testpbar
0.

```

testpbar.f05 input file

```

*809      Exotic: pion 1s1/2 2p@
          eneram_det max :
          mod_lightspeed=n
          nz=6
          mdf do_ener=y keep_ener=n binary_ener=y do_scf=y
          Breit=full mag_scf=n diag_afterscf=n
          vacpol_scf=y
          energy

```

```

ret_Lorentz=n
opt_qedel=n :
mod_mesh=y
hx=0.02 r(1)=0.01 amesh=0.1 :
exotic=y pion
mod_nuc=n
nbel=2
def_config=given
c 1 (1s)1 (2p@]1 : end
  jjt=1 mjt=1
  negative_cont=n
  part_finsize=y
  neigv=1 icmul=0 iprfgr=1
  norbsc=00 ndep=0 nlec=0 nec=0 0 0 1 :
  nstep=0
  lregul=n modtest=n
  modsolv_orb=n
  mod_odlm=n
# data for uwfrdf
:
*818      Exotic: pbar 1s1/2 (6h@])
:
mod_lightspeed=n
nz=2
mdf do_ener=y keep_ener=n binary_ener=y do_scf=y
Breit=full mag_scf=n diag_afterscf=n
vacpol_scf=y
gm2p
inuc=41 gnuc=1.0 diag=y
ret_Lorentz=n
opt_qedel=n :
mod_mesh=y
hx=0.021 r(1)=0.01 amesh=0.2 :
exotic=y pbar
mod_nuc=n
nbel=2
def_config=given
c 1 (1s)1 (6h@])1 : end
  jjt=12 mjt=12
  negative_cont=n
  part_finsize=y
  neigv=1 icmul=0 iprfgr=1
  norbsc=00 ndep=0 nlec=0 nec=1 0 0 1 :
  nstep=0
  lregul=n modtest=y

```

```

    teste=1.e-7 rap=1000. :
    modsolv_orb=n
    mod_odlm=n
# data for uwfrdf
:
*819      Exotic: pbar 1s1/2 (39+35[0])
:
mod_lightspeed=n
nz=2
mdf do_ener=y keep_ener=n binary_ener=y do_scf=y
Breit=full mag_scf=y ret_scf=n diag_afterscf=n
vacpol_scf=y
energy
ret_Lorentz=n
opt_qedel=n :
mod_mesh=y
hx=0.021 r(1)=0.01 amesh=0.2 :
exotic=y pbar
mod_nuc=n
nbel=2
def_config=given
c 1 (1s)1 (39+35[0])1 : end
  jjt=72 mjt=72
  negative_cont=n
  part_finsize=n
  neigv=1 icmul=0 iprfgr=1
  norbsc=00 ndep=0 nlec=0 nec=0 0 0 1 :
  nstep=0
  lregul=n modtest=y
  teste=1.e-7 rap=1000. :
  modsolv_orb=n
  mod_odlm=n
# data for uwfrdf
:
**

```

APPENDIX N: TEST CASE FOR RCI CALCULATION

mdfgme.dat input file

```

:
testrci
0.

```

testrci.f05 input file

```

*826   he-like 1s2p 3P1 z=83 preparation for RCI example
      :
      mod_lightspeed=n
      nz=83
      mdf do_ener=y keep_ener=n binary_ener=y do_scf=y
      Breit=full mag_scf=n diag_afterscf=n
      vacpol_scf=n
      energy
      ret_Lorentz=y
      opt_qedel=n :
      mod_mesh=n
      exotic=n
      mod_nuc=n
      nbel=2
      def_config=given
      1 (1s)1 (2p)1 :
end
      jjt=2   mjt=2
      negative_continuum=y
      neigv=1   icmul=0   iprfgr=0
      norbsc=00  ndep=0   nlec=0   nec=1   :
      nstep=0
      lregul=n  modtest=n
      modsolv_orb=n
      mod_odlm=n
# data for uwfrdf
      :
*827   he-like 1s2p 3P1 z=83 rci nsn'p   z=83, coulomb, short
example
      :
      mod_lightspeed=n
      nz=83
      rci do_ener=y keep_ener=n binary_ener=y do_scf=y modrci=y
      Breit=full mag_scf=n diag_afterscf=n
      vacpol_scf=n
      energy
      ret_Lorentz=y
      opt_qedel=n :
      mod_mesh=n
      exotic=n
      mod_nuc=n
      nbel=2
      def_config=given
      1 (1s)1 (2p)1 :
      2 (2s)1 (2p)1 :

```

```

3 (2p)1 (3s)1 :
4 (1s)1 (3p)1 :
5 (2p)1 (4s)1 :
6 (1s)1 (4p)1 :
7 (2p)1 (5s)1 :
8 (1s)1 (5p)1 :
end
  jjt=2  mjt=2
  negative_continuum=y
  neigv=1  icmul=0  iprfgr=1
  norbsc=00  ndep=3  nlec=1  nec=2  :
  nstep=0
  lregul=y  modtest=n
  modsolv_orb=n
  mod_odlm=n
# since modrci=y, list of orbitals to be generated with BSplines
  BSpline=19 kspline=5
# list the first orbital (lower nq) that will be generated by
BSplines
  2s 3p* 3p :
end # data for uwfrdf
  :
**

```

APPENDIX O: TEST CASE FOR BORN CROSS SECTION CALCULATION

mdfgme.dat input file

```

:
testborn
0.

```

testborn.f05 input file

```

*b01  Be 1s2 -> 1s2p 1P1 Born cross section
:
mod_lightspeed=n
nz=4
mdf do_ener=y keep_ener=n binary_ener=y do_scf=y
Breit=full mag_scf=n diag_afterscf=y keep_scfcoeff=y
vacpol_scf=n
born
use_mcdfener=n eexp=5.277433 eV sub_offset=n
opt_relax=n
ret_Lorentz=n

```

```

opt_qedel=n :
mod_mesh=n
exotic=n
mod_nuc=n
nbeli=4 nbelf=4
select_cfg=given
c 1 1s2 2s2 : end c 1 1s2 2s1 2p1 : end
jjti=0 mjti=0
jjtf=2 mjtf=2
negative_continuum=n
# initial state parameters
neigv=1 icmul=0 iprfgr=0
norbsc=00 ndep=0 nlec=0 nec=1 :
nstep=0
lregul=n modtest=n
modsolv_orb=n
mod_odlm=n
# data for uwfrdf
:
#final state parameters
neigv=2 icmul=0 iprfgr=0
norbsc=00 ndep=0 nlec=0 nec=2 :
nstep=6
1 1 50 4. 0.01 0.90 1.0 1.0
1 1 50 4. 0.001 0.90 1.0 1.0
1 1 50 4. 0.0001 0.95 1.0 1.0
1 1 50 4. 0.00001 0.95 1.0 1.0
1 1 50 4. 0.00001 1.00 1.0 1.0
1 1 50 4. 0.000001 1.00 1.0 1.0
lregul=n modtest=n
modsolv_orb=n
mod_odlm=n
# data for uwfrdf
:
# this the beginning of specific input data for Born cross section
# first optional options to builds the Q grid
:
# followed by values of incident energy
TEV=6. 7. 8. 9. 10. 20. 50. 100.
500. 1000. :
**

```