2. General theory

The theoretical basis of the Dirac *R*-matrix method was already described more than 30 years ago by Chang (1975,1977). A general numerical implementation (DARC), was developed by Norrington and Grant (1981, 1987). Comprehensive review of further developments are summarized in books of Burke (2011) and Grant (2007). Recent developments of the method and some applications can be found in publications (…).

The present work is an entirely independent implementation of the same basic theory, albeit with two distinctive features that have proven to be of significant advantage, especially for the application to truly complex systems. The first of these features concerns the orthogonality requirements for the one-electron radial functions. Although the option is still available, we generally do not impose any orthogonality conditions on the one-electron radial functions used to represent different target states, and the continuum orbitals do not have to be orthogonal to the bound orbitals either. The use of nonorthogonal orbital sets avoids the need to introduce additional (*N*+1)-electron terms in the *R*-matrix expansion for the continuum electron. Most importantly, however, it makes it possible to optimize, and then to use in the subsequent collision calculation, the radial wave functions independently for each target state. Consequently, the size of otherwise extensive multiconfiguration expansions, often with correlated pseudo-orbitals being employed to improve the target states, can be reduced significantly.

The second feature is the use of *B*-splines as a numerically convenient, universal, and effectively complete basis to expand the radial orbitals of interest. It turns out, however, that the relativistic implementation of this basis poses new challenges, particular in collision calculations. These will be further discussed below.

2.1. The Dirac *R*-matrix method

We use the Dirac-Coulomb (DC) Hamiltonian to describe the *N*-electron target and the (*N*+1)-electron collision systems, respectively. In atomic units, the DC Hamiltonian for electrons in a central field $V_{\text{nuc}}(r)$ made by an infinitely heavy nucleus of charge *Z* is given by

$$H_{DC} = \sum_i h_D(r_i) + \sum_{i<j} \frac{1}{r_{ij}} \ , \tag{2.1}$$

$$h_D = c\boldsymbol{\alpha} \cdot \mathbf{p} + (\boldsymbol{\beta} - 1)c^2 + V_{\text{nuc}}(r) \ , \tag{2.2}$$

where *i* and *j* index the individual electrons, $\mathbf{p} = -i\nabla$ is the momentum operator of electron, *c* is the speed of light, and the electron rest mass has been subtracted. The components of the vector $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are the usual Dirac matrices constructed from Pauli spin and unit matrixes

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix} \qquad \boldsymbol{\beta} = \begin{pmatrix} \mathbf{1} & 0 \\ 0 & -\mathbf{1} \end{pmatrix}$$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{2.3}$$

The solution of the time-independent Dirac equation

$$H_{DC}\Psi^{JM\pi} = E\Psi^{JM\pi} \tag{2.4}$$

is required for each set of conserved quantum numbers *J*, *M*, and π, where *J* is the total angular momentum quantum number, *M* is the corresponding magnetic quantum number in some preferred

direction and π is the total parity. The total wave function $\Psi^{JM\pi}$ is constructed from Dirac four-component spinors

$$\phi_{n\kappa m}(\mathbf{r}) = \frac{1}{r}\begin{pmatrix} P_{n\kappa}(r)\eta_{\kappa m}(\hat{\mathbf{r}},\sigma) \\ iQ_{n\kappa}(r)\eta_{-\kappa m}(\hat{\mathbf{r}},\sigma) \end{pmatrix}, \tag{2.5}$$

where the real and imaginary parts are referred as the large and small components, respectively, κ is the relativistic angular momentum quantum number, and $\eta_{\kappa m}$ is the spinor spherical harmonic

$$\eta_{\kappa m}(\hat{\mathbf{r}},\sigma) = \sum_{m_\ell m_s}(\ell m_\ell \tfrac{1}{2}m_s \mid jm)Y_{\ell m_\ell}(\theta,\phi)\chi_{\frac{1}{2}m_s}(\sigma), \tag{2.6}$$

where $(\ell m_\ell \tfrac{1}{2}m_s \mid jm)$ are Clebsch-Gordon coefficients, $Y_{\ell m_\ell}(\theta,\phi)$ are spherical harmonic and $\chi_{\frac{1}{2}m_s}(\sigma)$ are the usual two-component Pauli spin functions. The separation of variables in (2.6) representation allows the Hamiltonian matrix element to be split so that angular integrals are calculated using Racah algebra and radial integrals by numerical quadrature.

In the spirit of the *R*-matrix method, the configuration space is partitioned into two regions separated by the *R*-matrix boundary at $r = a$. The latter is chosen in such a way that the magnitude of the radial spinors describing the bound electrons in the target is sufficiently small that exchange between the incident electron and any target electron outside the *R*-matrix sphere is negligible. Within the sphere $r \le a$, the motion of the *N* electrons of the target atom or ion and the scattering electron is described by close-coupling equations with specified boundary conditions at $r = a$. Computationally, the internal region is treated in a similar way to an atomic structure calculation. In the external region the electron moves in the long-range multipole potential of the target. The wave function for a scattering process can be constructed by matching interior and exterior solutions on the *R*-matrix boundary; its asymptotic behavior as $r \to \infty$ determines the scattering matrix and physical observables. When the residual ionic charge is not high and the electron is moving in the external region with a velocity much less than c, non-relativistic asymptotic solutions are adequate.

In the inner region, the total scattering wave function is expanded in terms of a basis set,

$$\Psi_k^{N+1} = \sum_{ij}c_{ijk}A\left[\Psi_i^N \otimes \phi_{ij}\right]^{J\pi} + \sum_m d_{mk}\Theta_m^{N+1}. \tag{2.7}$$

Here Ψ_i^N is the wave function of the *N*-electron target state *i* while the ϕ_{ij} form the *R*-matrix basis for the scattering electron. The target wave functions Ψ_i^N have zero values on the boundary, whereas the one electron scattering orbitals ϕ_{ij} should have no-zero value at $r = a$, in order to provide connection with solutions in the external regions. The symbol A in (2.x) represents the antisymmetrization between the incident projectile and the target electrons and the notation $\otimes$ implies that the angular momentum and parity of the target, J_i, π_i, and that of the continuum orbital j_j, π_j are coupled total angular momentum and parity J, π. The Θ_m^{N+1} functions are (*N*+1)-electron square-integrable functions constructed by adding an outer electron to a target state. They must be included to compensate for any orthogonality constraints imposed on ϕ_{ij}. Due to non-orthogonal technique employed in the present code, these functions are usually avoided in our treatment, but they can be used under special circumstances.

For the further discussion, it is convenient to re-write the expansion (2.7) for the basis function Ψ_k^{N+1} with explicit introduction of radial functions for the continuum orbitals

$$\Psi_k^{J\pi}(\mathbf{X}_{N+1}) = A \sum_{i=1}^{n_c} \sum_{j=1}^{n} c_{ijk} \overline{\Phi}_i^{J\pi}(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1} \sigma_{N+1}) r_{N+1}^{-1} u_{ij}(r_{iN+1})$$

$$+ \sum_{m=1}^{n_b} d_{mk} \Theta_m^{J\pi}(\mathbf{X}_{N+1}), \qquad k = 1, \dots, n_k, \tag{2.8}$$

where n_c is the number of scattering channels retained in the expansion, n is the number of continuum basis functions retained in each channel, n_b is the number of the bound-like functions, and $n_k = nn_c + n_b$ is the total number of linearly independent basis functions in the inner-region expansion. The functions $\overline{\Phi}_i^{J\pi}$ are usually referred as *channel functions* and are defined by coupling the target states with the relativistic spin-angle functions describing the scattering electron

$$\overline{\Phi}_i^{JM\pi}(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1} \sigma_{N+1}) = \sum_{M_i m_i} (J_i M_i j_i m_i \mid JM) \, \Phi_i^{J_i M_i \pi_i}(\mathbf{X}_N) \phi_i^{j_i m_i}(\hat{\mathbf{r}}_{N+1}, \sigma_{N+1}) \tag{2.9}$$

where we introduce the four-component spin-angle function

$$\phi^{jm}(\hat{\mathbf{r}}, \sigma) = \begin{pmatrix} \eta_{\kappa m}(\hat{\mathbf{r}}, \sigma) \\ i \eta_{-\kappa m}(\hat{\mathbf{r}}, \sigma) \end{pmatrix}. \tag{2.10}$$

In this notation, the radial motion of the scattered electron in the internal region is described by the two-component reduced radial continuum basis function

$$u_i(r) = \begin{pmatrix} P_i(r) \\ Q_i(r) \end{pmatrix}. \tag{2.11}$$

The coefficients c_{ijk} and d_{mk} in expansion (2.8) are obtained by diagonalizing the (N+1)-electron Dirac-Coulomb Hamiltonian (2.1). However, with nonzero scattering orbitals ϕ_{ij} on the boundary, the Hamiltonian matrix becomes non-Hermitian. In *R*-matrix theory, it is customary to apply a Bloch operator that enforces the boundary conditions as well as symmetry. In contrast to the non-relativistic case, the Bloch operator for the Dirac Hamiltonian can be chosen in different ways. We use the Bloch operator in the form

$$L = c\delta(r-a) \begin{pmatrix} -p\eta & \eta \\ \eta-1 & (1-\eta)/p \end{pmatrix}, \tag{2.12}$$

where matrix indexes refer to large and small components of the scattering orbitals and constant p defines the boundary conditions

$$\frac{Q_i(a)}{P_i(a)} = \frac{b + \kappa_i}{2ac} = p \tag{2.13}$$

for all channels i. Parameters b here is an arbitrary constant. In the limit $c \to \infty$, this boundary conditions reduce to well-known non-relativistic form for the logarithmic derivatives at boundary:

$$\frac{dP_i(a)}{dr}\bigg|_{r=a} = \frac{b}{a} P_i(a). \tag{2.14}$$

In calculations, b is normally taken as zero. Note that the boundary conditions (2.13) are different from that used by Chang in his pioneer work (Chang 1975). Chang's boundary conditions omit the κ value for each channel, and do not reduce to the above non-relativistic form. The modification (2.13) was first suggested by Norrington and Grant (1981, 1987).

The Bloch operator (2.12) contains another arbitrary constant η. For $\eta = 0.5$, the Bloch operator has the symmetrical form suggested by Grant (2008) whereas for $\eta = 1$ it takes the form used by

Szmytkowski and Hinze (1996). We found a negligible dependence of the accuracy of R-matrix calculations on the value of η.

After adding the Bloch operator to the Hamiltonian, the resulting matrix $\boldsymbol{H+L}$ has symmetric form and can be diagonalized readily to obtain the desired set of solutions. From this finite set of solutions, an R-matrix relation can be derived [xx] that connects the solutions in the inner and outer regions. For a given energy E, this relation has the form

$$P_i(a) = \sum_j R_{ij}(E)[2ac Q_j(a) - b P_j(a)] \tag{2.15}$$

where the relativistic R-matrix is defined as

$$R_{ij}(E) = \frac{1}{2a} \sum_k \frac{P_{ik}(a) P_{jk}(a)}{E_k^{N+1} - E} \tag{2.16}$$

Here the E_k^{N+1} are the R-matrix poles while the P_{ik} are the surface amplitudes of Ψ_k in channel i. We note that a more rigorous expression for the R-matrix contains the correction $-(b+\kappa)/[(b+\kappa)^2 + (2ac)^2]$, first obtained by Szmytkowski and Hinze (1996). This correction is due to the fact that the set of relativistic basis functions (P_i, Q_i) is incomplete on the surface $r = a$. In most realistic cases, however, it is small and thus usually omitted.

An important point in the R-matrix method is the choice of the radial continuum basis functions u_j. Although members of any complete set of functions satisfying arbitrary boundary conditions can be used, a careful choice will speed up the convergence of the expansion (2.13). In the standard R-matrix approach developed by the Belfast group (Burke 2011) numerical basis functions satisfying homogeneous boundary conditions at $r = a$ were adopted. This approach gives accurate results provided that corrections proposed by Buttle (1967), to allow for the omitted high-lying poles in the R-matrix expansion, are included. In the standard approach, the basis functions u_i are constructed to be orthogonal to the bound orbitals u_{nl} used for construction of the target wavefunctions. To compensate for the resulting restrictions on the total wavefunctions, the basis states Ψ_k must contain the correlation functions Θ_m as in equation (2.7). In the case of complex atoms, when extensive many-configuration expansions are used for accurate representations of the target state wave functions, this may lead to a very large number of the correlation functions Θ_m which must be included in the close-coupling expansion to compensate for the orthogonality constraints. The present program has the option to imply a fully non-orthogonal set of basis functions u_j in equation (2.8). It allows us to use the close-coupling expansions without any correlation functions at all. Nevertheless, in practical calculations some restricted orthogonality constraints are usually imposed on the basis functions u_j, depending on the physical model under consideration.

The other key point of the present approach is the use of the B-splines instead of the one-electron basis functions $u_i(r)$ in the R-matrix representation (2.14) of the inner region. The full description of B-splines is given in section 12. The B-splines possess properties as though they were especially created for the R-matrix theory. They form a complete basis on the finite interval $[0,a]$, have a universal nature, and are very convenient in numerical calculations because they allow us to avoid finite-difference formulae. Here we have to distinguish between using B-splines as another basis for representation of the one-electron orbitals and using B-splines for generating the complete pseudo-spectrum for some one-electron Hamiltonian as is done in many atomic structure calculations (Bachau 2001). The present program provides both options. In the first case, the coefficients a_{ijk} are found from the diagonalization of the full Hamiltonian in the B-spline representation. Such an approach is more suited for bound-state calculations. In the second case, we first perform a preliminary diagonalization of the Hamiltonian blocks corresponding to one channel. This generates a complete set of one-electron orbitals for each channel. We can transform the Hamiltonian matrix to the new representation based on these one-

electron orbitals, and now we are able to reduce the dimension of the full interaction matrix by dropping some of the basis orbitals, depending on the problem under consideration.

The boundary conditions in the *B*-spline basis define only the first and the last basis functions, which are the only non-zero terms, respectively, for $r = 0$ and $r = a$. The boundary conditions for the scattering function at the origin are satisfied in the form $u(0) = 0$ and by simply removing the first *B*-spline from the basis set. For the definition of the *R*-matrix at the boundary (2.16), the amplitudes of the radial functions $u(r)$ at $r = a$ are required. These values are defined by the coefficients of the last spline, which is equal to one at the boundary. The summation over the entire expansion (2.15) now gives the surface amplitudes in a straightforward manner. The details for using *B*-splines in the construction and diagonalization of the Hamiltonian matrix are given in sections 7 and 8, respectively, along with a description of the corresponding programs.

In contrast to the nonrelativistic case, however, the direct implementation of *B*-splines for the solution of the Dirac equations encounters a problem related to the occurrence of spurious states (Johnson et al 1988). Fortunately, the wave functions of these states oscillate rapidly, and hence they play a negligible role in the summation over states in many-body perturbation theory (MBPT). For this very reason, these pseudo-solutions have been disregarded in practical atomic calculations based on the MBPT (Sapirstein and Johnson 1996). However, since the presence of the spurious states disturbs the spectrum, it worsens the convergence properties of such basis-set calculations (Shabaeb et al 2004). This is of particular concern in *R*-matrix calculations, where one needs the surface amplitudes for each solution. The appearance of these kinds of pseudostates completely destroys the *R*-matrix in the vicinity of such a state.

Several schemes for solving the problem of spurious states have been presented to date. Most recently this problem was investigated in detail by Igarashi (2006) who used a variety of methods and boundary conditions. In particular, he explored the use of *B*-splines of different order, k_p and k_q, as a way of avoiding spurious solutions. In a subsequent paper (Igarashi 2007), he concluded that "kinetic balance" also provided a good basis. Rather than *B*-splines alone, combinations of the form $B'(r) \pm \kappa B(r) / r$, with the prime denoting the first derivative, are employed instead in this case. The kinetic balance basis, however, and even more so the dual kinetic balance approach proposed by Shabaev et al (2004), is very difficult to implement, particularly in multichannel *R*-matrix calculations, since different bases are needed for different values of κ. This makes such a basis impractical for calculations with extensive multi-configurational expansions.

A practically feasible solution was recently proposed by Froese Fischer and Zatsarinny (2009). They noticed that the (B_k, B_{k+1}) functions are a numerically very stable basis, thereby avoiding the occurrence of spurious solutions. At the same time, this basis retains the simplicity and effectiveness of the original *B*-spline basis and provides the same accuracy as the kinetic balance bases proposed by Igarashi (2006).

Based on these findings, we expand the radial functions for the large and small components $P(r)$ and $Q(r)$ in separate *B*-spline bases as

$$P(r) = \sum_{i=1}^{n_p} p_i B_i^{k_p}(r), \quad Q(r) = \sum_{i=1}^{n_q} q_i B_i^{k_q}(r). \tag{2.17}$$

Both *B*-spline bases are defined on the same grid, with the same number of intervals, n_v. Only in this case the calculations of various matrix elements and integrals of interest can be performed with the same routines and at the same level of required computational resources as in the case of a single *B*-spline basis in non-relativistic calculations.

The coefficients p_i and q_i are found by diagonalizing the total $(N+1)$-electron Hamiltonian plus Bloch operator inside the *R*-matrix box. More specifically, using the *B*-spline basis leads to a generalized eigenvalue problem of the form

$$\mathbf{Hc} = E\mathbf{Sc} \tag{2.18}$$

where S is the overlap matrix between the basis functions. If orthogonality conditions are imposed between the scattering orbitals, S reduces to a banded matrix whose elements are the overlaps between individual B-splines. In the general case of nonorthogonal orbital sets, however, it has a more complicated structure. In result of the (2.18) diagonaliztion we obtain the surface amplitudes $P_i(a)$ and the relativistic R-matrix as defined in (2.16).

2.2. The external region

The next step in the calculation is to solve the scattering problem in the external region and to match the solutions on the boundary $r = a$ in order to obtain the K-matrices, S-matrices, or phase shifts. Since the radius a is chosen such that electron exchange is negligible in this region, we can expand the total wavefunction in the form

$$\Psi_{jE}^{JM\pi}\left(x_1,...,x_{N+1}\right) = \sum_{i=1}^{n} \overline{\Phi}_i^{JM\pi}\left(x_1,...,x_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1}\right) r_{N+1}^{-1} F_{ij}^{J\pi}\left(r_{N+1}\right), \qquad r_{N+1} > a, \tag{2.24}$$

where n is the number of channels, j labels the linearly independent solutions, the channel functions $\overline{\Phi}_i^{JM\pi}$ are the same as those retained in the internal region expansion (2.8), and the reduced radial functions $F_{ij}^{J\pi}(r)$ can be written as energy-dependent two-component functions

$$F_{ij}^{J\pi}(r) = \begin{pmatrix} P_{ij}^{J\pi}(r) \\ Q_{ij}^{J\pi}(r) \end{pmatrix}, \qquad i = 1,\ldots,n. \tag{2.25}$$

By substituting wavefunction (2.24) into Dirac equation (2.4) and projecting onto the channel function $\overline{\Phi}_i^{JM\pi}$, we obtain coupled first-order differential equations satisfied by the reduced radial continuum orbitals $P_{ij}^{J\pi}(r)$ and $Q_{ij}^{J\pi}(r)$ in the external region

$$\left(\frac{d}{dr} + \frac{\kappa_i}{r}\right)P_{ij}^{J\pi}(r) - \frac{1}{c}\left(2c^2 + e_i + \frac{Z-N}{r}\right)Q_{ij}^{J\pi}(r) = -\frac{1}{c}\sum_{i'=1}^{n}V_{ii'}^{J\pi}(r)Q_{ij}^{J\pi}(r), \tag{2.26}$$

and

$$\left(\frac{d}{dr} - \frac{\kappa_i}{r}\right)Q_{ij}^{J\pi}(r) + \frac{1}{c}\left(e_i + \frac{Z-N}{r}\right)P_{ij}^{J\pi}(r) = \frac{1}{c}\sum_{i'=1}^{n}V_{ii'}^{J\pi}(r)P_{ij}^{J\pi}(r), \tag{2.27}$$

where e_i are the channel energies in atomic units. The potential matrix $V_{ii'}^{J\pi}(r)$ is defined by

$$V_{ii'}^{J\pi}(r_{N+1}) = \left\langle r_{N+1}^{-1}\overline{\Phi}_i^{JM\pi}\left(x_1,...,x_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1}\right)\left|\sum_{k=1}^{N}\frac{1}{r_{kN+1}} - \frac{N}{r_{N+1}}\right|r_{N+1}^{-1}\overline{\Phi}_{i'}^{JM\pi}\left(x_1,...,x_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1}\right)\right\rangle' \tag{2.28}$$

where $i,i' = 1,\ldots,n$ and the prime on the Dirac bracket means that the integration is carried out over the space and spin coordinates of all $N+1$ electron except the radial coordinate r_{N+1} of the scattering electron. The potential matrix can be simplified using a well-known expansion for inter-electron interaction in terms of Legendre polynomials

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{\lambda=0}^{\infty}\frac{r_<^\lambda}{r_>^{\lambda+1}}P_\lambda(\hat{\mathbf{r}}_1 \bullet \hat{\mathbf{r}}_2), \tag{2.29}$$

where $r_<$ is the smaller and $r_>$ is the larger of r_1 and r_2. We obtain

$$V_{ii'}^{J\pi}(r_{N+1}) = \sum_{\lambda=1}^{\lambda_{max}}\alpha_{ii'\lambda}^{J\pi}r^{-\lambda-1}, \qquad r > a, \qquad i,i' = 1,\ldots,n, \tag{2.30}$$

where the long-range potential coefficients $\alpha_{ii'\lambda}^{J\pi}$ are defined by

$$\alpha_{ii'\lambda}^{J\pi} = \left\langle r_{N+1}^{-1}\overline{\Phi}_i^{JM\pi}\left(x_1,\ldots,x_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1}\right)\left|\sum_{k=1}^{N}r_k^{\lambda}P_{\lambda}(\hat{\mathbf{r}}_k \bullet \hat{\mathbf{r}}_{N+1})\right|r_{N+1}^{-1}\overline{\Phi}_{i'}^{JM\pi}\left(x_1,\ldots,x_N;\hat{\mathbf{r}}_{N+1}\sigma_{N+1}\right)\right\rangle'. \quad (2.31)$$

The multipole expansion (2.30) is truncated to $\lambda_{\max}$ terms since the range of λ where $\alpha_{ii'\lambda}^{J\pi} \neq 0$ is determined from triangular relations satisfied by the angular momenta of involved channels. In practical calculations, the long-range potential coefficients are the by-product of generating the Hamiltonian matrix and defined by the coefficients of the relevant Slater integrals R^k, describing the direct interaction between channels in the internal region. Note that $\alpha_{ii'0}^{J\pi} = N\delta_{ij}$ because of the orthogonality of the target wavefunctions Φ_i. This relation is used to check the target representation in the present program.

For low-energy collisions with atoms and atomic ions, where the ionic interaction potential $(Z-N)/r$ in the external region and the channel energies are both small compared with c^2, then the coupled differential equations (2.26) and (2.27) can be reduced to non-relativistic limiting form

$$\left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + \frac{2(Z-N)}{r} + k_i^2\right)P_{ij}^{J\pi}(r) = 2\sum_{i'=1}^{n}V_{ii'}^{J\pi}(r)P_{ij}^{J\pi}(r), \quad (2.32)$$

where $k_i^2 = 2e_i$. In this non-relativistic limit we also have

$$P_{ij}^{J\pi}(a) = \sum_{i'=1}^{n}R_{ii'}^{J\pi}(E)\left(a\frac{dP_{i'j}^{J\pi}}{dr} - bP_{i'j}^{J\pi}\right)_{r=a}, \qquad i=1,\ldots,n. \quad (2.33)$$

Equations (2.32) can be integrated outwards from $r=a$ and fitted to an asymptotic expansion at large r as described by Burke and Noble (1995). If all n scattering channels are open, the asymptotic form of the radial wavefunctions $\mathbf{P}^{J\pi}(r)$ may be written in the form

$$\mathbf{P}^{J\pi}(r) \underset{r\to\infty}{\sim} \mathbf{k}^{-1/2}(\mathbf{F}+\mathbf{G}\mathbf{K}^{J\pi}), \quad (2.34)$$

where we have written the channel momenta, $\mathbf{k}$, as a diagonal matrix. The diagonal matrices $\mathbf{F}$ and $\mathbf{G}$ correspond to regular and irregular Coulomb (or Riccatti-Bessel) functions in each scattering channel. The asymptotic expression (2.27) defines the scattering K-matrix, $\mathbf{K}^{J\pi}$, appropriate for standing-wave boundary conditions. The K-matrix is related to the scattering S-matrix and to the transition T-matrix by relations

$$\mathbf{S}^{J\pi} = \frac{1+i\mathbf{K}^{J\pi}}{1-i\mathbf{K}^{J\pi}}, \qquad \mathbf{T}^{J\pi} = \mathbf{S}^{J\pi} - \mathbf{I}. \quad (2.35)$$

It may be used directly to calculate cross sections and other scattering observables. The cross section for a transition from an initial state $\alpha_i J_i$ to a final state $\alpha_f J_f$ is given by

$$\sigma(\alpha_i J_i \to \alpha_f J_f) = \frac{\pi a_o^2}{2k_i^2(2J_i+1)}\sum_{J\pi,j_ij_f}(2J+1)|T_{fi}^{J\pi}|^2, \quad (2.36)$$

where α_i and α_f distinguish target states with the same total angular momentum J_i and J_f, and j_i anf j_f are the initial and final angular momenta of the scattered electron.

The long-range coefficients $\alpha_{ii'\lambda}^{J\pi}$ together with the target energies and the definition of the structure of the close-coupling equations constitute the information needed to solve the scattering problem in the external region. This problem is well developed, and there is a set of general computer codes for its solution. We mention to program in this respect which is recommended to use in connection with the

present DBSR code at low scattering energies. The outer region program FARM, written by Burke and Noble (1995), uses the *R*-matrix propagator technique. A parallel version of FARM (PFARM) has been developed by Sunderland et al (2002). The STGF program, initially written by Seaton and partly described by Berrington et al (1987), calculates solutions which are correct to second order in the long-range potentials. A parallel version PSTGF is also available for calculations [20]. These programs enable the *K*-matrix, *T*-matrix and hence collision cross sections to be determined. The last version of STGF can be find in the site http://amdpp.phys.strath.ac.uk/UK_RmaX/codes.html.

For electron collisions with highly ionized ions, *Z-N* and hence the excitation energies are large, the use of non-relativistic limit (2.32) in the external region can lead to errors. In this case, the original relativistic equations (2.25) and (2.26) should be integrated outwards from *r=a*, using the standard approach for solving these first-order differential equations. The discussion and possible algorithms were presented by Young and Norrington (1994), however, we are not aware of any publicly-available program for the relativistic treatment of the external region. We are planning to develop such program in future as one of the possible extension of the present DBSR complex.

2.3. Breit and QED corrections

The Breit interaction describes the relativistic corrections to the electronic motion due to magnetic and retardation effects. These are important corrections and they should be included into accurate atomic-structure calculations. An effective operator for the Breit interaction can be derived from quantum electro-dynamics (QED) in perturbation theory with respect to the number of virtually exchanged photons (Grant 2007). In Coulomb gauge and in the long-wavelength approximation, the Breit operator reads as

$$H_B = -\frac{1}{2r_{12}}\left[\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2 + \frac{(\boldsymbol{\alpha}_1 \cdot \mathbf{r}_{12})(\boldsymbol{\alpha}_2 \cdot \mathbf{r}_{12})}{r_{12}^2}\right],\tag{2.37}$$

where $\boldsymbol{\alpha}$ are the Dirac matrices (2.3). Discussion of the Breit Hamiltonian and its implementation in the present code is given in section XX. Here we just note that Breit interaction can be included either for scattering calculations or just for description of target states. The Breit interaction considerably complicates the calculations and inclusion for scattering on neutral atoms or ions with low charge is not worth the computational efforts. However, its inclusion to the description of the target often lead to higher accuracy of target wave functions, and consequently, it improves the description of low-energy scattering. Breit corrections may also be important when using DBSR complex in the bound-state mode.

The QED corrections in the present code are used only for the target description. They are calculated in the same approximations as in the GRASP (Jönsson et al 2007) and RELCI (Fritzsche et al 2002) programs. The dominant corrections arise from the self-energy of the electrons and the polarization of the vacuum due to the nuclear field. The effect of the vacuum polarization can be represented in terms of the Uehling potential (Uehling 1935, Fullerton and Rinker 1976) and has been included in relativistic structure calculations for many years. The computation of the self-energy requires a considerably larger effort. The self-energy contributions are usually estimated from tabulations that are available for the hydrogen-like ions (Mohr 1974, 1983, Mohr and Kim 1992). Different methods have been proposed to determine an *effective* nuclear charge, in order to interpolate these data for individual subshells of a many-electron system. We refer the reader to the description of the DBSR_HF program for different options for the inclusion of the QED corrections in the DBSR complex.

2.4. Bound-state and pseudostate calculations

Electron-atom collision theory is concerned with states of an (N+1)-electron system for which N electrons are bound in an atom or atomic ion and one electron can escape to infinity. Such states may be represented accurately using the close-coupling expansion (2.8). This expansion is obviously also suitable for representing states with one electron highly excited and the other N electrons more tightly bound. When the close-coupling approximation is used to calculate bound states of atomic systems, it is referred to as the frozen-core (FCS) approximation, and the Φ_i are usually labelled 'core' rather than 'target' functions.

The FCS method has several advantages. It can readily be extended to highly excited states. The multichannel form of Eq. (2.8) allows us to include explicitly the interaction between different Rydberg series, as well as the interaction of the Rydberg series with perturbers that can be represented in the second part of the expansion. The energies and wavefunctions can be computed efficiently with an accuracy comparable to that obtainable using the best alternative methods, from which large amount of radiative data can be generated. The same expansions can be used for close-coupling collision calculations as for FCS bound-state calculations. Often a comparison of the calculated bound-state energies with experimental energies provides a check on the accuracy of the collision calculations. At the same time, one can take advantage of the extensive experience accumulated from close-coupling collision calculations and the codes developed for such calculations, and one can apply them to the study of Rydberg series. The first extensive FSC calculations for many-electron systems were made using the computer program IMPACT (Crees et al 1978) that solved the resulting integro-differential equations. Further developments of the FCS method for the study of Rydberg series were obtained in connection with the R-matrix method (Seaton 1985). A good example of such a calculation is given by Berrington and Seaton (1985) .

The accuracy of both the above-mentioned methods is restricted through the use of finite-difference methods for computing the radial functions. More accurate numerical results can be obtained by using a spline FCS method for Rydberg series, in which the wavefunctions of the outer electrons are expanded directly in B-splines in some finite region $r \leq a$, with a sufficiently large value of a. Such a method is implemented in the present package. The zero boundary conditions are imposed by deleting from the expansion the first and the last splines, i.e., the only splines with a nonzero value at the boundary. We also delete the next to last spline, in order to guarantee a zero derivative at the boarder for all bound solutions.

The choice of B-splines as basis functions has some advantages. The completeness of the B-spline basis ensures that, in principle, we can study the entire Rydberg series. The number of physical states we can obtain in one diagonalization is defined by the box radius a, which can easily be varied in the B-spline representation. The exponential grid was found to be quite suitable for bound states, and it allows us to use a rather large radius with a relatively small number of B-splines. For example, in order to obtain Rydberg states up to n=10 in neutral atoms, it is often sufficient to choose the box radius equal to 300 au and the number of splines as 45. If we aim to study Rydberg series up to n=20, we should increase the border radius to 1200 au. With an exponential grid, this increases the number of splines only to 51. Hence, the size of the interaction matrix, which is proportional to the number of splines, does not increase considerably. Of course, these numbers somewhat depend on the nuclear charge Z. For very high Z, it is advisable to add a few splines at very small radii to achieve an accurate representation of the orbitals near the nucleus.

The wavefunctions in this method are obtained for all radii and for all Rydberg states under consideration. There is no need to obtain an asymptotic solution and to match it to the inner-region solution as in the R-matrix method discussed above. This considerably simplifies the calculations and

the codes, but the use of a finite B-spline basis limits the upper n-value for the Rydberg states. Consequently, this method can be efficient for the study of moderately excited states with values of n not too large, typically in the range 10-30.

Our implementation of the spline method differs from all previous ones through the use of non-orthogonal orbitals, both for the construction of target wavefunctions and for the representation of the outer electron. It provides us with a great deal of flexibility in the choice of the 'target' wavefunctions, which can be optimized for each atomic state separately, and in the introduction of different correlation corrections. In the present program, the core-core correlation may be taken into account by using extensive multi-configuration target states. The core-valence correlation can be introduced, in principle, in two ways, either by using a large set of excited target states in the close-coupling expansion or by introducing additional (N+1)-electron states, specially designed for this purpose. The convergence of the close-coupling expansion can be very slow, and hence the first approach is much more time consuming. Nevertheless, our experience shows that this method gives a more accurate description of the core-polarization potential, and the (N+1)-electron terms in Eq. (2.5) are better used only for the inclusion of the short-range correlation.

The bound-state mode becomes as an important part of any large-scale scattering calculations. Usually, the scattering calculations consist following steps. First, calculations of the ground and other low-lying states of target by programs that the user prefers, e.g. the GRASP program or DBSR_MCHF, or others. Here the user defines the level of accuracy for the target description. In the next state, the wavefunctions for higher lying target states (and continuum pseudostates if needed) are added by using DBSR in the bound-state mode. Finally, DBSR is employed for the inner-region calculation in the chosen model, with desirable number of target states in the close-coupling expansions. The resulting surface amplitudes, and consequently, R-matrix, are used in the external region to generate cross sections or other scattering parameters. Here the user is supposed to use STGF or FARM program, or any other programs or utilities, depending on the specific problem (see section 7 for the further discussions).