22. Program BSR_POL   (version 3)

The BSR_POL program is designed to determine the so-called polarized atomic pseudo-states. These pseudo-states can be used to determine the atomic polarizabilities or simulate the core-valence correlation for outer bound or scattering electron. The typical example is the elastic scattering at small energies, where it is very important to include the polarization of the target ground state to full extent.

22.1 Related theory

As typical example, consider the one-electron atoms such as the alkali-metal atoms. The main correlation effects for the valence electron are related with the core-valence interaction. In most existing calculations for one- or two-electron atoms, a phenomenological one-electron core polarization potential was usually added to account for the core-valence correlation. Although such a potential simplifies the calculations significantly and can provide accurate excitation energies and oscillator strengths, the question always remains how well the model potential can simulate whole core-valence correlation, including non-dipole contributions. The core-valence correlation can also be included *ab initio* by adding the states with an excited core in the corresponding configuration or close-coupling expansions. This is the most consistent approach, but it may lead to very large close-coupling expansions and extensive computational efforts. Besides, in many cases, such as np^6 core, typically 50% or more of the core polarizability comes from the continuum that is very difficult to incorporate into close-coupling expansions. One solution to this problem in the case of electron-hydrogen scattering was given by Damburg and Karule (1967). They pointed out that it was possible to define a pseudo-state which could be included in the close coupling expansion in the same way as an atomic eigenstate but which allowed for the full polarizability of the ground state. We will refer to this state as a polarized pseudo-state to distinguish it from pseudo-states which have been widely used to represent other aspects of the collision process. For example, in the RMPS (R-matrix pseudo-state, Bartschat et al 1996) or CCC (convergent close-coupling, Bray et al 2002) methods, pseudo-states are used to mimic the target continuum and they are usually determined from diagonalization of the atomic Hamiltonian in the bases of L^2 integrable wave functions.

First attempt to employ polarized pseudo-states in scattering problem was made by Burke and Mitchell (1974), who obtained the polarized pseudo-states as linear combination of configurations based on analytic orbitals. Further development of using polarized pseudo-states in the multiconfigurational approach for calculation of atomic polarizabilities has been reported in a series of papers by Hibbert *et al* (1977). In the present calculations we follow these developments but employ the different numerical technique which is based on the B-spline expansions.

The polarized pseudo-state ϕ_p is defined by the requirement that the static polarizability of atomic state ϕ_0 can be expressed by a single term

$$\alpha = 2\frac{|<\phi_0\,|\,\mathbf{D}^{(1)}\,|\,\phi_p>|^2}{E_p - E_0} \tag{22.1}$$

where $\mathbf{D}^{(1)}$ is a dipole operator and ϕ_p is a normalized solution of the atomic Hamiltonian, that is,

$$<\phi_p\,|\,\phi_p> = 1 \tag{22.2}$$

and E_p is defined by

$$<\phi_p\,|\,H\,|\,\phi_p> = E_p. \tag{22.3}$$

As shown by Burke and Mitchell (1974), the ϕ_p can be written as

$$\phi_p = N^{-1/2}\tilde{\phi}_p \tag{22.4}$$

where $\tilde{\phi}_p$ is a solution of the equation

$$(H - E_o)\tilde{\phi}_p = D_0^{(1)}\phi_0 \tag{22.5}$$

and the factor $N^{-1/2}$ ensures that Eq. (6) is satisfied. The generalization to any higher multipole k is straightforward by using multipole operator $\mathbf{D}^{(k)}$.

Consider as example our calculations of photoionization of potassium atoms from the ground and excited states, $3p^6nl$. In the calculations of the core polarization, we take into account the excitations from both the $3s^2$ and $3p^6$ subshells, so that the expansions for the polarized pseudo-state have the form

$$\varphi_p^{(k)} = A[\Phi(3s^2 3p^5)\bullet\varphi_1(l_1)]^{J\pi} + A[\Phi(3s3p^6)\bullet\varphi_2(l_2)]^{J\pi} \tag{22.6}$$

where A denotes the antisymmetrization operator and we consider all possible channels for the outer electron. The unknown radial function for the pseudo-orbitals $\varphi_i(l_i j_i)$ in Eq. (22.6) were expanded in the B-spline basis. The coefficients of the B-spline expansions were found from the inhomogeneous Eq. (22.5). In the B-spline basis, this equation has the form

$$(\mathbf{H} - E_0\mathbf{S})\mathbf{c} = \mathbf{D}\mathbf{c}_0 \tag{22.7}$$

where $\mathbf{H}$, $\mathbf{S}$, and $\mathbf{D}$ are the Hamiltonian, overlap, and dipole matrices between the basis functions for the $(N\text{-}1)$-electron system of K^+, and $\mathbf{c}$ and $\mathbf{c}_0$ are the vectors of B-spline expansions for the polarized pseudo-states and the initial $K^+(3p^6)$ bound state, respectively. In actual calculations, we do not need the $\mathbf{D}$-matrix and $\mathbf{c}_0$ vector explicitly, but rather their product $\mathbf{d}=\mathbf{D}\,\mathbf{c}_0$ which can be obtained by using BSR_DMAT program. Note that BSR_DMAT can employ both B-spline (BSR) and standard configurational (MCHF) representation for the ground state, ϕ_0.

The polarized pseudo-states then can be incorporated into the corresponding close-coupling expansions. In our example of potassium, the K^+ polarized pseudo-states with multipole ind*exes* $k = 1, 2, 3$ together with the ground state $K^+(3p^6)$ were used as target states in the *B*-spline bound-state close-coupling calculations to generate the low-lying states of atomic K. The corresponding close-coupling expansion has the structure

$$\Psi(3p^6nl; J\pi) = A[\Phi(3s^2 3p^6) \bullet \varphi(nl)]^{J\pi} + A \sum_{k=1-3} [\phi_p^k \bullet \varphi(n'l')]^{J\pi} \ . \tag{22.8}$$

The first term describes the physical states, whereas the other terms describe the core-polarization effects. The unknown radial components for the outer valence electron, $\varphi(nlj)$, were again expanded in individual B-spline bases. The coefficients of these expansions were found by diagonalizing the atomic Hamiltonian in the usual way, see BSR_HD program. Sometimes, when our close-coupling contains additionally some excited physical states, we need to described not full polarization of the ground state, but only the part of polarization not included into the close-coupling expansion. In this case we need to impose the orthogonality constraints on our pseudo-state function to the included physical states. It can be done with Lagrange multipliers in the equation (22.5):

$$(H - E_o)\tilde{\phi}_p + \sum_i \lambda_i < \tilde{\phi}_p \mid \phi_i > \ = D_0^{(1)}\phi_0 \tag{22.9}$$

In B-spline basis we then have

$$(\mathbf{H} - E_0\mathbf{S})\mathbf{c} + \sum_i \lambda_i \mathbf{B}\mathbf{c}_i = \mathbf{D}\mathbf{c}_0 \tag{22.10}$$

where $\mathbf{B}$ is the overlap matrix between individual B-splines, $\mathbf{c}_i$ are the expansion coefficients for ionic state i, and we solve the equation (22.10) both for pseudo-state expansion coefficient $\mathbf{c}$ and Lagrange multipliers λ_i.

10.3. Structure and data flow

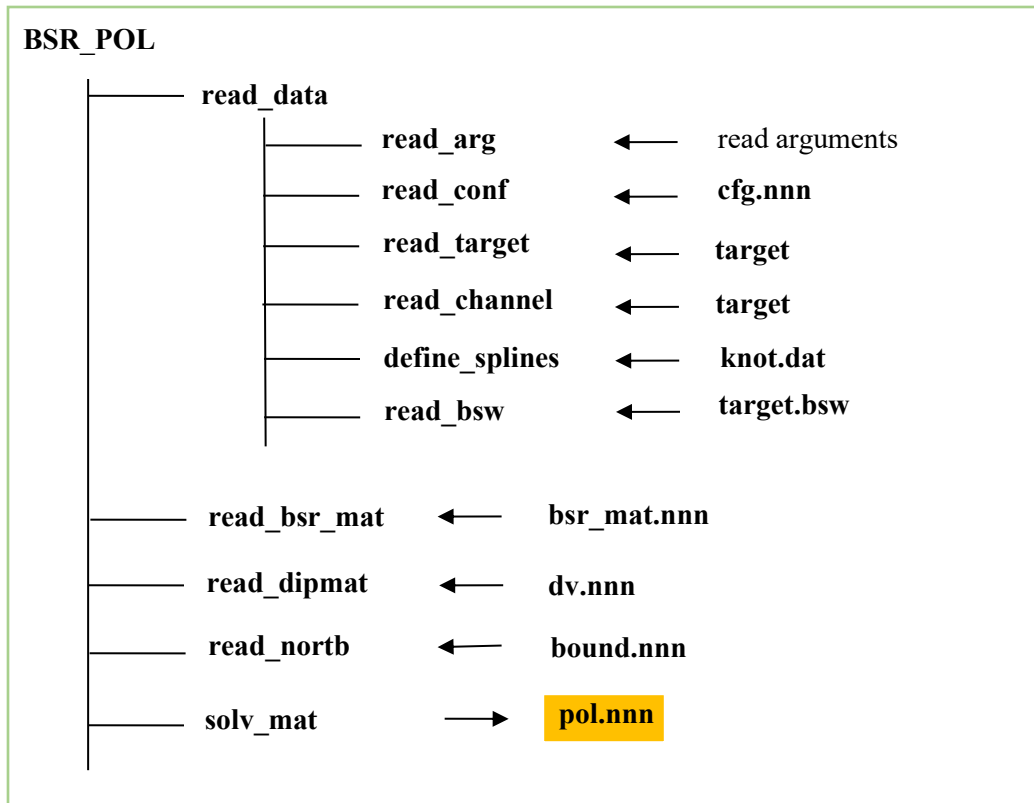The block diagram of the program BSR_POL, along with the data flow, is given in Fig. 12.1.

Fig. 22.1. Block diagram for the program BSR_POT3 and data flow (see text).

22.3 Input parameters

klsp	index of partial wave, **nnn**
ilzero [1]	number of initial B-splines to be excluded from orbital expansions
ibzero [1]	number of final B-splines to be excluded from orbital expansions
ilzero [1]	number of initial B-splines to be excluded from orbital expansions
nortb [0]	number of additional orthogonal conditions
inorb	if nortb > 0, indexes of solutions in **bound.nnn** file which will be used for orthogonality

22.4. Data files

bsr_par	File type: formatted sequential input. Written by user. Read by routine **read_arg**. Description: input parameters for given run.
target	File type: formatted sequential input. Written by user and modified by BSR_PREP and BSR_CONF programs. Read by routine **read_target.** Description: contains description of the target states and scattering channels, optional.
knot.dat	File type: formatted sequential input. Written by user. Read by routine **define_grid** from BSPLINE library. Description: input parameters that define the B-spline grid.
cfg.nnn	File type: formatted sequential input. Created BSR_CONF programs. Read by routine **read_conf**. Description: contains the configuration expansion for the polarized pseudo-state
target.bsw	File type: unformatted sequential input. Created by program BSR_PREP. Read by routine **read_bsw.** Description: target one-electron orbitals in the B-spline basis, optional.
bsr_mat.nnn	File type: unformatted sequential input Created by program BSR_MAT. Description: Overlap/Hamiltonian matrix in B-spline basis.
dv.nnn	File type: formatted sequential input. Written by program BSR_DMAT. Read by BSR_POL. Description: dipole vector for the given initial state.
bsr_pol.nnn	File type: formatted sequential input. Written by program BSR_POL. Read by user. Description: running information.
pol.nnn	File type: formatted sequential output **(main result)**. Written by program BSR_POL. Read by **bound_bsw** utility. Description: bound-state solutions for given psedo-state in the B-spline close-coupling representation (8.2).