

BSR ionization approach

The scattering amplitude

Let us consider the ionization of an atom by electron impact, schematically written as

$$e_0(\mathbf{k}_0\mu_0) + A(L_0S_0) \rightarrow e_1(\mathbf{k}_1\mu_1) + e_2(\mathbf{k}_2\mu_2) + A^+(L_fS_f) \quad (1)$$

where \mathbf{k}_i and μ_i ($i=0,1,2$) are the linear momenta and spin components of the incident, scattered, and ejected electrons, respectively. L_0 , S_0 and L_f , S_f are the orbital and spin angular momenta of the initial $(N+1)$ -electron atom and the residual N -electron ion.

For complete description of this process, we need the ionization amplitude

$$f(L_0M_0S_0M_{S_0}, \mathbf{k}_0\mu_0 \rightarrow L_fM_fS_fM_{S_f}, \mathbf{k}_1\mu_1\mathbf{k}_2\mu_2), \quad (2)$$

where we have introduced the magnetic quantum numbers of the atomic (M_0) and ionic (M_f) orbital angular momenta as well as the corresponding spin components M_{S_0} and M_{S_f} .

To begin the discussion, let's consider the first-order amplitude that can be written as

$$f(L_0M_0S_0M_{S_0}, \mathbf{k}_0\mu_0 \rightarrow L_fM_fS_fM_{S_f}, \mathbf{k}_1\mu_1\mathbf{k}_2\mu_2) = \left\langle \phi_{\mathbf{k}_1\mu_1}^{(-)}(x) \Psi_{L_fM_fS_fM_{S_f}}^{\mathbf{k}_2\mu_2(-)}(X) \middle| V(x, X) \middle| \Phi_{L_0M_0S_0M_{S_0}}(X) \phi_{\mathbf{k}_0\mu_0}^{(+)}(x) \right\rangle \quad (3)$$

Here $X = \{\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_{N+1}, \sigma_{N+1}\}$ denotes a set of electronic spatial and spin coordinates in the $(N+1)$ -electron atom, while $x = \{\mathbf{r}, \sigma\}$ denotes the coordinates of the colliding electron. The Coulomb potential

$$V(x, X) = \sum_{n=1}^{N+1} \frac{1}{|\mathbf{r} - \mathbf{r}_n|} - \frac{Z}{r} \quad (4)$$

describes the interaction between the projectile and the atomic electrons as well as the nucleus of charge Z . Although the two outgoing electrons are, in principle, indistinguishable, we will refer to the faster (slower) one of these as the scattered (ejected) electron. This notation makes sense for sufficiently high incident energies (many times the ionization threshold) and strongly asymmetric energy sharing between the two outgoing electrons. The post-collision interaction as well as exchange effects between the two final continuum electrons are neglected in (3) above

The functions $\phi_{\mathbf{k}_0\mu_0}^{(+)}(x)$ and $\phi_{\mathbf{k}_1\mu_1}^{(-)}(x)$ represent the incident and outgoing projectile with the linear momenta \mathbf{k}_0 and \mathbf{k}_1 , respectively. In the simplest case, they are chosen as plane waves and the integral over the projectile coordinates can be performed analytically through the Bethe integral. In more sophisticated treatments, they are represented by distorted waves via a partial-wave expansion.

Another important aspect is the treatment of the ejected-electron–residual-ion interaction, i.e. the function $\Psi_{L_fM_fS_fM_{S_f}}^{\mathbf{k}_2\mu_2(-)}(X)$ in (3). A common approximation is to write this function as a product of the final ionic state of

interest and another distorted wave for the ejected electron. In addition, the dependence of the radial orbitals for the spectator electrons (i.e. those remaining in the ion) on the charge state and the various angular momentum couplings is often ignored. In that case, the integral over all spectator coordinates is unity and it becomes relatively straightforward to calculate the ionization amplitude (3).

A more rigorous treatment is the close-coupling expansion

$$\Psi_{L_f M_f S_f M_{S_f}}^{k_2 \mu_2 (-)}(X) = \frac{1}{\sqrt{k_2}} \sum_{l_2 m_2} i^{l_2} \exp(-i\sigma_{l_2}) Y_{l_2 m_2}^*(\hat{\mathbf{k}}_2) \sum_{L, M, S, M_S} (L_f M_f, l_2 m_2 | LM)(S_f M_{S_f}, \frac{1}{2} \mu_2 | SM_S) \Psi_{LMSM_S}^{L_f M_f S_f M_{S_f}, k_2 (-)}(X) \quad (5)$$

where $\Psi_{LMSM_S}^{L_f M_f S_f M_{S_f}, k_2 (-)}$ is an ion-ejected-electron eigenstate of total orbital angular momentum L and total spin S with ingoing-wave boundary conditions for well-defined orbital spin angular momenta L_f and S_f of the ion, and $(j_1 m_1, j_2 m_2 | j m)$ is a standard Clebsch-Gordan coefficient. These channel functions are being constructed in typical collision calculations by coupling the X coordinates of the target with the angular and spin coordinates of the free electron. The expansion (5) then allows us to obtain well-defined final-state wave functions for each residual ionic state and the ejected electron. As will be shown below, having these functions available is an important part of generating the final results by projection.

To illustrate the situation further, let us consider the limit of a single target state (here the final ionic state) and also assume that the scattering phase for the ejected electron does not depend on the total momenta L and S . In this case the close-coupling expansion is reduced to the product of that ionic state and the familiar distorted-wave partial-wave expansion

$$\varphi_{k\mu}^{(\pm)}(\mathbf{r}) = \frac{1}{\sqrt{k}} \sum_{l=0}^{\infty} \sum_{m=-l}^l i^l \exp[\pm i(\sigma_l + \delta_l)] Y_{lm}^*(\hat{\mathbf{k}}) \times \frac{1}{r} P_{el}(r) Y_{lm}(\hat{\mathbf{r}}) \chi_{\mu} \quad (6)$$

for the ejected electron with the wave-vector normalization

$$\langle \varphi_{\mathbf{k}'m'}^{(\pm)}(\mathbf{r}) | \varphi_{\mathbf{k}m}^{(\pm)}(\mathbf{r}) \rangle = \delta(\mathbf{k} - \mathbf{k}') \delta(m_s - m_s')$$

Here σ_l is the Coulomb phase shift while δ_l is the phase shift due to the deviation of the short-range potential from the pure Coulomb case. The + and - subscripts denote the outgoing-wave and ingoing-wave boundary conditions that are appropriate, respectively, for the initial- and final-state continuum electrons.

An alternative to the fully or at least partially perturbative methods is the **CONTINUUM PSEUDOSTATE APPROACH**, which does *not* start with the separation of the projectile from the rest of the problem as in (3). Specifically, one begins by replacing the true continuum orbitals in the wave function $\Psi_{L_f M_f S_f M_{S_f}}^{k_2 \mu_2 (-)}(X)$ by a square-integrable representation, usually obtained by diagonalizing the atomic Hamiltonian in an appropriate basis. The diagonalization procedure results in a number of discrete states, with the negative-energy (with respect to the ionization threshold) states representing a few low-lying physical bound states and an approximation for the

infinite Rydberg spectrum, while the positive-energy states represent the ionization continuum. **EXCITATION OF THE POSITIVE-ENERGY PSEUDOSTATES IS THEN REGARDED AS IONIZATION.**

As a first step, the electron-impact *excitation* problem for both the physical and the pseudostates needs to be treated. This can be done, for example, by using the *R*-matrix approach. A significant challenge, however, remains. It concerns the procedure of extracting the information from the wave function obtained for the atom left in an excited pseudostate. The total angle-integrated ionization cross section can be obtained directly as the sum of the excitation cross sections for all the pseudostates above the ionization threshold. To obtain the more detailed angle-differential cross sections, on the other hand, one needs to relate the discrete finite-range pseudostate functions to the true continuum functions at the proper ejected electron energy and construct the appropriate ionization amplitude (2). Even the extraction of the angle-integrated ionization cross section for a specific final ionic state is by no means trivial, due to the fact that configuration interaction (CI) effects make it difficult to uniquely assign the contribution of an individual pseudostate to the result for a particular ionic state.

The pseudostate approach, especially the CCC method, was successfully applied to (quasi-) one and (quasi-)two-electron atomic systems, where model potentials were used, if necessary, to describe the effect of a inert closed core. Very importantly, only one of the electrons in the two-electron targets was considered active, while the other remained a spectator. This methodology cannot be applied directly to more complex systems or more correlated ionization processes, such as ionization with simultaneous excitation of the residual ion. Below we extend the capability of the pseudostate approach by using a flexible *B-spline basis* and the *nonorthogonal orbital technique*. Also, we introduce a direct projection approach to extract the relevant information.

Pseudo-states in the B-spline basis (the box-based approach).

In the present method, the atomic wavefunction describing the total $(N+1)$ -electron system is expanded in terms of products of the N -electron ion states and radial functions for the outer electron. The latter, in turn, are expanded in a *B-spline basis*. In case of He, as example, $N=1$ and we employed the following close-coupling expansion

$$\Phi(nln'l', LS) = A \sum_{i,j} a_{ij} \{ \varphi(n_i l_i) P(n_j l_j) \}^{LS} + \Phi(1s^2) \quad (7)$$

$$P_{nl}(r) = \sum_k a_k B_k(r) \quad (8)$$

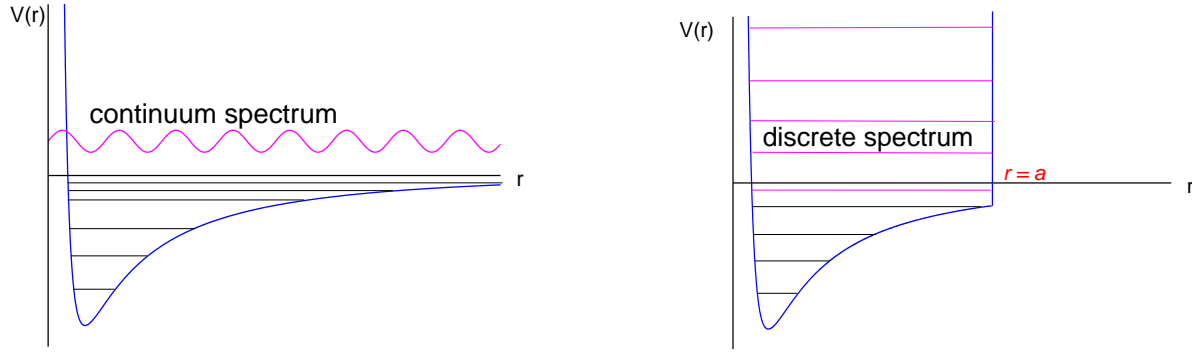
The operator A includes antisymmetrization and implies that the target function is coupled to the outer electron according to the usual angular momentum rules. The functions $\varphi(n_i l_i)$ are the hydrogen-like ($Z=2$) orbitals $1s, 2s, 2p$, and the multi-configuration expansions for the $1s^2$ state was directly included in the expansion as correlation functions (called as "perturber" in the BSR complex). The radial functions $P(n_j l_j)$ were forced to be orthogonal only to the $1s$ orbital. The above scheme yields non-orthogonal, term-dependent valence orbitals for each LS term, i.e., we directly include term-dependent effects in our atomic wavefunctions. Besides, the non-

orthogonal orbital technique allows us to use the independently optimized multi-configuration expansions for the $1s^2$ state.

The sets of unknown expansion coefficients $\{a\}$ for each orbital and given set of $LS\pi$ are found by diagonalizing the atomic Hamiltonian interaction matrix inside the box of radius a , with zero boundary conditions. In the B -spline basis, this leads to a generalized eigenvalue problem of the form

$$\mathbf{Hc} = E\mathbf{Sc}, \quad (9)$$

where \mathbf{S} is the overlap matrix. A detailed description of the structure of the \mathbf{H} and \mathbf{S} matrices in the B -spline representation is given in the description of BSR_MAT program. The choice of B -splines as basis functions has some advantages. An important property of B -splines is that they form an effectively *complete* basis on the interval spanned by the knot sequence. The number of physical states that we can generate by this method depends on the radius a of the B -spline box. Along with the physical states, the above scheme also provides a set of pseudo-states, with the lowest states representing the remaining bound states and the rest representing the continuum..



Scattering calculations for excitation of pseudo-states.

The scattering calculations are carried out with a general R -matrix code BSR in standard way. The RMPS close-coupling expansions usually contain from 500 to 1000 target states (including pseudo-states). Such calculations are possible only with MPI version of BSR and require supercomputers with 1000 or more cores. It is found convenient to make calculation separately for each partial wave, using the separate folders. As result, we get set of h.nnn files for each partial wave, which then used to generate the collision strengths and T-matrix elements for desired incident-electron energies using the stgf or farm programs. The corresponding files are very extended and we use special format only to record only the part of information (see the SCT_LS utils description).

The T-matrix elements are then used to generate the scattering amplitudes for all energy-accessible atomic pseudo-states Φ^p as

$$f^P(L_0 M_0 S_0 M_{S_0}, \mu_0 \rightarrow L M S M_S, \mu_1) = \sqrt{\frac{\pi}{k_0 k_1}} \sum_{l_0, l_1, L_T, S_T, \Pi_T, M_{L_T}, M_{S_T}} i^{(l_0 - l_1)} \sqrt{(2l_0 + 1)} \times C_{M_0 0 M_{L_T}}^{L_0 l_0 L_T} C_{M_{L_1} m_{L_1} M_{L_T}}^{L_1 l_1 L_T} C_{M_{S_0} \mu_0 M_{S_T}}^{S_0 \frac{1}{2} S} C_{M_S \mu_1 M_{S_T}}^{S \frac{1}{2} S} T_{l_0 l_1}^{L_T S_T \Pi_T}(\alpha_0 L_0 S_0 \rightarrow \alpha L S) Y_{l_1 m_1}(\theta_1, \phi_1) \quad (11)$$

where $T_{l_0 l_1}^{L_T S_T \Pi_T}(\alpha_0 L_0 S_0 \rightarrow \alpha L S)$ is an element of the T matrix for a give total angular momentum L , total spin S_T and parity Π_T of the $(N+2)$ -electron system. We assume the z axes is chosen along the direction of the incident beam, i.e., $m_0 = 0$. The generation of all needed amplitudes (11) is provided by utility **dif_sec_He** (see details in the description of this utility).

Ionization amplitude.

According to the pseudo-state approach, ionization amplitudes (2) can be obtain by projection of the atomic amplitudes (14) to the true continuum functions $\Psi_{L_f M_f S_f M_{S_f}}^{k_2 \mu_2 (-)}$ and summing over all energy-accessible pseudo-states:

$$f(L_0 M_0 S_0 M_{S_0}, k_0 \mu_0 \rightarrow L_f M_f S_f M_{S_f}, k_1 \mu_1 k_2 \mu_2) = \sum_p \langle \Psi_{L_f M_f S_f M_{S_f}}^{k_2 \mu_2 (-)} | \Phi^P(LS) \rangle f^P(L_0 M_0 S_0 M_{S_0}, k_0 \mu_0 \rightarrow L M S M_S, k_1 \mu_1) \quad (12)$$

This requires the determination of the overlaps factors $\langle \Psi_{LS}^{f, k_2 (-)} | \Phi^P(n l n' l', LS) \rangle$ between real continuum states and corresponding pseudo-states. The continuum state $\Psi_{L M S M_S}^{L_f M_f S_f M_{S_f}, k_2 (-)}$ have been obtained using R-matrix method with the same close-coupling expansion (10), which was employed for pseudo-states. Computationally, the only difference was that now we use R-matrix boundary conditions by adding corresponding Bloch operator. Both pseudo-states and continuum solutions in the B -spline basis can be considered as a vectors \mathbf{b}_p and \mathbf{b}_c , which length depends on the number of open channels.

The computational advantage of the present approach is that the needed overlap factors are obtained in a straightforward way as $\langle \mathbf{b}_p | \mathbf{S} | \mathbf{b}_c \rangle$ using the already calculated overlap matrix from (9). Note that the one-electron pseudo-state and continuum orbitals are not orthogonal. Our non-orthogonal orbital technique takes this nonorthogonality into account in full extent, without any simplifications. Note that standard R-matrix approach provide continuum function with real \mathbf{K} -matrix asymptotic, and to obtain the required solutions with ingoing-wave boundary conditions, we should normalized the R-matrix solutions with factor of $[1 + i\mathbf{K}]^{-1}$

Before proceeding further, it is worth pointing out an important subtlety of the approach. Note that $\Psi_f^{k_2 -}$ and $\Phi^P(LS)$ have *different* energies for the continuum electron represented by k_2 and the electron in the pseudostate. Due to energy conservation, excitation of $\Phi^P(LS)$ leads to $k_{1p} = k_1$ for the projectile. Having noted numerical instabilities in some cases, Bray and Fursa (1996) suggested interpolating the transition-matrix elements as an alternative. While this interpolation, indeed, worked very well for the single-channel case, our direct projection

method is necessary to maintain the crucial channel information in multichannel situations. This makes Eq. (12) a suitable approximation for the true ionization amplitude, provided the spectrum of the pseudostates is sufficiently dense.

The triple-differential cross-section for ionization-excitation process to the final state f is then given by

$$\frac{d\sigma^f}{d\Omega_1 d\Omega_2 dE} = \frac{k_1 k_2}{k_0} \frac{1}{2(2L_0+1)(2S_0+1)} \sum_{\substack{M_0, M_f, M_{S_0}, M_{S_f} \\ \mu_0, \mu_1, \mu_2}} |f(L_0 M_0 S_0 M_{S_0}, \mu_0 \rightarrow L_f M_f S_f M_{S_f}, \mu_1 \mu_2)|^2 \quad (13)$$

where we use atomic units $[a_0^2 / (sr^2 \text{hartree})]$. We are working in nonrelativistic LS -coupling scheme and summation on the spin magnetic quantum numbers, for the specific case, can be done analytically. In case of closed shells atoms with $L_0=0$ and $S_0=0$, the TDCS can be represented with simplified notation as

$$\frac{d\sigma^f(\mathbf{k}_1, \mathbf{k}_2)}{d\Omega_1 d\Omega_2 dE} = \frac{k_1 k_2}{k_0} \sum_{M_f} \sum_S |f^S(M_f)|^2 \quad (17)$$

where $f^S(M_f)$ is the amplitude (11) obtained for the pseudo-state spin S (0 or 1 in our case). In above formula we explicitly introduce additional notation $(\mathbf{k}_1, \mathbf{k}_2)$ to stress that in the pseudo-state treatment primary and ejected electron are not treated symmetrically. For comparison with experiment, we should also add another ionization process, where the primary electron has momentum \mathbf{k}_2 and the ejected electron has momentum \mathbf{k}_1 and which cannot be experimentally distinguished from the former. For highly asymmetric energy sharing ($k_1 \gg k_2$) the first process will be dominant, whereas for equal energy sharing ($k_1 \sim k_2$) both processes become comparable. As shown by Stelbovics et al (2005), the corresponding amplitudes should be added coherently using expressions for redefined S -dependent amplitudes F^S

$$F^0(\mathbf{k}_1, \mathbf{k}_2) = f^0(\mathbf{k}_1, \mathbf{k}_2) - \frac{1}{2} f^0(\mathbf{k}_2, \mathbf{k}_1) - \frac{\sqrt{3}}{2} f^1(\mathbf{k}_2, \mathbf{k}_1) \quad (15)$$

$$F^1(\mathbf{k}_1, \mathbf{k}_2) = f^1(\mathbf{k}_1, \mathbf{k}_2) + \frac{1}{2} f^1(\mathbf{k}_2, \mathbf{k}_1) - \frac{\sqrt{3}}{2} f^0(\mathbf{k}_2, \mathbf{k}_1) \quad (16)$$

While the above expressions were specifically derived for equally shared energies ($k_1 = k_2$), they can also be used for the asymmetric case.