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Generalizations of the R-Matrix Method to the Treatment of the Interaction of Short Pulse Electromagnetic Radiation with Atoms

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1 **Abstract:** Since its initial development in the 1970's by Phil Burke and his collaborators, the
2 R-matrix theory and associated computer codes have become the *de facto* approach for the cal-
3 culation of accurate data for general electron-atom/ion/molecule collision and photoionization
4 processes. The use of a non-orthonormal set of orbitals based on B-splines, now called the B-spline
5 R-matrix (BSR) approach, was pioneered by Zatsarinny. It has considerably extended the flexibility
6 of the approach and improved particularly the treatment of complex many-electron atomic and
7 ionic targets, for which accurate data are needed in many modelling applications for processes
8 involving low-temperature plasmas. Both the original R-matrix approach and the BSR method
9 have been extended to the interaction of short, intense electromagnetic (EM) radiation with atoms
10 and molecules. Here we provide an overview of the theoretical tools that were required to facilitate
11 the extension of the theory to the time domain. As an example of a practical application, we show
12 results for two-photon ionization of argon by intense short-pulse extreme ultraviolet radiation.

13 **Keywords:** B-spline R-matrix, R-matrix with time dependence, intense short-pulse extreme ultra-
14 violet radiation, time-dependent Schrödinger equation; Arnoldi-Lanczos propagation

15 **1. Introduction**

16   The evolution of R-matrix theory from a useful but largely phenomenological ap-
17 proach for the description of nuclear resonances [1,2] to an accurate computational
18 method in atomic physics in the 1970's is primarily due to Phil Burke and his col-
19 laborators at The Queen's University of Belfast [3–6]. The refinement of the original
20 theory to include long-range interactions and the associated computer codes have
21 become the *de facto* approach for the calculation of accurate data for general electron-
22 atom/ion/molecule collision and photoionization processes in general and cross sections
23 in particular. These data are needed for many modeling applications for processes in-
24 volving low-temperature plasmas, in addition to providing critical insights into how
25 electrons and photons interact with atomic systems. The atomic R-matrix methods were
26 subsequently extended to the study of electron-molecule collisions [7–9] and ultimately
27 led to the now widely used UKRmol+ package [10].

28   A significant advance in the practical use of the R-matrix method was made by
29 Oleg Zatsarinny when he introduced a non-orthogonal (NO) basis set representation of
30 the wavefunction using B-splines. The B-spline R-matrix (BSR) approach [11,12] is based
31 on an idea that had been very successfully introduced into atomic structure calculations
32 by Charlotte Froese Fischer [13].

33   Oleg pioneered using non-orthogonal sets of orbitals in the R-matrix method and
34 showed that by using a flexible radial B-spline basis, it was possible to greatly improve

the accuracy of the calculated results. The NO basis enables the efficient incorporation of correlation into the atomic expansion, using individually optimized, i.e., term-dependent one-electron orbitals. The B-splines provide a very accurate description of the atomic bound and continuum orbitals, together with excellent and well-studied numerical properties. B-splines as the primitive numerical basis, together with their use to expand the non-orthogonal set of physical and pseudo-orbitals in them, provide a potent mix that may improve significantly on the standard versions of the atomic R-matrix codes.

Recently, the finite-difference representation of the orbitals in the well-known atomic code [14] has indeed been replaced by B-splines [15]. At this point, however, the individual orbitals expanded in this basis are still assumed to be orthogonal, thereby limiting their flexibility to represent the generally existing term dependence. In principle, of course, this term dependence can be represented in large configuration-interaction expansions, as done very successfully in the convergent close-coupling (CCC) [16] and R-matrix with pseudo-states (RMPS) [17] formulations. Hence, while nonorthogonal orbital sets are not an advantage *per se* in the general formulation of close-coupling theory, they can be highly beneficial in reducing the required size of the expansion in practical applications. Undoubtedly, they come with their own challenges, which is the main reason they tend not to be used in collision problems, where both the N-electron target and the $(N + 1)$-electron collision problem need to be handled at a comparable and consistent level of sophistication. A significant difference between atomic and molecular structure calculations and those involving scattering is that the former more commonly employ methodologies that optimize orbitals for specific states. In studying dynamical systems where there is a strong interplay between neutral, excited and ionic states, this is far greater challenge.

The BSR method has been demonstrated to be capable of computing highly accurate electron-collision and photoionization amplitudes and cross sections for complex atomic and ionic targets. There are now non-relativistic, semi-relativistic (Breit-Pauli), and full-relativistic (Dirac-Coulomb) versions. In some cases, the BSR calculations were shown to be more accurate than the available experimental data, and sometimes the calculations suggested strong evidence of problems with existing experimental data that were later corrected by newer experiments. For just one such example, see Ren *et al.* [18].

Around 2006-2007, it became clear that input from BSR calculations could be used to treat the interaction of intense laser radiation with complex atoms such as Ne [19] and Ar [20]. All the key ingredients were available; namely, the Hamiltonian matrix and the dipole length and/or velocity matrix elements required for the coupling of the target system to the external EM field. Since these could be "easily" extracted from the BSR code, this would provide a general *ab initio* and non-perturbative treatment to the problem that goes beyond quasi-one-electron or quasi-two-electron models.

The only other required ingredient is an efficient method to propagate the time-dependent wavefunction and a way to extract the information from that wavefunction at long times, when i) the external field has died down and ii) a possibly ejected electron has moved sufficiently far away from the target center. Schneider, Bartschat, and Guan had been working on the numerical propagation techniques using the short iterative Lanczos (SIL) method, and they convinced Oleg that using his BSR matrix elements would be a very useful contribution to atomic physics. The four of us combined our talents to examine the multi-photon, single-ionization of Ne and Ar, which are significantly more challenging targets than He for this process. Eventually, the method that we hereafter term TDBSR, was generalized to treat two-photon, double ionization of He [21,22]. The late Cliff Noble also joined the group and was instrumental in parallelizing the codes we had developed. With the addition of Johannes Feist, we later examined the question of time delays in the photoionization of Ne [23].

The generalization of the Belfast R-matrix method to treat arbitrary time-dependent EM fields actually goes much further back to a paper written by Phil and Valerie Burke in 1997 [24]. Subsequent theoretical [25] developments lead to the generation of the

89 Time-Dependent R-matrix method (TDRM) [26], which used a B-spline basis approach
90 in the R-matrix inner region. Combining this with an outer region based on the finite
91 difference techniques used in the HELIUM code [27] led to the first incarnation of the
92 R-matrix with time dependence method (RMT) [28] in 2011. Since then the code has
93 undergone extensive redevelopment, with extensions to treat arbitrary light fields [29],
94 molecular targets [30], and spin-orbit interaction using input from the RMATRX-I suite
95 of codes [31], and improvements to the parallelization scheme [32]. It is still under active
96 development by researchers located mostly in the UK.

97   Both the BSR code and the RMT suite are available from a number of sources, such
98 as Computer Physics Communications [11,32] and designated github sites [33,34]. A
99 good place to start with these and other codes in this field is the Atomic, Molecular, and
100 Optical Sciences (AMOS) Gateway [35].

101   In this contribution, we take the opportunity to examine and contrast how the
102 TDBSR and RMT methods are structured today. Specifically, we highlight the contribu-
103 tions of the collaboration between Schneider at NIST and the Bartschat group at Drake
104 University to this topic. The basic ideas are outlined in Section 2. As one representative
105 example, we compare the TDBSR and RMT results for two-photon ionization of Ar
106 atoms by an intense short-pulse extreme ultraviolet (XUV) laser field in Section 3. We
107 finish in Section 4 with a summary and an outlook to suggest that a very worthwhile
108 long-term goal is the unification or at least the interoperability of the two codes through
109 the development of an appropriate interface.

110 **2. Solving the TDSE via the R-Matrix Method**

The general solution of the time-dependent Schrödinger equation (TDSE) in the internal R-matrix region is

$$[i\frac{\partial}{\partial t} - \mathcal{K}(\mathbf{X}_{N+1}) - \mathcal{D}(\mathbf{X}_{N+1}, t)]|\Psi(\mathbf{X}_{N+1}, t)\rangle = -\mathcal{L}|\Psi(\mathbf{X}_{N+1}, t)\rangle ; \quad (1a)$$

$$\mathcal{K}(\mathbf{X}_{N+1}) = \mathcal{H}(\mathbf{X}_{N+1}) + \mathcal{L} ; \quad (1b)$$

$$\mathcal{L} = \sum_{\alpha} L_{\alpha} ; \quad (1c)$$

$$L_{\alpha} = \frac{1}{2}\sum_{i} |\phi_{\alpha}(\mathbf{X}_N)\rangle \delta(r_i - R_0)[\frac{\partial}{\partial r_i} - b]\langle\phi_{\alpha}(\mathbf{X}'_N)|. \quad (1d)$$

where $\mathbf{X}_q = [\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3 \ldots, \mathbf{x}_q]$ and $\mathbf{x}_i = \mathbf{r}_i\sigma_i$ represents the space and spin coordinates of electron i. Here $\mathcal{K}(\mathbf{X}_{N+1})$ is the time-independent Hamiltonian, $\mathcal{D}(\mathbf{X}_{N+1}, t)$ represents the interaction of the system with the EM field, $\mathcal{L}$ is the Bloch operator, and $\mathbf{X}_{N+1}$ is used to label the entire set of $(N + 1)$ internal coordinates of the system. The states $|\phi_c\rangle$ that are being summed over in Eq. (1c) are the channel functions that are non-zero at the R-matrix boundary R_0. Their definition depends on how asymptotically exact quantum states are constructed as the interaction between the target and projectile approaches zero. Once that choice has been made, those parts of the wavefunction involving the internal coordinates $\mathbf{X}_N$ of the target and the projectile can be coupled to form the channel functions, and those can be projected out of the calculation leaving only the

wavefunction in the relative coordinate r in the asymptotic region to be determined. In the external region, therefore, we have a time-dependent one-electron problem:

$$[i\frac{\partial}{\partial t} - \mathbf{h}(r) - \mathbf{d}(r,t)]\mathbf{f}(r,t) = \mathbf{L}\mathbf{f}(r,t); \tag{2a}$$

$$\mathbf{h}(r) + \mathbf{d}(r,t) = \begin{pmatrix} h_{1,1}(r,t) & h_{1,2}(r,t) & h_{1,3}(r,t) & \cdots & h_{1,n}(r,t) \\ h_{2,1}(r,t) & h_{2,2(r,t)} & h_{2,3}(r,t) & \cdots & h_{2,n}(r,t) \\ h_{3,1}(r,t) & h_{3,2(r,t)} & h_{3,3}(r,t) & \cdots & h_{3,n}(r,t) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ h_{n,1}(r,t) & h_{n,2}(r,t) & h_{n,3}(r,t) & \cdots & h_{n,n}(r,t) \end{pmatrix}; \tag{2b}$$

$$\mathbf{f}(r,t) = \begin{pmatrix} f_1(r,t) \\ f_2(r,t) \\ f_3(r,t) \\ \vdots \\ f_n(r,t) \end{pmatrix}; \tag{2c}$$

$$h_{i,j}(r,t) = -\frac{1}{2}\frac{d^2}{dr^2} + \frac{l_\alpha(l_\alpha+1)}{2} + v_{\alpha,\beta}(r) + d_{\alpha,\beta}(r,t). \tag{2d}$$

111 The bold-faced notation represents matrices and vectors in the channel space. The
112 explicit inclusion of the Bloch operator in both the internal and external region is done
113 to emphasize that it is this term that couples the two regions. Note that it is entirely
114 independent of the specific numerical method used to solve the set of equations in the
115 two regions. In the current implementation of RMT [32], a five-point finite difference
116 (FD) is used to represent the first and second derivatives.

Since the value of the logarithmic derivative to the solution to the TDSE in the inner and outer region must be the same at R_0,

$$[\frac{\partial}{\partial r} - b](\psi_\alpha|\Psi(\mathbf{X}_{N+1},t))|_{r=R_0} = [\frac{\partial}{\partial r} - b]f_\alpha(r,t)|_{r=R_0};$$
$$(\psi_\alpha|\Psi(\mathbf{X}_{N+1},t))|_{r=R_0} = f_\alpha(r,t)|_{r=R_0}. \tag{3}$$

The round brackets mean integration over all degrees of freedom save r. In a somewhat unorthodox fashion, one can replace the operation of $\mathcal{L}|\Psi(\mathbf{X}_{N+1},t)\rangle$ on the right-hand side of Eq. (1a) with the values of the projected external wavefunction and, similarly, $\mathbf{L}\mathbf{f}(r,t)$ on the right-hand side of Eq. (2a) with the projected $|\Psi(\mathbf{X}_{N+1},t)\rangle$. Then there are additional coupling terms due to approximating the derivatives of $f_\alpha(r,t)$ by difference formula. At present, the formalism only treats cases where a single free electron can be explicitly in the external region. This is a restriction of the current R-matrix formalism. Removing it is a fundamental challenge. Equations (1a) and (2a) can be elegantly rewritten using the identity,

$$i\frac{\partial}{\partial t}[\exp(i\mathcal{K}(\mathbf{X}_{N+1})t)|\Psi(\mathbf{X}_{N+1},t)\rangle] =$$
$$- \mathcal{K}(\mathbf{X}_{N+1})\exp(i\mathcal{K}(\mathbf{X}_{N+1})t)|\Psi(\mathbf{X}_{N+1},t)\rangle$$
$$+ \exp(i\mathcal{K}(\mathbf{X}_{N+1})t)i\frac{\partial}{\partial t}|\Psi(\mathbf{X}_{N+1},t)\rangle \tag{4}$$

and then integrating between t_0 and t to obtain

$$|\Psi(\mathbf{X}_{N+1},t)\rangle = \exp(-i\mathcal{K}(\mathbf{X}_{N+1})(t-t_0))|\Psi(\mathbf{X}_{N+1},t_0)\rangle$$
$$-i\exp(-i\mathcal{K}(\mathbf{X}_{N+1})t)\int_{t_0}^t dt' \exp(i\mathcal{K}(\mathbf{X}_{N+1})t')[\mathcal{D}(\mathbf{X}_{N+1},t') - \mathcal{L}]|\Psi(X_{N+1},t')\rangle. \tag{5}$$

117 The same can be done for Eq. (2a), replacing $\mathcal{K}(\mathbf{X}_{N+1})$ and $\mathcal{D}(\mathbf{X}_{N+1}, t)$ by $\mathbf{h}(r)$ and
118 $\mathbf{d}(r, t)$. It is always possible to add to $\mathcal{K}(\mathbf{X}_{N+1})$ and subtract from $\mathcal{D}(\mathbf{X}_{N+1}, t)$ any
119 time-independent operator without changing the form of Eq. (5). A customary and
120 advantageous choice is to use the value of $\mathcal{D}(\mathbf{X}_{N+1}, t_m)$, where t_m is the midpoint of
121 the integration interval. By doing that, we may re-interpret the values of $\mathcal{K}(\mathbf{X}_{N+1})$ and
122 $\mathcal{D}(\mathbf{X}_{N+1}, t)$ to reflect that addition and subtraction.

123 The short iterative Lanczos (SIL) or Arnoldi method is directly employed in both
124 the inner and outer region to evaluate the action of the matrix exponential on the vector
125 known from the previous time step. Turning to the second term, for sufficiently short
126 times only the part in the integral involving the Bloch operator contributes. This can be
127 justified by noting that the term involving $\mathcal{D}(\mathbf{X}_{N+1}, t)$ would vanish if the integration
128 was performed using the midpoint rule for sufficiently small time intervals.

129 To evaluate the term involving the Bloch operator, the suggested procedure is to
130 expand $\mathcal{L}|\Psi(\mathbf{r}, t)\rangle$ in a power series and then evaluate the integral between t_0 and t
131 involving the exponential operator. It can be demonstrated that these terms may also
132 be computed using a modification of the SIL suggested by Saad [36]. A further sim-
133 plification is to use the external-region Hamiltonian rather than the internal-region
134 Hamiltonian and the already computed outer-region vector to make that procedure even
135 more computationally efficient. One thing to notice is that the integral involving the
136 Bloch operator as well as the finite-difference operator contains information from points
137 that are shared between the outer and inner regions. This requires some updating or
138 iteration of that information at each time step.

139 For the remaining discussion, we assume that the short-time approximation is valid.
140 There are separate investigations underway to remove this approximation, but those are
141 beyond the scope of the present paper. However, it emerges from the above derivation
142 that the accuracy of an n-step SIL or Arnoldi propagation is *not* proportional to the nth
143 power of the step size for a time-dependent potential. The formal accuracy of the method
144 is clearly second order, as follows from the midpoint formula.

145 Before concluding this section, some comments on the actual application of the
146 two time-dependent R-matrix approaches is in order. The RMT grew out of a many-
147 decades effort by Phil Burke and his collaborators to provide high-quality software for
148 the solution of a broad class of problems in atomic and molecular physics. One should
149 not underestimate the perseverance and dedication of all those scientists to develop
150 the R-matrix software, which is now being used by researchers all over the world. In
151 contrast, the BSR code was essentially due to a single individual, Oleg Zatsarinny. It
152 was Oleg who maintained and added features to the code over a couple of decades. The
153 Drake University / NIST effort to produce a code based on BSR to treat the interaction
154 of EM radiation with atoms was neither planned for the long term nor was it initiated
155 by Oleg himself. Nevertheless, Oleg was always helpful and did his best to enable the
156 effort to move forward.

157 At the time, those of us interested in a TDBSR wanted to get out proof-of-principle
158 results quickly and only later worry about questions of efficiency. The SIL had already
159 been very successfully employed using a finite-element discrete-variable representation
160 (FEDVR) approach in atomic He. While this approach could be generalized to more than
161 two-electron systems, already having at our disposal the necessary ingredients from the
162 BSR code enabled us to quickly study systems such as Ne and Ar. The idea was simple:
163 take the field-free Hamiltonian and dipole matrices from the time-independent BSR
164 calculations and propagate the initial bound state (also given by BSR as the initial vector)
165 using the SIL. No attention was paid to an internal and external region. The R-matrix
166 box was taken to be sufficiently large, so that after the SIL propagation we could already
167 project onto asymptotic states.

3. Example Results

Figure 1 shows one example of a comparison between the previous TDBSR [19] and new RMT calculations performed for the present paper. As expected, the agreement between the two sets of predictions is excellent, as is the agreement with the Floquet results of McKenna and van der Hart [37]. The latter, of course, are effectively a steady-state approach, i.e., the natural width of the window resonances and the effect of the intermediate $(3p^54s)^1P$ state, which acts as a stepping stone, are fully resolved. In the calculations with a finite-length pulse, on the other hand, the pulse width enters as well and smears out some of the sharp structures.
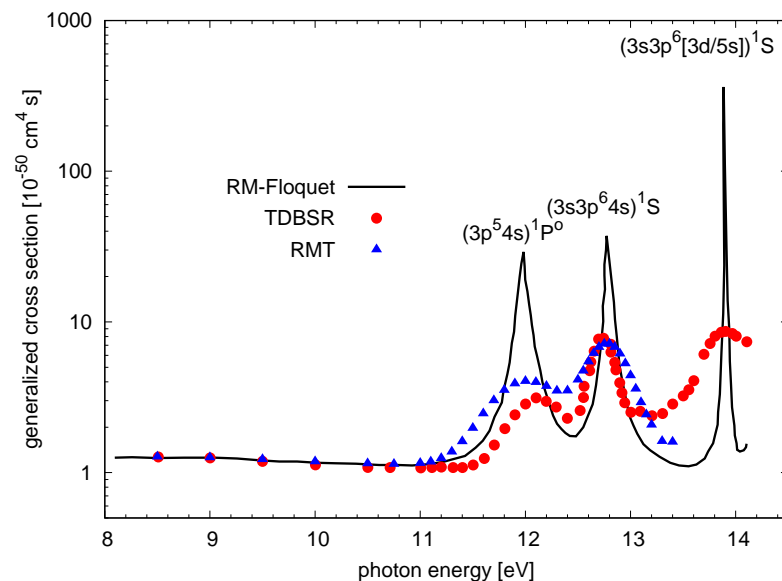

Figure 1. Generalized cross section for two-photon ionization of $Ar(3p^6)^1S$ as a function of photon energy. A 30-cycle laser pulse with a sine-squared field envelope and a peak intensity of 10^{12} W/cm^2 was used in the calculations. The Floquet results of McKenna and van der Hart [37] are compared with those from the previous TDBSR [19] and the current RMT calculations.

The remaining small disagreement between the TDBSR and the RMT results is due to the differences in the respective structure descriptions. Both the Floquet and the RMT results were obtained with the structure description developed by Burke and Taylor [38], who designed pseudo-orbitals to account for the strong term dependence of the 3s and 3p orbitals in the neutral $(3s^23p^6)^1S$ ground state as well the coupled final ionic $(3s^23p^5)^2P$ and $(3s3p^6)^2S$ states. This was particularly important to obtain accurate ionization potentials as well as the position (i.e., the excitation energy) of the intermediate $(3p^54s)^1P$ state. No such special effort was devoted to this issue in the TDBSR calculations, but apparently a sufficient number of short-range orbitals were included in this case to obtain accurate results. This is definitely a topic that BSR, in principle, can handle extremely well. On the other hand, if only the bare minimum of orbitals is included, problems can arise. An example is depicted in Fig. 4 of Guan *et al.* [19] in a similar calculation for two-photon ionization of $Ne(2p^6)^1S$. In that very first TDBSR calculation, the ionization potential is too small, i.e., the ground state lies too high, and hence the theoretical excitation energy of the $(2p^53s)^1P$ state is too small.

4. Summary and Outlook

In this contribution, we revisited some of the early work on the extension of the R-matrix (close-coupling) method, which was originally designed to treat – accurately and efficiently – electron and photon collisions with atoms, ions, and molecules in a steady-state scenario, to include the reaction of these targets to short-pulse intense electromagnetic radiation in a time-dependent framework. While the RMT code of

198 the Belfast group has now been interfaced with both their atomic/ionic and molecular
199 codes, we are currently working on interfacing the package with Oleg Zatsarinny's
200 suite of BSR programs. The interface will take full advantage of the BSR approach for
201 complex targets by allowing multiple orbitals with the same nodal structure (i.e., a
202 non-orthogonal physical basis) to describe term-dependence and correlation effects with
203 relatively compact configuration expansions. If the success of the BSR method for the
204 steady-case scenarios is any indication of likely future success, there is every reason to
205 expect BSR+RMT to be another major step forward.

206 The authors have had significant interactions with Oleg Zatsarinny for a number
207 of years. For details, interested readers are referred to the "Memories" contribution to
208 this Special Issue in Oleg's honor [39]. We hope that the BSR+RMT development will
209 contribute to ensure Oleg's legacy for many years to come.

210 **Author Contributions:** The project was conceived by BIS who also wrote the intial draft. The
211 RMT calculations were performed by KRH. All authors prepared and agreed to the final version
212 of this manuscript.

218 **Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the
219 design of the study; in the collection, analyses, or interpretation of data; in the writing of the
220 manuscript, or in the decision to publish the results.

Abbreviations

222 The following abbreviations are used in this manuscript:

TDSE	time-Dependent Schrödinger Equation
BSR	B-Spline R-Matrix
RMT	R-Matrix with Time Dependence
TDBSR	Time-Dependent B-Spline R-matrix
SIL	Short Iterative Lanczos
XUV	Extreme Ultraviolet

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