Multichannel single center method

Nikolay M Novikovskiy\textsuperscript{1,2}, Anton N Artemyev\textsuperscript{1}, Dmitrii V Rezvan\textsuperscript{1}, Boris M Lagutin\textsuperscript{3} and Philipp V Demekhin\textsuperscript{1,\ast}

\textsuperscript{1} Institut für Physik und CINSaT, Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany
\textsuperscript{2} Institute of Physics, Southern Federal University, 344090 Rostov-on-Don, Russia
\textsuperscript{3} Rostov State Transport University, 344038 Rostov-on-Don, Russia

E-mail: demekhin@physik.uni-kassel.de

Received 15 May 2022, revised 4 July 2022
Accepted for publication 7 July 2022
Published 10 August 2022

Abstract

A multichannel single center (MCSC) method for the theoretical description of the electron continuum spectrum in molecules is reported. The method includes coupling between different continuum channels via electron correlations and describes, thereby, photoelectron continuum in the Tamm–Dancoff (configuration interaction singles) approximation. Basic equations of the non-iterative one-channel single center (SC) method and their extension to the MCSC method are presented, and an efficient scheme for their numerical solution is outlined. The method is tested on known illustrative examples of the Ar 3s\textsuperscript{−}, HCl 4σ\textsuperscript{−} and N\textsubscript{2} 1σ\textsuperscript{−} photoionization processes, where inter-channel coupling plays a very important role. Unlike our previous SC studies, the present MCSC method can be reliably applied to photoionization of outer and valence molecular orbitals, where inter-channel correlations in the continuum might be relevant.

Keywords: computational and mathematical techniques in atomic and molecular physics, photon interactions with molecules, photoionization and photodetachment

(Some figures may appear in colour only in the online journal)

1. Introduction

Theoretical description of the electron continuum spectrum in molecules is a nontrivial task, which is difficult to solve with standard quantum chemistry methods implementing basis orbitals localized on atomic centers. Therefore, in the last decades, many comprehensive theoretical and computational approaches to solve the electron-continuum problem in molecules were developed. Just to mention a few currently used methods: Stieltjes imaging techniques [1–4]; different scattering [5–8], multichannel Schwinger [9–12], and R-matrix [13–17] methods; random phase approximation with exchange (RPAE) for diatomic molecules [18–22]; density functional theory [23, 24] (DFT) or time-dependent density functional theory [25–29] (TDDFT) B-spline LCAO formalisms; continuum multiple scattering method (CMS-X\textsubscript{α}) with local exchange correlation [30–32]; single center (SC) method [33–38]; and other approaches.

Some of the available methods [5–8, 30–37] describe the electron continuum in one-channel approximation, where the photoelectron leaves a system in the well-defined ionic state. Thereby, correlations of the photoelectron with electrons in the ionic core are neglected. A prominent example of such correlations is the so-called inter-channel interaction, where two continuum channels are coupled via an electron-electron interaction. A physical picture behind this effect is as follows: a photoelectron emitted from one bound orbital knocks-out electron from another bound orbital being itself recaptured to the original one. In many cases, it is impossible to satisfactorily describe a near-threshold region of the photoionization cross section without accounting for the inter-channel interaction [39, 40].

In the photoionization of atoms, importance of the inter-channel coupling was first predicted theoretically [41, 42] and then verified experimentally [43–46]. It resulted in a near-threshold correlation minimum in the 3s-photoionization cross...
section of Ar, which emerges owing to the inter-channel coupling between the 3s- and 3p-photoionization channels \([13, 41, 42, 47]\). Similar effect of the inter-channel coupling (between the 4s-, 5s-, and 2p-photoionization continua) was also found in the 4e-photoionization of HCl molecule \([48, 49]\). The effect is present not only in the outer-shell photoionization, but also in the inner-shell photoionization of molecules \([19, 20]\). As predicted in those works, coupling between the 1\(\sigma_g\) and 1\(\sigma_u\) channels shares a near-threshold shape-resonance between the two partial channels, while without coupling it is present only in the 1\(\sigma_g\) channel.

The methods which enable accounting for the inter-channel correlations can be conveniently grouped in two classes. The post-coupling methods, such as, e.g., different realizations of the RPAE \([18–22, 50–53]\) or K-matrix theory \([53–55]\), couple photoelectron continua obtained in the one-channel approximation. On the contrary, the pre-coupling methods, such as, e.g., multichannel Schwinger \([9–12]\) and R-matrix \([13–16]\) methods, or different realizations of the multichannel multi-configuration interaction methods \([56–58]\), focus on the direct calculation of the multichannel photoelectron continuum wave functions. However, most of those methods are restricted to atoms, and less \([9–16, 18–22]\) in molecules.

As predicted in those works, coupling between the 1\(\sigma_g\)–5\(\pi\)-photoionization continua \([19, 20]\) is present not only in the outer-shell photoionization, but also in the inner-shell photoionization of molecules \([19, 20]\). Below, we outline the one-channel SC method. According to the method, the spatial part of the one-particle molecular orbital with a kinetic energy \(\varepsilon\) is represented with respect to a molecular center as an expansion over spherical harmonics \(Y_{lm}\) with a given projection \(m\) of the angular momentum \(\ell\) on the quantization \(z\)-axis \([36, 37]\):

\[
\Psi_c(r) = \sum_{lm} \frac{P_{c,lm}(r)}{r} Y_{lm}(\theta, \varphi),
\]

where \(\{r, \theta, \varphi\}\) are spherical coordinates. In the one-channel approximation, the variational principle yields the following system of coupled inhomogeneous Hartree–Fock equations for the radial partial waves \(P_{c,lm}(r)\) of the photoelectron in continuum \([36, 37]\) (atomic units are used throughout):

\[
\frac{d^2 P_{c,lm}(r)}{dr^2} = \sum_{l'm'} \left[ \frac{(\ell\ell' + 1) - 2\varepsilon}{r^2} \delta_{\ell\ell'} \delta_{mm'} + 2V_{lm}^{\sigma}(r) + 2V_{lm'}^{\sigma}(r) \right] P_{c,l'm'}(r) + \sum_{c} 2b_c \\
\times \sum_{kq} \sum_{l'l'c} (-1)^{l'c} \sqrt{(2\ell' + 1)(2\ell' + 1)} Y_{kq}(\varepsilon, \Psi_c, \Psi_c) Y_{l'l'}(\varepsilon, \Psi_c, \Psi_c) \times P_{c,l'l'c},
\]

with the following normalization condition for a positive photoelectron kinetic energy \(\varepsilon > 0\):

\[
\sum_{lm} \langle P_{c,lm} | P_{c',lm} \rangle = \delta(\varepsilon - \varepsilon').
\]

In the system of equation (2), the nuclear–electron interaction potential is given as

\[
V_{lm}^{\sigma} = - \sum_{a} Z_a \sum_{kq} (-1)^{l} \sqrt{(2\ell + 1)(2\ell' + 1)} \times \left( \begin{array}{ccc} \ell & k & \ell' \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} \ell & k & \ell' \\ -m & q & m' \end{array} \right) \times \sqrt{4\pi} \frac{Y_{kq}(\theta_n, \phi_n)}{r_0^{\ell+1}},
\]

where \(r_c = \min(r, R_c)\), \(r_0 = \max(r, R_c)\), and \(R_c, \theta_n, \phi_n\) are the spherical coordinates of the nucleus \(n\) with charge \(Z_n\). The potential describing the direct electrostatic Coulomb interaction \(J_{lm}^{\sigma}\) between the photoelectron \(\Psi_c\) and all electrons in the molecular orbitals \(\Psi_c\) bound to the ion reads:
\[
\begin{align*}
  r_{\text{ion}m'}^c &= \sum_c a_c \sum_{\ell,m_c} \sum_{\ell',m'_c} (-1)^{\ell_c + \ell'_c} \\
  &\times (2\ell_c + 1)(2\ell'_c + 1)(2\ell + 1)(2\ell' + 1) \\
  &\times \left( \ell_c \; k \; \ell'_c \right) \left( \ell_c \; k \; \ell'_c \right) \\
  &\times \left( \ell' \; k \; \ell \right) \left( \ell' \; k \; \ell \right) \\
  &\times \sqrt{r_{c}} \left( \ell_c \; m_c \; \ell'_c \; m'_c \right).
\end{align*}
\]

Here, \( a_c \) are coefficients for the direct Coulomb interactions, which are determined by the electronic configuration formed by the photoelectron and the ionic core electrons, and \( y_{l_c}(\ell_c, m_c, \ell'_c, m'_c) \) are the partial harmonics of the Coulomb potential defined as
\[
y_l(\ell, m, \ell', m') = \int_0^\infty \frac{r'^2}{r^2} P_{l,m}(r')P_{l',m'}(r') dr'.
\]

with \( r_c = \min(r, r') \) and \( r_c' = \max(r, r') \).

The last term on the right-hand side of equation (2) with respective coefficients \( b_c \) represents the exchange Coulomb interaction of the photoelectron and all bound electrons (the two lower lines in the equation). Because of its non-locality, the system of equation (2) is inhomogeneous, which usually implies iterative solution schemes. This term contains generalized potentials \( Y_{l}(\Psi_c, \Psi_c) \), which represent harmonics of the multiplicity \( k_q \) of the exchange interaction of the photoelectron \( \Psi_c \) with the core electron \( \Psi_c \), and explicitly read [36]:
\[
Y_{l}(\Psi_c, \Psi_c) = \sum_{\ell,m} \sum_{\ell',m'} (-1)^{m_c} \sqrt{2\ell_c + 1}(2\ell' + 1) \\
\times \left( \ell_c \; k \; \ell' \right) \left( \ell_c \; k \; \ell' \right) \\
\times \left( \ell' \; k \; \ell \right) \left( \ell' \; k \; \ell \right) \\
\times r \cdot y_{l}(\ell_c, m_c, \ell'_c, m'_c).
\]

It is straightforward to show [71] that the generalized exchange potentials (7) satisfy the following differential equation of the second order:
\[
\frac{d^2 Y_{l}(\Psi_c, \Psi_c)}{dr^2} = F_{l}(\Psi_c, \Psi_c),
\]

satisfies the following homogeneous system of coupled differential equations of the second order:
\[
\frac{d^2 \Psi}{dr^2} = \hat{F} \Psi
\]

with the quadratic matrix
\[
\hat{F} = \begin{pmatrix} F_{l}(\Psi_c, \Psi_c) & F_{l}(\Psi_c, \Psi_c) \\ F_{l}(\Psi_c, \Psi_c) & F_{l}(\Psi_c, \Psi_c) \end{pmatrix},
\]

The matrix elements of \( \hat{F} \) are given by [36, 37]:
\[
F_{l}(\Psi_c, \Psi_c) = \frac{2\hbar}{r} \sum_{\ell,m} (-1)^{m_c} \sqrt{2\ell_c + 1}(2\ell' + 1) \\
\times \left( \ell_c \; k \; \ell' \right) \left( \ell_c \; k \; \ell' \right) \\
\times \left( \ell' \; k \; \ell \right) \left( \ell' \; k \; \ell \right) \left( \ell \; m \; \ell' \right) \left( \ell \; m \; \ell' \right)
\]

One can see that the system of equation (2) for the radial partial photoelectron waves \( P_{l,m}(r) \) and equation (8) for the generalized exchange potentials \( Y_{l}(\Psi_c, \Psi_c) = Y_{l}(r) \) are coupled to each other. As a consequence, the combined vector solution \( \Psi(r) \)
\[
\Psi = \begin{pmatrix} P_{l,m} \\ Y_{l} \end{pmatrix}
\]

satisfies the following homogeneous system of coupled differential equations of the second order:
\[
\frac{d^2 \Psi}{dr^2} = \hat{F} \Psi
\]

3. Multichannel single center method

We now go beyond the one-channel HF approximation for the photoelectron in continuum and introduce the MCSC method. Let us, for simplicity, consider an electronic configuration of a molecule with two doubly-occupied molecular orbitals \( a^2b^2 \) (extension of the theory to more coupled channels is straightforward). Both orbitals can be ionized, creating at a given total energy two continuum channels of similar symmetries and multiplicities:
\[
\Psi_{\text{ion}} = \left| a^2b^2 \right| e',
\]
\[
\Psi_{\text{ion}} = \left| a^2b^2 \right| e''.
\]
It is straightforward to show that these continuum channels are coupled via the following electron–electron Coulomb interaction matrix element
\[
\langle \psi^{(bc)} | \hat{H}^{\text{exch}} | \psi^{(ac')} \rangle = c^{\text{dir}} \left\langle a \left| \frac{1}{r_{12}} b \right| c^{\prime} \right\rangle + c^{\text{exch}} \left\langle a \left| \frac{1}{r_{12}} c^{\prime} \right| b \right\rangle, \quad (14)
\]
where, in the closed-shell case, the coefficient in front of the direct contribution is equal to \(c^{\text{dir}} = -1\) for both, singlet and triplet multiplicities of the channels, and that for the exchange contribution \(c^{\text{exch}} = 2\) for the singlet or \(c^{\text{exch}} = 0\) for the triplet multiplicities.

Applying the variational principle, one can derive coupled differential equations for the unified vector solution (9) of each channel in (13). Those solutions are designated below as \(\tilde{\pi}^{(bc)}\) and \(\tilde{\pi}^{(ac')}\). For each channel, this system resembles equation (10) from the one-channel SC method. However, because of the inter-channel interaction (14), the two systems of equations are coupled to each other by the direct and exchange contributions. If one combines the solutions for two channels in a single vector
\[
\tilde{\mathbf{F}} = \begin{pmatrix} \tilde{\pi}^{(bc)} \\ \tilde{\pi}^{(ac')} \end{pmatrix}, \quad (15)
\]
one arrives at the system of coupled homogeneous differential equations of the second order, which is similar to that solved in the one-channel SC method (equation (10)):
\[
\frac{d^2 \tilde{\mathbf{F}}}{dr^2} = \mathbf{H} \tilde{\mathbf{F}}, \quad (16)
\]
The respective quadratic matrix \(\mathbf{H}\) can be constructed from the one-particle matrices \(\tilde{\mathbf{F}}^{(bc)}\) and \(\tilde{\mathbf{F}}^{(ac')}\) of the two independent channels as follows
\[
\mathbf{H} = \begin{pmatrix} \{ \tilde{\mathbf{F}}^{(bc)} \} & F^{(bc') \text{lmbq}} \\ F^{(bc') \text{lmml}} & \{ \tilde{\mathbf{F}}^{(ac')} \} \end{pmatrix}, \quad (17)
\]
The matrix elements of the one-channel matrices \(\tilde{\mathbf{F}}^{(bc)}\) and \(\tilde{\mathbf{F}}^{(ac')}\) in the diagonal of \(\mathbf{H}\) are defined in equations (11)–(12d).

The non-diagonal matrix elements represent the direct \(F^{(bc') \text{lmbq}}\) and \(F^{(ac') \text{lmml}}\), as well as exchange \(F^{(bc') \text{lmbq}}\) and \(F^{(ac') \text{lmml}}\), contributions of the inter-channel coupling (14). Their explicit expressions read:
\[
F^{(bc') \text{lmbq}} = 2c^{\text{dir}} \sum_{\ell_a m_a \ell'_b m'_b} \sum_{k q} (-1)^{m_a + m'_b} \times \\
\sqrt{(2\ell + 1)(2\ell' + 1)(2\ell_a + 1)(2\ell'_b + 1)} \times \\
\left( \begin{array}{ccc} \ell_a & k & \ell'_b \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} -m_a & k & \ell'_b \\ 0 & 0 & 0 \end{array} \right) \times \\
y_k(\ell_a m_a, \ell'_b m'_b), \quad (18a)
\]

### 4. Applications

As mentioned in the introduction, 3s-photoionization of Ar atom is the first example of a manifestation of the inter-channel correlations in atomic photoionization [41, 42]. It is, therefore, appropriate to test the MCSC method on this example. The present calculations included the inter-channel coupling between the 3s- and 3p-photoionization continua (four coupled 3s-, 3p\(_{-z}\), 3p\(_{y}\), and 3p\(_{z}\)-channels) and were performed in two ways. In the first set of calculations, the Ar atom was placed in the center, and the SC expansions (1) of the occupied and continuum orbitals were restricted by \(\ell_c \leq 1\) and \(\ell \leq 2\), respectively. In order to simulate a molecule in the second set of calculations, the atom was shifted from the coordinate origin by +0.5 a.u. along the \(z\)-axis, and the SC expansions were extended to \(\ell_c \leq 99\) and \(\ell \leq 29\). Both sets of the present calculations yielded equal results, which are depicted in figure 1.

As one can see, the 3s-photoionization cross section of Ar, computed with accounting for the inter-channel coupling by the MCSC method (red solid curve), exhibits a correlation minimum around the photon energy of about 40 eV. This is in agreement with the previous theoretical results, obtained by the RPAE [42] and R-matrix [13] methods, and with the selected experimental results [43, 44, 46]. Note that this minimum emerges in the theoretical results at somewhat different photon energies, owing to different relative values of the 3s and 3p binding energies used in the calculations. Note also
that this minimum in the cross section is not present in the one-channel SC calculations, which neglect the inter-channel coupling (black dashed curve).

A similar correlational minimum exists in the 4σ-photoionization cross section of the argon-like HCl molecule [48, 49]. We, therefore, performed the respective MCSC calculations which account for the inter-channel coupling between the 4σ-, 2πx-, 2πy-, and 5σ-photoionization continua (analogies of the four 3s- and 3p-continua in Ar). Calculations were performed at the equilibrium internuclear distance with the CI atom being placed in the coordinate origin. The SC expansions (1) of the occupied and continuum orbitals were restricted by ℓc ≥ 99 and ℓ ≤ 29. As one can see from figure 2, the inter-channel coupling results in the appearance of the correlational minimum in the 4σ-photoionization cross section of HCl around the photon energy of about 40 eV (cf, the black dashed and red solid curves, which represent the present one-channel and multichannel calculations, respectively), which is in accord with the experiment [48] and the previous calculations [49]. Quantitative disagreement between the theory and experiment can be related to a multi-reference character of the final 4σ-ionized state [49], which was neglected in the present calculations.

We, finally, considered prominent example of manifestation of the inter-channel coupling in the inner-shell photoionization of molecules [19, 20]. To this end, we studied the 1σ-photoionization of N2 molecule (note a controversial discussion on the existence of the shape resonance in the 1σg-channel [101–103], which was finally confirmed in reference [104] experimentally and theoretically). The present calculations were performed in the relaxed-core approximation at the equilibrium internuclear distance of the neutral molecule. The molecular center was set in between the two nitrogen atoms, and the SC expansions of the occupied and continuum orbitals were restricted by ℓc ≥ 99 and ℓ ≤ 29. Results of the present calculations are depicted in figure 3, and they are in accord with the original predictions of references [19, 20] and also with the final results from reference [104] (see figure 2 in this reference for an overview of all available theoretical and experimental data). As one can see from figure 3 around the photon energy of about 420 eV, in the one-channel SC calculations, the shape resonance is present only in the partial 1σg-photoionization cross section (cf, magenta dash-dot-dotted and
violet dotted curves). After the coupling between the 1σg- and 1σu-channels is included, it emerges in both channels (cf, red dashed and blue dash-dotted curves). In the experimental total 1σ cross section [105] (circles), this shape resonance is somewhat broader than in the theory (black solid curve), which can be attributed to the effect of vibrational broadening neglected in the calculations.

5. Summary and outlook

The present work reports a further step in the development of the single center method. In its previous realization [36, 37], the method described the photoelectron continuum of the single center method. In its previous realization, the latter method relates values of the unknown vector solution only at two neighboring points.

The present work reports a further step in the development of the single center method. In its previous realization, the latter method relates values of the unknown vector solution only at two neighboring points. This development significantly broadens applicability of the method to the photoionization of outer and valence molecular orbitals, for which electron correlations in the continuum and electrons bound in the ion can be accurately accounted for. This development significantly broadens applicability of the method to the photoionization of outer and valence molecular orbitals, for which electron correlations in the continuum may play a significant role.

Acknowledgments

The authors would like to thank Victor L Sukhorukov for many valuable discussions. NMN, ANA, DVR and PhVD acknowledge support from the Deutsche Forschungsgemeinschaft (DFG)—Project No. 492619011—DE 2366/6-1. NMN acknowledges support from the Ministry of Science and Higher Education of the Russian Federation under State Task in the field of scientific activity, Project No. 0852-2020-0032 (BAS0110/20-3-081F). PhVD would like to thank the Rostov State Transport University for the hospitality during his research stay there, which was supported from traveling funds of the DFG Project DE 2366/1-2.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Appendix A. Numerical procedure

In order to solve the system of linear homogeneous differential equations of the second order (10), we employ a combination of the Numerov finite-difference and the vector sweep methods. The former method relates values of the unknown vector solution at three neighboring points as

\[ \hat{a}_{n+1} \times \mathbf{P}_{n+1} - \hat{b}_n \times \mathbf{P}_n + \hat{a}_{n-1} \times \mathbf{P}_{n-1} = O(h^6), \quad (A.1) \]

where matrices \( \hat{a} \) and \( \hat{b} \) are given by

\[ \hat{a}_n = \begin{bmatrix} \hat{E} - \frac{h^2}{12} \hat{F}_n \end{bmatrix} \quad \text{and} \quad \hat{b}_n = \begin{bmatrix} 2\hat{E} + \frac{10h^2}{12} \hat{F}_n \end{bmatrix}. \quad (A.2) \]

Here, \( h \) is a constant integration step, and \( \hat{E} \) is a unity matrix. The latter method relates values of the unknown vector solution only at two neighboring points

\[ \mathbf{T}_{n-1} = \mathbf{V}_{n-1} \times \mathbf{P}_n. \quad (A.3) \]

Substituting this relation in equation (A.1) yields the following recurrent relation for the unknown sweep matrix \( \mathbf{V}_n \):

\[ \hat{V}_n = \left( \hat{b}_n - \hat{a}_{n-1} \times \mathbf{V}_{n-1} \right)^{-1} \times \hat{a}_{n+1}. \quad (A.4) \]

Integration can be started by applying the \( \hat{V}_1 = \hat{V}_2 = \hat{V} \) boundary condition for the sweep matrix at \( r \to 0 \), which yields

\[ \hat{V} = \left( \hat{b}_2 - \hat{a}_1 \times \hat{V} \right)^{-1} \times \hat{a}_3. \quad (A.5) \]

Using now equation (A.4) allows one to find the unknown sweep matrix \( \mathbf{V}_n \) at all radial grid points.

The linearly independent solutions of the system of equation (2) satisfy at \( r \to \infty \) the following asymptotical behavior [72]:

\[ p_{LM}^{Jm}(r) = \delta_{Jm}^{J_0} \delta_{m0}^{J_0} \mathbf{P}_{LM}(r) + \mathbf{R}_{LM}^{Jm} H_{J_0}(r), \quad (A.6) \]

where \( J_0(r) \) and \( H_{J_0}(r) \) are the regular and non-regular Coulomb functions [106], respectively, \( \mathbf{R}_{LM}^{Jm} \) is the reaction matrix, and indices \( LM \) enumerate linear-independent solutions, while \( \delta \) their components. A similar condition at \( r \to \infty \) for the generalized exchange potentials, which are solutions of equation (8), reads [71]:

\[ Y_{ckq}(r) = \frac{B_{ckq}}{r}. \quad (A.7) \]

We now designate unknown values of the vector solution (9) at the last grid point \( N \) (where a short-range molecular potential vanishes) as

\[ \mathbf{P}_N^M = \begin{bmatrix} p_{LM}^{Jm}(r) \end{bmatrix}_N. \quad (A.8) \]

Applying the asymptotical conditions (A.6) and (A.7) together with the relation (A.3) to the last two points \( N \) and \( N - 1 \) of the radial grid, one can write

\[ \begin{bmatrix} \mathbf{P}_N^M \ \mathbf{R}_{LM}^{Jm} \mathbf{H}_{J_0}(r) \end{bmatrix}_N = \begin{bmatrix} \delta_{Jm}^{J_0} \delta_{m0}^{J_0} \mathbf{P}_{LM}^{Jm}(r) + \mathbf{R}_{LM}^{Jm} H_{J_0}(r) \end{bmatrix}_N. \quad (A.9) \]
Being solved for all solutions \( LM \), the system of linear equation (A.9) allows one to determine the unknown values of the radial partial waves \( \{ P_{LM} l_m \} \) and of the generalized exchange potentials \( \{ v_{lq}^{LM} \} \) in the last grid point, as well as coefficients \( B_{lq}^{LM} \) from the asymptotic relation (A.7) and the complete \( R_{LM}^{LM} \) matrix. Using now the matrix swap relation (A.3), one can reconstruct the partial photoelectron waves in the complete radial grid. The mutually-orthogonal energy-normalized partial photoelectron waves \( P_{LM}^{LM}(r) \), which contain outgoing spherical waves only in the channel with \( \ell m = LM \), can be constructed as the following linear combinations of the found solutions [54, 55]:

\[
P_{LM} = \sum_{LM'} \left( U_{LM'}^{LM} \right)^{-1} e^{-i\eta_{LM'}^M} \cos \eta_{LM'}^M \sum_{LM''} U_{LM''}^{LM'} P_{LM''},
\]

(A.10)

where \( U \) are eigenvectors of the Hermitian \( \mathcal{R} \)-matrix with real eigenvalues \( -\tan \eta \).

Using the radial parts (A.10), the dipole transition amplitudes \( A_{LMK} \) for population of the partial continua waves with energy \( \varepsilon \), angular momentum \( L \), its projection \( M \), and absorption of a photon with polarization \( K \) can now be calculated via:

\[
A_{LMK} = \sum_{L \ell} \sum_{\ell_m \ell_n} (-1)^{M'} \sqrt{(2 \ell + 1)(2 \ell - 1)} \times \left( \begin{array}{ccc} \ell & 1 & \ell_c \\ 1 & 1 & \ell_c \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} -m & K & m_c \\ 0 & 0 & 0 \end{array} \right) \times \int_0^\infty P_{LM}^{LM}(r)^* r P_{\ell_l \ell_m}(r) dr.
\]

(A.11)

Here, \( K = 0 \) represents linear and \( K = \pm 1 \) circular polarizations, \( P_{\ell_l \ell_m}(r) \) are the radial parts of the single center expansion (1) of an ionized bound orbital, and the length gauge of the dipole transition operator is used explicitly. The respective transition amplitudes provide an access to different observable quantities. For introns, the total photoionization cross section, discussed in this work, can be computed as:

\[
\sigma(\varepsilon) = \frac{4\pi^2 \alpha a_0^2 \omega}{3} \sum_{LMK} |A_{LMK}|^2,
\]

(A.12)

where \( \alpha = 1/137.036 \) is the fine structure constant, the square of the Bohr radius \( a_0^2 = 28.0028 \) Mb converts the atomic units for cross sections to megabarns \( (1 \text{ Mb} = 10^{-22} \text{ m}^2) \), and \( \omega \) is the implied photon energy.

As a final point we mention, that an accuracy of the numerical integration can be considerably improved if one introduces a new integration variable \( \rho \), which is related to the radial variable \( r \) via [36]:

\[
\rho(r) = \alpha r + \beta \ln r + \sum_n \arctan \frac{R_n - r}{\gamma_n}.
\]

(A.13)

Here, integration is performed in constant steps of \( \rho \). The second term in equation (A.13) concentrates radial grid points in the origin, while the third makes it symmetrically around all nuclei. Introducing a new vector solution

\[
\mathcal{F} = \mathcal{P} \sqrt{\rho}
\]

(A.14)

converts the system of differential equations for this solution \( \mathcal{F} \) to the form of equation (10) [36].

**ORCID iDs**

Philipp V Demekhin https://orcid.org/0000-0001-9797-6648

**References**

[1] Caravetta V, Ågren H, Valtrav O and Jensen H J A 2000 J. Chem. Phys. 113 7799
[2] Averbukh V and Cederbaum L S 2005 J. Chem. Phys. 123 204107
[3] Kolorenç, Averbukh V, Gokhberg K and Cederbaum L S 2008 J. Chem. Phys. 129 244102
[4] Averbukh V et al 2011 J. Electron Spectrosc. Relat. Phenom. 183 36
[5] Zähringer K, Meyer H-D and Cederbaum L S 1992 Phys. Rev. A 45 318
[6] Zähringer K, Meyer H-D and Cederbaum L S 1992 Phys. Rev. A 46 5643
[7] Schimmelpfennig B, Nestmann B M and Peyerimhoff S D 1995 J. Electron Spectrosc. Relat. Phenom. 74 173
[8] Hjelte et al 2005 J. Chem. Phys. 122 084306
[9] Bonhoff S, Bonhoff K, Schimmelpfennig B and Nestmann B 1997 J. Phys. B: At. Mol. Opt. Phys. 30 2821
[10] Lin P and Lucchese R R 2002 J. Chem. Phys. 116 8863
[11] Lucchese R R, Laffosse A, Brenot J C, Guyon P M, Houwer J C, Lebech M, Rassee G and Dowek D 2002 Phys. Rev. A 65 020702
[12] Jin C, Le A-T, Zhao S-F, Lucchese R R and Lin C D 2010 Phys. Rev. A 81 033421
[13] Burke P G 1978 J. Phys. Colloq. 39 C4–27
[14] Tennyson J 2010 Phys. Rep. 491 29
[15] Burke P G 2011 R-Matrix Theory of Atomic, Collisions: Application to Atomic Molecular and Optical Processes (Berlin: Springer)
[16] Harvey A G, Brambila D S, Morales F and Smirnova O 2014 J. Phys. B: At. Mol. Opt. Phys. 47 215005
[17] Maên Z, Benda J, Gorinkiel J D, Harvey A G and Tennyson J 2020 Comput. Phys. Commun. 249 10792
[18] Semenov S K, Cherepkov N A, Fecher G H and Schönheide G 2000 Phys. Rev. A 61 032704
[19] Cherepokov N A, Semenov S K, Hikosaka Y, Ito K, Motoki S and Yagishita A 2000 Phys. Rev. Lett. 84 250
[20] Semenov S K and Cherepokov N A 2002 Phys. Rev. A 66 022708
[21] Semenov S K and Cherepokov N A 2003 J. Phys. B: At. Mol. Opt. Phys. 36 1409
[22] Semenov S K, Kuznetsov V V, Cherepokov N A, Bolognesi P, Feyer V, Lahmann-Bennani A, Staica Casagrande M E and Avaldi L 2007 Phys. Rev. A 75 032707
[23] Argenti et al 2012 New J. Phys. 14 033012
[24] Toffoli D and Decleva P 2012 J. Chem. Phys. 137 134103
[25] Stener M, Fronzoni G and Decleva P 2005 J. Chem. Phys. 122 234301
[26] Mizuno T, Adachi J, Miyauchi N, Kazama M, Stener M, Decleva P and Yagishita A 2012 J. Chem. Phys. 136 074305
[98] Fehre K et al 2021 Phys. Rev. Lett. 127 103201
[99] Fehre K et al 2021 (arXiv:2101.03375)
[100] Rist J et al 2021 Nat. Commun. 12 6657
[101] Hergenhahn U, Kugeler O, Rüdel A, Rennie E E and Bradshaw A M 2001 J. Phys. Chem. A 105 5704
[102] Lin P and Lucchese R R 2002 J. Chem. Phys. 117 4348
[103] Stener M, Fronzoni G and Decleva P 2002 Chem. Phys. Lett. 351 469
[104] Semenov S K et al 2006 J. Phys. B: At. Mol. Opt. Phys. 39 375
[105] Shigemasa E, Ueda K, Sato Y, Sasaki T and Yagishita A 1992 Phys. Rev. A 45 2915
[106] Burgess A 1963 Proc. Phys. Soc. 81 442