Lanczos-based equation-of-motion coupled-cluster singles-and-doubles approach to the total photoionization cross section of valence excited states

Cabral Tenorio, Bruno Nunes; Chaer Nascimento, Marco Antonio; Rocha, Alexandre Braga; Coriani, Sonia

Published in:
Journal of Chemical Physics

Link to article, DOI:
10.1063/1.5125125

Publication date:
2019

Document Version
Peer reviewed version

Link back to DTU Orbit

Citation (APA):
Lanczos-based equation-of-motion coupled-cluster singles-and-doubles approach to the total photoionization cross section of valence excited states

Bruno Nunes Cabral Tenorio,1,a) Marco Antonio Chaer Nascimento,1 Alexandre Braga Rocha,1 and Sonia Coriani2,b)

1) Universidade Federal do Rio de Janeiro, UFRJ, Instituto de Química, Av. Athos da Silveira Ramos, 149, Rio de Janeiro - RJ, 21941-909, Brasil.

2) DTU Chemistry, Technical University of Denmark, Kemitorvet, Building 207, DK-2800 Kongens Lyngby, Denmark

(Dated: 15 October 2019)

Excitation energies and oscillator strengths of the first two electronically excited states of helium, water, sulfur dioxide, molecular nitrogen and carbon monoxide were obtained from an asymmetric-Lanczos-based formulation of the equation-of-motion (EOM) coupled cluster singles and doubles (CCSD) approach. The total photoionization cross sections were generated by two different methodologies: an analytic continuation procedure based on the Padé approximants and the Stieltjes imaging technique. The results are compared with theoretical photoionization cross sections from ADC(2) and ADC(2)-x calculations [J. Chem. Phys. 140, 184107 (2014)] and with available experimental data.

Keywords: Ionization processes, excited states, coupled cluster methods

---

a)Electronic mail: b.nunes.bruno@gmail.com
b)Electronic mail: soco@kemi.dtu.dk
EOM-CCSD photoionization

I. INTRODUCTION

In recent years we have witnessed a steady increase in the number of experimental and theoretical works focusing on the light absorption of molecules in electronically excited states. With the advent of attosecond light pulses, photons lying in the ultraviolet (UV) and X-ray spectral regions can now be employed as the probing light in pump-probe spectroscopy experiments reaching the attosecond time scale. The development of new experimental techniques to access information on transient states of atoms and molecules asks for further improvements of the theoretical methods necessary to help in the interpretation of such experiments. The photoionization cross section of transient states may supply valuable information about the electronic and nuclear structure of the molecules. The lack of the continuum asymptotic information in the electronic wave functions computed with full quadratically-integrable basis sets (also known as $L^2$ basis sets) does not allow for the calculation of phase-shifts necessary to obtain partial photoionization cross sections and angular distributions. Nonetheless, accurate calculations of total photoionization cross sections of molecules in electronically excited states may be of value to guide experimentalists in the choice of suitable candidate transient states of molecules and in the development of new experiments.

Many computational studies of the photoionization/photoabsorption cross-sections of valence and/or core electrons of atoms and molecules in their electronic ground state relying on $L^2$ basis sets have been reported employing either the well known Stieltjes imaging procedure or an analytical continued procedure based on the Padé approximants to describe the continuum part of the spectra.

As for systems in an electronic excited state, Yeager, Nascimento, and McKoy obtained, already in the seventies, the photoionization cross section of the $3S$ and $1S$ metastable states of Helium (as well as the decay rate for the $1S$ metastable state) within the random phase approximation (RPA) by using an analytical continuation procedure based on the Padé approximants. In the past few years, Averbukh and co-workers extended the algebraic diagrammatic construction (ADC)-Stieltjes-Lanczos method to photoionization of transient valence-excited states and core-excited states. Recently, Tenório et al. reported the first extension and benchmark of Lanczos-based core-valence-separated coupled cluster approaches exploiting both analytic continuation with Padé approximants and Stieltjes
EOM-CCSD photoionization Imaging as strategies to compute the inner-shell photoionization cross sections.

Herein, we derive a Lanczos-based approach, at the equation-of-motion (EOM-) coupled cluster singles and doubles (CCSD) level of theory,\textsuperscript{25–28} to compute the pseudo-spectra of valence excited states. The pseudo-spectra thus obtained are subsequently used with both the Stieltjes Imaging and the Padé analytic continuation procedures to reconstruct the photoionization cross section of transient states of the water, carbon monoxide, nitrogen, sulfur dioxide molecules and of the helium atom. The results are compared with the theoretical results of Ruberti \textit{et al.}\textsuperscript{7} at the ADC level and with the available experimental data.

II. THEORY

A. Lanczos EOM-CCSD transition strengths between excited states

Following the notation introduced in Refs. 25, 28 and 29, we write the EOM-CC transition moments, $T^{XX}_{ij}$, between an initial excited state $|i\rangle$ and a final state $|j\rangle$ for an operator (component) $X$ as

$$T^{XX}_{ij} = (L_i A^X R_j) - (L_i \xi^X)(\bar{t} \cdot R_j) - (L_i \cdot R_j)(\bar{t} \cdot \xi^X) \quad (1)$$

where $\bar{t}$ are the ground state Lagrangian multipliers, and $\xi^X$ is the CC property gradient vector for operator $X$.\textsuperscript{30} By adopting the EOM-CC expression for the transition moments, the computation of transition strengths within the asymmetric Lanczos reformulation of CC response theory (\textit{vide infra}) is facilitated, since all terms involving the $B$ matrix transformation – that is, either the response amplitudes $t^X(\omega_i - \omega_j)$ or the Lagrangian vectors $\bar{N}^{ij}(\omega_i - \omega_j)\textsuperscript{30}$ – are avoided.

Given the transition moments in Eq. (1), the transition strength $S^{XX}_{ij}$ and the oscillator strength $f_{ij}$ are then written as often done in CC response theory\textsuperscript{30,31}

$$S^{XX}_{ij} = T^{XX}_{ij} \cdot T^{XX}_{ji} \quad (2)$$

$$f_{ij} = \frac{2}{3}(\omega_j - \omega_i)(S^{XX}_{ij} + S^{YY}_{ij} + S^{ZZ}_{ij}) \quad (3)$$

Within the EOM-CC framework for pure CC models, the right and left excitation vectors and their excitation energies $(\omega_i, \omega_j)$ are the same of CC linear response,\textsuperscript{30,31} obtained as eigenvectors and eigenvalues of the CC Jacobian matrix $A$

$$L_j A = \omega_j L_j; \quad A R_j = \omega_j R_j \quad (4)$$
EOM-CCSD photoionization

under the biorthogonality condition \( L_j R_l = \delta_{jl} \). The Jacobian matrix \( A \) is defined as

\[
A_{\mu\nu} = \langle \mu | \exp(-T)[H, \tau_\nu] \exp(T) | \text{HF} \rangle \equiv \langle \mu | [H^T, \tau_\nu] | \text{HF} \rangle
\] (5)

where we also introduced the similarity transformed Hamilton operator, \( H^T = \exp(-T)X \exp(T) \).

The cluster operator \( T \) is, as usual, a sum of excitation operators, \( \tau_\mu \), each one weighted by its corresponding amplitude \( t_\mu \),

\[
T = \sum_\mu t_\mu \tau_\mu.
\]

The excited Slater determinant \( | \mu \rangle \) is generated by the excitation operator \( \tau_\mu \) out of the reference Hartree-Fock state, \( | \mu \rangle = \tau_\mu | \text{HF} \rangle \).

The EOM-CC property Jacobian matrix \( A^X \) in Eq. (1) is different from the one of CC response theory (below identified with superscript RSP), but it can be easily obtained from it with minor modifications\textsuperscript{29}

\[
A^X_{\mu\nu} = A^X_{\mu\nu}^{\text{RSP}} + \langle \mu | \tau_\nu X^T | \text{HF} \rangle (1 - \delta_{\mu\nu})
\] (6)

where the elements \( A^X_{\mu\nu}^{\text{RSP}} \) are defined as in Eq. (5), with the operator \( X \) in place of the Hamiltonian \( H \) (per definition, \( A^X_{\mu\nu}^{\text{RSP}} \) is the derivative of the CC Jacobian with respect to the strength of the perturbation \( X \)). Eq. (6) also contains the similarity-transformed operator \( X^T = \exp(-T)X \exp(T) \).

Coriani and co-workers\textsuperscript{32,33} have proposed to use an asymmetric Lanczos algorithm to solve Eq. (4), yielding a discretized spectrum covering the whole frequency range. In the algorithm, a truncated tridiagonal representation \( T \) of the Jacobian matrix \( A \) is built and then straightforwardly diagonalized. The leading size of \( T \) is the chain length \( k \ll n \), where \( n \) is the full dimension of the excitation space. The non-zero elements of the tridiagonal matrix \( T = P^T A Q \), where \( P^T Q = 1 \), are given by

\[
T_{ll} \equiv \alpha_l = p_l^T A q_l;
\]

\[
T_{l+1,l} \equiv \beta_l = \sqrt{p_{l+1}^T q_{l+1}};
\]

\[
T_{l,l+1} \equiv \gamma_l = \text{sgn}(p_{l+1}^T q_{l+1}) \beta_l
\] (7)

with

\[
q_{l+1} = \beta_l^{-1}(A q_l - \gamma_l q_{l-1} - \alpha_l q_l);
\]

\[
p_{l+1}^T = \gamma_l^{-1}(p_l^T A - \beta_l^{-1} p_{l-1}^T - \alpha_l p_l^T)
\] (8)

where \( p_l \) and \( q_l \) are columns of the (rectangular, \( k \times n \)) matrices \( P \) and \( Q \), respectively. The initial seeds \( q_1 \) and \( p_1 \) were chosen as (bi-)normalized CC vectors \( \xi^X \) and \( \eta^X \), giving
EOM-CCSD photoionization directly access to the dipole-allowed transitions, i.e. an effective excitation spectrum. The effective excitation spectrum generated by diagonalization of $T$ is known to converge from the bottom and from the top towards the exact excitation spectrum.$^{32-34}$

Total photoionization cross-sections have been extensively studied applying both Stieltjes Imaging and analytic continuation procedures to the effective ground state excitation pseudo-spectrum yielded by the asymmetric Lanczos algorithm, and with oscillator strengths formulated according to CC response theory.$^{15,16,21,24}$

Herein, we are interested in obtaining the total photoionization cross sections for a valence excited state. Specifically, we aim at generating the pseudo-spectrum from a chosen excited state employing an asymmetric Lanczos algorithm and with strengths corresponding to the EOM-CCSD ones given in Eq. (1).

Our procedure for calculating the excited-state pseudo-spectrum within the EOM-CCSD framework, which bears similarities to the one adopted by Ruberti et al.$^{7}$ in the ADC context, can be summarized as follows:

1. First, we calculate the initial excitation vectors ($R_i$ and $L_i$) via a regular Davidson diagonalization of Eq. (4)

2. Next, we select the Lanczos seeds and build the tridiagonal representation of the CC Jacobian $T$ such as to span the space of final excited states ($j$) that are dipole allowed when starting from the initial

3. We diagonalize the tridiagonal matrix $T$, conveniently truncated to a dimension (chain length) $k$, to obtain the final space pseudo-spectrum.

4. We compute the oscillator strengths between the initial state state $i$ and the final states $j$ from the Lanczos eigenvectors and eigenvalues of states $j$, and the Davidson eigenvectors and eigenvalue of state $i$.

Crucial steps in our procedure are the proper choice of initial Lanczos seeds in order to generate the pseudo-spectrum in the final symmetry space (step (2)), and the computation of the EOM-CCSD transition strengths between excited states (step (4)).

As Lanczos starting vectors, we use the following normalized $q_1$ and $p_1^T$ vectors

$$
q_1 = Qe_1 = x_q^{-1} \left[ A^X R_i - (\bar{t} \cdot R_i) \xi^X \right] \tag{9}
$$

$$
p_1^T = e_1^T P^T = x_p^{-1} \left[ L_i A^X - (L_i \cdot \xi^X) \bar{t} \right]
$$

This is the author’s peer reviewed, accepted manuscript. However, the online version of record will be different from this version once it has been copied and typeset.
EOM-CCSD photoionization

where \( x_q \) and \( x_p \) are the normalization factors and \( e_m \) a vector of length \( k \) whose \( m \)-th element is equal to 1 and all other elements are equal to zero. Notice that these seeds depend on the choice of initial valence excited state \( i \).

The EOM-CCSD right-transformed vector \((A^X R_i)\) is obtained as described in the Appendix. The seeds in Eq. (9) were defined based on Eq. (1), where the last term was neglected since it eventually will not contribute because of the biorthogonality condition between excited states. With this choice of Lanczos seeds, we can straightforwardly calculate the EOM-CCSD transition strength between two excited states in Eq. (1) as

\[
S_{ij}^{XX} = \langle i x_p L_{j,1} \rangle \langle i x_q R_{j,1}^{(k)} \rangle
\]

where we used the orthogonality condition \( P^T Q = 1 \) (of dimension \( k \times k \)), and the back-transformations of the Lanczos eigenvectors \( L_{j}^{(k)} \) and \( R_{j}^{(k)} \) into full space, \( R_j = QR_j^{(k)} \) and \( L_j = L_j^{(k)} P^T \). The superscript \( i \) in the normalization factors highlights the implicitly-built dependence on the initial excited state.

It is worth mentioning that, as in the case of the ground state,\(^{32,33}\) the final expression for the transition moment between the excited states shown in Eq. (10) only involves the first element of the Lanczos left and right excitation vectors of the final state, \( e_1^T R_j^{(k)} = R_{j,1}^{(k)} \) and \( L_j^{(k)} e_1 = L_{j,1}^{(k)} \), making the computation of the transition moments very simple.

B. Analytic continued calculation of the photoionization cross section of excited states

Yeager, Nascimento, and McKoy\(^{23}\) obtained the photoionization cross sections of the \( 2\, ^3S \) and \( 2\, ^1S \) metastable states of the helium atom using an analytical continuation procedure based on the Padé approximants. By defining an initial excited state \(|\lambda_i\rangle\) from which all one-photon excitation energies \( \omega_{ij} = (\omega_j - \omega_i) \) and oscillator strengths \( f_{ij} \) are generated, \( \{\omega_{ij}, f_{ij}\}_{i<j} \), the photoionization cross section \( \sigma_{\lambda_i}(\omega) \) is obtained from the imaginary part of the averaged dynamic dipole polarizability function of the excited electronic state,

\[
\sigma_{\lambda_i}(\omega) = \frac{4\pi\omega}{c} \lim_{\eta \to 0} \text{Im}[\overline{\alpha}_{\lambda_i}(\omega + i\eta)]
\] (11)
EOM-CCSD photoionization

The averaged dynamic dipole polarizability function $\alpha_{\lambda,i}(z)$ of the excited state $i$ is approximated by a finite sum over the electronic pseudo-spectrum $\{\omega_{ij}, f_{ij}\}_{i<j}$ obtained in the $L^2$ basis set calculation

$$\alpha_{\lambda,i}(z) = \sum_{j=1}^{k} \frac{f_{ij}}{\omega_{ij}^2 + z^2}$$

(12)

and $z$ is the complex valued frequency.

Here, we build an approximation of Eq. (12) from the set of Lanczos EOM-CCSD excited-to-excited transition energies and oscillator strengths. Then, in the spirit of Ref. 23, having such approximation in hand, we calculate $\alpha_{\lambda,i}(z)$ at a number of points in the complex plane. These points are subsequently fitted by a continued fraction function – which is mathematically equivalent to the Padé approximants – providing a representation of $\alpha_{\lambda,i}(z)$ in the complex plane. The imaginary part of $\alpha_{\lambda,i}(z)$ on the real axis provides the cross section by Eq. (11).

The set of points in the complex plane is known to be arbitrary and not unique and we are here using the recipe previously described in Ref. 20 to select the complex points.

C. The photoionization cross section of an excited state from Stieltjes Imaging

Another approach to obtain the photoionization cross section from a discrete pseudo-spectrum obtained with an $L^2$ basis set calculation is the Stieltjes Imaging procedure, suggested by Langhoff.\textsuperscript{35,36} Similarly to the Padé analytic continuation procedure, it is assumed that the moments $s(k)$ of the continuum oscillator strength

$$s(k) = \sum_{l} \omega_l^k f_l + \int_{-\infty}^{\infty} \omega^k f(\omega) d\omega$$

(13)

can be approximated by the sum of $N$ discrete pseudo-states of the continuum, $S(k) \approx \sum_i^N \bar{\omega}_i^k \bar{f}_i$.

In the Stieltjes imaging, the “primitive” set of $M$ excitation energies and oscillator strengths are transformed in order to obtain a smoothed representation of the continuum spectrum. One first computes a number $(2r)$ of “spectral moments” $S(-k)$ of the primitive spectrum

$$S(-k) = \sum_{l=1}^{M} f_l \omega_l^{-k}; \quad k = 0, ..., 2r - 1 .$$

(14)
EOM-CCSD photoionization

Based on the results of previous works, we used here $r$ ranging from 2 to 20 and only plot in the figures the points that are well converged.

From the $2r$ spectral moments, the discretized spectra of order $m = 2, \cdots, r$, called principal pseudo-spectra, are generated as generalized (Gaussian) quadrature points (abscissae) $\omega^{(m)}_i$ and weights $f^{(m)}_i$:

$$S(-k) = \sum_{i=1}^{m} f^{(m)}_i (\omega^{(m)}_i)^{-k}; \quad k = 0, \ldots, 2m - 1$$  \hspace{1cm} (15)

From the Gaussian quadrature points and weights, one reconstructs the photoionization cross section spectra numerically as the Stieltjes derivative of the general discretized principal pseudo-spectra (see Refs. 15, 24, 37 for a more detailed description of the Stieltjes imaging procedure). Here, we used the computed values $\omega_{ij}$ and $f_{ij}$ as primitive set in the Stieltjes procedure to get the spectra for cross section points for the initial excited state.

III. COMPUTATIONAL DETAILS

The asymmetric Lanczos procedure discussed in the previous section for calculating the spectral moments between excited states at the EOM-CCSD level has been implemented in a development version of the Dalton program package. Chain-length subspaces of $k = 500$ were used for all molecules considered, adopting Dunning’s correlation consistent basis set aug-cc-pVTZ. The basis set was enriched with continuum-like basis functions proposed by Kaufmann, Baumeister, and Jungen. The continuum-like functions were added to the center of mass of each molecule, and includes $s$, $p$ and $d$ functions generated using quantum numbers $n$ ranging from 2 to 8, as employed in Ref. 24. The same notation introduced there will be used to indicate such set, namely $(7s7p7d)_{n=2-8}$.

The geometries for the water, nitrogen and carbon monoxide molecules are the same ones used in Ref. 7, in order to establish a ground for comparison between our results and their ADC ones. Like in Ref. 7, the water molecule ground state equilibrium geometry and the lowest-energy geometries for the $1^1B_1$ and $1^1A_2$ states were obtained from Ref. 41 calculated with the d-aug-cc-pVQZ basis set at the CASPT2 level. The carbon monoxide experimental ground state equilibrium geometry and the experimental lowest $1\Sigma^-$ and $1\Pi$ excited states equilibrium geometries were obtained from Ref. 42. For molecular nitrogen,
EOM-CCSD photoionization

the geometries used here and in Ref. 7 are experimental geometries.\textsuperscript{42}

The calculations for the Helium atom have been performed with Lanczos chain dimension equal to the full excitation space dimension (exact Full Configuration Interaction (FCI) results), using the aug-cc-pVQZ basis complemented with the Kaufmann’s (7s7p7d)\textsubscript{\textit{n}=2–8} continuum-like set.

It is worth mentioning that the photoionization cross-section results presented herein have been plotted using as energy scale the "photon energy", \textit{i.e.}, the energy of the final excited state minus the energy of the considered transient excitation. This was done in order to consider the photoabsorption by the system already prepared in the transient excited state.

\textbf{IV. RESULTS}

Table I collects the calculated vertical excitation energies of the initial valence excited states of each system considered in the present study. Corresponding experimental values are also included.

\textbf{A. Helium}

For the two-electron system Helium, the CCSD approximation is equivalent to a full CI (FCI) calculation and the EOM-CCSD results can then be considered as a benchmark. Moreover, there are no vibrational nor geometrical effects, making helium a perfect choice to validate our computational method.

In Figure 1, we present the computed photoionization cross sections from the \textit{1S} and the \textit{1P} excited states of the helium atom. together with the available experimental values. Experimental photoionization cross sections from the same excited states have been reported in Refs. 43 and 44, respectively, and they are also plotted in Figure 1.

The calculated excitation energies from the ground state to the \textit{1S} and the \textit{1P} excited states are 20.61 eV and 21.21 eV, respectively, in excellent agreement with the experimental values of 20.61 eV\textsuperscript{43} and 21.22 eV\textsuperscript{44} (see Table I). The accuracy of the calculated excitation energies reflects the above-mentioned equivalence between FCI and CCSD in this case.

The calculated photoionization cross section from the \textit{1S} state (top panel of Fig. 1) is in excellent agreement with the experimental points. The same agreement can be observed...
EOM-CCSD photoionization

for the cross section from the $^1P$ state (bottom panel of Fig. 1). For both states, there is a reasonable agreement between the analytic Padé curve and the Stieltjes points, but the Stieltjes points for the $^1P$ excited state are more scattered, possibly an indication of poor convergence of the principal pseudo spectrum in this case. Our results are also in good agreement with other calculations from Yeager et al.\textsuperscript{23} and Jacobs.\textsuperscript{45}

B. Water

Our EOM-CCSD results for water are compared with the ones obtained by Ruberti et al.\textsuperscript{7} at the ADC(2) and ADC(2)-x levels in Fig. 2.

Ruberti et al.\textsuperscript{7} also reported results at the ADC(1) level, which proved to be inadequate to obtain the photoionization cross sections, even at qualitative level, if compared to the more accurate accurate ADC(2) and ADC(2)-x levels. These results\textsuperscript{7} showed the need to include double excitation effects in order to obtain reasonable photoionization cross sections of transient states. Also, the authors have found that the inclusion of coupling between the double excitations in ADC(2) theory, leading to the ADC(2)-x approach, makes a substantial difference in the final results.

Our EOM-CCSD photoionization cross sections from the two lowest excited states of water, $^1B_1$ and $^1A_2$, are shown in the Figures 2 and 3, respectively, together with the ADC(2) and ADC(2)-x results from Ruberti et al.\textsuperscript{7} in order to have some ground for comparison. To compare our results with the ADC(2) and ADC(2)-x ones, we used the same geometries as reported by Ruberti et al.\textsuperscript{7} The results obtained at the ground state equilibrium geometry are shown in the top panels of Figures 2 and 3 and the ones obtained at the lowest-energy geometries of the excited states, as calculated in Ref. 41, are shown in the bottom panel of the same figures.

The vertical excitation energy at the ground state geometry for the $^1B_1$ state was calculated at 7.61 eV while a previous EOM-CCSD\textsuperscript{46} study, employing an aug-cc-pVTZ basis set, reported 7.58 eV. For the $^1A_2$ state, we calculated the excitation energy at 9.36 eV, whereas the previous EOM-CCSD result\textsuperscript{46} is 9.35 eV. Our vertical excitation energies are in good agreement with experimental values (7.40 eV and 9.09 eV\textsuperscript{47} for the $^1B_1$ and $^1A_2$ excited states, respectively, see Table I). Compared to the ADC(2) and ADC(2)-x results\textsuperscript{7} (obtained with a different basis set), the differences are of the order of 5%. The adiabatic
EOM-CCSD photoionization excitation energies at the lowest-energy geometry of the excited state were calculated at 7.30 and 9.14 eV for the $^1B_1$ and the $^1A_2$ states, respectively.

From Fig. 2, one can observe a reasonable agreement between our EOM-CCSD and the ADC(2)-x (Ref. 7) photoionization cross sections of the $^1B_1$ excited state. In the region above 30 eV, the EOM-CCSD and the ADC(2)-x cross sections exhibit the same cross section decay at both geometries here considered. In the region around 20 eV, the EOM-CCSD cross section is narrower and slightly shifted, falling in between the ADC(2)-x and the ADC(2) ones. Analogous behavior is observed for the EOM-CCSD cross section at the lowest-energy geometry of the excited state shown in the bottom panel of Fig. 2. All in all, the EOM-CCSD photoionization cross section agrees better the ADC(2)-x results than with the ADC(2) ones.

The photoionization cross sections of the $^1A_2$ excited state, shown in Fig. 3, shows more spectral structures than the ones of the $^1B_1$ state. Also, there is a large difference between the results computed at the equilibrium geometry and the one obtained at the excited state geometry. For example, taking the Padé analytic curves, the maximum cross section (27 Mb) obtained with the ground state equilibrium geometry occurs at 37 eV (24 Mb by the Stieltjes highest point) and at 20 eV with 22 Mb when the calculation is performed at the excited state geometry. This is a clear evidence that the photoionization cross sections from the $^1A_2$ transient state is much more sensitive to geometry changes than from the $^1B_1$ excited state.

The cross sections obtained with the analytic Padé procedure are in reasonable agreement with the Stieltjes cross section points. This was also observed in our recent work where the cross section of inner shell states were obtained within a CC-CVS approximation and the Padé and the Stieltjes cross sections were compared for a number of molecules. Here, the larger difference in the photoionization cross sections of excited states of water obtained with both procedures was found at the maximum point of the top panels (ground state geometry) of Figs. 2 and 3, where the analytic Padé results are approximately 3 Mb higher.

C. Carbon monoxide

The photoionization cross sections of the $^1\Sigma^-$ and $^1\Pi$ excited states of carbon monoxide are presented in Figs. 4 and 5, respectively. Similarly to the water molecule, we compare our
EOM-CCSD photoionization results with the ADC calculations from Ruberti et al.\textsuperscript{7} using the experimental geometries,\textsuperscript{42} i.e., \( r_{\text{CO}} = 1.128 \) Å in the ground state and \( r_{\text{CO}} = 1.391 \) and \( 1.235 \) Å in the \( ^1\Sigma^- \) and \( ^1\Pi \) excited state equilibrium geometry, respectively.

The EOM-CCSD vertical excitation energies for the CO were calculated at 10.08 eV and 8.62 eV for the \( ^1\Sigma^- \) and \( ^1\Pi \) excited states, respectively (see Table I). The results of Ruberti et al.\textsuperscript{7} at the ADC(2)-x and ADC(2) levels, respectively, are 9.64 and 10.15 eV for the \( ^1\Sigma^- \) excited state and 8.32 and 8.85 eV for the \( ^1\Pi \) excited state. The vertical excitation energies, 9.88 eV for the \( ^1\Sigma^- \) state and 8.51 eV for the \( ^1\Pi \) state, were obtained numerically by Nielsen, Jørgensen, and Oddershede\textsuperscript{48} using the experimental spectroscopic rovibronic constants obtained from Ref. 42. Our EOM-CCSD adiabatic excitation energies are 8.33 eV for the \( ^1\Sigma^- \) excited state and 8.24 eV for the \( ^1\Pi \) excited state, while the experimental values are 8.07 eV for both \( ^1\Sigma^- \) and \( ^1\Pi \) excited states (obtained from Ref. 42). Again, our results are in reasonable agreement with the available experimental values.

The cross sections in Fig. 4 for the excited \( ^1\Sigma^- \) state at the ground state (top panel) and at the excited state geometry (bottom panel) are intermediate between the ADC(2)-x and ADC(2) curves,\textsuperscript{7} in the whole spectral region, i.e., red shifted relative to the ADC(2) cross section and blue shifted relative to the ADC(2)-x curve. Our analytic Padé cross section calculated at the ground state equilibrium geometry presents a maximum at 28 eV with 24 Mb. This maximum is blue shifted by 6 eV relative to the ADC(2)-x maximum and red shifted by 10 eV relative to the ADC(2) maximum. ADC(2)-x is known to underestimate the excitation energies due to its unbalanced description of correlation effects in the ground and excited states, which leads to systematic red shift of the excitation energies.\textsuperscript{49} Conversely, ADC(2) is known to give a poor description of states with large contributions from double excitations, overestimating Rydberg excitations and ionization, see Ref. 49. CCSD re-establishes the correlation balance and yields excitation energies in between those obtained with the ADC(2)-x and the ADC(2) methods.

The results of our calculations for the \( ^1\Pi \) excited state of CO are shown in Figure 5 at the ground state equilibrium geometry (top panel) and at the excited state equilibrium geometry (bottom panel). As it can be observed from Fig. 5, our EOM-CCSD photoionization cross sections are in better agreement with the ADC(2)-x results than with the ADC(2) ones\textsuperscript{7} in the whole spectral region, but still in between the maximum positions of the ADC(2)-x and ADC(2) curves, due to the more balanced description of correlation effects yielded by the
EOM-CCSD photoionization

CCSD method.\textsuperscript{49}

The photoionization cross section calculated for the transient $^1\Pi$ state is not much sensitive to the different geometries, whereas it is possible to see that the EOM-CCSD cross sections as well as the ADC ones, presented in the top and bottom panels of Fig. 5, look very similar to each other.

In Figs. 4 and 5 is also evident that the analytic Padé photoionization cross sections are in excellent agreement with the Stieltjes cross section points obtained with both geometries and transient states of the CO molecule.

D. Nitrogen

The photoionization cross sections of the $^1\Sigma_u^-$ and $^1\Pi_g$ excited states of $\text{N}_2$ are presented in Figs. 6 and 7, respectively. Also for this molecule, our results were compared with the ADC(2) and ADC(2)-x ones from Ruberti \textit{et al.}\textsuperscript{7}

The EOM-CCSD vertical excitation energies of $\text{N}_2$ are calculated at 10.04 eV and 9.44 eV for the $^1\Sigma_u^-$ and $^1\Pi_g$ excited states, respectively (see Table I). The values obtained at the ADC(2)-x and ADC(2) levels,\textsuperscript{7} respectively, were 10.13 eV and 10.31 eV for the $^1\Sigma_u^-$ excited state and 8.98 eV and 9.55 eV for the $^1\Pi_g$ excited state. Reference values computed numerically\textsuperscript{50} with experimental rovibronic constants\textsuperscript{42} were obtained at 9.92 eV and 9.31 eV for the $^1\Sigma_u^-$ and $^1\Pi_g$ excited states, respectively. We notice that the EOM-CCSD vertical excitation energies are closer to the reference values\textsuperscript{50} than the ones calculated at the ADC(2) and ADC(2)-x levels.\textsuperscript{7} Also, our EOM-CCSD adiabatic excitation energies are 8.85 eV for the $^1\Sigma_u^-$ excited state and 8.84 eV for the $^1\Pi_g$ excited state, versus experimental values of 8.59 and 8.45 eV for the $^1\Sigma_u^-$ and $^1\Pi_g$ excited states,\textsuperscript{42} respectively. Once again, our results show reasonable agreement with experimental data.

In Figure 6, we present the EOM-CCSD cross sections for the excited $^1\Sigma_u^-$ state of $\text{N}_2$ at the ground state (top panel) and at the excited state (bottom panel) geometry. The cross section calculated at the ground state equilibrium geometry presents a maximum at 20 eV with 36 Mb, which corresponds to a 5 eV blue shift relative to the ADC(2)-x maximum and a 15 eV red shift relative to the ADC(2) maximum. As discussed previously, the better correlation balance in both ground and excited states of the CCSD method\textsuperscript{49} explains the EOM-CCSD cross section curve being in between the ADC ones, similar to
EOM-CCSD photoionization

what observed in the CO case. Also, the EOM-CCSD cross section calculated at the $^1\Sigma_u^-$ excited-state geometry (bottom panel) presents a sharp peak with maximum at 14 eV with 50 Mb. This feature is absent in the cross sections obtained both at the ADC(2) and ADC(2)-x levels, showing that, for this molecule, the EOM-CCSD cross section is more sensitive to the molecular geometry variations than the ADC curves.

Our results for the $^1\Pi_g$ excited state of N$_2$ are presented in Figure 7, again with those for the ground state equilibrium geometry in the top panel and the ones at the excited state equilibrium geometry in the bottom panel. The EOM-CCSD cross section computed at the ground state geometry shows a sharp peak at 18 eV reaching 60 Mb, a value much higher than the maximum in the ADC(2) curve. This sharp peak is missing in the EOM-CCSD cross section calculated at the $^1\Pi_g$ excited state geometry (bottom panel of Fig. 7) using Padé approximants, even though the Stieltjes points appear to still hint at its presence. In this case, the EOM-CCSD cross section presents a maximum in an intermediate position between the ADC(2)-x and ADC(2) ones. Roughly, it is possible to say that the EOM-CCSD results shown in Figure 7 resemble better the characteristics of the ADC(2)-x cross sections than the ADC(2) ones.

E. Sulfur Dioxide

Sulfur dioxide is a molecule of significant interest in atmospheric chemistry and the astrochemistry related fields of research.$^{51-53}$ Its UV photoabsorption cross section has been studied experimentally and theoretically.$^{53-56}$ The SO$_2$ UV spectrum exhibits a weak absorption band extending from 3.6 to 5.1 eV dominated by the $\tilde{X}$ $^1A_1 \rightarrow ^1B_1$ electronic transition, with additional contributions from the $\tilde{X}$ $^1A_1 \rightarrow ^1A_2$ transition, followed by a strong absorption band extending from 5.4 to 7.3 eV associated with the $\tilde{X}$ $^1A_1 \rightarrow ^1B_2$ electronic transition which is mainly related to the photodissociation pathway of the SO$_2$ molecule.$^{53,56}$

At the EOM-CCSD level, we obtained the $\tilde{X}$ $^1A_1 \rightarrow ^1B_1$ transition at 4.40 eV and with an oscillator strength of 0.0054; a $\tilde{X}$ $^1A_1 \rightarrow ^1A_2$ transition at 4.87 eV; and a $\tilde{X}$ $^1A_1 \rightarrow ^1B_2$ transition at 6.51 eV with oscillator strength 0.079. The calculated vertical transition energies are in rather good agreement with the experimental data, and we have chosen the first low-lying electronic state $^1B_1$ and the strongest transition $^1B_2$ as the target transient
EOM-CCSD photoionization states for the excited state photoionization cross section study of the SO$_2$ molecule.

In Fig. 8, the photoionization cross sections of the $1^1B_1$ (top panel) and $1^1B_2$ (bottom panel) excited states of the SO$_2$ molecule are presented. The correspondent geometries were taken from Ref. 55 as the lowest-energy geometries of the excited states computed at the multi-reference second order perturbation theory (MRPT2) level with the basis set cc-pVTZ. Our adiabatic electronically excited state energies are 4.02 and 4.61 eV for the $1^1B_1$ and $1^1B_2$ excited states, respectively, while the ones calculated in Ref. 55 with MRPT2 were 4.10 and 5.62 eV.

The photoionization cross sections of Fig. 8 show a less pronounced dependence on the molecular geometry than the previous molecules. The results for the transient $1^1B_1$ state (top panel) present a difference of approximately 10 Mb at the maximum of the cross section curve. For the ground state geometry, the maximum value of the cross section, 58 Mb, occurs at 27 eV, while at the excited state equilibrium geometry the maximum of 68 Mb occurs at 23 eV. In the region of higher energy, starting at 40 eV, both curves are virtually equivalent. For the transient $1^1B_2$ state (bottom panel), the photoionization cross section calculated at the excited state equilibrium geometry is slightly red shifted (about 2 eV) relative to the one obtained at ground state geometry. Also, the maximum of the cross section curves calculated with both geometries occurs at approximately 60 Mb and near 25 eV. The results presented in Fig. 8 indicate that the transient photoionization cross section profile of the SO$_2$ molecule is very similar when the molecule is prepared in the $1^1B_1$ or in the $1^1B_2$ excited state.

V. SUMMARY AND CONCLUSIONS

We have presented an asymmetric-Lanczos based formulation of EOM-CCSD to compute excitation energies and transition strengths between excited states. The methodology was used to compute the pseudo-spectra of selected valence excited states in the systems He, H$_2$O, CO, N$_2$ and SO$_2$. The pseudo-spectra were then employed with both the Stieltjes Imaging and the Padé analytic continuation procedures to calculate the photoionization cross sections of such transient states. The results were compared with other theoretical results by Ruberti et al.$^7$ and with the available experimental data.

For helium, our EOM-CCSD method yields FCI results and the photoionization cross
EOM-CCSD photoionization

sections calculated for the \(^1\)S and \(^1\)P excited states were found in excellent agreement with experimental data.\(^{43,44}\)

The CCSD photoionization cross sections of the \(^1\)A\(_2\) and the \(^1\)B\(_1\) transient states of the water, the \(^1\)\(\Sigma^−\) and \(^1\)\(\Pi\) excited states of carbon monoxide and of the \(^1\)\(\Sigma_u^−\) and \(^1\)\(\Pi_g\) excited states of nitrogen molecule were found in better agreement with the ones computed at the ADC(2)-x level\(^7\) than those obtained at the ADC(2) level.\(^7\) Generally, when compared to the ADC(2)-x and ADC(2) cross sections, the EOM-CCSD results present maxima in between the maxima of the two ADC methods. This behaviour can be understood if one considers the unbalanced description of correlation effects in the ground and excited states of the ADC(2)-x method, leading to a red shift in the ADC(2)-x excitation energies.\(^{49}\) ADC(2), on the other hand, is known to give a poor description of states with large contributions from double excitations overestimating Rydberg excitations and ionization.\(^{49}\) As the correlation balance is reestablished by CCSD, the CCSD excitation energies and the photoionization cross sections are found between the ADC(2)-x and the ADC(2) ones. We also analyzed the dependence of the EOM-CCSD cross sections on the geometry of the excited states and demonstrated that it is similar dependence to the one shown by the ADC(2)-x cross-sections.\(^7\)

The Stieltjes points and the Padé cross section curves were generally in good agreement with each other. In most of the cases, one could even compare the Padé curve to a smooth continuous curve connecting the Stieltjes points. A similar behavior was observed in a previous work where the photoionization cross sections of inner-shell states of a number of molecules were compared in both methodologies.\(^{24}\)

We also presented the EOM-CCSD photoionization cross sections for the \(^1\)B\(_2\) and the \(^1\)B\(_1\) exited states of the sulfur dioxide, a molecule of large interest in atmospheric chemistry and astrochemistry. The \(^1\)B\(_2\) exited state is particularly interesting because it is mainly involved in the photodissociation pathway of the \(\text{SO}_2\) molecule. We observed that, contrary to the case of water and carbon monoxide, the sulfur dioxide cross sections are less dependent on the geometry changes. The photoionization curves showed the maximum cross section values near 25 eV for both the \(^1\)B\(_2\) and the \(^1\)B\(_1\) exited states.

The approach is presently being extended to the calculation of core-level photoionization cross sections of transient valence-excited states.
EOM-CCSD photoionization

ACKNOWLEDGMENTS

B.N.C.T, M.A.C.N. and A.B.R. acknowledge Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfeiçoamento Pessoal de Nível Superior (CAPES) - Finance Code 001, and Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ) for financial support.

S.C. acknowledges support from DTU Chemistry and from the Independent Research Fund Denmark – DFF-Forskningsprojekt2 grant no. 7014-00258B.
EOM-CCSD photoionization

TABLE I: Calculated vertical excitation energies $\omega_i$ (in eV) for the initial excited states considered in this work, and corresponding experimental vertical excitation energies.

<table>
<thead>
<tr>
<th>Excited state</th>
<th>Vertical $\omega_i$/eV</th>
<th>Experimental value/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>He $^1S$</td>
<td>20.61</td>
<td>20.61$^{43}$</td>
</tr>
<tr>
<td>He $^1P$</td>
<td>21.21</td>
<td>21.22$^{44}$</td>
</tr>
<tr>
<td>H$_2$O $^1B_1$</td>
<td>7.61</td>
<td>7.40$^{47}$</td>
</tr>
<tr>
<td>H$_2$O $^1A_2$</td>
<td>9.36</td>
<td>9.09$^{47}$</td>
</tr>
<tr>
<td>CO $^1\Pi$</td>
<td>8.62</td>
<td>8.51$^{48}$</td>
</tr>
<tr>
<td>CO $^1\Sigma^-$</td>
<td>10.08</td>
<td>9.88$^{48}$</td>
</tr>
<tr>
<td>N$_2$ $^1\Pi_g$</td>
<td>9.44</td>
<td>9.31$^{50}$</td>
</tr>
<tr>
<td>N$_2$ $^1\Sigma_u^-$</td>
<td>10.04</td>
<td>9.92$^{50}$</td>
</tr>
<tr>
<td>SO$_2$ $^1B_1$</td>
<td>4.40</td>
<td>3.6 to 5.1$^{53}$</td>
</tr>
<tr>
<td>SO$_2$ $^1B_2$</td>
<td>6.51</td>
<td>5.4 to 7.3$^{53}$</td>
</tr>
</tbody>
</table>
FIG. 1: He. FCI photoionization cross sections from the 1s2s $^1S$ (top) and 1s2p $^1P$ (bottom) excited states, obtained via the Padé and Stieltjes imaging procedures. The experimental points were taken from Refs. 43 and 44.
FIG. 2: H$_2$O. EOM-CCSD total photoionization cross sections from the $^1B_1$ excited state at the ground state equilibrium geometry (top) and at the $^1B_1$ lowest-energy geometry of the excited-state of Ref. 41 (bottom), obtained by the Padé and Stieltjes imaging procedures. The EOM-CCSD cross sections are compared with the ADC(2) and ADC(2)-x results of Ruberti et al.$^7$
FIG. 3: H₂O. EOM-CCSD photoionization cross sections from the \(^1A_2\) excited state at the ground state equilibrium geometry (top) and at the \(^1A_2\) lowest-energy geometry of the excited-state (bottom) obtained by the Padé and Stieltjes imaging procedures. The EOM-CCSD cross sections are compared with the ADC(2) and ADC(2)-x results of Ruberti \textit{et al.}^7
FIG. 4: CO. EOM-CCSD total photoionization cross sections from the $^1\Sigma^-$ excited state at the ground state equilibrium geometry (top) and at the $^1\Sigma^-$ excited-state equilibrium geometry (bottom), obtained by the Padé and Stieltjes imaging procedures. The EOM-CCSD cross sections are compared with the ADC(2) and ADC(2)-x results of Ruberti et al.\textsuperscript{7}
FIG. 5: CO. EOM-CCSD photoionization cross sections from the \(^1\Pi\) excited state at the ground state equilibrium geometry (top) and at the \(^1\Pi\) excited state equilibrium geometry (bottom) obtained by the Padé and Stieltjes imaging procedures. The EOM-CCSD cross sections are compared with the ADC(2) and ADC(2)-x results of Ruberti et al.\(^7\)
EOM-CCSD photoionization

FIG. 6: $N_2$. EOM-CCSD total photoionization cross sections from the $1\Sigma_u^-$ excited state at the ground state equilibrium geometry (top) and at the $1\Sigma_u^-$ excited-state equilibrium geometry (bottom), obtained by the Padé and Stieltjes imaging procedures. The EOM-CCSD cross sections are compared with the ADC(2) and ADC(2)-x results of Ruberti et al.$^7$
FIG. 7: N₂. EOM-CCSD photoionization cross sections from the $^1\Pi_g$ excited state at the ground state equilibrium geometry (top) and at the $^1\Pi_g$ excited state equilibrium geometry (bottom) obtained by the Padé and Stieltjes imaging procedures. The EOM-CCSD cross sections are compared with the ADC(2) and ADC(2)-x results of Ruberti et al. 7
FIG. 8: SO$_2$. EOM-CCSD photoionization cross sections from the $^1B_1$ (top) and $^1B_2$ (bottom) excited states, obtained via the Padé and Stieltjes Imaging procedures. In the top panel, the results for the $^1B_1$ excited state at the ground state equilibrium geometry (black) and at the lowest-energy geometry of the excited-state (blue) are shown. In the bottom panel, the cross sections of the $^1B_2$ excited state at the ground state and relaxed excited state geometries are shown.
EOM-CCSD photoionization

Appendix A: Right transformed EOM-CCSD $A^X R_i$ vector

In the EOM-CC framework, the property Jacobian matrix $A^X$ is different from the CC-LR matrix, as shown in Eq. (6), and the right transformation with the right excitation vector ($R_f$) reads

$$
\sum_{\mu \nu} A_{\mu \nu}^X R_f^\mu = \sum_{\mu \nu} A_{\mu \nu}^{X, RSP} R_f^\mu + \sum_{\mu \nu} \langle \mu | \tau_{\nu} X^T | HF \rangle (1 - \delta_{\mu \nu}) R_f^\nu \quad (A1)
$$

Since the right transformed CC-LR vector $A_{\mu \nu}^{X, LR} R_f^\mu$ is already available, we take the second part of Eq. (A1) and treat it as a correction to the CC-LR right transformation. We call this correction term $\sigma_{\mu}$

$$
\sigma_{\mu} = \sum_{\nu} \langle \mu | \tau_{\nu} X^T | HF \rangle (1 - \delta_{\mu \nu}) R_f^\nu \quad (A2)
$$

In the CCSD case, $\sigma_{\mu}$ contains contribution for the double excitation manifold $\langle \mu | = \langle \tilde{c} \tilde{d} |$, scaled in the biorthonormal basis, and $\tau_{\nu} = E_{ai}$, where $E_{ai}$ is the singlet one-electron excitation operator. The CC similarity-transformed operator $X^T$ is a component of the electric dipole operator $\hat{X}$ transformed with the cluster operators of single ($T_1$) and double ($T_2$) excitation manifold, $X^T = e^{-T_2-T_1} \hat{X} e^{T_1+T_2}$, and in practice reduces to

$$
X^T = X^{T_1} + [X^{T_1}, T_2] \quad (A3)
$$

with the $T_1$-transformed operator as

$$
X^{T_1} = \sum_{pq} X_{pq}^{T_1} E_{pq} \quad (A4)
$$

$X_{pq}^{T_1}$ are the $T_1$-similarity transformed molecular orbital integrals of the dipole operator, and $T_2 = \frac{1}{2} \sum_{bejm} t_{be}^{jm} E_{oj} E_{em}$.

We now re-write $\sigma_{\mu}$ as

$$
\sigma_{\mu}^{\tilde{c} \tilde{d}} = \sum_{ai} \langle \tilde{c} \tilde{d} | E_{ai} X^T | HF \rangle R_f^a_i (1 - \langle \tilde{c} \tilde{d} | a_i \rangle) \quad (A5)
$$

$$
= \sum_{ai} \left\{ \langle \tilde{c} \tilde{d} | E_{ai} X^{T_1} | HF \rangle + \langle \tilde{c} \tilde{d} | E_{ai} [X^{T_1}, T_2] | HF \rangle \right\} R_f^a_i
$$
EOM-CCSD photoionization

After some algebraic manipulations, the following expressions are obtained

\[ \sum_{ai} \langle \tilde{c}d | E_{ai} X_{T1}^T | \text{HF} \rangle R_{ai}^f = R_{ck}^f X_{dl}^T + R_{dl}^f X_{ck}^T \]  
\[ \sum_{ai} \langle \tilde{c}d | E_{ai} [X_{T1}, T_2] | \text{HF} \rangle R_{ai}^f = \sum_{em} \left\{ 2(R_{ck}^f X_{me}^T t_{ed}^{t_{de}} + R_{dl}^f X_{me}^T t_{ed}^{t_{de}}) - (R_{ck}^f X_{me}^T t_{ed}^{t_{de}} + R_{dl}^f X_{me}^T t_{ed}^{t_{de}}) \right\} \]  

Now we define an effective amplitude contracted with the one-electron property integrals

\[ \tilde{t}_{dl}^X = \sum_{em} X_{me}^T (2t_{de}^{t_{de}} - t_{ed}^{t_{de}}) \]  

which, inserted into Eqs. (A6) and (A5), yields

\[ \sigma_{cd}^{ed} = R_{ck}^f (X_{dl}^T + \tilde{t}_{dl}^X) + 2R_{dl}^f (X_{ck}^T + \tilde{t}_{ck}^X) \]  
\[ = P_{kl}^{cd} R_{ck}^f (X_{dl}^T + \tilde{t}_{dl}^X) \]  

where we used the permutation operator \( P_{kl}^{cd} \) in the final expression.

The final expression for \( A^X R_f \) of EOM-CCSD thus reads

\[ A^X R_f = A^{X,RSP} R_f + \sum_{ck,dl} P_{kl}^{cd} R_{ck}^f (X_{dl}^T + \tilde{t}_{dl}^X) \]  

REFERENCES

EOM-CCSD photoionization

12A. Palacios and F. Martín, Wiley Interdisciplinary Reviews: Computational Molecular Science 0, e1430.
EOM-CCSD photoionization

(2019).


EOM-CCSD photoionization

53 D. Blackie, R. Blackwell-Whitehead, G. Stark, J. C. Pickering, P. L. Smith, J. Rufus, and
EOM-CCSD photoionization


Stieltjes CCSD cross-section

Padé CCSD cross-section

ADC(2) Stieltjes

ADC(2)x Stieltjes

Photon energy (eV)

Cross section (Mb)
Stieltjes CCSD cross-section

Padé CCSD cross-section

ADC(2) Stieltjes

ADC(2)x Stieltjes

Photon energy (eV)

Cross section (Mb)
Stieltjes CCSD cross-section GS geometry
Padé CCSD cross-section GS geometry
Stieltjes CCSD cross-section ¹B₂ geometry
Padé CCSD cross-section ¹B₂ geometry

Photon energy (eV) vs Cross section (Mb)
Stieltjes CCSD cross-section $^1\text{B}_1$ geometry

Padé CCSD cross-section $^1\text{B}_1$ geometry

Stieltjes CCSD cross-section GS geometry

Padé CCSD cross-section GS geometry
Stieltjes CCSD cross-section
Padé CCSD cross-section
ADC(2)
Stieltjes

Photon energy (eV)

Cross section (Mb)

- Stieltjes CCSD cross-section
- Padé CCSD cross-section
- ADC(2) Stieltjes
- ADC(2)x Stieltjes
Stieltjes CCSD cross-section

Padé CCSD cross-section

ADC(2)

Stieltjes

Photon energy (eV)
Stieltjes CCSD cross-section
Padé CCSD cross-section
ADC(2)

Photon energy (eV)

Cross section (Mb)

- Stieltjes CCSD cross-section
- Padé CCSD cross-section
- ADC(2) Stieltjes
- ADC(2)x Stieltjes
Stieltjes CCSD cross-section
Padé CCSD cross-section
ADC(2)

\[
\text{Stieltjes}
\]

\[
\text{Padé}
\]

\[
\text{ADC(2)}
\]

Photon energy (eV)
Cross section (Mb)
Stieltjes CCSD cross-section

Padé CCSD cross-section

ADC(2) x Stieltjes

Photon energy (eV)

Cross section (Mb)
Stieltjes CCSD cross-section

Padé CCSD cross-section

ADC(2)

Photon energy (eV)

Cross section (Mb)

Crystals (Mb)

ADC(2)x Stieltjes
Stieltjes CCSD cross-section

Padé CCSD cross-section

ADC(2)

ADC(2)x Stieltjes

Photon energy (eV)

Cross section (Mb)