The role of initial-state electron correlation in one-photon double ionization of atoms and molecules

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Synopsis By decomposing the initial state wave function into its unique natural orbital expansion we analyze the role of electron correlation in the initial state of an atom or molecule in determining the angular distribution of one-photon double ionization (OPDI). Numerically accurate calculations on the OPDI of He, H^- and H_2 were considered. For the atomic systems the triply differential cross section (TDCS) was relative insensitively to initial state correlation. However, for oriented H_2 the TDCS was particularly sensitive to left-right initial state correlation along the bond.

A central argument motivating a long history of theoretical and experimental interest in one-photon double-ionization (OPDI) of atoms and molecules is that this process is particularly sensitive to the effects of electron correlation. In two-electron systems, there are two types of electron correlation that contribute to the triply differential cross section (TDCS) of OPDI. First, there is the strong correlation of the two electrons in the final double-continuum state. Second, and the focus of this presentation, is the electron correlation in the initial state.

The initial state correlation effects can be treated as a sum of terms when the initial state is written as a linear combination of basis functions. Using the natural orbital expansion of the configuration interaction two-electron initial-state wave function leads to a systematic ordering of such a linear combination based on natural orbital occupation numbers. The initial bound and final double continuum states were computed using numerical grid methods. For the continuum states, the numerical grids were extended using exterior complex scaling.

We considered three two-electron systems, He, H^-, and H_2 [1]. By traditional measures of initial state correlation, He is the least correlated system, H_2 at its equilibrium geometry is intermediate, and H^- is the most correlated. For He, the TDCS in OPDI has the correct order of magnitude with only one term in the natural orbital expansion and is fairly well converged including five terms. In H^- the convergence is slower, taking two terms to get the correct shape and magnitude. In contrast, for H_2, as seen in Fig. 1, with the light polarized parallel to the molecular axis, it takes all 14 terms with CI coefficients $> 5 \times 10^{-3}$ before the shape and magnitude resemble the converged answer as well as the one-term Hartree-Fock initial state does in the case of He and H^-.

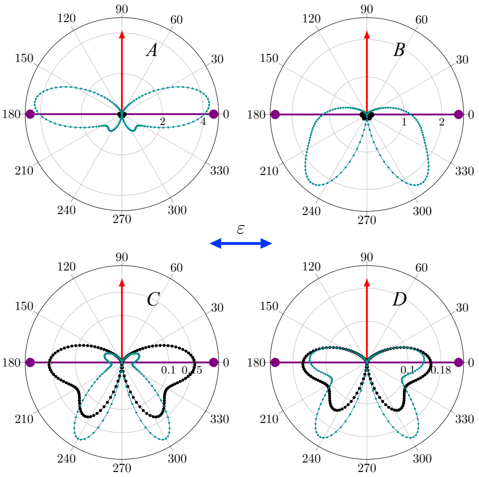

Figure 1. TDCS for OPDI of H_2 at 75 eV for in-plane geometry. Fixed electron (single ended red arrows) with 90% of the available energy and perpendicular to the polarization (double ended blue arrow at the center of the figure). The green lines in panels A, B, C, and D, contain $n = 1, 4, 5,$ and 14 terms, respectively, in the natural orbital expansion of the initial state. The black points give the same data in all panels for the converged calculation.

References

[1] Bello R Y, Yip F L, Rescigno T N, Lucchese R R, and McCurdy C W 2019 *Phys. Rev. A* **99** 013403

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