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

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By decomposing the initial-state wave function into its unique natural orbital expansion, as defined in the 1950s by Löwdin and used in modern studies of entanglement, 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. Final-state correlation of the two ejected electrons is treated completely in numerically accurate calculations as the initial states of He, H^-, and H_2 are built up from correlating configurations in strict order of decreasing natural orbital occupations. In the two-electron atoms it is found that the initial-state correlation plays a sometimes modest but generally measurable role. In striking contrast, for H_2 a large number of correlating configurations in the ground state is often necessary to produce angular distributions even approximately resembling the correct ones. One-photon double photoionization of oriented H_2 is found to be particularly sensitive to left-right correlation along the bond.

I. INTRODUCTION

A central argument motivating a long history of theoretical and experimental interest in single-photon double photoionization of atoms and molecules is that this process is particularly sensitive to the effects of electron correlation. The two ejected electrons must share the energy of a single photon, but the operator for interaction of the electrons with the electromagnetic field is a one-body operator, which for the conditions of most experiments is simply the dipole operator. This fact strongly suggests that the dynamics of double photoejection are correlated, and that expectation has been verified by a large number of experimental measurements showing strong correlation in the angular dependence of the two ejected electrons in double photoionization of both atoms [1–9] and molecules [10–19], only a selection of which we cite here.

The history of theoretical studies of one-photon double photoionization is characterized by an evolution of ever more sophisticated treatments of electron correlation in the context of overcoming the considerable difficulties imposed by the incorporation of appropriate boundary conditions for three-body Coulomb breakup. A sample of that literature employing various theoretical and computational approaches includes many studies of double photoionization of atoms [20–46] and of the more challenging problem of single-photon double photoionization of molecules [47–61].

A number of these calculations, especially the more recent ones, seek to treat the problem exactly in principle. In other words, to the degree such calculations are converged, they can completely treat electron correlation in both the initial and final states. The focus of these studies is generally on the calculation of the triply differential cross section (TDCS) for double photoionization which depends on the emission directions of the two electrons and on the energy sharing between them. Thus the TDCS contains the signatures of the contributions of various types of electron correlation to the dynamics. The implicit assumption in all these studies is that correlation in both the initial and final states must be treated well to achieve accurate results. The literature contains numerous detailed comparisons between these methods, for example, between the time-dependent close-coupling method, the convergent close-coupling method, and the exterior scaling approach we use here, that verify their agreement and validity [33], and there is now no question that we can calculate the TDCS accurately for two-electron systems by a variety of means.

In this study we explore the effects of electron correlation in the initial state of a neutral atom or molecule on the final angular distribution of the ejected electrons. We seek to answer the following question: "To what degree does the observation of one-photon double photoionization of an atom or molecule measure the degree and nature of correlation in the initial neutral system?" The theoretical studies mentioned above have focused extensively on the nature of correlation in the final state and the dynamics of the double-ionization process. To our knowledge, although there are certainly some previous studies that have addressed the question in one way or another [36,40,57], there have been, somewhat suprisingly, no quantitatively systematic studies of the degree to which the correlation of the two ejected electrons in the neutral system prior to double photoionization leaves a distinct signature in the TDCS. To make such a study we must treat final-state correlation completely and accurately, independent of the approximation being used to treat the initial state as it is made more correlated, and we will describe in Sec. III how we can do that using grid methods and exterior complex scaling of the electronic coordinates.

To make this analysis meaningful, we need a rigorous and systematic way of increasing the degree of correlation in the initial state. Fortunately, there is a well-established way to do so using the idea of the natural orbital expansion of the exact

wave function, which was introduced in 1955 by Löwdin [62]. The special properties of the natural orbital expansion for two-electron systems were initially explored by Löwdin and Shull [63] in the early days of electronic structure theory. The concept of the expansion of the exact wave function "as a sum of Slater determinants of all 'ordered' configurations" originates with that early work, and natural orbital expansions have become a standard tool in modern electronic structure theory [64,65]. For a two-electron system, the natural orbital occupations give the ordering of the configurations in terms of their coefficients in an expansion of the exact wave function, as explained in Sec. IV. For two electrons the natural orbital expansion is a special case of the Schmidt decomposition of the density matrix of a quantum system into reduced density matrices of two (in this case identical) subsystems. In the context of quantum information theory it plays a central role in discussions of entanglement [66–71] and its quantification in particular [66].

The procedure we will follow to analyze the role of initial-state correlation in one-photon double photoionization is to start with an effectively converged, highly correlated wave function for the ground state of three systems, He, H⁻, and H_2, and decompose them in terms of their natural orbital expansions. For these systems we can effectively calculate converged final states and construct the TDCS to observe how it changes as correlation contributions are added to the initial state. We find dramatic differences between the signature in the TDCS of the correlation in the initial state in the atoms versus that in H_2. This is a surprising result because the degree to which H_2 is correlated compared to H⁻, for example, does not immediately suggest such radical differences in the sensitivity of the TDCS to small contributions of correlating configurations. The implication is that in other molecules one-photon double ionization may be a more sensitive and specific probe of initial-state correlation in bonds than of electronic correlation in general.

The outline of this paper is as follows. In Sec. II we define the double photoionization amplitude and show how it can be effectively decomposed into contributions of each correlating term in the initial-state wave function. Section III briefly summarizes our computational approach to solving both for the initial state and for the double photoionization amplitude using a combination of a finite-element discrete variable representation of the wave function with exterior complex scaling (ECS) of the electronic coordinates. Then in Sec. IV we review the natural orbital expansion for two-electron singlet states and its particular form for the ground states of the systems we consider here, making a connection with the recent literature on Schmidt decomposition of fermionic systems in the context of discussions of entanglement in quantum information theory. We present the results of calculations on He and H⁻ in Sec. V on the sensitivity of the TDCS to initial-state correlation by considering the convergence of the TDCS with respect to the natural orbital expansion. In Sec. VI we present a similar analysis of H_2 where we find that, in a system less correlated near its equilibrium internuclear distance than H⁻, there is a dramatically stronger signature of initial-state correlation in the TDCS. Finally in Sec. VII we make some concluding remarks about the prospects for experiments on polyatomic molecules that could probe correlation in the ground state in a way that in principle tests the most subtle details of electronic structure.

II. CONNECTION OF INITIAL ELECTRON CORRELATION TO IONIZATION AMPLITUDES

Independent of the theoretical method employed in the calculations, it is useful to look at the formal definition of the TDCS to see why it might be sensitive to initial-state correlation. The TDCS, which depends on the angles of ejection of the two electrons, Ω_1 and Ω_2, and the energy sharing specified by the energy of one of the electrons E_1, is given by (atomic units throughout, $\hbar = e = a_0 = 1$)

$$\frac{d^3\sigma}{dE_1 d\Omega_1 d\Omega_2} = \frac{4\pi^2}{\omega c} k_1 k_2 |f(\mathbf{k}_1, \mathbf{k}_2)|^2, \quad (1)$$

with the double photoionization amplitude defined by (see e.g. [22])

$$f(\mathbf{k}_1, \mathbf{k}_2) = \langle \Psi_{\mathbf{k}_1 \mathbf{k}_2}^{(-)} | \mu_1 + \mu_2 | \Phi_0 \rangle, \quad (2)$$

where $\mu_i = \boldsymbol{\epsilon} \cdot \boldsymbol{\nabla}_i$ is the "velocity form" of the dipole operator for linearly polarized light and $\boldsymbol{\epsilon}$ is the polarization direction of the photon defining the z axis in the laboratory frame. The exact initial state Φ_0 and final state $\Psi_{\mathbf{k}_1 \mathbf{k}_2}^{(-)}$, which is a continuum wave function with two electrons initially in the continuum with incoming wave boundary conditions, must both obviously be represented by correlated wave functions.

While it may be difficult to see directly from the matrix element in Eq. (2) how small correlation contributions to $|\Phi_0\rangle$ contribute to the amplitude, the equivalent "first-order equation" from perturbation theory provides a path to rigorously identifying those contributions. The first-order equation is

$$(E_0 + \omega - H)|\Psi_{sc}^+\rangle = \mu|\Phi_0\rangle, \quad (3)$$

where the solution, $|\Psi_{sc}^+\rangle$, satisfies purely outgoing boundary conditions and E_0 is the energy of the initial state. Considering a two-electron atom, with electronic coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ and infinitely heavy nucleus, the asymptotic form of the solution in the region Ω_0 where all three particles are well separated can be written by using the result for the three-body Coulomb Green's function in Ref. [72] and is found to be [31,32]

$$\Psi_{sc}^+ \underset{\substack{\rho \to \infty \\ \text{in } \Omega_0}}{\longrightarrow} \sqrt{2\pi i} \left(\frac{K^3}{\rho^5} \right)^{1/2} e^{iK\rho + \zeta \ln 2K\rho + i\sigma_0} f(\mathbf{k}_1, \mathbf{k}_2). \quad (4)$$

In Eq. (4) the total energy in terms of the outgoing momenta of the electrons, $\mathbf{k}_1$ and $\mathbf{k}_2$, is $K^2/2 = k_1^2/2 + k_2^2/2$; the hyperradius and hyperangle are $\rho = \sqrt{r_1^2 + r_2^2}$ and $\alpha = \tan^{-1} r_2/r_1$. The other quantities are defined by

$$\zeta = \frac{1}{K} \left(\frac{Z}{\cos\alpha} + \frac{Z}{\sin\alpha} + \frac{1}{\sqrt{1 - \hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_1 \sin 2\alpha}} \right), \quad (5)$$

$$\sigma_0 = \frac{1}{K} \left(\frac{Z \ln \cos^2\alpha}{\sin\alpha} + \frac{Z \ln \sin^2\alpha}{\sin\alpha} \right.$$
$$\left. - \frac{\ln[(1 - \sin 2\alpha \hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2)/2]}{(1 - \sin 2\alpha \hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2)^{1/2}} \right). \quad (6)$$

As we will discuss in detail in Sec. IV the exact wave function can be uniquely decomposed into a sum of determinants, $|\Phi_k\rangle$, of natural spin orbitals,

$$|\Phi_0\rangle = \sum_k c_k |\Phi_k\rangle, \tag{7}$$

the first of which is essentially identical to the Hartree-Fock wave function. Because of the linearity of Eq. (3), the corresponding $|\Psi_{sc}^+\rangle$ is then a sum of functions,

$$|\Psi_{sc}^+\rangle = \sum_k c_k |\Psi_{sc}^{(k)}\rangle, \tag{8}$$

each separately satisfying that equation with the asymptotic form in Eq. (4) containing a contribution to the double photoionization amplitude, $f(\mathbf{k}_1, \mathbf{k}_2)$, which is therefore a sum of contributions due to each of the contributions to $|\Phi_0\rangle$ in Eq. (7).

This is the approach we use here, solving Eq. (3) accurately for different numbers of terms in Eq. (7) on the right-hand side, treating correlation completely on the left-hand side. Even though the coefficient of the dominant ($\approx$ Hartree-Fock) contribution to Eq. (7) is far larger than that of the correlating terms, we will find that the resulting contribution to the photoionization amplitude can be smaller than the contributions of correlating terms with much smaller coefficients. The contributions to $f(\mathbf{k}_1, \mathbf{k}_2)$ can of course interfere in the coherent sum that produces the TDCS. Although one might expect that the importance of initial-state correlation in double photoionization would be larger for more correlated systems, we will see that this is not necessarily the case.

To address that question we must specify what we mean by a "more correlated system." There are at least two commonly used measures of the degree of electronic correlation in a system. In bound-state electronic structure theory, one standard measure of the degree of correlation is the correlation energy, defined as the difference between the Hartree-Fock energy, E_{HF}, and the exact nonrelativistic energy, E_{NR} [73]. The degree of correlation, K_E, based on energy can then be expressed as the exact nonrelativistic electronic energy divided by the Hartree-Fock electronic energy, i.e., $K_E = E_{NR}/E_{HF}$, and we note that $K_E \geqslant 1$. Alternatively, Grobe *et al.* [74] make a strong argument that the amount by which the trace of the square of the one-electron density matrix is less than one is a better quantitative measure of correlation in the wave function. They therefore propose the definition of the degree of correlation as $K = 1/\text{tr}(\boldsymbol{\rho}^2)$, a quantity also used in discussions of entanglement quantification [66]. That quantity is of course equal to one if there is only one occupied natural orbital and the wave function is exactly expressible as one determinant, and is greater than one otherwise. In Secs. V and VI we will explore the sensitivity of the TDCS to initial-state correlation and see to what extent that sensitivity is related to traditional measures of the degree of correlation in the two-electron systems considered here.

III. CALCULATION OF THE TRIPLE DIFFERENTIAL CROSS SECTION FOR DOUBLE PHOTOIONIZATION USING EXTERIOR COMPLEX SCALING

A. Double photoionization amplitudes

The method for combining numerical grids with exterior complex scaling of the electronic coordinates to solve the double ionization and electron-impact ionization problems has been described in detail elsewhere [41,52,75], and so here we give only a summary of the essential ideas. The correct outgoing boundary conditions for both single and double ionization are imposed on Ψ_{sc}^+ in Eq. (3) by applying the ECS transformation [75–77] to the radial coordinates of both electrons, which scales those coordinates by a complex factor $e^{i\theta}$ beyond some radius $\mathcal{R}_0$,

$$r \rightarrow \begin{cases} r, & \text{if } r \leqslant \mathcal{R}_0, \\ \mathcal{R}_0 + (r - \mathcal{R}_0)e^{i\theta}, & \text{if } r > \mathcal{R}_0, \end{cases} \tag{9}$$

and requiring Ψ_{sc}^+ to vanish for large r_1 or r_2 on the complex contour. The amplitude $f(\mathbf{k}_1, \mathbf{k}_2)$ for single-photon double ionization associated with Ψ_{sc}^+ is given, up to an irrelevant overall phase, by a volume integral over a finite volume [30,52,75],

$$\begin{aligned} &f(\mathbf{k}_1, \mathbf{k}_2) \\ &= \langle \Phi^{(-)}(\mathbf{k}_1, \mathbf{r}_1) \Phi^{(-)}(\mathbf{k}_2, \mathbf{r}_2) | E - T - V | \Psi_{sc}^+ \rangle, \end{aligned} \tag{10}$$

where $E = E_0 + \omega$ is the excess energy above the double ionization threshold, T is the two-electron kinetic-energy operator, and V in the case of an atom with nuclear charge Z is the sum of the one-electron potentials,

$$V = -Z/r_1 - Z/r_2, \tag{11}$$

while in the molecular case (with nuclei fixed with coordinates $\pm \mathbf{A}$) the potential in Eq. (10) is the sum of the nuclear attraction potential seen by each of the electrons,

$$V = -\frac{1}{|\mathbf{r}_1 - \mathbf{A}|} - \frac{1}{|\mathbf{r}_1 + \mathbf{A}|} - \frac{1}{|\mathbf{r}_2 - \mathbf{A}|} - \frac{1}{|\mathbf{r}_2 + \mathbf{A}|}. \tag{12}$$

The "testing functions" $\Phi^{(-)}(\mathbf{k}, \mathbf{r})$ in Eq. (10) for the *atomic case* are momentum-normalized Coulomb functions with charges Z equal to the charge of the nuclear potential in V [30,41]. With that choice Eq. (10) exactly projects out the single-ionization contributions from the double-ionization channels by orthogonality of the Coulomb functions to the residual bound one-electron atom. Following the same logic, in the molecular case the testing functions are the H_2^+ continuum wave functions [52]. The triple-differential cross section (TDCS) for double photoionization is directly related to the amplitude $f(\mathbf{k}_1, \mathbf{k}_2)$ by Eq. (1).

B. Representation of the wave function in ECS calculations

We solve the driven equation, Eq. (3), by expanding both the first-order wave function, Ψ_{sc}^+, and the initial state, Φ_0, in products of spherical harmonics as was done in previous calculations on He [32], H^- [41], and H_2 [52], where a single center expansion around the middle of the molecule was used,

$$\Psi_{sc}^+ = \sum_{l_1 m_1} \sum_{l_2 m_2} \frac{1}{r_1 r_2} \psi_{l_1 m_1, l_2 m_2}(r_1, r_2) Y_{l_1 m_1}(\hat{\mathbf{r}}_1) Y_{l_2 m_2}(\hat{\mathbf{r}}_2). \tag{13}$$

The radial function $\psi_{l_1 m_1, l_2 m_2}(r_1, r_2)$ is described by the combination of a discrete variable representation further expanded in a product basis of one-dimensional finite-element-method (FEM) discrete-variable representation (DVR) functions. The DVR basis functions are the cardinal functions (polynomials) of a discrete variable representation based on a Gauss-Lobatto quadrature within each radial finite element:

$$\psi_{l_1 m_1, l_2 m_2}(r_1, r_2) = \sum_{i,j} C_{ij}^{l_1 m_1, l_2 m_2} \varphi_i(r_1)\varphi_i(r_2), \qquad (14)$$

where $\varphi_i(r)$ is a DVR basis function and the coefficients satisfy $C_{ij}^{l_1 m_1, l_2 m_2} = C_{ji}^{l_2 m_2, l_1 m_1}$.

We include all the terms, labeled by l_1, m_1, l_2, m_2 in Eq. (13), up to a maximum value, $l_{\max}$, of l that produce a scattered wave function with total angular momentum quantum numbers $L = 1$, $M = 0$, and Φ_0 with $L = 0$, $M = 0$ in the atomic case. For the molecular case, we include all the terms that contribute to Σ_u^+ ($M = 0$) and Π_u ($M = \pm 1$) for Ψ_{sc}^+ and Σ_g^+ ($M = 0$) for Φ_0. In all the calculations presented here the value of $l_{\max}$ for Ψ_{sc}^+ was held fixed at the value needed to converge calculations with a completely correlated initial state, while the degree of correlation in Φ_0 was varied. The numerical parameters we used are similar to those of previous calculations [32,41,52], where extensive convergence tests were performed. For H^- and He we used $l_{\max} = 7$, and for H_2 we also used $l_{\max} = 7$ for both Σ_u^+ and Π_u symmetries. The values of $l_{\max}$ are the same for the initial and final states in all cases.

The radial basis and ECS parameters were also similar to those of previous studies. For H^- 15th-order Gauss quadrature was used in 11 finite elements, with ECS scaling beginning at $\mathcal{R}_0 = 95$ bohr and a maximum value of r for each electron of 130 bohr. For He the radial grid was nine finite elements with 15th-order quadrature in each, with the value of $\mathcal{R}_0 = 65$ bohr and a maximum value of r of 95 bohr. In the calculations on H_2 we used a radial basis of nine finite elements with 15th-order quadrature in each, $\mathcal{R}_0 = 65$ bohr, and a maximum value of r of 95 bohr. In all cases the ECS scaling angle, θ, was $30°$ and, as expected [78], there was essentially no variation in the results of grid based calculations with varying θ.

This representation of the wave functions reduces the solution of Eq. (3) to the solution of large sets of linear equations, described in Refs. [41] and [52]. The fully correlated ground-state wave function (and natural orbitals) are obtained in our calculations using the finite element method and discrete variable representation (FEM-DVR) by diagonalizing the full Hamiltonian of each system using only the real portions of the radial FEM-DVR grid, truncated at a value of r large enough to contain the ground state completely. The corresponding natural orbitals are constructed by applying the algorithm of Sec. IV once the coefficients $C_{ij}^{l_1 m_1, l_2 m_2}$ in Eq. (14) have been calculated.

IV. NATURAL ORBITALS OF TWO-ELECTRON SYSTEMS

The initial states of the systems we treat here, namely nondegenerate singlet states (^1S and $^1\Sigma_g^+$), are examples of the simplest version of the natural orbital expansion of the exact

wave function. In that case, as Löwdin originally showed [63] the exact wave function can be expanded as a sum of Slater determinants of only doubly occupied natural orbitals, $\chi_k(\mathbf{r}_1)$,

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = \sum_k^N c_k |\chi_k(\mathbf{r}_1)\alpha(1)\,\chi_k(\mathbf{r}_2)\beta(2)|, \qquad (15)$$

where $\mathbf{x}_i$ denotes spin and space coordinates of electron i and N is the number of the natural orbitals with nonzero occupations. The coefficients of the expansion, c_k, are square roots of the natural orbital occupations, and thus the natural orbital expansion in Eq. (15) expresses the exact wave function as a uniquely defined sum of Slater determinants, which can be ordered by the magnitudes of their contributions. A natural orbital expansion of the initial electronic state ordered by occupation number thus provides a well-defined basis with which to study the convergence of the TDCS for the double photoionization process with respect to increasing the initial-state correlation.

The phases of the coefficients, c_k, in Eq. (15) in general are not all the same, and so we describe here how they are calculated as well as the general applicability of the expansion. "Natural spin orbitals" were introduced by Löwdin [62,63] as the functions which diagonalize the one-electron reduced density matrix. The one-electron density matrix for an N-electron system is defined by the expression familiar in the electronic structure literature [64],

$$\rho(\mathbf{x}; \mathbf{x}') = \int \Phi(\mathbf{x}, \mathbf{x}_2, \ldots, \mathbf{x}_N)\Phi^*(\mathbf{x}', \mathbf{x}_2, \ldots, \mathbf{x}_N)$$
$$\times d\mathbf{x}_2 \ldots d\mathbf{x}_N, \qquad (16)$$

where $\mathbf{x}_i$ denotes space and spin coordinates, and its eigenfunctions satisfy

$$\int \rho(\mathbf{x}; \mathbf{x}')\chi_n(\mathbf{x}')d\mathbf{x}' = \lambda_n \chi_n(\mathbf{x}), \qquad (17)$$

where the eigenvalues λ_n are called the natural orbital occupations and, with the normalization of Φ and Eq. (16) for ρ, they satisfy $\sum_n \lambda_n = 1$. They are a standard tool of electronic structure theory, where they reduce the number of determinants required to represent the wave function to any particular accuracy when compared to being expressed in other orbital bases.

Systems with only two electrons are an important special case in which simplifications appear that do not apply to many-electron systems. The essential theorem is that for a two-electron system; the wave function Φ is expressible in the explicitly diagonal form [64,68]

$$\Phi = \sum_i \mu_i f_i(\mathbf{x}_1)t_i^*(\mathbf{x}_2), \qquad (18)$$

where the natural spin orbitals in this expansion are eigenfunctions of the density matrix with the same eigenvalues

$$\int \rho(\mathbf{x}; \mathbf{x}')f_i(\mathbf{x}')d\mathbf{x}' = |\mu_i|^2 f_i(\mathbf{x}),$$
$$\qquad (19)$$
$$\int \rho(\mathbf{x}; \mathbf{x}')t_i(\mathbf{x}')d\mathbf{x}' = |\mu_i|^2 t_i(\mathbf{x}).$$

The diagonal form of Eq. (18) applies to both ground and excited states [79], and specializes [63,68] to the simpler form

in Eq. (15) for our cases. It almost always radically reduces the number of terms in the expansion relative to full CI in the natural orbital basis.

The centrality of the natural orbital expansion of the wave function in the understanding of correlation derives from the fact that Eqs. (18) and (19) are an example of the Schmidt decomposition of a many-particle wave function in terms of the eigenfunctions of the reduced density matrices corresponding to dividing the particles into two groups. The idea of the Schmidt decomposition [80] also appears extensively in recent treatments of quantum entanglement [66–71]. Although Eq. (18) does not explicitly display permutational symmetry or the property of being a spin eigenfunction, there are general discussions in the literature of how to construct versions that do so for both fermionic and bosonic systems [68]. The natural orbital expansion has also been used to provide a quantitative measure of correlation in two-electron systems [74,81].

Our construction of the two-electron wave function in Eq. (13) for singlet states is an expansion in terms of basis functions

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = \sum_{i,j} C_{ij}\, \psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2) \frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}}, \quad (20)$$

with

$$\psi_j(\mathbf{r}) = \varphi_j(r) Y_{l_j, m_j}(\hat{r}) \quad (21)$$

being the products of FEM DVR radial functions and spherical harmonics. The density matrix is defined in terms of this basis as

$$\rho(\mathbf{x}; \mathbf{x}') = (\alpha\,\alpha' + \beta\,\beta') \sum_{kl} \psi_l(\mathbf{r})\psi_k^*(\mathbf{r}')\rho_{l,k}, \quad (22)$$

where

$$\rho_{l,k} = \sum_m C_{lm}C_{km}^*, \quad \boldsymbol{\rho} = \mathbf{CC}^\dagger. \quad (23)$$

Because the spin eigenfunction for a singlet state is antisymmetric, the matrix $\mathbf{C}$ must be symmetric. For the ^1S and $^1\Sigma_g^+$ states we consider here, where the sum of the quantum numbers in the spherical harmonics of the product basis must sum to zero, $m_1 + m_2 = 0$, the matrix $\mathbf{C}$ is also real (as is the two-electron ground wave function), and that fact simplifies the algebra of constructing the natural orbital coefficients [82].

In this case the real-valued orthogonal matrix $\mathbf{U}$ that diagonalizes $\mathbf{C}$ also diagonalizes the density matrix:

$$\mathbf{CU} = \mathbf{Uc}, \quad \boldsymbol{\rho}\mathbf{U} = \mathbf{Uc}^2 = \mathbf{U}\boldsymbol{\lambda}. \quad (24)$$

The natural orbitals are then defined by the matrix relation

$$\boldsymbol{\chi} = \mathbf{U}^T \boldsymbol{\psi} \quad (25)$$

and the eigenvalues of $\mathbf{C}$ satisfy $c_k^2 = \lambda_k$ and are thus the square roots of the occupation numbers of the natural orbitals χ_k, but with well-defined phases. Substituting Eq. (25) into the wave function in Eq. (20) leads to the natural orbital expansion

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = \frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}} \sum_k^M c_k \chi_k(\mathbf{r}_1)\chi_k(\mathbf{r}_2), \quad (26)$$

where M is the number of the natural orbitals with nonzero occupations and thus to Eq. (15).

V. EFFECTS OF INITIAL-STATE CORRELATION IN He AND H⁻

To systematically analyze the effects of initial-state correlation we first solve Eq. (3) for Ψ_{sc}^+ using only the first term in the natural orbital expansion of Φ_0 that was calculated with the value of $l_{\max}$ necessary to converge the completely correlated calculation, and then add the remaining terms in order of increasing natural orbital occupation. In every such calculation we use the same value of $l_{\max}$ and the other numerical parameters to represent both sides of the equation. While optical selection rules dictate that each term in the natural orbital expansion of the initial state is only connected by the dipole operator to a subset of all angular momentum contributions to Ψ_{sc}^+, the electron repulsion potential, $1/r_{12}$, can of course connect all such contributions of the $l_1 m_1$, $l_2 m_2$ contributions in Eq. (13). Thus in these calculations we are varying the amount of initial-state correlation, adding terms in the order of their contribution to Φ_0 while always allowing the final doubly ionized state to be fully correlated.

In Table I we compare the natural orbital coefficients for the two electron atoms He and H⁻. In both cases the first natural orbital is graphically indistinguishable from the Hartree-Fock $1s$ orbital. The Hartree-Fock energy of H⁻ is above that of the hydrogen atom, as given in Table II, and so it is physically bound only because of correlation energy. The absolute correlation energy of H⁻ is less than that of He although much larger relative to its total energy. Thus the value of K_E is larger for H⁻ than it is for He. This same trend is seen in the values of K obtained from the density matrix verifying that H⁻ is the more correlated of the two atoms.

The convergence of the TDCS calculated in the velocity gauge for He at a photon energy of $\hbar\omega = 99$ eV with increasing number of terms in the natural orbital expansion is shown in Fig. 1. The convergence is so rapid that adding only the natural orbital term with the next largest coefficient ($2s$ in Table I) produces essentially the converged result. The convergence of the TDCS for H⁻ for a photon energy of $\hbar\omega = 18$ eV, chosen to produce two electrons whose shared energy is the same fraction of the double ionization potential, is shown in Fig. 2. In this case adding the second term in the natural orbital expansion ($2s$) is insufficient to produce a result indistinguishable from the exact TDCS, but adding one more orbital shell ($2p$) converges the TDCS.

In Fig. 1 we also show results in the length gauge. In all cases the cross sections calculated in the length gauge converge somewhat more slowly. For example, in Fig. 1 the contributions of three natural orbitals are necessary in the length gauge to recover a result close to that obtained with only the Hartree-Fock initial state in the velocity gauge. However, all the trends we observe here in the velocity gauge (for the atoms as well as for H$_2$) are reproduced in the length gauge, with more terms always being required in the length gauge. For that reason, and simplicity of presentation, we restrict the results we present in the other figures to the more rapidly convergent velocity gauge. Of course, length and velocity gauges give

TABLE I. Coefficients of the natural expansion of the He and H⁻ ground states, with comparison to earlier calculations employing analytic basis sets and the present calculations in the case of He. Reference [64] comments on the signs. Note that the $3p$, $4p$, $3d$, and $4d$ orbitals with the other possible values of m have coefficients with the same magnitude, but with sometimes different signs.

NO (m)	Ref. [83] He	Ref. [84] He	Present He	Present H⁻
$1s$ (0)	+0.99599	+0.99598	$+9.95973 \times 10^{-1}$	$+9.71958 \times 10^{-1}$
$2s$ (0)	−0.06148	−0.06163	-6.15655×10^{-2}	-2.05838×10^{-1}
$3s$ (0)	−0.00786	−0.00790	-7.89868×10^{-3}	-1.44055×10^{-2}
$4s$ (0)	−0.00197	−0.00192	-1.99462×10^{-3}	-2.92130×10^{-3}
$2p$ (0)	−0.03563	−0.03574	-3.57540×10^{-2}	-6.33681×10^{-2}
$2p$ (+1)			$+3.57540 \times 10^{-2}$	$+6.33681 \times 10^{-2}$
$2p$ (−1)			$+3.57540 \times 10^{-2}$	$+6.33681 \times 10^{-2}$
$3p$ (0)	−0.00638	−0.00643	-6.41313×10^{-3}	-8.96297×10^{-3}
$4p$ (0)	−0.00180	−0.00189	-1.82277×10^{-3}	-2.23093×10^{-3}
$3d$ (0)	−0.00566	−0.00566	-5.72895×10^{-3}	-7.98852×10^{-3}
$4d$ (0)	−0.00178	−0.00174	-1.80151×10^{-3}	-2.34227×10^{-3}

precisely the same results when enough terms for convergence are included in the natural orbital expansion of the initial state.

In Fig. 2 we see that the TDCS converges slightly more slowly for H⁻, as one would expect by any measure of the degree of correlation in the initial state. Nonetheless, in both cases the Hartree-Fock initial state is sufficient to produce the general shape and the rough magnitude (within a factor of three in the case of H⁻) of the cross section. It has been argued previously [41] that extreme unequal energy sharing minimizes correlation in the final state. While that is certainly true at very high photon energies, we find that for equal energy sharing at these energies (not shown) the conclusions about the convergence of the TDCS with the inclusion of initial-state correlation are the same. For the atomic cases, in general the Hartree-Fock wave function is nearly adequate. The molecular case is very different.

VI. EFFECTS OF INITIAL-STATE CORRELATION IN H₂

To understand the more dramatic effects of correlation on one-photon double ionization of H₂, it is useful first to analyze the convergence of the natural orbital expansion itself. The natural orbital coefficients calculated with the procedure in

TABLE II. Energies and degree of correlation for He, H⁻, and H₂ at several internuclear distances. Hartree-Fock energies, E_{HF}, are from Ref. [85] for He, Ref. [86] for H⁻, and computed using an aug-cc-pV6Z basis set [87] for H₂. Exact nonrelativistic energies, E_{NR}, are from Ref. [88] for He and H⁻ and from Ref. [89] for H₂.

System	E_{HF}	E_{NR}	K_E	K
He	−2.86168	−2.90372	1.01469	1.01625
H⁻	−0.48793	−0.52775	1.08161	1.11819
H₂($R = 1.0$ bohr)	−1.08513	−1.12454	1.03631	1.02614
H₂($R = 1.2$ bohr)	−1.12502	−1.16494	1.03548	1.03057
H₂($R = 1.4$ bohr)	−1.13363	−1.17448	1.03603	1.03653
H₂($R = 1.6$ bohr)	−1.12635	−1.16858	1.03750	1.04450
H₂($R = 1.8$ bohr)	−1.11096	−1.15507	1.03971	1.05475
H₂($R = 2.0$ bohr)	−1.09162	−1.13813	1.04261	1.06786
H₂($R = \infty$)	−0.71580	−1.00000	1.39704	2.00000

Sec. IV are listed at the H₂ equilibrium internuclear distance in Table III. The table is organized in terms of n, which is the effective principal quantum number for each orbital in the united atom limit. More specifically, the value of n for the orbital with the highest occupation in a given symmetry is the principal quantum number for the lowest atomic state in the united atom limit. For example, the most important σ_g orbital is assigned $n = 1$, corresponding to the $1s$ atomic orbital. Then the lowest σ_u and π_u orbitals are given by $n = 2$

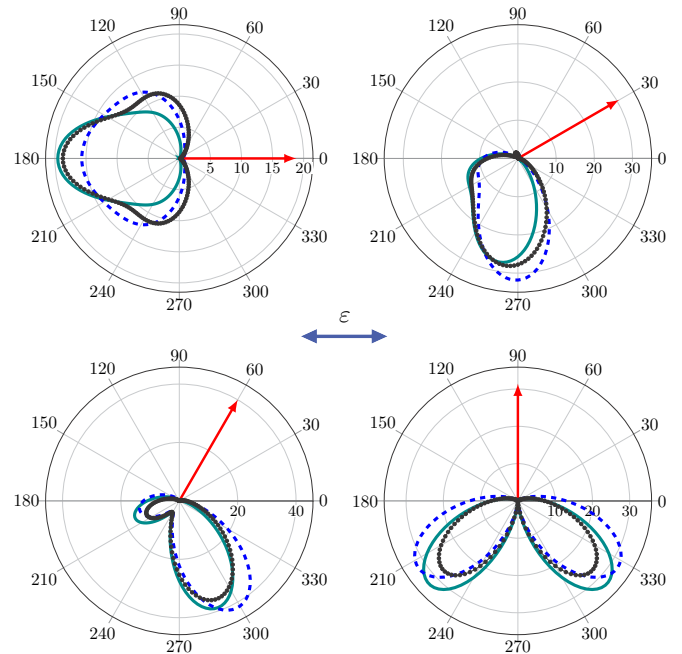
FIG. 1. TDCS at $\hbar\omega = 99$ eV for double ionization of He for in-plane geometries with unequal energy sharing. Fixed electron (single ended red arrows) with 90% of the available energy and various directions with respect to the polarization (double ended blue arrow). Solid dark-cyan line (velocity gauge): including only the first term ($1s^2$) in the natural orbital expansion of the initial-state wave function. Dashed blue line (length gauge): including three terms ($1s^2 + 2s^2 + 2p^2$). Black points: including all the natural orbitals in the expansion (converged wave function). Units are barn/eV/sr².

TABLE III. Coefficients in the natural expansion of H_2 ground state at $R = 1.4$ bohr. Coefficients for the configurations corresponding to orbitals with $\pm m$ are the same. n is the effective principal quantum number as defined in the text.

n	σ_g	σ_u	π_u	π_g	δ_g	δ_u
1	$+9.91039 \times 10^{-1}$					
2	-5.47711×10^{-2}	-9.95069×10^{-2}	$+4.62621 \times 10^{-2}$			
3	-9.97783×10^{-3}	-9.68934×10^{-3}	$+6.57201 \times 10^{-3}$	$+8.48462 \times 10^{-3}$	-6.66464×10^{-3}	
4	-6.56733×10^{-3}	-2.77750×10^{-3}	$+2.59382 \times 10^{-3}$	$+2.28040 \times 10^{-3}$	-1.83612×10^{-3}	-2.28496×10^{-3}
5	-2.69258×10^{-3}	-2.25059×10^{-3}	$+1.68292 \times 10^{-3}$	$+1.04529 \times 10^{-3}$	-9.69261×10^{-4}	-8.49212×10^{-4}

corresponding to the $2p$ orbital in the united atom limit. The natural orbitals of that symmetry are then numbered in order of their importance starting at that number. This arrangement of the orbitals reflects the fact that for H_2, as shown in Table III, the configurations constructed from orbitals with the same n have expansion coefficients of very similar magnitude. The same relationship is also present in the atomic systems presented in Table I.

The rate of convergence with respect to n of the occupation for the orbitals in each symmetry is presented in Fig. 3. We also present in Fig. 3 a comparison of the convergence natural orbital occupations with respect to n for both H_2 at $R = 1.4$ bohr with those of He and H^-. We can see that, in agreement with the relative values of K and K_E shown in Table II, the convergence of correlation of the H_2 system is intermediate between He and H^-. We note, however, at higher

values of n the molecular system converges somewhat more slowly. It is interesting to consider how the correlation of H_2 varies a function of R. Of course, in the united atom limit, the electronic state of H_2 just becomes the ground state of He. In contrast, in the separated atom limit, H_2 becomes two isolated H atoms. In that limit, the restricted Hartree-Fock wave function contains both covalent and ionic terms leading to rather a large correlation energy and as shown in Table II and the value of $K \equiv 1/\text{tr}(\boldsymbol{\rho}^2)$ rigorously limits to 2.

The convergence of the TDCS with respect to the addition of terms in the natural orbital expansion of the wave function is, however, radically different from that for either atom. In the comparisons in this section we focus on the case of strongly unequal energy sharing that was investigated by experiment and theory in an earlier study [53] that explored the changes with varying internuclear distance in the TDCS. The photon energy here is $\hbar\omega = 75$ eV, as in that study, and the internuclear distances for which we report results here are the ones for nuclear kinetic-energy release of 0.55 and 0.7 hartrees that appear there together with comparison of the converged TDCS with experiment. The results for equal energy sharing at this photon energy are similar to what we find below.

In Fig. 4 we plot the TDCS for unequal energy sharing with the polarization vector along the axis of the molecule. With just the first term (again nearly indistinguishable from the Hartree-Fock wave function) the cross section not only has a completely incorrect angular dependence, but is more
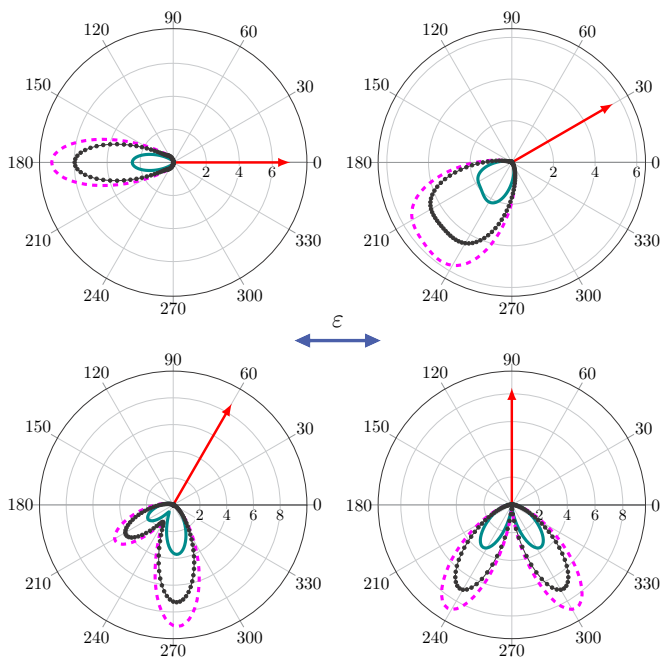

FIG. 2. TDCS for double ionization of H^- at $\hbar\omega = 18$ eV for in-plane geometries with unequal energy sharing. Fixed electron (single ended red arrows) with 90% of the available energy and various directions with respect to the polarization (double ended blue arrow). Solid dark-cyan line: including the first term in the natural orbital expansion of the initial-state wave function. Dashed magenta line: including two terms ($1s^2 + 2s^2$). Black points: including all the natural orbitals in the expansion (converged wave function). Units are kbarn/eV/sr^2.
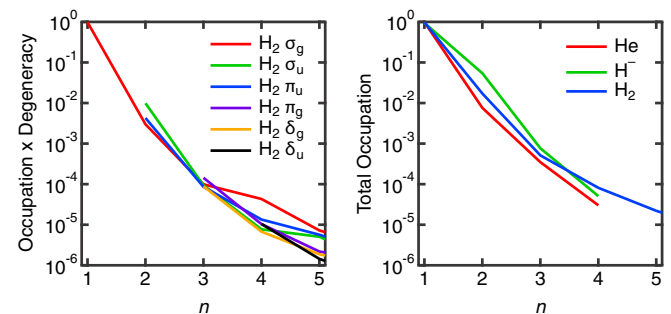

FIG. 3. Convergence of the natural expansions for the two-electron systems considered here. Left panel: convergence of the contributions from the orbitals of different symmetry in H_2 at $R = 1.4$ bohr as a function of n. Right panel: comparison of the convergence of the H_2 natural orbital expansion, summed over all symmetries for each n, and the convergence of the corresponding natural orbital expansions in He and H^-. In all cases, the contributions from degenerate orbitals have been summed.
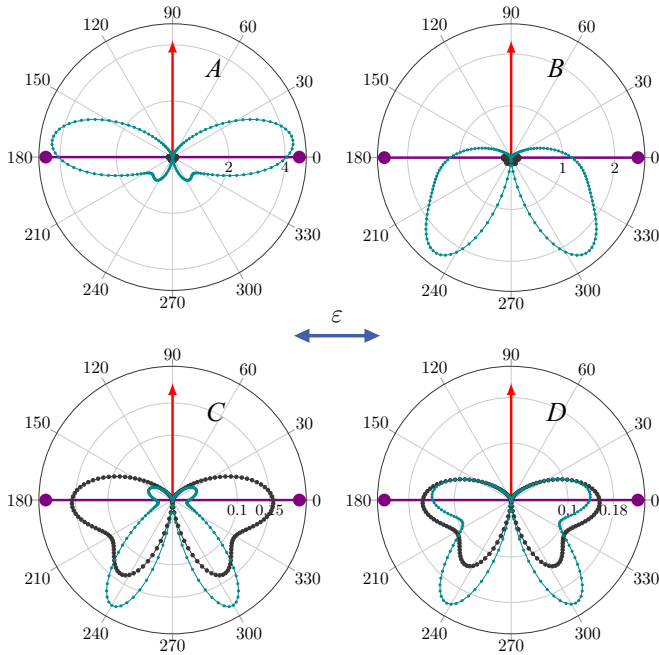
FIG. 4. TDCS for double ionization of H_2 at 75 eV for in-plane geometry at $R = 1.43$ bohr and $\theta_{mol} = 0°$ for which only the $^1\Sigma_u^+$ continuum final-state symmetry contributes. Fixed electron (single ended red arrows) with 90% of the available energy and perpendicular to the polarization (double ended blue arrow at the center of the figure). Light dotted curve (cyan points): increasing amounts of correlation in the initial state as contributions to the natural orbital expansion of its wave function are added. **A**: $1\sigma_g$, **B**: **A** $+ 1\sigma_u + 1\pi_u$, **C**: **B** $+ 2\sigma_g$ (all coefficients greater than 10^{-2}), and **D**: including all natural orbital configurations with coefficients greater than 5×10^{-3}. The darker curve (black points) gives the same data in all panels (note the changing radial scales) and includes all the natural orbitals in the expansion (converged wave function). Units are barn/eV/sr^2.

FIG. 5. Same as Fig. 4 but for molecular orientation $\theta_{mol} = 90°$ for which only the $^1\Pi_u$ continuum final-state symmetry contributes.

the cross sections for perpendicular polarization in Fig. 5, which shows the calculations analogous to those in Fig. 4, to show a more "atomic" behavior, and that is in fact the case. The convergence with respect to the inclusion of correlating terms in the natural orbital expansion is similar to that shown in Fig. 2 for H^-.

The comparison between Figs. 4 and 5 is evidence that the sensitivity to initial-state correlation is a *molecular* effect. For

than a factor of 10 larger than the converged result. Adding the first two natural orbital configurations of σ_u and π_u symmetry, which are the first two terms describing angular correlation, also produces the wrong order of magnitude and incorrect shape. Only after adding the $2\sigma_g^2$ with a smaller occupation than either the σ_u and π_u configurations does the cross section have the correct order of magnitude but still not the right shape. Even adding all the terms with coefficients greater than 5×10^{-3}, a total of 10 more configurations (with degenerate pairs) that can be identified in Table III, does not produce a completely converged TDCS. This result from the systematic addition of initial-state correlation supports the assertion [53] that one-photon double photoionization "is exquisitely sensitive to electron correlation in both the initial and final state," at least for the case of molecules.

It has been pointed out that in one-photon double ionization of H_2 [57] and in photoionization of H_2^+ [90] the ionization dynamics in the final state for polarization perpendicular to the axis, which has Π_u symmetry, is dominated by p waves at all internuclear distances, whereas that is not true of the Σ_u^+ component that contributes solely in Fig. 4 and for which the p-wave component is near a minimum at the equilibrium internuclear distance. Following that logic, one would expect
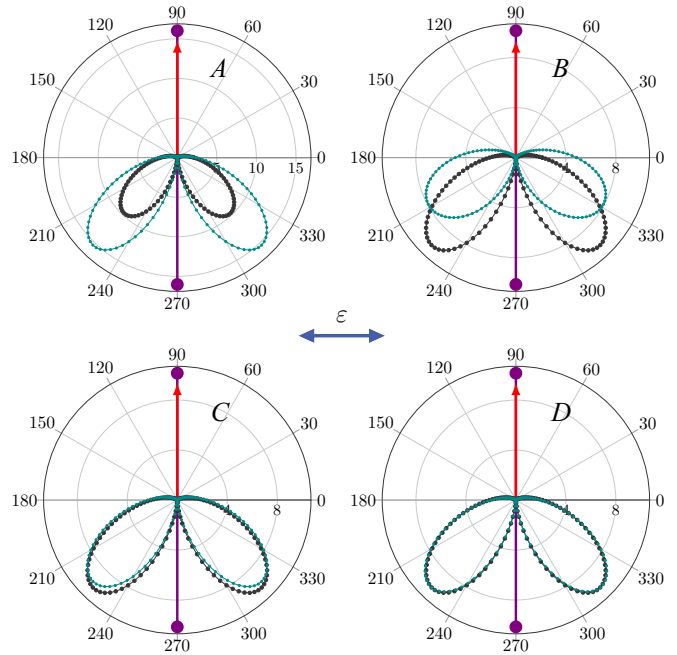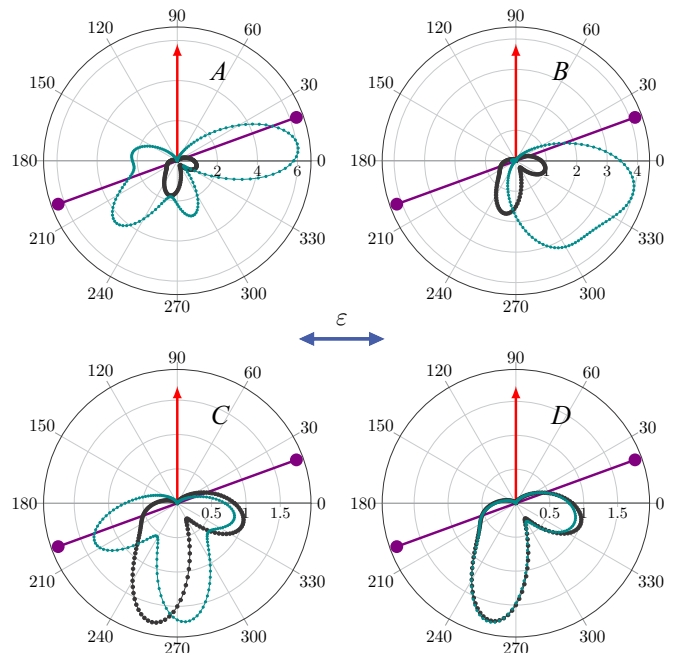

FIG. 6. Same as Fig. 4 but for molecular orientation $\theta_{mol} = 20°$ and internuclear distance $R = 1.43$ bohr corresponding to kinetic-energy release of 0.7 hartrees.

TABLE IV. Occupation numbers c_k^2 for the natural orbitals of the H_2 ground state for different internuclear distances (in bohr). These are the dominant contributions to the natural orbital expansion over this range of R. The contribution from the $1\pi_u$ orbital includes both of the degenerate orbitals.

NO	$R = 1.0$	$R = 1.2$	$R = 1.4$	$R = 1.6$	$R = 1.8$	$R = 2.0$
$1\sigma_g$	9.8716×10^{-1}	9.8502×10^{-1}	9.8216×10^{-1}	9.7836×10^{-1}	9.7351×10^{-1}	9.6737×10^{-1}
$1\sigma_u$	5.0910×10^{-3}	7.0773×10^{-3}	9.9016×10^{-3}	1.3783×10^{-2}	1.8775×10^{-2}	2.5088×10^{-2}
$1\pi_u$	3.9014×10^{-3}	4.1284×10^{-3}	4.2804×10^{-3}	4.3328×10^{-3}	4.3260×10^{-3}	4.2830×10^{-3}
$2\sigma_g$	3.2629×10^{-3}	3.1500×10^{-3}	2.9999×10^{-3}	2.8371×10^{-3}	2.6894×10^{-3}	2.5467×10^{-3}

polarization parallel to the molecular axis, the electromagnetic field drives the electrons parallel to the bond and thus across the nuclei. The terms in Table III that contribute to left-right correlation, namely the σ_u^2 configurations, are connected directly by the dipole operator to the correlated $^1\Sigma_u^+$ double continuum to which this motion causes the transition. The σ_g^2 configurations are dipole connected to the same configurations in the double continuum, and the coefficients of the σ_u^2 and σ_g^2 configurations decay most slowly in Table III. So the sensitivity of the TDCS to initial-state correlation in the molecule is a result of the fact that left-right correlation is the most important correlating contribution in both the initial and (in this orientation) final states.

The sensitivity of the TDCS in H_2 to varying internuclear distance has been studied previously [53,57]. It is directly observable from the variation in the angular distributions of the two electrons with kinetic-energy release of the nuclei, which via the Coulomb explosion of the molecule following double ionization maps directly onto the internuclear distance. This effect is revealed most strongly in the TDCS for molecular orientations that are neither parallel nor perpendicular to the polarization vector, for which the $^1\Sigma_u^+$ and $^1\Pi_u$ continuum contributions are mixed coherently. In Fig. 6 we show the

slow convergence with respect to the natural orbital expansion of a case shown in Ref. [53] for kinetic-energy release of 0.70 hartrees corresponding to 1.43 bohr, near the equilibrium internuclear distance.

It has been known since the early history of molecular physics and the Heitler-London [91] model for bonding in H_2 that the correlation contributions, in particular the contribution of the first σ_u^2 configuration, vary rapidly with increasing internuclear distance in H_2 as the wave function converts into that of two separated atoms, and this behavior can be seen in Table IV. For that reason it was expected [53,57] that variations in the TDCS with kinetic-energy release might contain a signature of changes in initial-state correlation combined with changes in the correlation of the final double continuum. In Fig. 7 we show the convergence of the TDCS for a kinetic-energy release that was studied previously of 0.55 hartrees corresponding to an internuclear distance of 1.82 bohr. With only a few natural orbital configurations, the calculated TDCS is only slightly further from convergence than at 1.43 bohr, even though the coefficient of the first correlating configuration, $1\sigma_u^2$, is nearly twice as large.

One of the most dramatic variations with kinetic-energy release was seen in the experimental results for an "out of
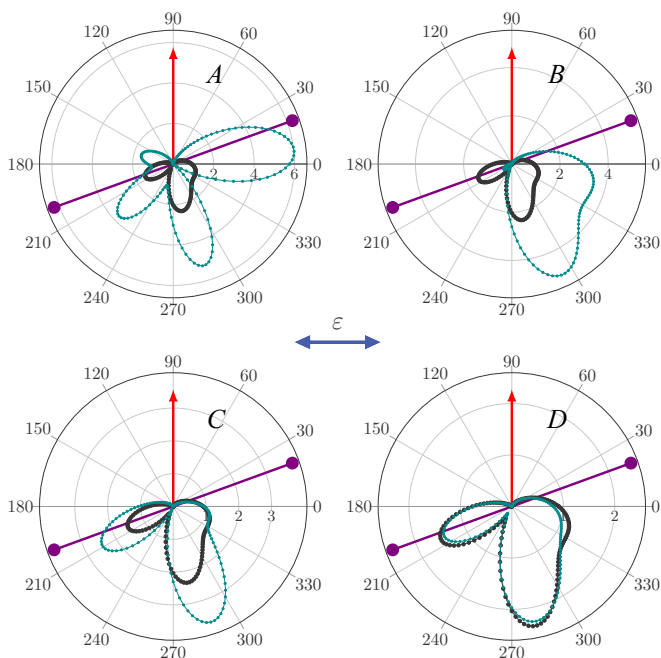

FIG. 7. Same as Fig. 6 but for $R = 1.82$ bohr corresponding to kinetic-energy release of 0.55 hartrees.
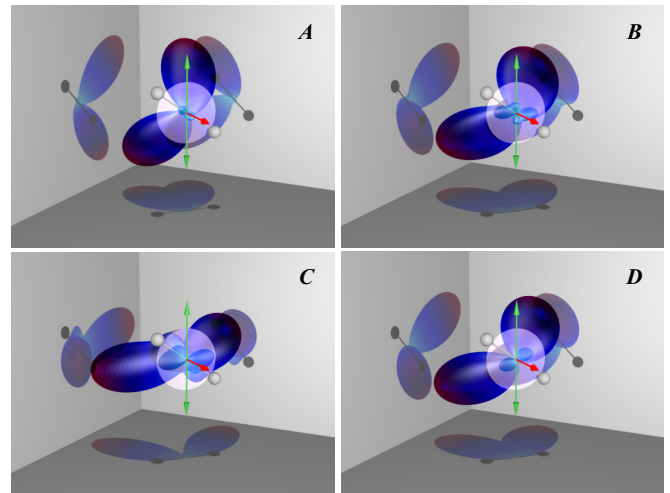

FIG. 8. TDCS for double ionization of H_2 for out-of-plane geometries with equal energy sharing at $R = 1.43$ bohr and $\theta_{mol} = 55°$. Fixed electron (single ended red arrows) is perpendicular to the plane formed by the polarization (vertical double arrow) and the molecule. Panels showing increasing amounts of correlation in the initial state A: $1\sigma_g$, B: $A + 1\sigma_u$, C: $B + 1\pi_u$, and D: converged result. TDCSs have been multiplied by factors of A: 1, B: 1.42, C: 3.79, and D: 2.59 to appear on the same scale.

plane" geometry with the fast electron emerging perpendicular to the plane of molecule and polarization vector. The entire angular distribution twists relative to the molecular axis as the internuclear distance varies, as shown in the comparison of theory and experiment in the second figure in Ref. [53]. In Fig. 8 we show that, in addition to large changes in magnitude, the convergence of the TDCS there involves a similar twisting of the angular distribution that would have obscured the comparison of experiment with theory in the absence of a fully correlated initial-state wave function.

VII. CONCLUSION

While it has long been understood that initial-state correlation must play a role in one-photon double ionization, the extent of its effect and the difference between atomic and molecular cases have not been widely understood and quantified. The natural orbital analysis of nearly exact initial-state wave functions has provided a systematic way to do so, and shown that in molecular systems the role of initial-state correlation can be strikingly greater than in similarly correlated atomic systems.

In molecular targets, the sensitivity to electron correlation in double photoionization is by far best revealed by measurements in the molecular frame [11–18], and for that reason we have limited ourselves here to the exploration of this question to oriented molecules. While those measurements thus far have been almost exclusively limited to the cases of the H_2 and D_2 molecules, this study suggests that double photoionization experiments on other oriented molecules will contain strong signatures of initial-state correlation in molecular bonds of more complicated systems. Such measurements in H_2O have

been explored already [92,93], where the dissociation of some states of the dication into two protons and a neutral oxygen atom creates the opportunity for body frame coincidence measurements.

For future theoretical treatments of molecular double photoionization, however, these results may suggest the problem is more difficult than for many-electron atoms. For atomic cases, there is a large number of studies of double ionization in the "two-active-electron" model [35,36,38,40,42–45], which involves freezing all but two electrons in orbitals from which they are not excited, thereby ignoring their correlation with the active electrons. If initial-state correlation in polyatomic molecules is indeed generally much more important in determining the angular correlation of the ejected electrons than in atoms, that approximation may be much less successful in the molecular case, and one-photon double ionization may be expected to be particularly sensitive to electron correlation associated with bonds.

[1] L. Avaldi and A. Huetz, J. Phys. B **38**, S861 (2005).

[2] O. Schwarzkopf, B. Krässig, J. Elmiger, and V. Schmidt, Phys. Rev. Lett. **70**, 3008 (1993).

[3] R. Dörner, T. Vogt, V. Mergel, H. Khemliche, S. Kravis, C. L. Cocke, J. Ullrich, M. Unverzagt, L. Spielberger, M. Damrau, O. Jagutzki, I. Ali, B. Weaver, K. Ullmann, C. C. Hsu, M. Jung, E. P. Kanter, B. Sonntag, M. H. Prior, E. Rotenberg, J. Denlinger, T. Warwick, S. T. Manson, and H. Schmidt-Böcking, Phys. Rev. Lett. **76**, 2654 (1996).

[4] R. Dörner, J. M. Feagin, C. L. Cocke, H. Bräuning, O. Jagutzki, M. Jung, E. P. Kanter, H. Khemliche, S. Kravis, V. Mergel, M. H. Prior, H. Schmidt-Böcking, L. Spielberger, J. Ullrich, M. Unversagt, and T. Vogt, Phys. Rev. Lett. **77**, 1024 (1996).

[5] R. Dörner, H. Bräuning, J. M. Feagin, V. Mergel, O. Jagutzki, L. Spielberger, T. Vogt, H. Khemliche, M. H. Prior, J. Ullrich, C. L. Cocke, and H. Schmidt-Böcking, Phys. Rev. A **57**, 1074 (1998).

[6] L. Malegat, P. Selles, P. Lablanquie, J. Mazeau, and A. Huetz, J. Phys. B **30**, 263 (1997).

[7] H. Bräuning, R. Dörner, C. L. Cocke, M. H. Prior, B. Krässig, A. S. Kheifets, I. Bray, A. Bräuning-Demian, K. Carnes, S. Dreuil, V. Mergel, P. Richard, J. Ullrich, and H. Schmidt-Böcking, J. Phys. B **31**, 5149 (1998).

[8] S. Cvejanovic, J. P. Wightman, T. J. Reddish, F. Maulbetsch, M. A. MacDonald, A. S. Kheifets, and I. Bray, J. Phys. B **33**, 265 (2000).

[9] P. Bolognesi, V. Feyer, A. Kheifets, S. Turchini, T. Prosperi, N. Zema, and L. Avaldi, J. Phys. B **41**, 051003 (2008).

[10] T. J. Reddish, J. P. Wightman, M. A. MacDonald, and S. Cvejanović, Phys. Rev. Lett. **79**, 2438 (1997).

[11] R. Dörner, H. Bräuning, O. Jagutzki, V. Mergel, M. Achler, R. Moshammer, J. M. Feagin, T. Osipov, A. Bräuning-Demian, L. Spielberger, J. H. McGuire, M. H. Prior, N. Berrah, J. D. Bozek, C. L. Cocke, and H. Schmidt-Böcking, Phys. Rev. Lett. **81**, 5776 (1998).

[12] D. P. Seccombe, S. A. Collins, T. J. Reddish, P. Selles, L. Malegat, A. K. Kazansky, and A. Huetz, J. Phys. B **35**, 3767 (2002).

[13] T. Weber, A. Czasch, O. Jagutzki, A. Müller, V. Mergel, A. Kheifets, J. Feagin, E. Rotenberg, G. Meigs, M. H. Prior, S. Daveau, A. L. Landers, C. L. Cocke, T. Osipov, H. Schmidt-Böcking, and R. Dörner, Phys. Rev. Lett. **92**, 163001 (2004).

[14] T. Weber, A. O. Czasch, O. Jagutzki, A. K. Muller, V. Mergel, A. Kheifets, E. Rotenberg, G. Meigs, M. H. Prior, S. Daveau, A. Landers, C. L. Cocke, T. Osipov, R. Diez Muino, H. Schmidt-Böcking, and R. Dörner, Nature (London) **431**, 437 (2004).

[15] T. Weber, L. Foucar, T. Jahnke, M. Schoeffler, L. Schmidt, M. Prior, and R. Doerner, J. Phys. B **50**, 164002 (2017).

[16] T. Weber, A. O. Czasch, O. Jagutzki, A. K. Muller, V. Mergel, A. Kheifets, E. Rotenberg, G. Meigs, M. H. Prior, S. Daveau, A. Landers, C. L. Cocke, T. Osipov, R. Diez Muino, H.

Schmidt-Böcking, and R. Dörner, Nature (London) **443**, 1014 (2006).

[17] M. Gisselbrecht, M. Lavollée, A. Huetz, P. Bolognesi, L. Avaldi, D. P. Seccombe, and T. J. Reddish, Phys. Rev. Lett. **96**, 153002 (2006).

[18] D. Akoury, K. Kreidi, T. Jahnke, T. Weber, A. Staudte, M. Schöffler, N. Neumann, J. Titze, L. P. H. Schmidt, A. Czasch, O. Jagutzki, R. A. C. Fraga, R. E. Grisenti, R. D. Muiño, N. A. Cherepkov, S. K. Semenov, P. Ranitovic, C. L. Cocke, T. Osipov, H. Adaniya, J. C. Thompson, M. H. Prior, A. Belkacem, A. L. Landers, H. Schmidt-Böcking, and R. Dörner, Science **318**, 949 (2007).

[19] P. Bolognesi, B. Joulakian, A. A. Bulychev, O. Chuluunbaatar, and L. Avaldi, Phys. Rev. A **89**, 053405 (2014).

[20] F. Maulbetsch and J. S. Briggs, J. Phys. B **28**, 551 (1995).

[21] F. Maulbetsch and J. S. Briggs, J. Phys. B **27**, 4095 (1994).

[22] M. Pont and R. Shakeshaft, Phys. Rev. A **51**, R2676 (1995).

[23] A. S. Kheifets and I. Bray, Phys. Rev. A **54**, R995 (1996).

[24] S. P. Lucey, J. Rasch, C. T. Whelan, and H. R. J. Walters, J. Phys. B **31**, 1237 (1998).

[25] A. S. Kheifets and I. Bray, J. Phys. B **31**, L447 (1998).

[26] A. S. Kheifets and I. Bray, Phys. Rev. A **57**, 2590 (1998).

[27] J. S. Briggs and V. Schmidt, J. Phys. B **33**, R1 (2000).

[28] L. Malegat, P. Selles, and A. Huetz, J. Phys. B **30**, 251 (1997).

[29] P. Selles, L. Malegat, and A. K. Kazansky, Phys. Rev. A **65**, 032711 (2002).

[30] C. W. McCurdy, D. A. Horner, T. N. Rescigno, and F. Martín, Phys. Rev. A **69**, 032707 (2004).

[31] A. Palacios, C. W. McCurdy, and T. N. Rescigno, Phys. Rev. A **76**, 043420 (2007).

[32] A. Palacios, T. N. Rescigno, and C. W. McCurdy, Phys. Rev. A **77**, 032716 (2008).

[33] D. A. Horner, J. Colgan, F. Martín, C. W. McCurdy, M. S. Pindzola, and T. N. Rescigno, Phys. Rev. A **70**, 064701 (2004).

[34] J. Colgan, M. S. Pindzola, and F. Robicheaux, Phys. Rev. A **72**, 022727 (2005).

[35] M. S. Pindzola, F. Robicheaux, S. D. Loch, J. C. Berengut, T. Topcu, J. Colgan, M. Foster, D. C. Griffin, C. P. Ballance, D. R. Schultz, T. Minami, N. R. Badnell, M. C. Witthoeft, D. R. Plante, D. M. Mitnik, J. A. Ludlow, and U. Kleiman, J. Phys. B **40**, R39 (2007).

[36] D. C. Griffin, M. S. Pindzola, C. P. Ballance, and J. Colgan, Phys. Rev. A **79**, 023413 (2009).

[37] A. S. Kheifets, D. V. Fursa, C. W. Hines, I. Bray, J. Colgan, and M. S. Pindzola, Phys. Rev. A **81**, 023418 (2010).

[38] M. S. Pindzola, C. P. Ballance, S. A. Abdel-Naby, F. Robicheaux, G. S. J. Armstrong, and J. Colgan, J. Phys. B **46**, 035201 (2013).

[39] Y. Li, M. S. Pindzola, and J. Colgan, J. Phys. B **49**, 195205 (2016).

[40] A. S. Kheifets and I. Bray, Phys. Rev. A **75**, 042703 (2007).

[41] F. L. Yip, D. A. Horner, C. W. McCurdy, and T. N. Rescigno, Phys. Rev. A **75**, 042715 (2007).

[42] F. L. Yip, T. N. Rescigno, and C. W. McCurdy, Phys. Rev. A **94**, 063414 (2016).

[43] F. L. Yip, T. N. Rescigno, C. W. McCurdy, and F. Martín, Phys. Rev. Lett. **110**, 173001 (2013).

[44] F. L. Yip, C. W. McCurdy, and T. N. Rescigno, Phys. Rev. A **81**, 063419 (2010).

[45] F. L. Yip, F. Martín, C. W. McCurdy, and T. N. Rescigno, Phys. Rev. A **84**, 053417 (2011).

[46] J. M. N. Djiokap, A. V. Meremianin, N. L. Manakov, S. X. Hu, L. B. Madsen, and A. F. Starace, Phys. Rev. A **96**, 013405 (2017).

[47] J. M. Feagin, J. Phys. B **31**, L729 (1998).

[48] M. Walter and J. S. Briggs, Phys. Rev. Lett. **85**, 1630 (2000).

[49] A. S. Kheifets and I. Bray, Phys. Rev. A **72**, 022703 (2005).

[50] A. S. Kheifets, Phys. Rev. A **71**, 022704 (2005).

[51] W. Vanroose, F. Martín, T. N. Rescigno, and C. W. McCurdy, Science **310**, 1787 (2005).

[52] W. Vanroose, D. A. Horner, F. Martín, T. N. Rescigno, and C. W. McCurdy, Phys. Rev. A **74**, 052702 (2006).

[53] D. A. Horner, W. Vanroose, T. N. Rescigno, F. Martín, and C. W. McCurdy, Phys. Rev. Lett. **98**, 073001 (2007).

[54] L. Tao, C. W. McCurdy, and T. N. Rescigno, Phys. Rev. A **82**, 023423 (2010).

[55] D. A. Horner, S. Miyabe, T. N. Rescigno, C. W. McCurdy, F. Morales, and F. Martín, Phys. Rev. Lett. **101**, 183002 (2008).

[56] J. Colgan, M. S. Pindzola, and F. Robicheaux, Phys. Rev. Lett. **98**, 153001 (2007).

[57] T. J. Reddish, J. Colgan, P. Bolognesi, L. Avaldi, M. Gisselbrecht, M. Lavollée, M. S. Pindzola, and A. Huetz, Phys. Rev. Lett. **100**, 193001 (2008).

[58] J. Colgan, M. S. Pindzola, and F. Robicheaux, J. Phys. B **41**, 121002 (2008).

[59] X. Guan, K. Bartschat, and B. I. Schneider, Phys. Rev. A **83**, 043403 (2011).

[60] I. A. Ivanov and A. S. Kheifets, Phys. Rev. A **85**, 013406 (2012).

[61] W.-C. Jiang, L.-Y. Peng, J.-W. Geng, and Q. Gong, Phys. Rev. A **88**, 063408 (2013).

[62] P.-O. Löwdin, Phys. Rev. **97**, 1474 (1955).

[63] P.-O. Löwdin and H. Shull, Phys. Rev. **101**, 1730 (1956).

[64] E. R. Davidson, Rev. Mod. Phys. **44**, 451 (1972).

[65] E. R. Davidson, in *Advances in Quantum Chemistry*, edited by P.-O. Löwdin (Academic Press, New York, 1972), Vol. 6, pp. 235–266.

[66] M. C. Tichy, F. Mintert, and A. Buchleitner, J. Phys. B **44**, 192001 (2011).

[67] A. Ekert and P. L. Knight, Am. J. Phys. **63**, 415 (1995).

[68] R. Paškauskas and L. You, Phys. Rev. A **64**, 042310 (2001).

[69] J. Schliemann, D. Loss, and A. H. MacDonald, Phys. Rev. B **63**, 085311 (2001).

[70] E. Eckert and J. Schliemann, Ann. Phys. (N.Y.) **299**, 88 (2002).

[71] F. Buscemi, P. Bordone, and A. Bertoni, Phys. Rev. A **73**, 052312 (2006).

[72] A. S. Kadyrov, A. M. Mukhamedzhanov, A. T. Stelbovics, I. Bray, and F. Pirlepesov, Phys. Rev. A **68**, 022703 (2003).

[73] P.-O. Löwdin, Phys. Rev. **97**, 1509 (1955).

[74] R. Grobe, K. Rzazewski, and J. H. Eberly, J. Phys. B **27**, L503 (1994).

[75] C. W. McCurdy, M. Baertschy, and T. N. Rescigno, J. Phys. B **37**, R137 (2004).

[76] B. Simon, Phys. Lett. A **71**, 211 (1979).

[77] C. A. Nicolaides and D. R. Beck, Phys. Lett. A **65**, 11 (1978).

[78] C. W. McCurdy and F. Martín, J. Phys. B **37**, 917 (2004).

[79] S. Rothenberg and E. R. Davidson, J. Chem. Phys. **45**, 2560 (1966).

[80] E. Schmidt, Math. Ann. **63**, 433 (1906).

[81] M. Y. Ivanov, D. Bitouk, K. Rzążewski, and S. Kotochigova, Phys. Rev. A **52**, 149 (1995).

[82] If **C** is complex symmetric, the unitary matrix **U** calculated from the *symmetric* singular value decomposition [94] $\mathbf{C} = \mathbf{UcU}^T$, where T denotes transpose, can be used to construct the natural orbital expansion.

[83] E. R. Davidson, J. Chem. Phys. **39**, 875 (1963).

[84] K. E. Banyard and C. C. Baker, J. Chem. Phys. **51**, 2680 (1969).

[85] R. Celeste, H. F. M. da Costa, A. B. F. da Silva, and M. Trsic, Chem. Phys. Lett. **183**, 31 (1991).

[86] J. M. G. d. l. Vega, J. Phys. B **27**, L447 (1994).

[87] K. A. Peterson, D. E. Woon, and T. H. Dunning, J. Chem. Phys. **100**, 7410 (1994).

[88] K. Frankowski and C. L. Pekeris, Phys. Rev. **146**, 46 (1966).

[89] J. S. Sims and S. A. Hagstrom, J. Chem. Phys. **124**, 094101 (2006).

[90] J. Colgan, A. Huetz, T. J. Reddish, and M. S. Pindzola, J. Phys. B **41**, 085202 (2008).

[91] W. Heitler and F. London, Z. Phys. **44**, 455 (1927).

[92] Z. L. Streeter, F. L. Yip, R. R. Lucchese, B. Gervais, T. N. Rescigno, and C. W. McCurdy, Phys. Rev. A **98**, 053429 (2018).

[93] D. Reedy, J. B. Williams, B. Gaire, A. Gatton, M. Weller, A. Menssen, T. Bauer, K. Henrichs, P. Burzynski, B. Berry, Z. L. Streeter, J. Sartor, I. Ben-Itzhak, T. Jahnke, R. Dörner, T. Weber, and A. L. Landers, Phys. Rev. A **98**, 053430 (2018).

[94] A. Bunse-Gerstner and W. B. Gragg, J. Comput. Appl. Math. **21**, 41 (1988).