Dynamic exchange in the strong field ionization of molecules

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We show that dynamic exchange is a dominant effect in strong field ionization of molecules. In CO₂ it fixes the peak ionization yield at the experimentally observed angle of 45° between polarization direction and the molecular axis. In N₂ it changes the alignment dependence of yields by up to a factor of 2. The effect appears on the Hartree-Fock level as well as in full ab initio solutions of the Schrödinger equation.

Experimental techniques like molecular orbital tomography [1, 2], laser-driven electron diffraction [3, 4], and high harmonic imaging [5] are based on the control of ionization by the strong field of a laser. They share the concept that an electron is emitted by a strong laser field and re-directed by the same field to its parent system, where it produces a snapshot of the system’s time evolution in the angle-resolved electron-momentum or harmonic spectra. The analysis of these experiments relies on the idea that the steps of initial electron emission, propagation, and scattering of the returning electron can be considered as largely independent. Adequate understanding of each of these three steps is a pre-requisite for proper use of the techniques.

In this letter we deal with the ionization step. With atoms, there are several models that deliver correct ionization yields at infrared (IR) wavelength. In contrast, for molecules a disquieting discrepancy between theoretical predictions and experiment appeared: two independent experiments at two different intensities [6, 7] reported maximal ionization of CO₂ when the molecular axis was aligned at 45° to the polarization direction of a linearly polarized pulse. In contrast, most theoretical calculations found angles in the range 30° ∼ 40°.

It is usually assumed that ionization at IR wavelength is a tunneling process and yields can be obtained as the integral over the tunneling rates computed at the instantaneous field strengths. As the field ionization rates drop exponentially with the ionization potential, one expects that the highest occupied molecular orbital (HOMO) in a molecule determines ionization. In particular, the angle dependence of the ionization rate should reflect the electron density distribution of the HOMO. Combining this idea with the Ammosov-Delone-Krainov (ADK) [8] formula for tunneling from effective single-electron systems, the molecular ADK (MO-ADK) approach was formulated [9]. In more complicated molecular systems with energetically closely spaced ionic states this approach may become invalid [5, 10]: at the nodal directions of the HOMO, where MO-ADK would show nearly no ionization, the energetically next lower orbital HOMO-1 could contribute.

On this level of theory there remains a striking discrepancy to experimental findings for the ionization of CO₂: while maximum ionization is predicted for an alignment of molecules at ∼ 30° between laser polarization and molecular axis, experiments find the maximum at 45° [6, 7].

Several attempts were undertaken to resolve the discrepancy by more elaborate computations. From density functional theory (DFT) calculations it was concluded that the contribution of energetically lower molecular orbitals could account for the experimental observation [11]. In a time-dependent DFT calculation reported in Ref. [12] peak yield was found at 40° alignment. On the other hand, a single electron model with a frozen core potential produced the experimental value of 45° [13]. The only fully numerical calculations beyond single electron or electron density based methods was reported in Ref. [14] where it was shown that a single channel picture leads to peak angles ∼ 30° and it was conjectured that inter-channel couplings could explain the experimental observation. Other efforts using the semi-classical WKB approximation [15] and the strong field eikonal Volkov approximation [5] also fail to yield accurate predictions. A recent work [16] analyzes the problem using an adiabatic strong field approximation to show that field-distortion of the orbitals plays a role, but the predicted angles of 36° to 39° fall short of the experimental values. In spite of all efforts, the discrepancy remained unresolved.

In the discussion so far, little attention has been paid to exchange symmetry that must be respected not only in the initial state but also during the ionization process. Ideally, in DFT such effects would be included, but in practice this is hardly ever fully achieved due to limitations of the exchange-correlation potentials. The value reported closest to experiment was obtained with a single electron potential including DFT-based exchange, but the good agreement there was attributed to excited state dynamics rather than exchange [13].

In this letter, we show that exchange occupies a central place in strong field ionization (SFI). Specifically, in CO₂ the non-local exchange forces lead to peak ionization at an alignment of 45°. Effects on the alignment-dependence of N₂ ionization are sizable but less conspicuous. The mechanism is truly dynamical and independent of exchange and correlation in the initial states. Qualitatively it appears also on the Hartree-Fock level.

We compute SFI rates and solutions of the time-
dependent Schrödinger equation (TDSE) by the \textit{ab initio} hybrid anti-symmetrized coupled channels (haCC) approach [17], haCC uses a multi-electron wavefunction in terms of several ionic states $|I\rangle$ that are fully anti-symmetrized with a numerical single electron basis, $|i\rangle$. In addition, the neutral ground and excited states, $|N\rangle$, can be included resulting in the wavefunction

$$|\Psi_A\rangle = \sum_{i,I} A(|i\rangle|I\rangle) C_{i,I} + \sum_{N} |N\rangle C_{N}, \quad (1)$$

which we will refer to as ansatz A in the following. The $C_{i,I}, C_{N}$ are the respective expansion coefficients and $A$ indicates anti-symmetrization. The $|I\rangle$ and $|N\rangle$ states were obtained from the COLUMBUS quantum chemistry package [18]. For $|i\rangle$ we use a high-order finite element radial basis combined with single center spherical harmonics. A complete description of the method can be found in [17]. It is important that the basis can accurately describe the asymptotic behavior of the ionizing orbital, as discussed in Ref. [19]. Neutral and ionic states can be systematically included to examine multi-electron effects like field-free correlation, inter-channel coupling and ionic core polarization. Independently the importance of exchange can also be investigated.

Tunneling ionization rates are computed using exterior complex scaling [20-22]: the Hamiltonian is analytically continued by transforming the electron coordinates into the complex plane. For radii $r > R_0$ one uses $r_\theta = e^{i\theta}(r-R_0) + R_0$ with the complex scaling angle $\theta > 0$. The resulting Hamiltonian is non-Hermitean with a complex ground state eigenvalue $W = E_0 + E_\pi - \frac{1}{2}\Gamma$, where $E_0$ is the field-free ground state energy, $E_\pi$ is its dc-Stark shift and $\Gamma/h$ is the static field ionization rate. Apart from errors due to finite computational approximation, $W$ is independent of $\theta > 0$ and $R_0 \geq 0$.

We treat the CO$_2$ molecule with nuclear positions fixed at the equilibrium C-O bond length of 116.3 pm. The multi-electron states of neutral and ion are computed using COLUMBUS with the minimally augmented cc-pvtz basis at the multi-reference configuration interaction singles level. We used up to 6 ionic channels which include the doubly degenerate $X^2\Pi_g$, $A^2 \Pi_u$, and the singly degenerate $B^2\Sigma^+_u$, $C^2\Sigma^+_g$ states. Single electron functions with up to 84 linear coefficients with finite element orders 12 on a radial box of 30 a.u. and up to 269 spherical harmonics ($L_{\text{max}} = 12, M_{\text{max}} = 12$) were used for the stationary problem. For solutions of the TDSE the number of spherical harmonics was increased up to 324. This numerical basis is complemented by the atom-centered Gaussians that constitute the neutral and ionic functions. For complex scaling, we chose $R_0$-values well outside the range of neutral and ionic orbitals, such that only the coordinate of the single-electron basis had to be continued to complex values. Basis and scaling the parameters $R_0$ and $\theta$ were systematically varied to ensure that results are converged to better than 2%. The main approximation is introduced by the limited number of ionic channels. With all 6 ionic channels, we obtain a first ionization potential of $I_p \approx 13.85$eV (Experimental value: 13.78eV [23]), which decreases by about 0.14 eV with fewer ionic channels.

The main results of this letter are given in figures 1 and 2. In Fig. 1, one sees that the static field ionization rates peak at an alignment angle of 45°. They have minima at 0° and 90° due to the nodal planes in the HOMO orbital of CO$_2$. These findings are in good agreement with experiments [6, 7]. As the dominant multi-electron effect, we see a reduction of ionization rates as the number of ionic channels is increased. This can be understood as a larger number of ionic channels results in larger polarizability of the ground state, whereas the more tightly bound ionic states are less affected. The difference in de-Stark shifts increases the ionization potentials in presence of the field and the ionization rates drop.

Figure 2 shows the angle of peak rate as a function of intensity: except for the highest intensities, the rate varies by $\lesssim 2\%$, depending on the number of ionic channels included. We cannot confirm any intensity dependence as was predicted in Ref. [15] based on analytic arguments. Dependence on the number of channels is strongest at the higher intensities $I > 2.5 \times 10^{14}$W/cm$^2$. There, the tunneling picture ceases to be applicable: according to a simple estimate [22] at intensities $I_0 \approx I_p^2/4 = 1.5 \times 10^{14}$W/cm$^2$ the molecular binding barrier of CO$_2$ is suppressed to below the field free ground state energy. In this regime, the importance of virtual continuum states for polarization of the ionic core may become important, which is not modeled by the haCC ansatz as used here and therefore no dependable statement about the accuracy of our results can be made.

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{fig1.png}
\caption{Alignment angle dependent CO$_2$ ionization rates at selected intensities $I$ (in W/cm$^2$). The convergence with the number of ionic channels indicates the role of multi-electron effects. Blue: including only the neutral ground state and ionic $X^2\Pi_g$ ground states, green: as blue with the ionic $A^2 \Pi_u$ channel added. Red: as green with $B^2\Sigma^+_u$ channel. Black: as red with $C^2\Sigma^+_g$ channel. Computation were performed for static fields of strengths $F = 0.05, 0.07$ and 0.09 atomic units corresponding to intensities $I = F^2/2$ that label the plots. $\Gamma_{\text{max}}$ indicates maximal decay width in atomic units at the inclosing circle. A total of 6 ionic channels are used in the calculations.}
\end{figure}
shows that the first excited state of the neutral X$^2\Pi_g$ yields found in one of the experiments [14] that the experimental result may be artificially narrowed due to the deconvolution procedure.

The alignment dependence of ionization obtained in quasi-static approximation (QSA) by integrating the tunnel ionization rate is confirmed by solutions of the complete TDSE. In figure 3, normalized angle dependent yields obtained from TDSE and QSA within the single channel model are compared with experimental results. The angle-dependence in TDSE is well approximated in QSA, with better agreement for higher intensities, where the QSA is more appropriate [22]. This agreement is gratifying, considering that in the intensity range $3 \times 10^{13} - 1.1 \times 10^{14} \text{W/cm}^2$ with Keldysh parameters $\gamma = 2 \sim 1$, one can hardly expect ionization to be of pure tunneling type. A failure of the tunneling picture is exposed in the magnitudes of the yields, where the TDSE results exceed the QSA by a factor 2 at $1.1 \times 10^{14} \text{W/cm}^2$ and by nearly two orders of magnitude at $3 \times 10^{13} \text{W/cm}^2$. The peak angle is consistent with the experiments, but yields found in one of the experiments [6] are more narrowly confined around the maximum angle. It was noted in Ref. [19] that the experimental result may be artificially narrowed due to the deconvolution procedure.

The failure of earlier theory in reproducing the peak angle of 45° is due to the absence or insufficient inclusion of dynamical exchange. This is clearly seen by omitting from the haCC ansatz A the anti-symmetrization of the single-electron basis against the multi-electron states in an otherwise identical wavefunction, ansatz B:

$$|\Psi_B\rangle = \sum_{i,I} |i\rangle |C_{i,I} + \sum_N |\mathcal{N}\rangle C_N,$$

In figure 4 one sees that with ansatz B one obtains the peak rate at an angle around 30° at low intensities that then dips-off as intensity is increased, see also Fig. 2.

Our results without anti-symmetrization for the dynamics are consistent with Ref. [14], where it was proposed that the remaining discrepancy to the experimental value was caused by neglecting coupling between X$^2\Pi_g$, A$^2\Pi_u$ ionic channels in the calculation. In contrast, in Ref. [13], the angle near 45° was attributed to dynamics of excited neutral states, mostly the first excited neutral state. However, neither excited state dynamics nor coupling of ionic channels, in absence of dynamical exchange, result in correct angles.

![FIG. 2. Peak ionization angles as a function of intensity. Solid lines: results with the anti-symmetrized ansatz A, Eq. (1). Dashed lines: results without anti-symmetrization, ansatz B, Eq. (2). Colors correspond to different numbers of neutral states and ionic channels, see Fig. 1 (solid) and Fig. 4 (dashed).](image)

![FIG. 3. Normalized angle dependent yields from TDSE (lines), QSA (dash-dotted lines) in the single channel picture and experiments [6, 7] (dashed lines). The laser parameters are 800 nm central wavelength, 40 fs duration with peak intensities of $3 \times 10^{13} \text{W/cm}^2$ (Upper panel) and $1.1 \times 10^{14} \text{W/cm}^2$ (lower panel).](image)

![FIG. 4. The role of exchange in CO$_2$ ionization: alignment angle-dependence of normalized static SFI rates in different single-channel models. Blue: anti-symmetrized ansatz A with the neutral ground state and ionic X$^2\Pi_g$ ground state channels. Green: ansatz B with the same states as blue, red: as green, with the addition of ionic A$^2\Pi_u$ ground state channels. Cyan: as green with the addition of first excited neutral state. The green and cyan lines coincide at the two higher intensities.](image)
shows that also here exchange shifts the peak angle.

Apart from the exchange term, ansatz A effectively en-
forces orthogonality of the active electron orbital against
the ionic HF orbitals \(\langle \psi | \phi_k \rangle = 0\), \(k \geq 2\). If this were
the dominant effect of anti-symmetrization, one would
expect that in absence of the constraint (ansatz B) the
ground state energy would be lowered. On the other
hand, anti-symmetrization effectively enlarges the ansatz
space: it operates in the \(2^N\) fold larger space containing
all permutations of \(\psi\) through the \(\phi_2 \ldots \phi_N\), but
including explicitly only the dynamically accessible subspace
of anti-symmetrized linear combinations. By this reason-
ning, Stark-shift (polarization) should be larger in ansatz
A and B. Field strength = 0.06 a.u.

In Ref. [19] it was pointed out that the long-range interac-
tions also affect emission. To exclude those, we smoothly
truncate the Coulomb tail of the potential at 10 a.u. Fig-
ure 5 shows that also here exchange shifts the peak angle
by \(\sim 7^\circ\).

Apart from the exchange term, ansatz A effectively en-
forces orthogonality of the active electron orbital against
the ionic HF orbitals \(\langle \psi | \phi_k \rangle = 0\), \(k \geq 2\). If this were
the dominant effect of anti-symmetrization, one would
expect that in absence of the constraint (ansatz B) the
ground state energy would be lowered. On the other
hand, anti-symmetrization effectively enlarges the ansatz
space: it operates in the \(N\)-fold larger space containing
all permutations of \(\psi\) through the \(\phi_2 \ldots \phi_N\), but
including explicitly only the dynamically accessible subspace
of anti-symmetrized linear combinations. By this reason-
ning, Stark-shift (polarization) should be larger in ansatz
A. Indeed, we find the latter in our calculations. We also
directly verified that an orthogonality constraint on \(\psi(t)\)
against the \(\phi_k\) in ansatz B causes only \(\lesssim 1\%\) of the over-
all difference between the results of A and B. This finally
establishes that indeed the dynamical effects of exchange
play the decisive role in ionization.

Dynamical exchange is most conspicuous in \(CO_2\) be-
cause of the node-structure of the HOMO and the re-
sulting non-trivial angle dependence of the yields. How-
ever, the mechanism as such is universal and must be
included for obtaining correct ionization rates from any
system. As an example, we studied the effect on the ni-
trogen molecule, which is one of the main model system
for strong field physics. Figure 6 shows normalized 
ionization rates for \(N_2\) at equilibrium nuclear position with
a single channel in ansatz A and B. Here, dynamical ex-
change leads to a broadening of the ionization profile,
where the ratio between the rates at 0° and 90° changes
by up to a factor \(\sim 2\).

In conclusion, we have established that dynamical
exchange takes a central place in the ionization of
molecules. The effects on \(CO_2\) are striking, but also for
\(N_2\) results can change by up to a factor 2 merely due to
exchange. This indicates that dynamical exchange must
be considered in any attempt to understand strong field
ionization also of more complex multi-electron systems.
Apart from the ionization yields discussed here, the an-
gular distribution of electron emission at fixed alignment
may be affected. A critical assessment of the importance
of these distributions for rescattering-based attosecond
experiments appears in place. On the other hand, sim-
ple anti-symmetrization may enhance single-electron and
single-channel models that have been applied so far, even
without the comparatively heavy numerical apparatus
used to establish the fact in the present paper.

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\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5}
\caption{Normalized ionization yields of \(CO_2\) as a function
of alignment angle. Including neutral ground state and the
\(X^\ddagger\Sigma_u^+\) ionic ground state channel. Solid: with dynamic
exchange, ansatz A, and dashed, without exchange, ansatz B.
}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6}
\caption{Normalized ionization rates of \(N_2\) as a function
of alignment angle. Including neutral ground state and the
\(\Sigma^+\Sigma_u^+\) ionic ground state channel. Solid: with dynamic
exchange, ansatz A, and dashed, without exchange, ansatz B.
}
\end{figure}

\[I = 0.9 \times 10^{14}\]

\[I = 1.7 \times 10^{14}\]

\[I = 2.8 \times 10^{14}\]
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