

Single-active-electron potentials for molecules in intense laser fields

M. Abu-samha and L. B. Madsen

*Lundbeck Foundation Theoretical Center for Quantum System Research,
Department of Physics and Astronomy,
Aarhus University, DK-8000 Aarhus C, Denmark.*

Abstract

Single-active-electron potentials are computed for selected molecules, and molecular wavefunctions with the correct asymptotic behavior are produced. Asymptotic expansion coefficients are extracted from the wavefunctions, and used to compute alignment-dependent ionization yields from molecular tunneling theory. The predictions of molecular tunneling theory are benchmarked by *ab initio* calculations based on the solution of the time-dependent Schrödinger equation within the single-active-electron approximation.

I. INTRODUCTION

Understanding the initial ionization step of molecules in intense laser fields is fundamental for high harmonic generation, time-resolved studies and dynamic imaging of molecules [1–3]. In the past couple of years, several experiments emerged on strong-field ionization [4–7] from aligned molecules, where the molecular axis is fixed at a particular angle relative to the laser polarization axis. In [7], alignment-dependent ionization yields were measured for ionization from the highest occupied molecular orbital (HOMO) of N_2 , O_2 and CO_2 . The experimental results were modeled using the molecular tunneling theory (MO-ADK) for fixed internuclear distances [8]. For N_2 and O_2 , very good agreement was found between MO-ADK predictions and the experiment. For CO_2 , on the other hand, the MO-ADK predicted the maximum ionization yield at about 24° , in disagreement with the experimental ionization peak at an alignment angle of 45° . This issue was addressed by theory [9–12], and no consensus has been reached regarding its origin. By solving the time-dependent Schrödinger equation (TDSE) for frozen nuclei, within the single-active-electron model [9] or including multi-electron effects [10], the maximum ionization yield for CO_2 is found at about 45° , in agreement with the experiment. In [11], it was suggested that intermediate core excitations are needed to reproduce the experimental ionization yields for CO_2 . Yet in [12], the discrepancy between the MO-ADK results and the experiment was attributed partly to an inaccurate asymptotic behavior of the wavefunctions for the CO_2 HOMO orbital. Using wavefunctions with a better asymptotic form (in the MO-ADK analysis) results in a maximum ionization yield for CO_2 at about 35° , still in disagreement with the experiment. Nevertheless, the CO_2 case served to demonstrate the importance of using molecular wavefunctions with correct asymptotic behavior in MO-ADK theory.

Molecular wavefunctions are usually derived from standard quantum chemistry calculations, whereby Slater-type orbitals (with $\exp[-cr]$ asymptotic behavior) are represented by a linear combination of Gaussian-type orbitals (with $\exp[-\zeta r^2]$ asymptotic behavior). To produce alignment-dependent ionization yields by MO-ADK theory (cf. Eq. (14) in section II C), the long-range part of the wavefunction is fitted by coefficients that depends on l and m quantum numbers, C_{lm} in Eq. (10). However, since the long-range part of the wavefunction behaves like a Gaussian function, the C_{lm} coefficients obtained from standard quantum chemistry calculations are not necessarily accurate.

Several numerical techniques exist for obtaining molecular wavefunctions with correct asymptotic behavior. For instance, one can either perform direct diagonalization of the Hamiltonian matrix, or propagate the TDSE for a single electron, in imaginary time. These techniques, however, require a priori knowledge of the molecular potential, including electron exchange.

In this paper, single-active-electron (SAE) potentials are computed for selected molecules (N_2 , O_2 , CO_2 , CS_2), and molecular wavefunctions with correct asymptotic behavior and accurate C_{lm} coefficients are produced. Alignment-dependent ionization yields are computed from MO-ADK theory, based on the present C_{lm} coefficients. For N_2 , O_2 and CO_2 , we provide alignment-dependent ionization yields from *ab initio* calculations to benchmark the MO-ADK predictions.

The paper is organized as follows. In sections II and III, we present the theoretical models and computational details. The main results and discussion are given in section IV, and the conclusions in section V.

II. THEORETICAL MODELS

A. Single-active-electron potentials

The potential describing the interaction of the active electron with the frozen core is defined (atomic units are used throughout) as

$$V(\mathbf{r}) = V_x(\mathbf{r}) + V_{en}(\mathbf{r}) + V_{ee}^{cl}(\mathbf{r}), \quad (1)$$

where $V_x(\mathbf{r})$ is the electron exchange potential and $V_{en}(\mathbf{r})$ is the electron-nuclear attraction, i.e.,

$$V_{en}(\mathbf{r}) = - \sum_i^{\text{nuclei}} \frac{Z_i}{|\mathbf{r} - \mathbf{R}_i|}, \quad (2)$$

with Z_i and $\mathbf{R}_i$ the charge and position of nuclei i . In Eq. (1), $V_{ee}^{cl}(\mathbf{r})$ is the classical electron-electron repulsion, i.e.,

$$V_{ee}^{cl}(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (3)$$

where $\rho(\mathbf{r})$ is the total electron density. The classical electron-electron repulsion is computed from standard quantum chemistry programs (Gaussian [13] or GAMESS [14]).

The exchange potential $V_x(\mathbf{r})$ is evaluated within the local density approximation (LDA) [15]. The local density potential [16] reads

$$V_x^{LDA}(\mathbf{r}) = -\frac{3}{2}\alpha_0 \left(\frac{6\rho_\sigma(\mathbf{r})}{\pi} \right)^{1/3}, \quad (4)$$

where $\rho_\sigma(\mathbf{r})$ is the spin density at point $\mathbf{r}$ and α_0 is $2/3$. For closed-shell molecules such as, e.g., N_2 , CO_2 and CS_2 , one can use either the spin-up ($\sigma=+\frac{1}{2}$) or spin-down ($\sigma=-\frac{1}{2}$) density. For the open-shell O_2 molecule, the HOMO electrons have $\sigma=+\frac{1}{2}$, and the spin-up density is used in Eq. (4). The electron density is extrapolated to large r by employing a Slater-type function ($\exp[-cr]$). This help us evaluate the density gradient as $r \rightarrow \infty$, which, in turn, will be needed to determine the correct exchange potential.

Now, in order to obtain SAE potentials with a correct Coulombic ($-1/r$) asymptotic behavior, we apply a gradient correction (GC) to the local density. The correction term is [17]

$$GC(\mathbf{r}) = \frac{X(\mathbf{r})^2 \rho_\sigma(\mathbf{r})^{1/3}}{1 + 3\beta X(\mathbf{r}) \sinh^{-1}(X(\mathbf{r}))}, \quad (5)$$

with

$$X(\mathbf{r}) = \left| \frac{\partial \rho_\sigma(\mathbf{r}) / \partial r}{\rho_\sigma(\mathbf{r})^{4/3}} \right|. \quad (6)$$

Here, we assume that the angular part of the density is slowly varying and consider only the radial component of the density gradient. The final form of the exchange potential with correct asymptotic behavior is

$$V_x(\mathbf{r}) = \alpha V_x^{LDA}(\mathbf{r}) - \beta GC(\mathbf{r}), \quad (7)$$

where α and β are optimized to produce accurate ionization potentials. This approach was recently successfully applied to CO_2 [9].

1. A single-active-electron potential for CO_2

We consider the CO_2 molecule as an example illustrating our procedure for obtaining SAE potentials. The potential $V(\mathbf{r})$ is defined in partial waves as

$$V(\mathbf{r}) = \sum_{lm} V_{lm}(r) Y_{lm}(\theta, \phi). \quad (8)$$

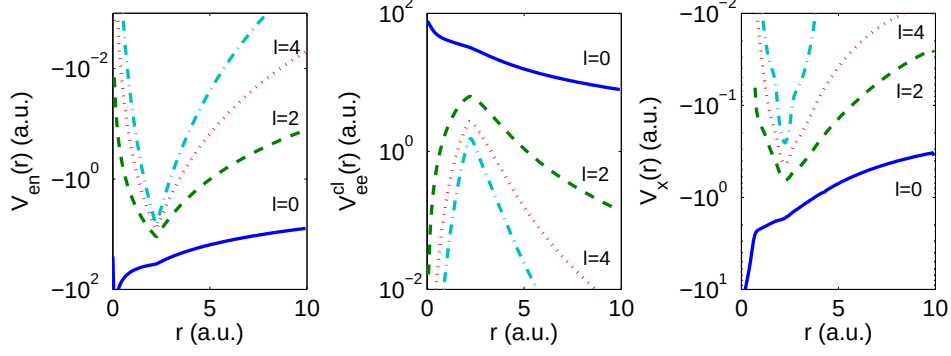


FIG. 1: (Color online) Partial waves expansions of $V_{en}(\mathbf{r})$ (Eq. (2)), $V_{ee}^{cl}(\mathbf{r})$ (Eq. (3)), and $V_x(\mathbf{r})$ (Eq. (7)) potentials for CO_2 at equilibrium atomic positions. The expansion goes to $l=20$, but for clarity we only show here the $l=0, 2, 4$ and 6 terms.

For a linear symmetric molecule, within the frozen nuclei approximation, the potential is azimuthally symmetric ($m=0$) and l is even. In Fig. 1, we show partial wave expansions of the $V_{en}(\mathbf{r})$ (Eq. (2)), $V_{ee}^{cl}(\mathbf{r})$ (Eq. (3)) and $V_x(\mathbf{r})$ (Eq. (7)) potentials for the CO_2 molecule. In general, the contribution from terms with $l > 0$ is important only close to the atomic positions. At large r , the terms $V_{ee}^{cl}(\mathbf{r})$ and $V_{en}(\mathbf{r})$ cancel out each other, as they should, and the active potential is indeed $V_x(\mathbf{r})$. It is therefore important that $V_x(\mathbf{r})$ shows the correct asymptotic $-1/r$ behavior.

The parametrization of the molecular potentials in terms of analytical expressions, as has been done for atoms [18, 19], is unattractive since the parametrization of each partial wave will typically need 6-10 terms and we used up to, e.g., 21 partial waves for the CO_2 molecule.

B. Wavefunctions with correct asymptotic behavior

The wavefunction is expressed in a partial wave expansion [20, 21], i.e.,

$$\Psi(\mathbf{r}) = \sum_{lm} \frac{f_{lm}(r)}{r} Y_{lm}(\theta, \phi), \quad (9)$$

where $Y_{lm}(\theta, \phi)$ are the spherical harmonics and $f_{lm}(r)$ are the reduced radial wavefunctions, discretized on an equidistant spatial grid. At large r , where the monopole dominates (cf. Fig. 1),

$$f_{lm}(r) = C_{lm} r^{Z/\kappa} \exp[-\kappa r], \quad (10)$$

where C_{lm} is the asymptotic coefficient, Z is the asymptotic charge and $\kappa = \sqrt{2I_p}$ with I_p the ionization potential. In principle, the C_{lm} coefficients are independent of r , but due to numerical inaccuracy, they show some dependency on r as can be seen in Fig. 2.

For both O₂ and CO₂, the HOMO orbital is the lowest electronic state with Π_g symmetry, and can thus be obtained by propagating the TDSE in imaginary time ($t \rightarrow -i\tau$), i.e.,

$$\Psi(\tau + \Delta\tau) = \exp[-\mathbf{H}_0\Delta\tau]\Psi(\tau), \quad (11)$$

where $\mathbf{H}_0$ is the field-free Hamiltonian. The time evolution operator $\exp[-\mathbf{H}_0\Delta\tau]$ is solved numerically using the split-operator technique [21].

For N₂ (CS₂), the HOMO orbital is not the lowest electronic state of Σ_g (Π_g) symmetry, and can not be obtained by following the same procedure as for O₂ and CO₂. Instead, we obtain the HOMO wavefunction as [22]

$$\Psi = \frac{1}{\tau} \int_0^\tau dt \Psi^G(t) A(t) e^{-iI_p t}, \quad (12)$$

where $\Psi^G(0)$ is the HOMO wavefunction obtained from calculations in GAMESS [14], and $A(t)$ is a Hanning function. While $\Psi^G(0)$ is not necessarily an eigenfunction of $\mathbf{H}_0$, we can think of it as a superposition of eigenfunctions of $\mathbf{H}_0$. To resolve these eigenfunctions, we field-free propagate $\Psi^G(t)$ for a time τ . Note that generation of the orbital wavefunction by means of Eq. (12) requires prior knowledge of the orbital energy. This is obtained from the Fourier transform of the correlation function ($C(t) = \langle \Psi^G(0) | \Psi^G(t) \rangle$) [22], i.e.,

$$P(E) = \frac{1}{\tau} \left| \int_0^\tau dt C(t) A(t) e^{iEt} \right|. \quad (13)$$

The function $P(E)$ displays a resonant peak at the HOMO orbital energy ($-I_p$). For N₂ and CS₂, we run field-free propagation for a time $\tau=1000$ a.u. The integrals in (12) and (13) are performed by simple summation involving the saved wavefunction at each integration time step, $200 \times \Delta t$, with $\Delta t=0.005$ a.u. the propagation time step. These choices of τ and time steps produce wavefunctions with correct asymptotics up to $r \approx 15$ a.u. Equation (12) allows us to obtain wavefunctions with correct asymptotics for any molecule for which the SAE potential is at hand.

C. MO-ADK analytical formula

In MO-ADK theory [8], the ionization rate of a linear molecule aligned at an angle β with respect to a slowly varying field (with field strength E_0) may be expressed as

$$W = \sqrt{\frac{3E_0}{\pi\kappa^3}} \sum_{m'} \frac{|B(m')|^2}{2^{|m'|} |m'|! \kappa^{2Z/\kappa-1}} \left(\frac{2\kappa^3}{E_0}\right)^{2Z/\kappa-|m'|-1} \exp\left(-\frac{2\kappa^3}{3E_0}\right), \quad (14)$$

where

$$B(m') = \sum_{l \geq |m'|} (-1)^{\frac{m'+|m'|}{2}} \sqrt{\frac{(2l+1)(l+|m'|)!}{2(l-|m'|)!}} \times C_{lm} d_{m,m'}^{(l)}(\beta), \quad (15)$$

and where $d_{m,m'}^{(l)}(\beta)$ is the Wigner's (small) d-matrix, and m is the projection of the orbital angular momentum on the molecular axis ($m=0, 1, \dots$ for $\Sigma, \Pi, \dots$ orbitals). From Eq. (14), the tunneling rate depends on the field strength (E_0), the ionization potential (I_p) and the asymptotic coefficients (C_{lm}) of the probed orbital.

III. COMPUTATIONAL DETAILS

All quantum chemistry calculations concerning the SAE potential were carried out at the Hartree-Fock level of theory in conjunction with the triple- ζ valence (aug-cc-pVTZ for O_2) basis set, as implemented in GAMESS [14].

Alignment-dependent ionization yields are computed using the MO-ADK theory [8] (cf. section II C). To benchmark the MO-ADK predictions, we solve the TDSE describing the HOMO electron in the combined fields of the laser pulse and the frozen core. The calculations are performed in the velocity gauge [21]. The external field, linearly polarized along $\vec{\epsilon}$, is characterized by the vector potential $\vec{A}(t) = A_0 \sin^2(\omega t/2N) \cos(\omega t + \frac{\pi}{2}(1-2N) + \phi) \vec{\epsilon}$, where N is the number of optical cycles, ω is the angular frequency, ϕ is the carrier-envelope phase and $A_0(=E_0/\omega)$ is the amplitude. We use an equidistant grid with 2048 points for N_2 and CO_2 (4096 points for O_2) that extends up to 160 a.u. The laser pulses contain 7 cycles for N_2 and O_2 (10 cycles for CO_2), and the calculations were performed at 800 nm and peak intensity of $1.0 \times 10^{14} \text{ W/cm}^2$ for N_2 , $1.3 \times 10^{14} \text{ W/cm}^2$ for O_2 and $0.56 \times 10^{14} \text{ W/cm}^2$ for CO_2 . The alignment-dependent ionization yields are calculated by applying an absorbing boundary [20]. For O_2 and CO_2 , the HOMO orbital is degenerate, and we add the contributions to the ionization signal from the two orbitals incoherently—consistent with the statistical mixture in the density matrix representing the initial state.

Molecule	$I_p^{theo}(\text{eV})$	$I_p^{exp}(\text{eV})$
N ₂	15.67	15.6 [23]
O ₂	12.24	12.3 [24]
CO ₂	13.71	13.78 [25]
CS ₂	9.77	10.08 [25]

TABLE I: The HOMO orbital energy ($-I_p^{theo}$) of N₂, O₂, CO₂ and CS₂, from the present approach. For N₂, O₂ and CO₂, α and β in Eq. (7) are set to 1.1 and 0.05. For CS₂, α and β are set to 1.2 and 0.1. Experimental vertical ionization potentials (I_p^{exp}) are shown for comparison.

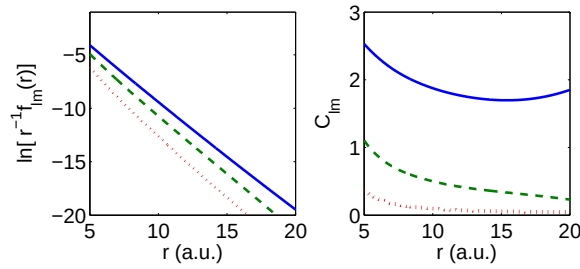


FIG. 2: (Color online) Radial wavefunctions ($r^{-1}f_{lm}(r)$) and C_{lm} coefficients for the CO₂ HOMO orbital ($m=1$), obtained from solving Eq. (11). The solid, dashed and dotted lines denote $l=2, 4$ and 6, respectively.

IV. RESULTS AND DISCUSSION

A. Wavefunctions with correct asymptotic behavior

It is important that the computed SAE potentials produce accurate orbitals, both in terms of energy and l -decomposition. In Table I, we compare the HOMO orbital energies for N₂, O₂, CO₂ and CS₂, obtained using the present approach, with the experimental vertical ionization potentials. The agreement is very good, indicating the accuracy of the SAE potentials. For the CO₂ molecule, the excited states are accurately described by the SAE potential [9].

In Fig. 2, we show the radial wavefunctions ($r^{-1}f_{lm}(r)$) and C_{lm} coefficients for the HOMO orbital of CO₂, as obtained from numerical calculations. The radial wavefunctions have the correct asymptotic behavior. Although, due to numerical inaccuracy, the slope of

$\ln[r^{-1}f_{lm}(r)]$ depends on l . To circumvent this problem, the C_{lm} coefficients need to be averaged over a region of r . In Table II, we show C_{lm} coefficients averaged over different r regions. One can clearly see that in the region where $r=6-10$ a.u., the C_{lm} coefficients vary quickly with r (cf. Fig. 2). This indicates that one needs to extend the range of r in order to get more stable C_{lm} coefficients. This is obtained by extracting C_{lm} coefficients in the region where r is extended to 20 a.u. What should be emphasized is that the molecular wavefunctions obtained from GAMESS fall off rapidly at r values above 10 a.u. [12], thereby limiting the accuracy of the C_{lm} coefficients obtained from GAMESS wavefunctions.

We carried out analysis on the molecular wavefunctions of the remaining molecules, and Table III includes C_{lm} coefficients for N_2 , O_2 , CO_2 and CS_2 , obtained from the present calculations and previous works [8, 12, 26]. Starting with N_2 , the absolute values of the C_{lm} coefficients are apparently dependent on the method. Yet, the ratios are similar. The present approach produces a C_{20}/C_{00} ratio of 0.44. Numerical Hartree-Fock calculations predicts a C_{20}/C_{00} ratio of 0.48 [26]. Yet another approach for obtaining asymptotic wavefunctions based on multiple scattering [8], produces a C_{20}/C_{00} ratio of 0.39. In keeping with this, our results for N_2 and O_2 , are in generally good agreement with the values cited in [8, 26].

For CO_2 , we compute somewhat larger C_{lm} coefficients, compared to those reported in [12]. One should be aware that the C_{lm} coefficients are sensitive to the computational method and the quality of basis set (grid). In the CO_2 case, changing the density of grid points leads to somewhat different C_{lm} coefficients. On a positive note, the ratios of the C_{lm} coefficients are less sensitive to the computational details than the absolute C_{lm} values.

Regarding CS_2 , we compare the C_{lm} coefficients with those based on the wavefunctions obtained in GAMESS [14]. The C_{41}/C_{21} ratio is 0.43 and 0.60, respectively, for the newly calculated wavefunction vs. the GAMESS wavefunction. Therefore, we do expect the alignment-dependent ionization yields for CS_2 molecules, computed within MO-ADK theory, to change considerably upon using the revised C_{lm} coefficients.

B. Alignment-dependent ionization yields

We first comment on the accuracy of our new C_{lm} coefficients for N_2 , O_2 , CO_2 and CS_2 . The alignment-dependent ionization yields are shown in Fig. 3, as obtained from the MO-ADK theory (cf. Eq. (14) in section II C). For N_2 and O_2 , we compare to ionization yields

r (a.u.)	C_{21}	C_{41}	C_{61}
6-10	2.07	0.65	0.12
6-20	1.84	0.43	0.06
10-20	1.75	0.35	0.04

TABLE II: C_{lm} coefficients for the HOMO orbital of CO₂, sampled over different r ranges.

Molecule	I_p (eV)	C_{0m}	C_{2m}	C_{4m}	C_{6m}	C_{8m}
N ₂	15.67	2.47	1.08	0.07		
N ₂ ^a		3.35	1.62	0.12		
N ₂ ^b	15.58	2.02	0.78	0.04		
O ₂	12.24		0.88	0.05		
O ₂ ^c	12.03		0.62	0.03		
CO ₂	13.71		1.75	0.35	0.04	
CO ₂ ^d	13.77		1.27	0.188	0.014	
CS ₂	9.78		1.86	0.79	0.188	0.03
CS ₂ ^e	10.22		1.78	1.06	0.29	0.06

^aRef. [26]

^bRef. [8]

^cRef. [8]

^dRef. [12]

^eCalculations at the HF level of theory in conjunction with the TZV basis set as implemented in GAMESS [14].

TABLE III: C_{lm} coefficients and ionization potentials (I_p) for the HOMO orbitals of N₂ ($m=0$), O₂ ($m=1$), CO₂ ($m=1$) and CS₂ ($m=1$), as obtained from the present calculations and literature [8, 12, 26].

based on the C_{lm} coefficients from [8], and the agreement is very good.

For CO₂ and CS₂, we compare with ionization yields based on the C_{lm} coefficients extracted from GAMESS wavefunctions. Starting with CO₂, the maximum ionization yield is predicted at an alignment angle of 33°, based on the revised C_{lm} coefficients. By contrast, the C_{lm} coefficients extracted from the GAMESS wavefunctions produce the maximum ionization yield at about 24° [12]. Therefore, the revised C_{lm} coefficients give better results, in

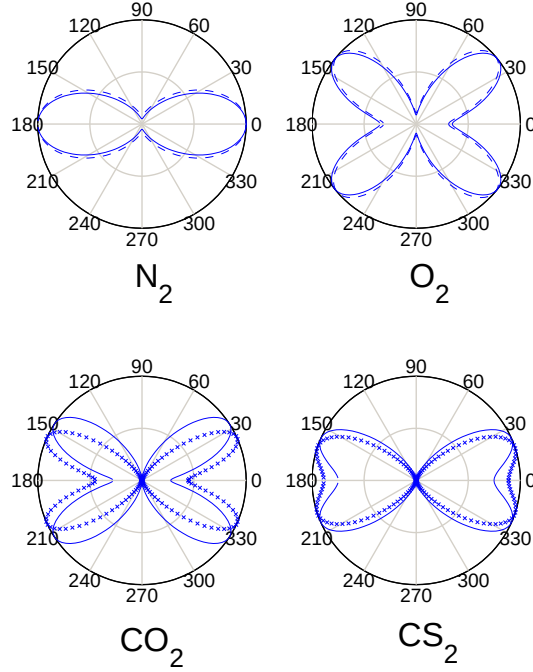


FIG. 3: (Color online) Alignment-dependent ionization yields from the HOMO orbitals of N_2 , O_2 , CO_2 and CS_2 molecules, computed using the MO-ADK theory [8] at laser intensities of $1.0 \times 10^{14} \text{W/cm}^2$ for N_2 , $1.3 \times 10^{14} \text{W/cm}^2$ for O_2 , $0.56 \times 10^{14} \text{W/cm}^2$ for CO_2 and $0.77 \times 10^{14} \text{W/cm}^2$ for CS_2 . Solid lines denote MO-ADK results based on revised C_{lm} coefficients; dashed lines: C_{lm} coefficients from Ref. [8], and crosses: C_{lm} coefficients extracted from GAMESS [14] wavefunctions.

comparison with the experiment [7], wherein the maximum ionization yield is predicted at 45° . Our MO-ADK results for CO_2 are in agreement with the main findings of Ref. [12].

The dependence of the maximum ionization yield for CO_2 on the C_{lm} coefficients is illustrated in Fig. 4(c), wherein several C_{41}/C_{21} ratios are considered (the C_{61} term is neglected). In the extreme case when the ratio $C_{41}/C_{21} \rightarrow 0$, the maximum ionization yield is predicted at 45° , in agreement with the maximum for the $|Y_{21}(\theta, \phi = 0)|^2$ in Fig. 4(a). By increasing the C_{41}/C_{21} ratio, the angle decreases monotonically, and at $C_{41}/C_{21} \rightarrow \infty$, the maximum ionization yield is predicted at about 22° , also in agreement with the maximum for the $|Y_{41}(\theta, \phi = 0)|^2$ in Fig. 4(b). Fig. 4 demonstrates the importance of extracting accurate C_{lm} coefficients for correct predictions by the MO-ADK theory.

Turning to CS_2 , the maximum ionization yield is predicted at 18° , based on the C_{lm}

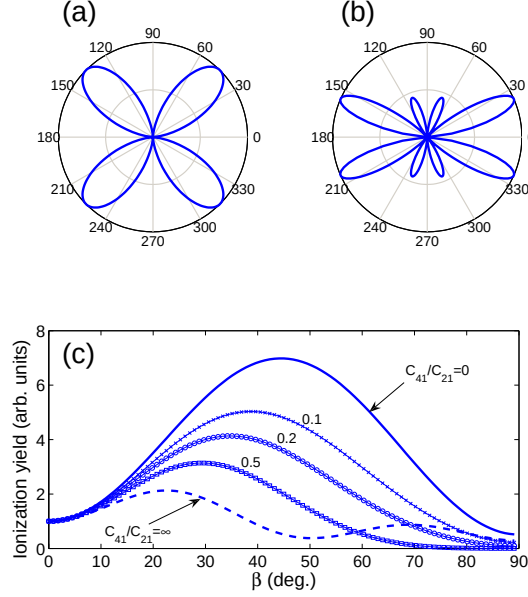


FIG. 4: (Color online) (a) $|Y_{21}(\theta, \phi = 0)|^2$, (b) $|Y_{41}(\theta, \phi = 0)|^2$ and (c) MO-ADK based alignment-dependent ionization yields from the HOMO orbital of the CO_2 molecule, assuming a varying C_{41}/C_{21} ratio and negligible C_{61} term. The ionization yields are given relative to those at alignment angle $\beta=0^\circ$.

coefficients obtained from GAMESS [14] wavefunctions. The ionization maximum shifts to 24° upon using the revised C_{lm} coefficients. The shift can be understood in terms of the change in C_{41}/C_{21} ratio, based on Fig. 4.

Now we compare the alignment-dependent ionization yields for N_2 , O_2 and CO_2 obtained from MO-ADK, with those from solving the TDSE. Since the same initial state and potential are used in both MO-ADK analysis and TDSE calculations, and taking into consideration that the population in, e.g., the HOMO-1 state [9] is reduced by the choice of laser intensity, large differences between MO-ADK and TDSE calculations should be understood as a failure of the MO-ADK theory to describe the ionization process.

The ionization yields are shown in Fig. 5, and do not account for focal-volume effects, fluctuation of laser intensity, or alignment distribution. For N_2 ($1.0 \times 10^{14} \text{W/cm}^2$) and O_2 ($1.3 \times 10^{14} \text{W/cm}^2$), the agreement between MO-ADK and TDSE results is generally good. For N_2 , the ionization yield is largest at 0° and monotonically decreases with alignment angle up to 90° . Regarding O_2 , both TDSE and MO-ADK predict the maximum ionization

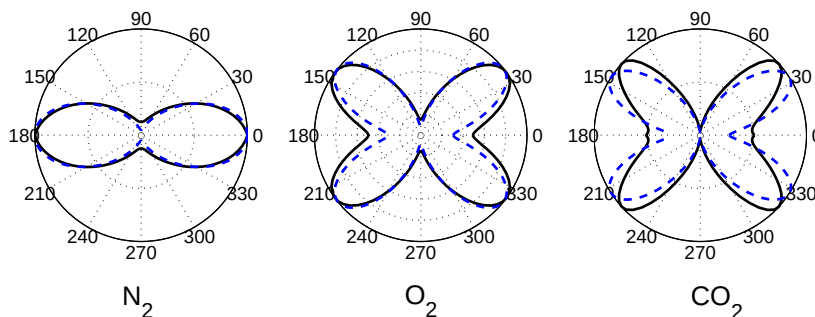


FIG. 5: (Color online) Alignment-dependent ionization yields for N_2 , O_2 and CO_2 molecules. The laser pulses have a central wavelength of 800 nm and peak intensities $1.0 \times 10^{14} \text{W/cm}^2$ for N_2 , $1.3 \times 10^{14} \text{W/cm}^2$ for O_2 and $0.56 \times 10^{14} \text{W/cm}^2$ for CO_2 . The solid (dashed) lines denote numerical (MO-ADK) results. The MO-ADK results are based on the present calculations of the C_{lm} coefficients using wavefunctions with improved asymptotics.

yield at 40° , slightly below the experimental value of 45° [7].

For CO_2 ($0.56 \times 10^{14} \text{W/cm}^2$), the TDSE calculations predict the maximum ionization yield at 45° , in agreement with the experimental observations [7]. By contrast, MO-ADK results based on the revised C_{lm} coefficients predict the maximum ionization yield at 33° . It is clear that MO-ADK fails to reproduce the ionization peak for CO_2 . In fact, alignment-dependent ionization of CO_2 is subject to several theory papers [9–11], and no consensus has yet been reached regarding the failure of MO-ADK theory.

V. SUMMARY AND CONCLUSIONS

Single-active-electron potentials are computed for the N_2 , O_2 , CO_2 and CS_2 molecules. The potentials rely on the local density approximation of electron exchange [15, 17], and produce accurate orbital energies. The potentials produce molecular wavefunctions with correct asymptotic behavior, and, therefore, accurate asymptotic coefficients can be extracted. For N_2 and O_2 , the computed asymptotic coefficients are in agreement with those based on numerical Hartree-Fock calculations of the ground-state wavefunctions [26] and the multiple scattering method [8]. For CO_2 and CS_2 , the computed asymptotic coefficients are superior to those obtained from molecular wavefunctions computed in GAMESS [14].

Alignment-dependent ionization yields are computed from MO-ADK theory, and are found to be very sensitive to the ratios of the asymptotic coefficients. The MO-ADK predictions for N₂, O₂ and CO₂ are benchmarked by *ab initio* calculations based on a solution of the time-dependent Schrödinger equation for the HOMO electron. The TDSE calculations take as input the same wavefunctions and SAE potentials used in MO-ADK analysis. For N₂ and O₂, the MO-ADK predictions are in generally good agreement with the TDSE calculations. However, the MO-ADK theory fails to reproduce the TDSE results for CO₂.

VI. ACKNOWLEDGMENTS

This work was supported by the Danish Research Agency (Grant No. 2117-05-0081).

-
- [1] C. Z. Bisgaard, O. J. Clarkin, G. Wu, A. M. D. Lee, O. Geßner, C. C. Hayden, and A. Stolow, *Science* **323**, 1464 (2009).
 - [2] S. Baker, J. S. Robinson, C. A. Haworth, H. Teng, R. A. Smith, C. C. Chirila, M. Lein, J. W. G. Tisch, and J. P. Marangos, *Science* **312**, 424 (2006).
 - [3] J. Itatani, J. Levesque, D. Zeidler, H. Niikura, H. Pépin, J. C. Kieffer, P. B. Corkum, and D. M. Villeneuve, *Nature* **432**, 867 (2004).
 - [4] A. S. Alnaser, S. Voss, X. M. Tong, C. M. Maharjan, P. Ranitovic, B. Ulrich, T. Osipov, B. Shan, Z. Chang, and C. L. Cocke, *Phys. Rev. Lett.* **93**, 113003 (2004).
 - [5] V. Kumarappan, L. Holmegaard, C. Martiny, C. B. Madsen, T. K. Kjeldsen, S. S. Viftrup, L. B. Madsen, and H. Stapelfeldt, *Phys. Rev. Lett.* **100**, 093006 (2008).
 - [6] I. V. Litvinyuk, K. F. Lee, P. W. Dooley, D. M. Rayner, D. M. Villeneuve, and P. B. Corkum, *Phys. Rev. Lett.* **90**, 233003 (2003).
 - [7] D. Pavičić, K. F. Lee, D. M. Rayner, P. B. Corkum, and D. M. Villeneuve, *Phys. Rev. Lett.* **98**, 243001 (2007).
 - [8] X. M. Tong, Z. X. Zhao, and C. D. Lin, *Phys. Rev. A* **66**, 033402 (2002).
 - [9] M. Abu-samha and L. B. Madsen, *Phys. Rev. A* **80**, 023401 (2009).
 - [10] S.-K. Son and S.-I. Chu, *Phys. Rev. A* **80**, 011403 (2009).
 - [11] M. Spanner and S. Patchkovskii, *Phys. Rev. A* **80**, 063411 (2009).

- [12] S.-F. Zhao, C. Jin, A.-T. Le, T. F. Jiang, and C. D. Lin, *Phys. Rev. A* **80**, 051402 (2009).
- [13] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant *et al.*, Gaussian 03, Revision C.02. Gaussian, Inc., Wallingford, CT, 2004.
- [14] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. J. Jensen, S. Koseki, N. Matsunaga, K. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.* **14**, 1347 (1993).
- [15] W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- [16] X.-M. Tong and S.-I. Chu, *Phys. Rev. A* **55**, 3406 (1997).
- [17] R. van Leeuwen and E. J. Baerends, *Phys. Rev. A* **49**, 2421 (1994).
- [18] X.-M. Tong and C. D. Lin, *J. Phys B* **38** 2593, (2005).
- [19] H. G. Muller and F. C. Kooiman, *Phys. Rev. Lett.* **81**, 1207 (1998).
- [20] L. A. A. Nikolopoulos, T. K. Kjeldsen, and L. B. Madsen, *Phys. Rev. A* **75**, 063426 (2007).
- [21] T. K. Kjeldsen, L. A. A. Nikolopoulos, and L. B. Madsen, *Phys. Rev. A* **75**, 063427 (2007).
- [22] M. R. Hermann and J. A. Fleck, *Phys. Rev. A* **38**, 6000 (1988).
- [23] A. Lofthus and P. Krupenie, *J. Phys. Chem. Ref. Data* **6**, 113 (1977).
- [24] P. Baltzer, B. Wannberg, L. Karlsson, M. Carlsson Gothe, and M. Larsson, *Phys. Rev. A* **45**, 4374 (1992).
- [25] A. W. Potts and G. H. Fattahallah, *J. Phys. B* **13**, 2545 (1980).
- [26] T. K. Kjeldsen and L. B. Madsen, *J. Phys. B* **37**, 2033 (2004).