

## LETTER TO THE EDITOR

## Antibonding molecular orbitals under the influence of elliptically polarized intense light

**Manfred Lein**

Max Planck Institute for the Physics of Complex Systems, Nöthnitzer Straße 38,  
D-01187 Dresden, Germany

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### Abstract

The strong-field dynamics of diatomic molecules with antibonding valence orbitals is investigated within classical and quantum mechanical model calculations. Due to the orbital symmetry, ejected electrons never return to the core if a linearly polarized laser field acts perpendicularly to the molecular axis. However, elliptical polarization can be used to achieve recollision so that high-order above-threshold ionization and high-order harmonic generation become maximal at nonzero ellipticity. Smaller ellipticities favour higher harmonic orders. For given ellipticity the probability for electron recollisions depends strongly on the orientation of the molecule. Thus, ellipticity can be used as a control parameter to select a range of orientations for recollision-induced processes.

The dynamics of molecules in strong laser fields has recently met with growing interest. The interplay between laser-induced electronic motion and nuclear vibrational motion in  $H_2$  has been used to measure the electron dynamics with sub-laser-cycle time resolution [1]. In this experiment the laser field removes an electron, accelerates it and drives it back to the molecular core where it can initiate dissociation by inelastic scattering. These results can also be interpreted such that the recolliding electron is used as a tool to probe the molecular dynamics. Besides inelastic scattering, recollisions can lead to the production of fast electrons through elastic scattering and subsequent acceleration in the field [2, 3], or to the generation of high-order harmonics, i.e. the emission of XUV photons [4]. Owing to quantum mechanical interference, both processes are very sensitive to the molecular geometry [5–7]. Thus, high-harmonic generation and high-order above-threshold ionization are promising candidates for probing. As a probe, recolliding electrons combine high current density with sub-fs time resolution, which is a great advantage as compared to other short-wavelength probing techniques based on external sources [8, 9].

Since the strong-field dynamics of molecules is sensitive to the molecular orientation, it is desirable to work with fixed orientation. When dissociation is involved (as in the case

of [1]) the orientation can be selected by detecting the fragments. Without dissociation, the molecules have to be prealigned by an appropriate aligning laser pulse [10–12] which is obviously a complication of the experiment. Laser-induced alignment would not be needed if the recollision probability was sufficiently dependent on the molecular orientation in such a way that only a narrow range of angles contributed significantly to the recollision-induced processes. In principle, charge-resonance-enhanced ionization [13, 14] offers this possibility since it enhances ionization (and therefore the probability for recollision) only for molecules oriented approximately parallel to the laser field. However, charge-resonance-enhanced ionization is effective only at internuclear distances much larger than the equilibrium distance, and it offers no controllable selection of orientations. In this letter, a method for *controlled selection* is proposed: it is demonstrated that in diatomic molecules with antibonding valence orbitals, the recollision probability depends strongly on the molecular orientation. Furthermore, this angle dependence changes with the ellipticity of the laser, so ellipticity can be used as a control parameter to select the orientation. This sort of orientation control can be used on its own, or it can be combined with alignment techniques, opening up new perspectives for experiments with aligned molecules.

Previous work has shown that the symmetry of the valence orbitals is of great importance in strong-field processes: antibonding valence orbitals are harder to ionize than bonding valence orbitals as a consequence of destructive interference of the electron waves emerging from the different atomic centres [15]. The experimentally found suppression of ionization in O<sub>2</sub> [16] can be explained along these lines. However, a different explanation was proposed in [17]. Suppressed ionization was also observed in organic molecules [18].

The impact of symmetry on recollision-related effects was seen in the experiment of [19]: as a consequence of the spatial antisymmetry of the highest occupied molecular orbitals in C<sub>6</sub>H<sub>6</sub>, the maximum double-ionization yield is obtained not for linear laser polarization but for small nonzero ellipticity. Qualitatively, the effect can be understood from the momentum-space wavefunction. For simplicity, consider an antibonding LCAO molecular orbital in a diatomic molecule,  $\psi(\mathbf{r}) = \beta[\phi(\mathbf{r} - \mathbf{R}_1) - \phi(\mathbf{r} - \mathbf{R}_2)]$ , where  $\beta$  is a normalization constant and  $\mathbf{R}_1, \mathbf{R}_2 = \mathbf{R}_1 + \mathbf{R}$  are the positions of the nuclei. From  $\tilde{\psi}(\mathbf{p}) = \int \psi(\mathbf{r})e^{-i\mathbf{p}\cdot\mathbf{r}} d^3r$  we obtain the momentum distribution

$$|\tilde{\psi}(\mathbf{p})|^2 = 4|\beta\tilde{\phi}(\mathbf{p})|^2 \sin^2\left(\frac{\mathbf{p}\cdot\mathbf{R}}{2}\right) \quad (1)$$

with  $\tilde{\phi}(\mathbf{p}) = \int \phi(\mathbf{r})e^{-i\mathbf{p}\cdot\mathbf{r}} d^3r$ . (Atomic units are used unless indicated otherwise.) We see that  $\tilde{\psi}(\mathbf{p}) = 0$  for  $\mathbf{p} \perp \mathbf{R}$ , i.e. the component of the electron momentum parallel to the molecular axis is always nonzero. Consider now the molecule being ionized by an intense laser polarized linearly with the polarization axis perpendicular to the molecular axis. In this configuration, the mirror symmetry of the system is not broken by the field. Therefore the wavefunction keeps its antibonding symmetry, and upon ionization the electron must drift away from the polarization axis due to the nonzero velocity component perpendicular to the field. The probability for recollision with the core is thus very small. In order to increase the recollision probability, however, the transverse drift motion can be compensated by introducing a small degree of ellipticity in the laser polarization. In [19] this effect was seen as an increase in the double-ionization yield.

In the present work, we investigate how the recollision probability in diatomic molecules with antibonding valence orbitals depends on the molecular orientation and on the laser ellipticity. We begin with a simple classical model for a laser with small ellipticity. First, consider the case where a linearly polarized laser is applied with its field perpendicular to the molecule. In the event of ionization at the time  $t_0$ , we assume that a free electron is

created at  $r = 0$  with zero velocity component in the field direction. The velocity component perpendicular to the field must be nonzero as a consequence of the antibonding symmetry. The initial velocity does not necessarily point along the molecular axis. This depends on the location of nodal planes other than the one giving rise to the antibonding character of the orbital. Since the free electron will never return to the molecular core in a linearly polarized laser, we add now a small ellipticity  $\xi$  to the laser and assume that this does not affect the initial conditions for the electron. We take the  $x$ -axis along the direction of the large component of the field and the  $y$ -axis along the direction of the small component so that the field is given by

$$E(t) = E_0[e_x \sin(\omega t) + e_y \xi \cos(\omega t)]. \quad (2)$$

The velocity of the ejected electron is taken to be in the  $(x, y)$  plane. This is an approximation where we restrict ourselves to electrons that can be steered back to the core if the ellipticity is appropriately chosen. Other electrons, i.e. electrons for which the initial velocity is outside the  $(x, y)$  plane, can never return to the core and are therefore expected to have little influence on the results. The classical equations of motion for the laser-driven free electron are

$$\ddot{x}(t) = -E_0 \sin(\omega t), \quad (3)$$

$$\ddot{y}(t) = -\xi E_0 \cos(\omega t). \quad (4)$$

With the initial velocity  $v_0 = (0, v_0)$ , we find

$$x(t) = \alpha[\sin(\omega t) - \sin(\omega t_0) - \omega(t - t_0) \cos(\omega t_0)], \quad (5)$$

$$y(t) = \xi \alpha[\cos(\omega t) - \cos(\omega t_0)] + \omega(t - t_0)[v_0/\omega + \xi \alpha \sin(\omega t_0)], \quad (6)$$

with  $\alpha = E_0/\omega^2$ . For a given starting time  $t_0$ , we can find from equation (5) the time  $t_1$  when the electron first returns to  $x = 0$ . In general, we have  $y(t_1) \neq 0$ . Yet, from equation (6), we can find the ‘recollision ellipticity’  $\xi_r$  that yields  $y(t_1) = 0$ . The travel time between departure and return of the electron is then  $\tau = t_1 - t_0$ .

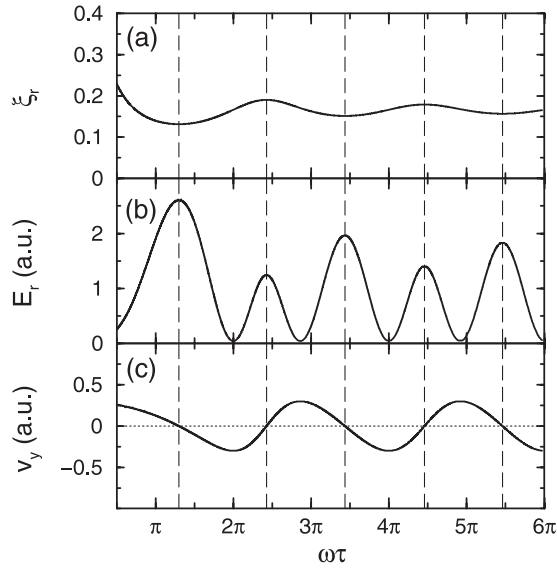
The laser intensity is given by

$$I = E_0^2(1 + \xi^2) \times 3.5094 \times 10^{16} \text{ W cm}^{-2}. \quad (7)$$

Thus, if the intensity is held constant, an increase in  $\xi$  leads to a decrease in  $E_0$ . This has been taken into account in figure 1 where we plot the results of the classical analysis for a realistic set of parameters (see figure caption) that correspond to the numerical results presented further below. The uppermost panel of the figure shows the recollision ellipticity  $\xi_r$  as a function of  $\omega\tau$ . The other panels display the kinetic energy  $E_r$  of the recolliding electron and the lateral component  $v_y$  of the recollision velocity, respectively. It is interesting to note that every local extremum in  $\xi_r$  coincides with a maximum in the recollision energy and with zero lateral recollision velocity. These positions are indicated by the dashed vertical lines in figure 1. The coincidence of maximum recollision energy and zero lateral velocity implies that the highest recollision energy occurs for the same travel time ( $\omega\tau = 4.09$ ) as in the standard recollision model for linear polarization [4] and is equal to  $3.17E_0^2/(4\omega^2) = 3.17U_p/(1 + \xi^2)$ . The most important conclusion from figure 1 is that the range of recollision ellipticities is rather small. (This is not true for very small travel times for which the recollision ellipticity grows larger and larger.) Thus, with an appropriately chosen fixed ellipticity, e.g.  $\xi \sim 0.15$  in the case of figure 1, we are able to steer the electron close by the nucleus irrespective of its travel time.

In the following, we proceed with quantum mechanical calculations. We use a two-dimensional one-electron model system with a double-well potential of the form

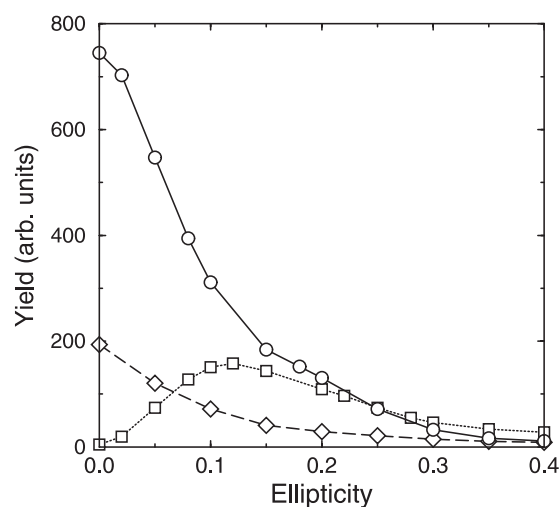
$$V(x, y) = - \sum_{k=1,2} \frac{1}{\sqrt{(x - x_k)^2 + (y - y_k)^2 + 0.5}}, \quad (8)$$



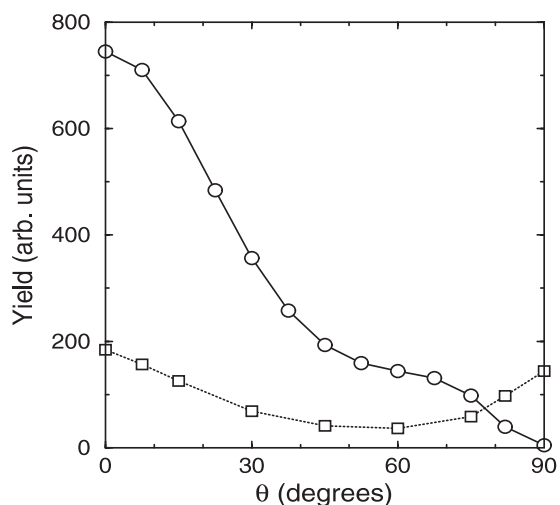
**Figure 1.** Results from the classical model for the molecular axis perpendicular to the large component of the laser field. The three panels show as a function of  $\omega\tau$  (a) the ellipticity required for electron recollision, (b) the recollision energy, (c) the lateral electron recollision velocity. The laser parameters are  $I = 4 \times 10^{14} \text{ W cm}^{-2}$ ,  $\lambda = 780 \text{ nm}$ . The initial lateral electron velocity is  $v_0 = -0.3$ .

where  $(x_k, y_k)$  are the positions of the nuclei. The same binding potential was used in [7]. Instead of the bonding lowest orbital, however, the initial state of the electron is here set to be the antibonding first excited state of the system. Keeping the internuclear distance fixed at 2 au, the vertical ionization potential of this orbital is  $I_p = 0.69 \text{ au}$  (19 eV). We solve the time-dependent Schrödinger equation for the system under the influence of a laser pulse numerically as described in [7]. This method allows us to calculate not only the wavefunction in a region around the nuclei, but also the spectrum and angular distribution of electrons ejected through ionization in the strong field. The calculation is performed for ten-cycle pulses of 780 nm wavelength and  $4 \times 10^{14} \text{ W cm}^{-2}$  intensity. The electric field envelope is trapezoidal with three-cycle linear ramps.

It is well known that the energies of direct electrons, i.e. electrons being ejected without rescattering, classically range up to  $2U_p$ . Electrons that recollide and scatter elastically from the core acquire energies up to  $10U_p$  [2, 3]. Hence the yield of such fast electrons is a good measure of recollisions in the system. In figure 2 we plot the yield of photoelectrons with energies higher than  $4U_p = 3.34 \text{ au}$  as a function of the laser ellipticity. We consider three different angles between the molecular axis and the large component of the electric field:  $\theta = 0^\circ, 45^\circ$  and  $90^\circ$ . In the first two cases we find that the electron yield drops quickly with increasing ellipticity: at  $\xi = 0.25$  the number of scattered electrons drops below 10% of the yield at  $\xi = 0$ . For  $\theta = 90^\circ$ , however, the maximum is obtained at  $\xi = 0.12$  while the yield is zero for linear polarization. This is in agreement with our classical considerations above. The result for the intermediate angle is somewhat surprising since we might have expected a maximum at nonzero ellipticity as well. However, we should keep in mind that in this case the mirror symmetry of the whole system (molecule plus field) is broken even for linear polarization, i.e. there are no symmetry restrictions on the initial electron velocity.

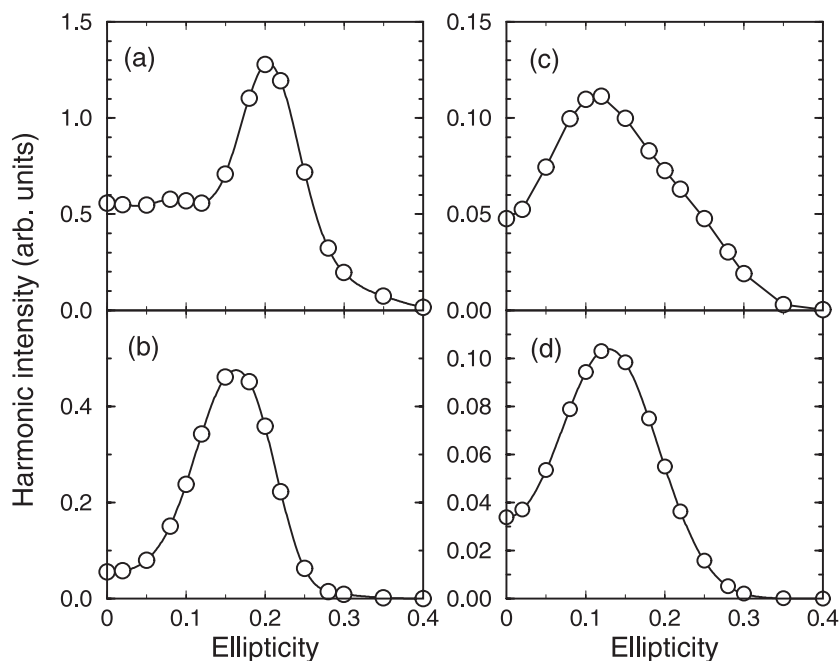


**Figure 2.** The yield of scattered electrons with energies above  $4U_p$  as a function of the laser ellipticity for the molecular orientations  $\theta = 0^\circ$  ( $\circ$ — $\circ$ ),  $45^\circ$  ( $\diamond$ — $\diamond$ ) and  $90^\circ$  ( $\square$ — $\square$ ). The laser parameters are as in figure 1.



**Figure 3.** The yield of scattered electrons with energies above  $4U_p$  as a function of the molecular orientation for the laser ellipticities  $\xi = 0$  ( $\circ$ — $\circ$ ) and  $0.15$  ( $\square$ — $\square$ ).

Let us now assume an ensemble of randomly oriented molecules. Then, it is obvious from figure 2 that zero ellipticity favours recollisions in molecules oriented parallel to the field while nonzero ellipticity also favours recollisions in molecules oriented in the perpendicular direction. This is evident in figure 3 where we plot the yield of scattered electrons as a function of the orientation for linear polarization and for  $\xi = 0.15$ . The contribution of  $\theta = 0$  remains significant even at  $\xi = 0.15$ , so we cannot isolate the perpendicular orientation. Nevertheless, it is clear that ellipticity acts as a control parameter that selects specific ranges of molecular orientations for recollision-induced processes. Although it seems impossible to select a very narrow range of orientations using this type of orientation control, one may combine it with



**Figure 4.** The ellipticity dependence of the intensities in high-order harmonic generation for perpendicular orientation of the molecule ( $\theta = 90^\circ$ ). (a) 31st, (b) 41st, (c) 51st, (d) 61st harmonic.

alignment techniques involving an additional external field. A very high effective degree of alignment will be achieved in this way.

Finally we briefly show that the effect of the antibonding symmetry is also seen in high-order harmonic generation. Figure 4 displays the ellipticity dependence of selected harmonics for the case of perpendicular alignment ( $\theta = 90^\circ$ ). For all harmonic orders shown in the figure, we find a maximum at nonzero ellipticity. This is analogous to what we found for the yield of fast electrons in figure 2. Furthermore, the maximizing ellipticity decreases with increasing harmonic order (except for the 61st harmonic which is maximal at about the same ellipticity as the 51st harmonic). This can be understood from the classical results in figures 1(a), (b): the smallest recollision ellipticity gives rise to the highest return energy  $E_r$  and thus to the highest harmonic order since the energy of the harmonic photon generated by recombination equals  $E_r + I_p$ . This effect offers the possibility of maximizing specific harmonics by varying the laser ellipticity. Note that this is different from harmonic generation in an atom where all harmonics become maximal at  $\xi = 0$  [20].

In experiment, harmonic generation is limited by phase mismatch due to ionization. Therefore, whether the variation of the harmonic intensities can be observed depends on the ellipticity dependence of the ionization. Regarding this point, we note that the calculated ionization probability (about 90% for the present parameters) is practically independent of the ellipticity since the laser intensity is held constant.

To summarize, we have investigated the strong-field behaviour of diatomic molecules with antibonding valence orbitals. When an electron is ejected by a laser polarized perpendicular to the molecular axis, it never recollides with the core, but it can be steered back to the core by using a small degree of ellipticity. Accordingly, if the large component of the field is perpendicular

to the molecule, the yield of scattered electrons and high-order harmonics is maximal at nonzero ellipticity. Different harmonic orders are maximized by different ellipticities. For a given ellipticity the probability for recollision is strongly orientation dependent, so a range of orientations is selected for recollision-induced processes. Hence, this effect is of great importance for experiments with aligned molecules since it can enhance the effective degree of alignment in a controllable way.

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