Chemical Physics 366 (2009) 85–90

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Strong-field approximation for high-order above-threshold ionization of randomly oriented diatomic molecules

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A R T I C L E   I N F O

Article history:
Received 27 May 2009
Accepted 1 September 2009
Available online 6 September 2009

Keywords:
Molecules
Attosecond
Above-threshold ionization
Electron spectra
Alignment
Double-slit interference

A B S T R A C T

High-order above-threshold ionization of diatomic molecules by a strong linearly polarized field is considered using the molecular strong-field approximation. Tunneling–rescattering as the mechanism of this ionization gives rise to a novel two-source double-slit interference, which involves the four geometrical paths that are available to an electron, which can be ionized from and rescattered off either of the two centers of the diatomic molecule. For a comparison of this theory with experiments in the absence of molecular alignment, it is necessary to average the theoretical results over the molecular orientation. This paper presents technical details of this averaging procedure. It is shown that, depending on the molecular symmetry, the destructive two-source double-slit interference minima can survive the orientation averaging and can be observed in the angle-resolved electron spectra. This is illustrated on the examples of N_2 and O_2 molecules. It is also shown that two- and three-dimensional versions of orientation averaging lead to qualitatively similar results.

1. Introduction

The strong-field approximation (SFA) is at the core of the semi-analytical theory of laser-induced strong-field ionization of atoms [1–4]. When it is extended to allow for rescattering and atom-specific electron-atom scattering potentials are introduced, its predictions are rather reliable, especially for the angle-resolved energy spectra (see [5] and references therein). In contrast, accurate results for total ionization rates are harder to come by because the latter are dominated by the emission of electrons of very low energy, which are only poorly represented by the SFA because it does not properly account for the atomic Coulomb potential [6].

The extension of the SFA to molecules has only recently come under closer scrutiny [7–11]. It is much more demanding not only because of the structure of the molecule that needs be taken into account but also because other problems that already hamper the atomic SFA, such as its neglect of all bound states except for the initial ground state and its notorious dependence [12] on the gauge employed, become much more severe [11,13]. Yet, many advances have recently been made and the molecular SFA has progressed to the point [14,15] – and sufficiently detailed experimental data have become available [16,17] – where a comparison with the latter has become meaningful [18].

The SFA provides the *T*-matrix element into a fully specified final continuum state. All parameters that are not observed have to be integrated over. This is one of the reasons of why a *T*-matrix computation of the total ionization rate is particularly cumbersome. In experiments and also in approaches based on the solution of the time-dependent Schrödinger equation the situation is the exact opposite. Inclusive results are easiest to obtain, and more differential ones require harder work [19] (see also [20] and references therein). For observations on molecules, one parameter that is difficult to fix in experiments with high precision is the orientation of the molecule. Interesting features that exist for well-defined orientation may be washed out in the average. This paper considers technical details of the orientation average in SFA calculations, especially the extent to which a planar geometry is sufficient, and applications to high-order above-threshold ionization of molecules. A novel interference phenomenon that goes beyond the phenomenology of the standard double slit and the question of whether its footprint in the data survives the orientation average provide a case in point [21].

The paper is organized as follows. In Section 2 we briefly summarize our earlier work in so much as it is indispensable for the present paper. In the next Section 3, we discuss the dependence of the *T* matrix on the various angles and define the problem of averaging over the orientation of the molecule. In Section 4, we simplify the problem by considering the case where all vectors are coplanar. Next, in Section 5 we present the results of full

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doi:10.1016/j.chemphys.2009.09.002

three-dimensional (3D) averaging. In Section 6 we consider for the coplanar case the partial rates for specific molecular orientation angles in order to explain the differences between the molecules N_2 and O_2, and in Section 7 we compare two-dimensional (2D) and 3D averaging.

2. General theory

In this paper, we will only be concerned with the part of the T matrix that is due to rescattering (in earlier work, this part was denoted by $T^{(1)}$; here we drop the superscript "(1)"). For all details of the molecular SFA, which underlies this paper, we refer to Refs. [11,15], for direct and rescattering ionization, respectively. The total rescattering T-matrix element can be decomposed into four terms that are distinguished by the geometrical pathway followed by the electron on its way from the molecule to the detector as illustrated in Fig. 1:

$$T = T^{++} + T^{--} + T^{+-} + T^{-+}. \tag{1}$$

The electron can tunnel out of either atom and after its excursion in the continuum rescatter at either atom, which gives rise to four terms. Note that the terms T^{+-} and T^{-+}, where the electron is ionized and rescatters off different atoms, describe topologically different pathways: in the lower left panel, the electron passes the second center, where it will subsequently rescatter, shortly after it was ionized, at the beginning of its excursion away from the molecule. In contrast, in the lower right panel, it encounters the second center for the first time when it returns to rescatter. In consequence, these two terms are different and exhibit, for example, slightly different cutoffs. However, for the comparatively small internuclear separations that we shall consider the differences are not very pronounced, and we shall assume that the four contributions depicted in Fig. 1 are identical up to respective phases, which are related to the length of the respective orbits. For the two "nontransfer" terms where the electron is born at and rescatters off the same atom this path-length difference is $R_0\cos(\theta_{fe}-\theta_L)$ so that

$$T^{++} + T^{--} = \left(e^{i\alpha} + s_{a\lambda}e^{-i\alpha}\right)A \tag{2}$$

with $\alpha = \mathbf{p}_f\cdot\mathbf{R}_0/2$. The quantity $s_{a\lambda}$ depends on the symmetry of the molecular orbital which is a linear combination of the atomic orbitals a. Hence, the right-hand side of Eq. (2) is proportional to $\cos\alpha$ or $\sin\alpha$, respectively, for $s_{a\lambda} = +1$ and $s_{a\lambda} = -1$. This gives rise to the well-known two-center destructive interference, which for "direct" processes (not involving rescattering) was predicted in Ref. [7] and first observed in Ref. [16].

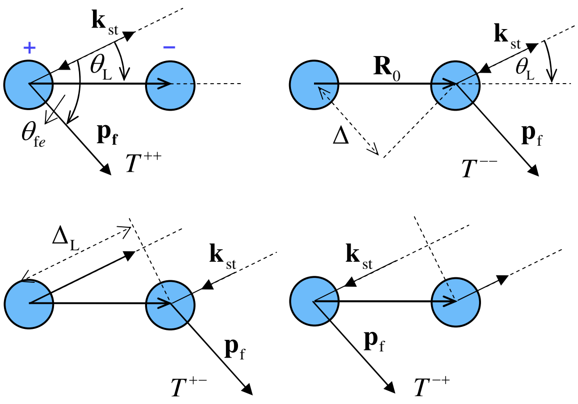

Fig. 1. Schematic diagram of the four rescattering T-matrix contributions to strong-field ionization of a diatomic molecule represented by two atomic centers denoted by "+" and "−". The electron drift momentum $\mathbf{k}_{st}$ between ionization and rescattering is along the laser polarization axis. The final momentum $\mathbf{p}_f$ and the relative nuclear coordinate $\mathbf{R}_0$ include the angles θ_{fe} and θ_L with respect to the former. In the upper panels the contributions T^{++} and T^{--} are depicted, where the electron rescatters at the same center at which it was born, and the corresponding electron path-length difference $\Delta = R_0\cos(\theta_{fe}-\theta_L)$ is indicated. The two lower panels show the contributions of the processes where ionization and rescattering occur at different centers. The path-length difference of these two contributions, before rescattering, is $2\Delta_L = 2R_0\cos\theta_L$.

With our assumption that all four terms have about the same magnitude, the above symmetry will not be observed owing to the contributions of the "transfer" terms T^{+-} and T^{-+}. The corresponding two paths differ from each other by twice the projection of the internuclear axis on the direction of the field polarization minus the projection of the internuclear axis on the direction of the final electron momentum:

$$T^{+-} + T^{-+} = \left(e^{i\beta} + s_{a\lambda}e^{-i\beta}\right)A \tag{3}$$

with $\beta = \mathbf{k}_{st}\cdot\mathbf{R}_0 - \mathbf{p}_f\cdot\mathbf{R}_0/2$. We note that the factor $s_{a\lambda}$ is associated with the center where the electron starts, not where it rescatters. The interference pattern (3) of the transfer terms is different from that of the nontransfer terms, Eq. (2). Because they overlap neither one can be observed separately. The sum of all four terms can be factorized as follows:

$$\begin{aligned} T^{++} + T^{--} + T^{+-} + T^{-+} &= \left[e^{\frac{i}{2}(\alpha-\beta)} + e^{-\frac{i}{2}(\alpha-\beta)}\right]\left[e^{\frac{i}{2}(\alpha+\beta)} + s_{a\lambda}e^{-\frac{i}{2}(\alpha+\beta)}\right]A \\ &= 4A\cos\gamma\begin{cases}\cos\delta & (s_{a\lambda}=1) \\ i\sin\delta & (s_{a\lambda}=-1)\end{cases}, \end{aligned} \tag{4}$$

where

$$\begin{aligned} 2\gamma &= \alpha-\beta = (\mathbf{p}_f - \mathbf{k}_{st})\cdot\mathbf{R}_0 \equiv 2(c\cos\theta_{fR} - \delta), \\ 2\delta &= \alpha+\beta = \mathbf{k}_{st}\cdot\mathbf{R}_0 \equiv 2b\cos\theta_L \end{aligned} \tag{5}$$

and we have introduced the parameters $b = k_{st}R_0/2$ and $c = p_fR_0/2$ for later use. Remarkably, when $\gamma = n\pi + \pi/2$ with integer n, Eq. (4) predicts destructive interference *regardless of the molecular symmetry*. No double slit can create this pattern. It requires four paths to contribute, such as they are generated by two sources plus two slits.

To be more specific, the total rescattering T-matrix element $T^{++} + T^{--} + T^{+-} + T^{-+}$ for the ath constituent of the molecular orbital having the symmetry σ (for N_2) or π (for O_2) is found to be proportional to [14,15]

$$\begin{aligned} &\cos\delta\cos\gamma \quad \text{for } a = s \text{ and } \sigma\ (s_{a\lambda} = +1), \\ &\cos\theta_L\sin\delta\cos\gamma \quad \text{for } a = p \text{ and } \sigma\ (s_{a\lambda} = -1), \\ &\sin\theta_L\sin\delta\cos\gamma \quad \text{for } a = 2p \text{ and } \pi\ (s_{a\lambda} = -1). \end{aligned} \tag{6}$$

As mentioned before, the magnitudes of the four terms T^{++}, T^{--}, T^{+-}, and T^{-+} are not exactly equal and, hence, the interference pattern predicted by Eq. (6) will not be exactly observed. However, for the moderate values of R_0 that we consider the destructive interference is very pronounced and, moreover, its position does not depend on the molecular symmetry, as predicted by Eq. (4).

3. Definition of the problem and 3D averaging

Theoretically, in the spherical coordinate system with the z axis along the polarization axis $\hat{\mathbf{e}}_L$ (see Fig. 2) the vectors of the internu-

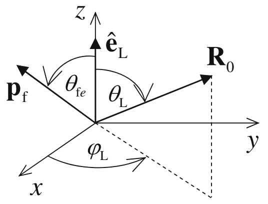

Fig. 2. Definition of the 3D coordinate system used in our theoretical considerations.