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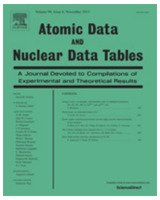

Structure factors for tunneling ionization rates of diatomic molecules

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ABSTRACT

Within the leading-order, single-active-electron, and frozen-nuclei approximation of the weak-field asymptotic theory, the rate of tunneling ionization of a molecule in an external static uniform electric field is determined by the structure factor for the highest occupied molecular orbital. We present the results of systematic calculations of structure factors for 40 homonuclear and heteronuclear diatomic molecules by the Hartree–Fock method using a numerical grid-based approach implemented in the program X2DHF.

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1. Introduction

The rate of tunneling ionization of atoms and molecules in an external static uniform electric field is an important property required for many applications in atomic, molecular, and optical physics. The current interest to this property is dictated by its applications in strong-field physics and attoscience [1], where tunneling ionization is the initial key process that triggers subsequent dynamics [2,3]. In the adiabatic regime of main interest for such applications, that is, at sufficiently low frequency and high intensity, tunneling ionization in an oscillating laser field proceeds as if the field were static and equal to its instantaneous value [4,5].

Recently, we have developed the weak-field asymptotic theory (WFAT) of tunneling ionization [6]. This theory generalizes the earlier treatments of tunneling ionization from spherically symmetric atomic potentials [7–10] to molecular potentials without any symmetry. In the WFAT, the ionization rate is sought as an asymptotic expansion in the field F. Such an approach is justified for sufficiently weak fields satisfying $F \ll F_c$, where F_c is a field at which over-the-barrier ionization becomes accessible. Since for neutral atoms and molecules in the ground state $F_c \sim 0.1$ a.u., which corresponds to a laser intensity $I \sim 3.5 \times 10^{14}$ W/cm^2, the WFAT applies to all truly static fields available in laboratories as well as to the majority of intense low-frequency laser pulses used in current experiments.

The leading-order term in the asymptotic expansion for the ionization rate of an arbitrary molecule treated in the single-active-electron (SAE) and frozen-nuclei (FN) approximations was obtained in Ref. [6]. Under these approximations, tunneling ionization occurs from the highest occupied molecular orbital (HOMO) taken at the equilibrium internuclear configuration. The ionization rate of a molecule depends on the field and orientation of the molecule with respect to the field; these two dependences are of main interest for applications. In the formula for the rate obtained in Ref. [6] these dependences factorize. The field-dependent factor is a simple analytic function of F and the ionization potential of the HOMO. The orientation-dependent factor, given by the *structure factor* squared, depends on the dipole moment of the HOMO and a coefficient appearing in its asymptotic tail. The structure factor is as fundamental a property of a molecule as, e.g., its static dipole polarizability; in fact, the two characteristics play similar roles in evaluating the tunneling ionization rate and second-order Stark shift, respectively. Since the field factor is known analytically, the calculation of the ionization rate within the WFAT reduces to calculating the structure factor. The techniques for calculating molecular structure factors based on the different quantum chemistry codes were developed in Refs. [11–13]. In this work, we present the results of systematic calculations of structure factors for 40 homonuclear and heteronuclear diatomic molecules by the Hartree–Fock (HF) method using the program X2DHF [14]. With these results at hands, the ionization rates of the molecules can be readily evaluated.

Let us emphasize that the structure factors presented below enable one to obtain only the leading-order term in the asymptotic expansion of the ionization rate in F evaluated in the SAE and FN approximations. This basic approximation of the WFAT [6] is now a well established theory, and this paper presents an extensive set of results within this theory. At the same time, it should be noted that a number of generalizations of the WFAT is already available. Thus the first-order correction terms in the asymptotic expansion of the rate in F were derived in Refs. [15,16]; the incorporation of the effects of nuclear motion within the WFAT was discussed in Refs. [17,18]; a generalization of the WFAT to many-electron systems was developed in Refs. [19,20]. The evaluation of the rate within these generalizations requires much more involved calculations beyond the basic WFAT employed in this work. Atomic units are used throughout the paper.

2. Theory

In this section, we summarize formulas needed to implement the basic WFAT [6] for linear molecules, which includes diatomic molecules as a particular case. We introduce laboratory and molecular coordinate frames. Let $\mathbf{r} = (x, y, z)$ and $\mathbf{r}' = (x', y', z')$ denote the Cartesian coordinates of the active electron in these frames, respectively, and $\hat{R}$ denote an Euler rotation [21] from the laboratory to the molecular frame, $\mathbf{r}' = \hat{R}\mathbf{r}$. By our convention, the z axis is directed along the electric field, thus the field is $\mathbf{F} = F\mathbf{e}_z, F > 0$; the z' axis coincides with the internuclear axis and lies in the xz plane; the y and y' axes coincide. Then the different orientations of the molecule with respect to the field are described by a single angle β, $0 \leqslant \beta \leqslant \pi$, defining the rotation $\hat{R}$ from z to z' about the $y = y'$ axis. Explicitly, the relations between the coordinates read

$$x' = x \cos\beta - y \sin\beta, \tag{1a}$$

$$y' = y, \tag{1b}$$

$$z' = x \sin\beta + z \cos\beta. \tag{1c}$$

Let $E < 0$ and $\psi(\mathbf{r}')$ be the energy and wave function of the unperturbed field-free HOMO in the molecular frame. The structure of $\psi(\mathbf{r}')$ assumed must be explained. The unperturbed orbitals $\psi_M(\mathbf{r}')$ of linear molecules can be generally characterized by the projection $M = 0, \pm 1, \pm 2, \ldots$ of the electronic angular momentum onto the internuclear axis. We have $\psi_M(\mathbf{r}') \propto e^{iM\varphi'}$, where φ' is the azimuthal angle in the molecular frame. The orbital energy does not depend on the sign of M, therefore states with $M \neq 0$ are doubly degenerate. This degeneracy is removed by an arbitrarily weak field, provided that the molecule is not aligned along the field. The correct zeroth-order orbitals (in the sense of perturbation theory for degenerate states [7]) in our geometry are given by

$$\psi^{(+)}_{|M|}(\mathbf{r}') = \frac{1}{\sqrt{2}}\left[\psi_M(\mathbf{r}') + \psi_{-M}(\mathbf{r}')\right], \tag{2a}$$