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First-principles insights into ultrashort laser spectroscopy of molecular nitrogen

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In this research, we employ accurate time-dependent density functional calculations for ultrashort laser spectroscopy of nitrogen molecule. Laser pulses with different frequencies, intensities, and durations are applied to the molecule and the resulting photoelectron spectra are analyzed. It is argued that relative orientation of the molecule in the laser pulse significantly influence the orbital character of the emitted photoelectrons. Moreover, the duration of the laser pulse is also found to be very effective in controlling the orbital resolution and intensity of photoelectrons. Angular resolved distribution of photoelectrons are computed at different pulse frequencies and recording times. By exponential growth of the laser pulse intensity, the theoretical threshold of two photons absorption in nitrogen molecule is determined.

1. Introduction

The recent progress in the field of ultra-short laser pulses has provided novel opportunities to capture fast dynamics of atoms and electrons in chemical reactions and photo ionization phenomena [1–4]. The studies of Ahmed Hassan Zewail, on the dynamic of chemical reactions by using femtosecond spectroscopy, awarded him the Nobel Prize of chemistry in 1999 [1]. In 2001, Ferenc Krausz succeeded to generate attosecond laser pulses [2], which provide invaluable abilities to investigate and even control electron dynamics in photo ionization phenomena [5]. Haessler and coworkers used a train of attosecond laser pulses in presence of a weak infrared field to ionize nitrogen molecule [6]. They identified two ionization channels in the system correspond to the ground state and excited state of the ionized molecule. Kelkensberg and others applied the same method to ionize hydrogen molecule and observe changes in charge distribution of the system on attosecond time scales [7]. Siu et al. found that the time delay between attosecond pulse train and a corresponding infrared field may be used to control the dissociative ionization of oxygen molecule [8]. Penka and others applied time dependent density functional theory in the nonlinear nonperturbative regime to investigate laser induced photo ionization in CO and H_2CO molecules [9]. They found that the interplay between the ionization potential, the orbital shape, and the laser polarization axis significantly influence the ionization process.

In the present work, we employ time-dependent ab initio calculations to study photo ionization of N_2 molecule under irradiation of short laser pulses. The effects of frequency and intensity of the pulse on the polarization will be investigated.

2. Computational method

Our calculations have been performed in the framework of time dependent Kohn–Sham (TDKS) density functional theory [10], which provides a proper single-particle description of many-body systems in the presence of time dependent external potentials (e.g. an electromagnetic pulse). Adiabatic local density approximation (ALDA) is adapted for description of the time dependent exchange correlation functional in this approach. It is already argued to be the proper functional for description of atomic clusters under intense electromagnetic fields [11]. We used the Octopus package to solve the TDKS equations by employing the norm-conserving pseudo potential technique [12]. The KS orbitals are expanded on a real space grid defined inside geometrical boxes around atoms or around whole system. Two general approaches are implemented in this package for solving the TDKS equations: linear response and explicit real time propagation methods. In the linear response regime, which is used to address the effects of a weak uniform white electromagnetic noise, the absorption spectra and the character of electronic excitations of the system are determined. While in the

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Table 1
Obtained molecular orbitals of the nitrogen molecule. The occupied orbitals are highlighted.

State	Energy (eV)	State	Energy (eV)
1	**−28.40** (σ)	11	0.53
2	**−13.38** (σ^*)	12	1.05
3	**−11.96** (π)	13	1.12
4	**−11.96** (π)	14	1.12
5	**−10.45** (σ)	15	1.13
6	−2.32 (π^*)	16	1.13
7	−2.32 (π^*)	17	1.21
8	0.03 (σ^*)	18	1.65
9	0.52	19	1.65
10	0.53	20	1.66

presence of strong laser pulses, explicit propagation of KS orbitals in real time domain is considered.

In order to calculate the emitted photoelectron spectra of a sample after strong laser irradiation, a detector region is defined around the system and then the Wigner quasi-probability distribution function in the phase space:

$$\omega(\mathbf{R},\mathbf{p},t)=\int\frac{d\mathbf{s}}{2\pi^2}e^{i\mathbf{p}\cdot\mathbf{s}}\rho\left(\mathbf{R}+\frac{\mathbf{s}}{2},\mathbf{R}-\frac{\mathbf{s}}{2},t\right)$$

is used to integrate the photoelectrons in the detector region. In the above equation, $\rho(\mathbf{r},\mathbf{r}',t)$ is a two body density matrix and R and s are the center of mass and relative coordinates. The momentum resolved photoelectron spectrum is then given by:

$$P(\mathbf{p})=\lim_{t\to\infty}\int d\mathbf{R}\;\omega(\mathbf{R},\mathbf{p},t)$$

In this equation the integral is calculated in the detector region after a sufficiently long time to ensure contribution of all photoelectrons. In the Kohn–Sham approach, the two body density matrix is defined by the following sum over occupied states:

$$\rho_{\mathrm{KS}}(\mathbf{r},\mathrm{r}',t)=\sum_{i}^{occ.}\psi_i(\mathbf{r},t)\psi_i(\mathrm{r}',t)$$

This procedure needs calculation area of hundreds Angstrom to give reliable photoelectron spectra. In order to reduce the required calculation area, a mask region is defined before the detector region [13].

3. Results and discussions

First, we performed some static DFT calculations to identify the equilibrium properties of N_2 molecule. The equilibrium bond length and binding energy of nitrogen was found to be about 1.09 Å and 8.89 eV, respectively, which agree with the measured data (1.1 Å and 9.79 eV) [14]. The energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) was determined to be about 8.2 eV (Table 1). Comparing this parameter with the experimental energy gap of N_2 is questionable, because of the frozen character of orbitals in the static DFT calculations, while in practice; electron excitation has non-trivial influences on orbital energy levels. This problem is well resolved in time dependent DFT, where orbitals are allowed to relax during electronic excitations. The obtained absorption spectrums of N_2 by using TDDFT within the Casida linear response and real time propagation approaches are presented in Fig. 1. The agreement between these two spectra is acceptable, especially in lower energies. In higher energies, the accuracy of the linear response approach decreases and hence the real time propagation approach is more reliable.

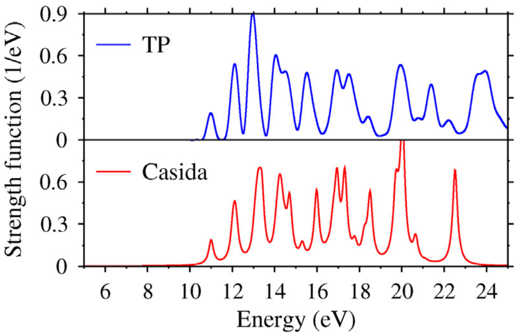

Fig. 1. Calculated absorption spectra of N_2 by using the Casida linear response and real time propagation (TP) methods.

The obtained energy gap within both Casida and real time approaches is about 11.0 eV. In order to compare the obtained absorption spectra with experiment, we note the complex absorption spectrum of nitrogen molecule [15], which includes weak dipole-forbidden transitions from 6 to 12.4 eV and strong dipole-allowed transitions from 12.4 to 18.8 eV [16]. The first 20 electronic excitations, identified within the Casida approach, are listed in Table 2. Our results confirm that the peaks below 11 eV have negligible dipole moment and very weak strength while strong dipole allowed peaks occur above this threshold. Moreover, we may conclude that the observed experimental transitions below 11 eV are likely non-electronic excitation transition (rotational or vibrational transitions). The ionization energy of nitrogen molecule, the difference of the minimized energy of the neutral and ionized molecule, was found to be 16.02 eV, which compares well with the measured value of 15.80 eV [17].

For calculations of photoelectron spectra, we used spherical boxes around the molecule with an optimum internal radius of 12 Å for region A, an external radius of 22 Å for detector region and a sine-mask function. The optimum grid spacing in the atomic spheres was found to be 0.18 Å while the time step for real time evolution was set to 1 m$\hbar$/eV (~0.66 as). We used Gaussian envelope laser pulses with a length of 4 $\hbar$/eV (2.63 fs). The frequency of the extreme ultraviolet (xuv) laser pulses was set to some specific odd (9–17th) multiples of a fundamental frequency of 1.565 eV. These odd harmonics have been already produced by propagating intense laser pulses in a gas jet and then used for photo ionization of nitrogen molecule [6]. The 12th multiple was also considered for more accurate inspection.

The calculated photoelectron spectra at the desired pulse frequencies and two different geometries are presented in Fig. 2. In these geometries, the molecule is either parallel or perpendicular to the direction of the laser pulse propagation. First, we focus on the perpendicular geometry. It is seen that at the lowest pulse frequency (14.08 eV), two peaks are appeared in the spectra, indicating emission of two different kinds of photoelectrons from the system. We will argue that these peaks are likely attributed to the two sigma molecular orbitals of the nitrogen molecule. Taking into account the calculated ionization energy of N_2 (16.02 eV), it seems that a laser pulses with frequency of 14.08 eV should not be able to create any photoelectrons. Therefore, the observed very weak ionization is either due to the multi-photon absorption or electron tunneling in strong laser field. The low kinetic energy of photoelectrons (~2 eV) rules out the multi-photon absorption mechanism. The suppressed electrostatic potential of a nucleus in a strong laser field is depicted in Fig. 3. It is clearly seen that the laser field may reduce the electrostatic confinement barrier of the nucleus and hence enhances electron tunneling. Therefore tunneling ionization may happen at energies lower than the normal ionization energy. The very low intensity of the photoelectron spectra (Fig. 2) provides