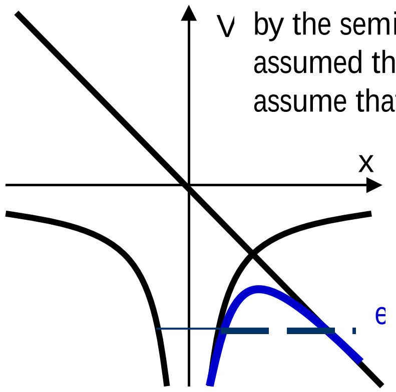
Exploration of a Method to Image an N_2 Molecular Orbital Using the ATI Spectrum

Dina Genkina
Dr. Andreas Becker, Dr. Agnieszka Jaron-Becker

Introduction

Finding a way to experimentally image molecular orbitals has been one of the main goals of strong field science for a few years. This field is well suited for such a task because the time scale on which measurements could be made, in the (sub-)femtosecond regime, is on the scale of molecular dynamics. Thus, the ability to image an orbital on this timescale would allow for amazing possibilities of watching phenomena such as dissociation of molecules or chemical reactions as they happen. The applications of this kind of method would be vast, and sure to be of interest to chemical engineers and pharmaceutical companies. However, this is very far from reality at this time. This paper will simply present the first steps of working out a technique to image a static molecular orbital of a homonuclear diatomic orbital, specifically N_2.

Background



The basic behavior of atoms and molecules in intense laser fields is well described by the semi-classical 3-step model, as proposed by Corkum[1]. In this model, it is assumed that only one electron is interacting strongly with the field. Also, we assume that the field is varying relatively slowly with respect to molecular dynamics, so that at a particular point in time we can approximate the superposition of the Coulomb potential and the potential due to the electric field as a tunneling problem, as shown in the figure. This quantum mechanical tunneling is the first step of the three-step process. In the second step, the electron that tunneled out is propagating in the electric field and its dynamics can be treated classically. If the electron was ªbornº (tunneled) at the peak of the electric field, it will return to the parent nucleus with zero energy. If it is born a short time before the peak, it will never return to the parent nucleus, and the molecule will be ionized. This is called above-threshold ionization. If it is born a short time after the peak, then it will return to the parent nucleus with some kinetic energy. In this latter case, once it comes back to the parent nucleus, it can scatter from it, or recombine with it in a process called high harmonic generation. It can also kick out another electron, causing double ionization.

Why the recombination process is called high harmonic generation is best understood through the quantum-mechanical equivalent of the semi-classical 3-step model. Instead of tunneling, the first step can be thought of as an electron in a bound state absorbing multiple photons from the intense laser field and getting excited to the continuum. Then, if it recombines with the parent molecule, it will emit the energy equivalent to that of those multiple photons as one photon, with an energy equal to $N\omega$ (in Hartree atomic units, where $\hbar=1$), producing a pulse of some higher harmonic frequency light than the initial laser light it was exposed to.

There has already been a proposal to use the high harmonic generation spectrum to image the molecular orbital of N_2[2]. The proposal is to use the fact that the emitted spectrum is proportional to the Fourier transform of the dipole moment produced by the interaction of the two parts of the electronic wavefunction: the original molecular orbital and the tunneled part as it recombines with the parent nucleus. From this dipole moment, and certain assumptions about the tunneled part to the wavefunction, the original molecular orbital is inferred. This is a promising method that has been under a lot of study for the past five years since it was first proposed.

Here, we intend to explore whether there is an alternative approach to this problem, whether there is a possibility to image the molecular orbital of N_2 by analyzing the electron yield as a function of energy of the electrons that are emitted through above-threshold ionization.

Methods

The ionization rate is calculated through the transition probability, which can be calculated using the time-dependent wave function of the system. In our approximation, the electron yield at a certain energy is approximated to be directly proportional to the ionization rate at that energy. Thus, in order to be able to analyze the electron yield, a theoretical way to calculate the ionization rate is necessary.

S-matrix Theory

The traditional way to determine the time-dependent wave function is through perturbation theory. However, in this case, the term in the Schrödinger equation due to the Coulomb forces within the molecule is on the same order as the term due to the electric field of the laser light, making perturbation theory inapplicable. This may seem like it would then necessitate a numerical solution of the Schroedinger equation. However, there is an alternative approximation method that is applicable to this case, called S-matrix theory. This method approximates the total time-dependent wave function assuming the knowledge of the initial state and final state (and sometimes even some intermediate state) wave function.

S-matrix theory creates a series expansion of the total wave function. Successive terms of this series are not shown to be decreasing, and the series may not even be convergent. However, the advantage of this method is that each of the terms represents a different physical mechanism which is immediately apparent from the mathematical expression of the term. In the words used above, there would in this case a different term corresponding to ionization, scattering, recombination, double ionization, etc. Therefore, if you know what physical mechanism you are considering, you could model it with the corresponding term of the S-matrix expansion.

In this case, since we are looking only at the above-threshold ionization, we can take only this (first) term of the S-matrix expansion. Using this term of the wave function, one can derive an expression for probability per unit time (or rate). For atoms, this probability as a function of the final momentum k_N, where N is the number of photons getting absorbed, is given by (for linearly polarized light)[3] $\frac{W_{KFR}}{d\vec{k}_N}=2\pi k_N(U_p-N\omega)^2 J_N^2(a_{\vec{k}_N},b)|\langle\phi_{\vec{k}_N}(\vec{r})|\phi_i(\vec{r})\rangle|^2$, where U_p is the pondermotive energy $U_p=I/4\omega^2$, where I is the intensity and ω is the angular frequency of the laser light, $a_{k_N}=k_N\sqrt{I}/\omega^2, b=U_p/2\omega$, the initial state wave function $\phi_i(\vec{r})$ is the orbital that we are trying to image, and the final state wave function $\phi_{\vec{k}_N}(\vec{r})$ is the spacial part of the Volkov wave function, which is simply a plane wave. This latter point is certainly an approximation, since the ionized electron is subject to the Coulomb forces from the nucleii as well, not simply the electric field, and the Volkov wave function solves the Schrödinger equation for an electron in an oscillating electric field. However, if the electron is traveling fast enough, and so will escape the range of the Coulomb potential relatively quickly, this approximation is a decent one.

Since the final state is just a plane wave, the superposition $\langle \phi_{\vec{k}_N}(\vec{r}) | \phi_i(\vec{r}) \rangle$ is simply the Fourier transform of the initial state wave function. This holds for the molecular case as well. The extension of the KFR formula to the molecular case, specifically the diatomic, homonuclear molecules simply introduces another factor which corresponds to an interference term which is dependent on the vector momentum of the electron and the internuclear radius. So now the problem becomes to see how much information about the Fourier transform we can get by observing the electronic yield, and thus the ionization probability. It is important to note that the use of this S-matrix term is an approximation in itself, and a strong influence comes from the modulating functions, specifically the generalized Bessel function J_N, in front of this Fourier transform. It is therefore not only very computationally difficult to just solve for the Fourier transform in the above equation, but also would likely not yield very accurate results. Therefore, care must be taken to try to get conditions from this ionization rate that solely depend on the Fourier transform, and not any of the modulating functions.

Since there is little experimental data available of specifically the momentum dependent electronic yield in above threshold ionization of N_2, it was necessary to somehow simulate this result. To do this, we used quantum chemistry programs, such as GAUSSIAN and GAMESS to get wave functions of the nitrogen molecule. Then, a Fortran code was used to calculate the ionization rate based on these wave functions. Then, the results of this code were used to try to reconstruct the initial wave function, and the reconstructed one could then be compared to the original wave function from the quantum chemistry programs, and thus the effectiveness of the method could be tested.

Linear Combination of Atomic Orbitals (LCAO)

In order to get any information about the molecular orbital without directly solving for the Fourier transform in the equation above, it is necessary to assume some form of this wave function. A common way to approximate molecular orbitals (and the technique used by the quantum chemistry programs above), is to treat it as a superposition of atomic orbitals, centered at the different nuclei of the molecule: $\Phi_{molecular} = \sum_{\vec{R}_i} a_i \varphi_{atomic}(\vec{r} - \vec{R}_i)$, where R_i is the position of the i^{th} nucleus. [4] This treatment is an approximation within itself. Furthermore, the form of the atomic wave function used is another approximation.

In the case of N_2, one can determine that the bond between the two atoms is a σ_g (bonding symmetry) orbital from a simple experiment that measures the total (non-energy dependent) electron yield as a function of internuclear orientation. In our treatment, we assume this is known. Therefore, only s and pz components should contribute to the molecular orbital. Also, N_2 is in the second row of the periodic table, so it is physically reasonable to guess that the electrons which will be contributing to the highest occupied molecular orbital (HOMO) will be coming from the second shell in the atomic structure. Therefore, the components that are most likely to contribute to the molecular wave function are the 2s and 2pz components. So, in this simplest possible treatment, it was assumed that the atomic wave function consists of a linear combination of the 2s and 2pz hydrogenic wave functions:
$\varphi_{atomic} = a_{2s}(1 - \alpha r) e^{-\alpha r} + a_{2pz} r \cos(\theta) e^{-\alpha r}$, where the coefficients a_{2s} and a_{2pz} as well as the exponent α are undetermined. Since N_2 is a homonuclear molecule, the a_i coefficients from the sum above are equal, and so can be absorbed into the a_{2s} and a_{2pz} coefficients. Thus, in order to image the wave function one need to determine those three parameters, and therefore needs three conditions. In principle one also needs the internuclear distance, but this can easily be determined by performing a

Coulomb explosion experiment, so we assume that this is also known.

This approach is admittedly extremely simplistic. However, as a first guess the simplest approach must be taken. Also, if this approach proves insufficient, one may learn something about the nature of the nitrogen wave function. Perhaps, if other contributions must be taken into account, there are physically other electrons contributing to the HOMO, which would give us insight into the structure of the molecule.

Conditions on the Fourier Transforms of the Wave functions

In order to obtain the three conditions listed above, it is first necessary to find the Fourier transform of the atomic wavefunction we are considering. The Fourier transforms were calculated to be:

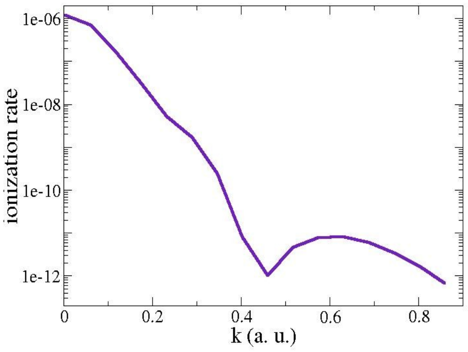
$$\tilde{\Phi}_{2pz} = a_{2pz} 4\pi i \cos(\theta_k) \frac{8k\alpha}{(\alpha^2+k^2)^3}$$

$$\tilde{\Phi}_{2s} = a_{2s} 16\pi\alpha \frac{k^2-\alpha^2}{(\alpha^2+k^2)^3}$$

The angle θ_k is defined as the angle between the momentum vector k of the outgoing electron and the internuclear axis of the molecule.

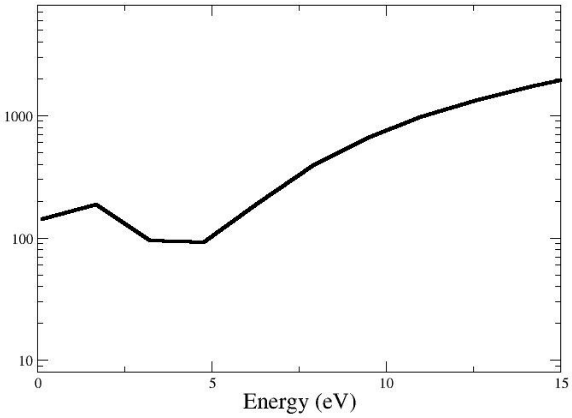
The first condition comes from the fact that if one looks at the electron yield in a direction perpendicular to the internuclear radius, the contribution to the number of electrons from the 2pz component is zero, because cos(90)=0. Therefore, in that direction the observed electron yield is due solely to the 2s contribution. It is also easy to see from the Fourier transform of the 2s part of the wave function that there is a zero at $k = \alpha$. Thus, looking in a direction perpendicular to the internuclear radius, a zero in the momentum-dependent ionization rate will be observed, from which the value of α follows immediately.

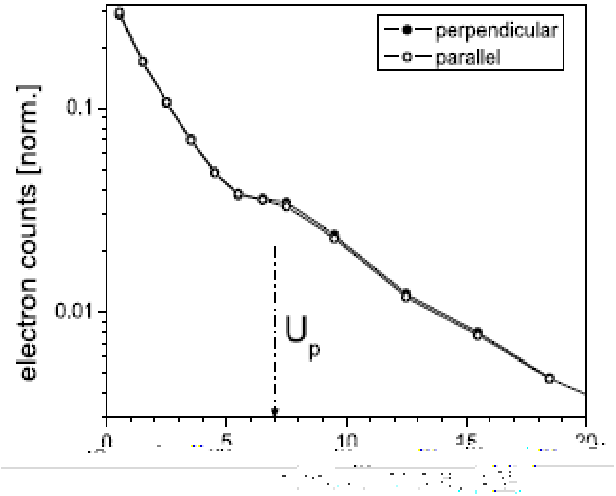
This zero was observed in the computational simulation, as seen in the figure.



However, it is likely that in experiment this zero would be harder to observe. Firstly, there is a limit to how small of a yield can be detected experimentally, so the momentum distribution plot might be cut off at some value, decreasing the resolution of the zero. Also, it is a great challenge experimentally to align molecules in a specific direction, such that the internuclear orientation is well known. So, there will be some error in the alignment of the molecule, and therefore some contribution from the 2pz orbital, which may make the zero harder to observe. As a first step, however, we do not consider these issues and leave them as future work.

The second condition comes from the observation of a ªshoulderº in the experimental data of the electron yield versus energy (figure below on the right)[5]. This observation is in fact what suggested the original idea of the possibility of this imaging method. We also observe this as a minimum in our computational simulation even when the contribution of the generalized Bessel function is not accounted for, demonstrating that this is indeed a feature of the Fourier transform of the total wave function (figure below on the left). This shoulder could be caused by a minimum in the Fourier transform of the total molecular wave function, and thus would obey the the condition $\frac{d}{dk}|\tilde{\Phi}_{mol}(\vec{k})|^2=0$, at the value of k where this shoulder is observed.

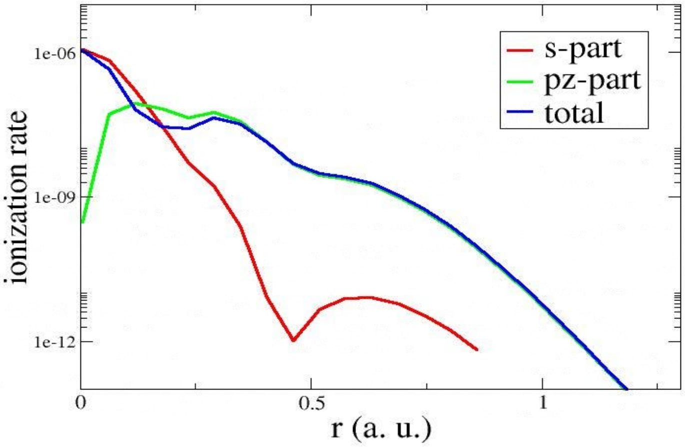




From this condition we can infer the relationship between the two coefficients a_{2s} and a_{2pz}. The last, 3rd condition is simply the normalization of the wave function, which gives another relationship between these two coefficients: $a_{pz} = \sqrt{\alpha^5/\pi - \alpha^2 a_s^2}$. Solving these two conditions with the help of Mathematica, one can obtain the values of the two coefficients, assuming α has already been determined.

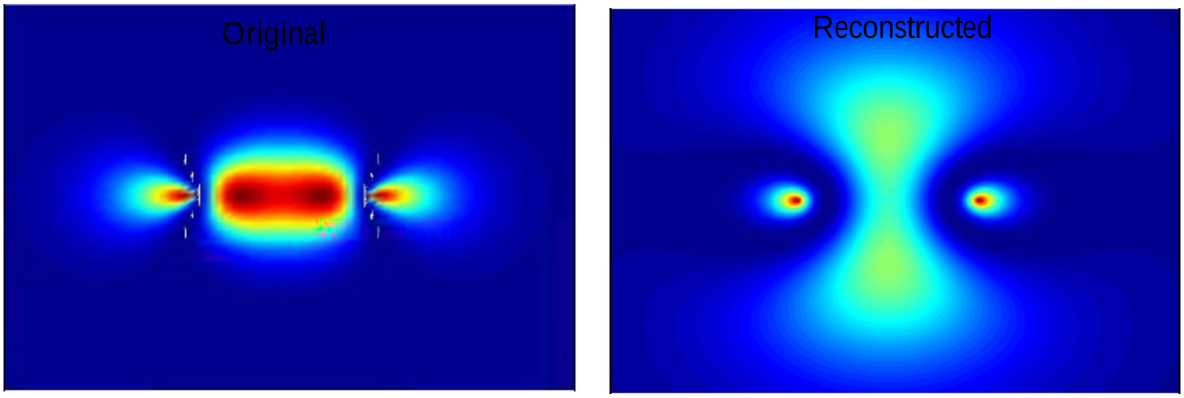
Simplifying the 2nd condition

Unfortunately, the original procedure for finding the coefficients using the 2nd and 3rd conditions described above had so far failed ± there was no real solution to the system of two equations at the value of alpha that was determined. Therefore, to try to analyze what went wrong, a slightly simpler second condition was adopted. Instead of considering the shoulder as a minimum of the total wave function, it was considered as the point at which the 2s and 2pz contributions are equal. This treatment is not entirely unreasonable, as the 2s part dominates for small k and the 2pz part begins to dominate at larger k, so there must be an intersection point at which the two are equal, and we observe this intersection point to be not too far from the supposed minimum (see figure). Using this simplified condition, we were able to get the coefficients, though not the relative sign between them.

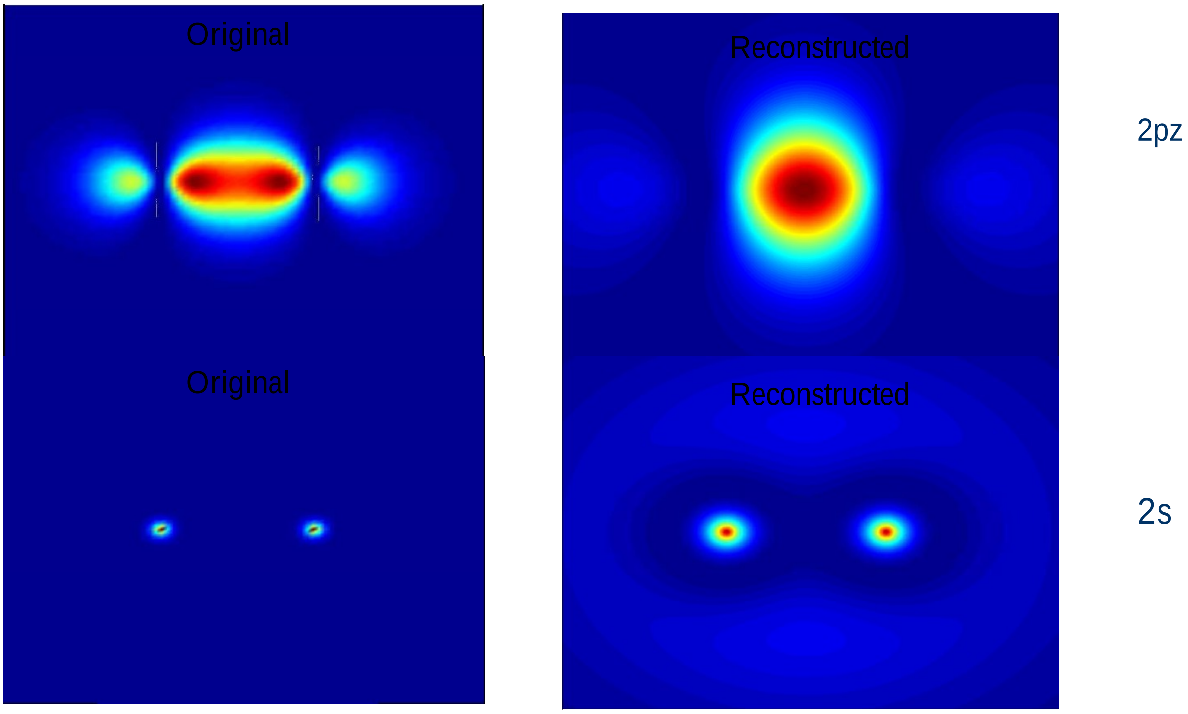


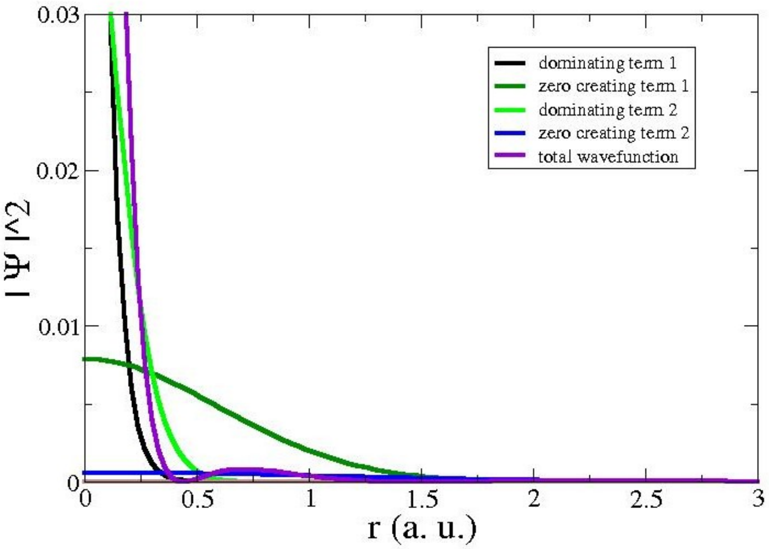
Results

Using the original 1st condition and the simplified 2nd condition, we obtained a reconstructed total wave function. Below are the reconstructed and original wave function, both normalized to one.



Clearly, this is not as good a result as we were hoping for . To analyze what where the problem lies, we decompose both the original and reconstructed wave functions into their 2s and 2pz components.





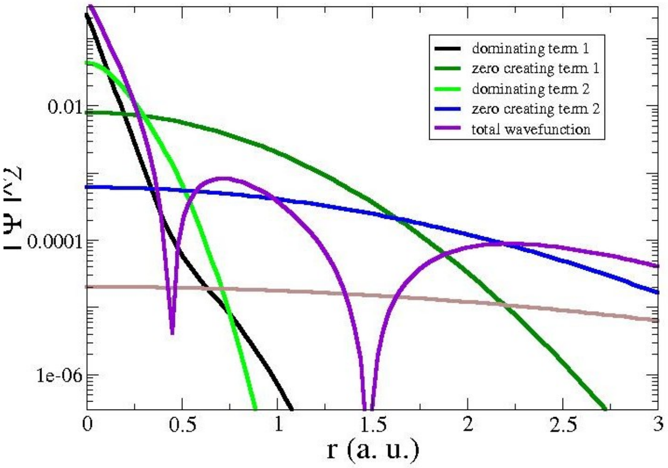
Comparing these graphs, especially the s components, it becomes apparent that the spread of our reconstructed wave function is much greater than that of the original one. The spread of the wave function is determined by the exponent α, therefore the problem is that this reconstructed exponent is far too small.

To analyze why that is the case, we took a more careful look at the original wave function. The quantum chemistry program uses a superposition of a number of gaussians. This particular wavefunction consisted of 5 sums of gaussians to construct the 2s component, and 4 sums of gaussians to construct the 2pz component. Since α is determined by a condition that is solely dependent on the 2s component, we decomposed that part of the original wave function into the 5 components, as seen here. When the simulation is run with just the ªzero creating termsº (dark green and blue on the figure), one still sees the zero that was used to determine α. Therefore, the interference between these two components is what produces the zero. However, the contribution of those components compared to the contribution of the ªdominating termsº (black and light green in the figure) near the nuclei is small. So, by using the zero to determine the value of α, we are imaging not the whole but only the delocalized part of the wave function, creating a much less localized result than the original. This could also explain why the original unsimplified 2nd condition did not produce results. Perhaps with a more adequate value of α the original condition could work.

Future Work

It is clear, however that the original assumption of just one 2s component in the atomic wave function cannot adequately reproduce the features of the above wave function. One solution to consider is including another, perhaps a 1s component in the total wave function. Doing this, or taking any more complicated kind of atomic wave function, would produce more parameters and thus require more conditions. One possibility may come from the second minimum we see in the total wave function when we replot it on a logarithmic scale (above). In order to be able to observe the effect of this minimum in the Fourier transform, one may need to go to higher values of the final momentum than we have here, which would pose another challenge in experiment.

It would also be important in the future to consider how this treatment is affected by imperfect alignment of the internuclear axis. Perhaps an uncertainty in alignment could be input into the Fortran simulation, and then the error at which the zero for the first condition could still be observed will be determined, helping to see how difficult it would be to perform the experiment.



[1] Corkum, P. B. & Krausz, F. Attosecond science. Nature Phys. 3, 381±387 (2007)
[2] Itatani et al., Nature 432, 867-871 (2004)
[3] Becker, A. & Faisal, F H M. J. Phys. B: At. Mol. Opt. Phys. 38 (2005) R1-R56
[4] Levine, Ira N. <u>Quantum Chemistry</u>. Upper Saddle River, NJ: Pearson Education, Inc, 2009.
[5] Zeidler et. al., *J. Phys. B: At. Mol. Phys.* 39 (2006), L159-L166