High-harmonic generation from molecules
Renewal proposal for FY08

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1   Introduction

As explained in detail in our original proposal submitted last fall, the purpose of this project is the implementation of the orbital approach to time-dependent configuration interaction singles (TDCIS). The theory underlying this method is developed in Ref. [1]. Using TD-CIS, we plan to perform *ab initio* investigations of high-harmonic generation (HHG) from molecules in a strong laser field.

The process of HHG takes place during a single optical cycle, which at a wavelength of 800 nanometers corresponds to about 2.5 femtoseconds. Thus, since the HHG spectrum is a function of the electronic structure of the molecule, and since the electronic structure depends on the instantaneous molecular geometry (the positions of the atomic nuclei within the molecule), HHG holds the promise that it may be utilized to study ultrafast conformational changes in a time-resolved manner. This requires few-cycle laser pulses—with well-defined relationship between the carrier phase and the pulse envelope. The technology for this is already available [2,3].

2   Progress report and plans for FY08

Within the TDCIS theory discussed in Ref. [1], each (spatial) orbital $|\varphi_i\rangle$ occupied in the Hartree-Fock ground state of the molecule under consideration is associated with an orbital $|\chi_i, t\rangle$ that describes the excitation of an electron from $|\varphi_i\rangle$. In atomic units, the equation of motion satisfied by $|\chi_i, t\rangle$ is given by

$$
\begin{aligned}
\mathrm{i}\frac{\partial}{\partial t}|\chi_i\rangle &= (\hat{H}_0 + I_i)|\chi_i\rangle + \sum_{i'} \hat{P}\{2\hat{K}_{i'i} - \hat{J}_{i'i}\}|\chi_{i'}\rangle \\
&\quad -\mathcal{E}(t)\hat{P}\hat{z}\left\{\alpha_0|\varphi_i\rangle + |\chi_i\rangle\right\} + \mathcal{E}(t)\sum_{i'} z_{i'i}|\chi_{i'}\rangle.
\end{aligned}
\tag{1}
$$

Here, $\hat{H}_0$ is the Fock operator associated with the Hartree-Fock ground state; I_i is the ionization potential of an electron in $|\varphi_i\rangle$; the projection operator $\hat{P}$ ensures that the $|\chi_i, t\rangle$ remain orthogonal to all $|\varphi_{i'}\rangle$; $\hat{J}_{i'i}$ and $\hat{K}_{i'i}$ are, respectively, generalized Coulomb and exchange operators; $\mathcal{E}(t)$ is the field strength of the laser; and $\hat{z}$ is the electric dipole operator. The amplitude of the Hartree-Fock ground state in the time-dependent many-electron wave function is denoted by $\alpha_0(t)$. The equation of motion for $\alpha_0(t)$ reads

$$
\mathrm{i}\dot{\alpha}_0 = -2\mathcal{E}(t)\sum_i \langle\varphi_i|\hat{z}|\chi_i, t\rangle.
\tag{2}
$$

Using α_0 and the $|\chi_i\rangle$'s, the time evolution of the laser-induced electric dipole moment may be calculated. It is the second derivative, with respect to time, of this dipole moment that gives rise to the generation of high harmonics of the driving-laser frequency.

After we were notified that funding of awards for the Joint Theory Institute had been approved by management at both Argonne National Laboratory and the University of Chicago, it took a little more than a month to identify a suitable graduate student for the project. Processing of the work order took additional time, so that the selected graduate student, Tamas Juhasz, began working on this project on April 15. Considering the short amount of time that was available before the deadline for this renewal proposal, the progress already made is quite good in our opinion. We decided to postpone the formal analysis of TDCIS for molecules with permanent electric dipole moment, which was originally planned for the first year of our JTI project, and currently focus on computer program development.

Tamas uses the *ab initio* quantum chemistry package GAMESS-US to perform the Hartree-Fock calculation for the electronic ground state. He wrote a program that allows him to read in from the GAMESS output file the primitive Gaussian orbital exponents, the contraction coefficients and the types for the Gaussian basis functions. Using this information and the definition for primitive Gaussian orbitals, Tamas evaluated Gaussian basis functions on a Cartesian grid. Currently, this is limited to s- and p-type basis functions, but will be straightforward to extend to d- and f-type basis functions at a somewhat later stage of the project. Following the Hartree-Fock calculation, GAMESS generates a file that contains the expansion coefficients of the molecular orbitals with respect to the Gaussian basis set. Tamas reads this transformation matrix into his program. All these steps combined give him access to the spatial representation of the occupied molecular orbitals $|\varphi_i\rangle$, which are required for the construction of the operators $\hat{H}_0$, $\hat{P}$, $\hat{J}_{i'i}$, and $\hat{K}_{i'i}$, and for the calculation of the electric dipole interaction in Eqs. (1) and (2). In order to determine the accuracy of the Cartesian grid representation initially chosen (more on this below), Tamas evaluated the overlap matrix of the molecular orbitals in the Cartesian grid representation. The relative error was about 0.1% using 100 uniformly spaced points extending over an interval of 10 Å in each direction (i.e., 10^6 grid points in three dimensions).

The primary challenge, from a computational point of view, of implementing a three-dimensional wave-packet propagation code for HHG applications is the size of the one-particle basis set that is needed. The reason for this is easily understood on the basis of the three-step model of HHG [4]. Atoms and molecules with an ionization potential above 10 eV require a laser intensity of the order 10^{14} W/cm^2 to become tunnel-ionized (the first step in the three-step model). Tunnel ionization occurs in the vicinity of electric field maxima during the optical cycle. After tunnel ionization at 10^{14} W/cm^2, depending on the optical phase during which tunneling has occurred, the excited electron may move more than 30 Å away from its parent ion (assuming an 800-nm laser) before being redirected by the laser field (the second step). The electron may then collide with its parent ion at a kinetic energy of up to 100 eV (the third step). If electron–ion recombination takes place, the kinetic energy of the electron may be released as high-harmonic radiation. The challenge, therefore, is to represent the electron wave function within a rather large volume (because the electron can propagate relatively far before recollision takes place) using a dense spatial grid (because the electron wave function oscillates much more rapidly than is usually the case in quantum chemistry calculations). This means, in particular, that Gaussian basis sets are not useful

for representing the $|\chi_i, t\rangle$. (Gaussians are, of course, perfectly fine for the $|\varphi_i\rangle$.) In our experience, Gaussian basis sets can be employed for scattering wave functions with a strong bound-state character (shape and Feshbach resonances), as long as the electron energy does not exceed 10 eV [5–7].

We had therefore proposed to divide space into different regions. In the innermost region, the TDCIS equations are solved without additional approximations. The electron de Broglie wavelength at a kinetic energy of 100 eV is about 1 Å. In order to resolve the electron wave function, we would like to have about 10 grid points per period, i.e., about 10 grid points per Å. The size of the inner region will probably approach 10 Å in each direction (depending on the system). Hence, it is likely that using a Cartesian grid in this inner region, up to 10^6 grid points in three dimensions will have to be used to converge results. Tamas tested whether a Cartesian grid is really suitable for this purpose. To this end, he evaluated the Coulomb operator $\hat{J}_{ii}$. He found that integration over one electron takes about 0.25 seconds with 100 gridpoints per dimension. This would have to be repeated 10^6 times when performing the loop over the second electron. Thus, it would take about three days to calculate the Coulomb or exchange operators for each orbital. The Coulomb operator would have to be calculated only once. However, if three excited orbitals are used, every time step during the temporal propagation of the TDCIS equations would take more than a week for the exchange operator on a 2.4 GHz Xeon (Pentium 4) computer.

We have therefore decided to employ for the inner region a so-called single-center expansion (SCE) [8] instead. The SCE has been used, for example, to successfully calculate elastic electron–molecule collisions [9] and the angular distribution of photoelectrons with respect to the molecular frame of the parent ion [10]. The combination of the SCE with TDCIS is quite straightforward. We make the ansatz

$$\chi_i(\boldsymbol{x}, t) = \chi_i(r, \theta, \phi, t) = \sum_{l,m} \frac{f_{l,m}^{(i)}(r, t)}{r} Y_{l,m}(\theta, \phi), \tag{3}$$

$$\varphi_i(\boldsymbol{x}) = \varphi_i(r, \theta, \phi) = \sum_{l,m} \frac{g_{l,m}^{(i)}(r)}{r} Y_{l,m}(\theta, \phi), \tag{4}$$

where r, θ, ϕ are spherical coordinates and $Y_{l,m}(\theta, \phi)$ is a spherical harmonic. In the atomic case, the expansion of the occupied orbitals in terms of spherical harmonics is trivial since the occupied orbitals may be chosen as eigenfunctions of the orbital angular momentum operators $\boldsymbol{l}^2$ and l_z. The ansatz for $\chi_i(\boldsymbol{x}, t)$ is inserted into the TDCIS equations of motion, and the result is projected onto $Y_{l,m}(\theta, \phi)$ in order to determine the TDCIS-SCE equations of motion for the $f_{l,m}^{(i)}(r, t)$. The evaluation of Coulomb and exchange matrix elements is particularly easy using the SCE. One simply employs the expansion

$$\frac{1}{|\boldsymbol{x}_1 - \boldsymbol{x}_2|} = \sum_{l=0}^{\infty} \frac{4\pi}{2l + 1} \frac{r_<^l}{r_>^{l+1}} \sum_{m=-l}^{l} Y_{l,m}^*(\theta_1, \phi_1) Y_{l,m}(\theta_2, \phi_2), \tag{5}$$

where $r_< = \min(r_1, r_2)$ and $r_> = \max(r_1, r_2)$. Hence, all matrix elements of $1/|\boldsymbol{x}_1 - \boldsymbol{x}_2|$ with respect to the spherical harmonics may be expressed in terms of the following well-known

integral

$$\int d\Omega Y_{l_3,m_3}^*(\Omega)Y_{l_2,m_2}(\Omega)Y_{l_1,m_1}(\Omega) = \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2l_3+1)}}C(l_1l_2l_3;m_1m_2m_3)C(l_1l_2l_3;000).$$

(6)

Here, $C(l_1l_2l_3;m_1m_2m_3)$ is a Clebsch-Gordan coefficient. The evaluation of the dipole operator is also trivial in the representation with respect to spherical harmonics, since $z = r\cos\theta$, and $\cos\theta$ is proportional to $Y_{1,0}(\theta,\phi)$.

Tamas has completed the derivation of the TDCIS-SCE equations of motion. He reads in the GAMESS output file and extracts from the spatial representation of the occupied molecular orbitals the functions $g_{l,m}^{(i)}(r)$ [Eq. (4)]. (In the current implementation of the program, this procedure is restricted to atoms.) Tamas evaluated both the Coulomb and the exchange operator in the SCE representation. Using three excited orbitals, and expanding each excited orbital $\chi_i(\boldsymbol{x},t)$ in a basis of 1681 spherical harmonics ($l = 0,\ldots,40$; $m = -l,\ldots,l$), Tamas found that with 100 radial gridpoints, it takes about 2 and 7 minutes, respectively, for the evaluation of the Coulomb and exchange operators. And this does not yet exploit that the evaluation of the exchange operator converges rapidly with respect to l. If angular momenta of only up to $l = 10$ are used, it takes 5 seconds instead of 7 minutes to evaluate the exchange operator for three excited orbitals and 100 gridpoints. For the radial kinetic energy operator, we will employ a finite-difference or spectral-difference [11–15] scheme. The time propagation of the TDCIS-SCE equations of motion will be performed using the second-order differencing scheme [16].

The size of the inner region is determined by the relative importance of the higher-order multipole effects in comparison with the electric monopole term and the laser electric field. To identify the relevant parameter range, Michelle Miller, a recent high-school graduate who participates in this year's pre-college research program at Argonne, is implementing a semiclassical description of HHG. In this approach, the initial tunnel ionization step is treated quantum mechanically. The electron motion, including the recombination step, is treated classically. The quantum and classical descriptions are combined using a Monte Carlo strategy. Michelle will perform simulations that will allow us to estimate the sensitivity of the HHG spectrum to the size of the inner region. The inner region is constructed such that outside, there is no channel coupling, and the Hamiltonian for the electron motion is that of a hydrogen atom in a laser field. Since the SCE makes it easy to define the inner region in terms of a sphere, matching solutions between the inner and outer regions is relatively simple. This can be accomplished by utilizing the time-dependent R-matrix theory for optical strong-field processes presented in Ref. [17]. The Coulomb interaction outside the inner region is only a perturbation compared to the interaction with the strong laser field. If the Coulomb interaction may be neglected, the electron wave function is analytically known and referred to as Volkov wave function. The perturbation by the Coulomb potential may then be taken into consideration by using the so-called Coulomb-eikonal Volkov states [18].

In order to test the accuracy of the TDCIS-SCE method, we will perform our first test calculations on experimentally well-studied atomic species such as helium, neon, and argon. In the atomic case, a comparison between calculations with and without an outer region should be feasible. The extensions to the computer code that are needed for molecular applications will follow after that.

3 Budget

In order to be able to continue our JTI-funded research, we would like to request financial support for a graduate student. The student will cost **$52,400** (FY08), as detailed in the following table.

base salary + health insurance	50% tuition	computer	travel	tax	total
12×$2.2k/month	$13.0k	$5.0k	$3.0k	$5.0k	$52.4k

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