November 16, 2012

Dr. Jeffrey L. Krause
Team Lead, Atomic, Molecular and Optical Sciences Program
Office of Basic Energy Sciences
SC-22.1/Germantown Building
U.S. Department of Energy
1000 Independence Avenue, SW
Washington, DC 20585-1290

Dear Dr. Krause,

I am pleased to propose Dr. Daniel J. Haxton for the Office of Science Early Career Research Program. Dr. Haxton has met the requirements, having received his Ph.D. in 2006, and holding an employment status of Staff Scientist.

The appended proposal, “The Multiconfiguration Time-dependent Hartree Fock (MCTDHF) Method for Interactions of Molecules with Strong Ultrafast High-energy Laser Pulses,” has my approval for consideration for the DOE Office of Science Early Career Research Program. This proposal supports Berkeley Lab’s mission in the area of Atomic, Molecular, and Optical Sciences (AMOS).

Sincerely,

[Signature]

A. Paul Alivisatos

FWP No.: CH13HAX1

Office of Science Program Office: Basic Energy Sciences (BES), Chemical Sciences, Geosciences, and Biosciences

Topic Area: Atomic, Molecular, and Optical Sciences (AMOS)
Topic Area Technical Contact: Dr. Jeffrey Krause, 301-903-5827, jeff.krause@science.doe.gov

Program Announcement: LAB 12-751

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Number of Times Previously Applied: 1
PECASE Eligible: Yes

Official signing for laboratory
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Requested funding for each year: FY13: $464K; FY14: $500K; FY15: $500K;
FY16: $500K; FY17: $500K

Total request: $2.5M

Use of human subjects in proposed project: No
Use of vertebrate animals in proposed project: No

Daniel J. Haxton, Principal Investigator

Ali Belkacem, Interim Division Director

November 20, 2012

November 20, 2011
Abstract
The mission of Basic Energy Sciences (BES) is to support fundamental research to understand, predict, and ultimately control matter and energy at the level of electrons, atoms, and molecules [00]. Such research requires the development of accurate quantum mechanical descriptions of properties and dynamical processes of such systems [0].

Fortunately, recent improvements in laser technology allow us to create pulses short enough to excite and probe molecules on the time scale of electronic motion, providing fundamental new capabilities. Next generation technology will open the door to a panoply of nonlinear experiments that provide information about chemical dynamics.

However, the dynamics probed cannot, in general, accurately be calculated with present methods. One must describe quantum dynamics with high levels of electronic excitation or perturbation that may result from X-ray excitation, the application of strong fields, or the absorption of multiple photons.

I have led the development [1,2] of the first computer code capable of calculating the physics of many electron atoms and diatoms subject to arbitrary laser pulses, using the ab initio MCTDHF method [3-18]. In it all electrons are active, the ionization continuum is treated exactly, and for diatoms it includes the capability to treat electronic and nuclear dynamics on the same footing without recourse to a Born-Oppenheimer expansion. These are the capabilities required of a numerical method capable of calculating current and next generation laser experiments. High-energy excitations of core hole electrons cause excitations of all electrons due to the change in nuclear screening. Ionization results from strong or energetic fields and may provide the experimental signal, and multiple electrons may be ionized. Nuclear dynamics causes decoherence of electronic excitations.

I propose to construct a nonadiabatic polyatomic implementation of MCTDHF that will become the standard for calculating ultrafast X-ray and strong field molecular physics. This is the overarching goal of the work through the five-year period, and development of it will proceed in steps. The proposal has several components that support this overarching goal.

1) Improve the coordinate system for nonadiabatic dynamics of diatomics.
2) Include nonadiabatic rotational motion for diatomics.
3) Implement fundamental algorithmic improvements of my own invention that will allow the method to be applied to large systems and that will improve its performance.
4) Optionally, pursue several capabilities such as the calculation of photon scattering (e.g. high harmonic generation, four wave mixing), the calculation of Floquet states, and a method to extract detailed ionization spectra without long time propagation.

Relevant applications will proceed throughout the course of the award and will be grounded in the current atomic and diatomic implementation, because the polyatomic code will become operational only toward the end of the award period. I will focus on three specific applications.

1) Ultrafast pump-probe experiments using X-ray light and possibly attosecond few-cycle probes.
2) Modification of X-ray processes using strong fields.
3) Nonadiabatic processes in strong fields.

The essence of the challenge in calculating ultrafast dynamics relevant to current and next generation experiments is the incorporation of all-active-electron dynamics with ionization into a method including nuclear dynamics for polyatomic molecules. My implementation of MCTDHF represents the most promising step to date toward tackling that challenge, and the funding of the proposed work will enable its maturation toward an indispensable tool for studying current and next generation experiments.
Narrative

New energy technologies may take many forms, but, with few exceptions, their design and behavior will hinge upon the quantum mechanics of underlying molecular and optical interactions. For instance, light harvesting complexes are fundamentally quantum systems supporting long-lived coherent electronic excitations, and the mechanism of coherence is understood to involve ultrafast evolution of electronic excitations toward different spatial locations on the molecule. To engineer such systems, one needs to create and probe electronic excitations on their fundamental timescale and in a site specific manner. To calculate such experiments, one must accurately represent highly excited, nonadiabatic electronic and nuclear dynamics involving many degrees of freedom.

Modern and next-generation experiments aim to describe and manipulate the electronic dynamics of such systems using ultrafast pulses of laser light. Such pulses reach the attosecond time scale of electronic motion in molecules. The goal is complete quantum control of the molecule: for instance, strong fields could create new pathways for coherent electronic and nuclear dynamics, and core hole stimulated Raman transitions may localize an excitation on one atomic site. Pump-probe spectroscopy, especially that using stimulated Raman core hole transitions, will further enable the monitoring of the electronic environment at given atomic centers and the elucidation of mechanisms of charge transfer and exciton migration.

Applications to this date have involved the use of high-harmonic generation to produce coherent attosecond pulses, but at present the intensity is insufficient for nonlinear experiments. Conversely, contemporary free electron lasers provide sufficient intensity, but both this intensity and the pulse shape are not well controlled. Next-generation light sources will provide pulses having both the necessary control and intensity to open up new studies of electronically excited state dynamics.

On the numerical front, the situation is less promising. Examples of processes whose calculation is currently prohibitive include all but the simplest experiments using X-ray light. The description of a two-electron coincidence experiment using double Auger decay to probe changes in nuclear geometry is far beyond the capability of modern numerical methods. Such multi-dimensional signals, containing a large amount of information, are necessary to disentangle complicated dynamics.

The excitation of a core electron causes excitations of all other orbitals, due to the loss of screening, such that no orbital in an accurate calculation may be frozen. Furthermore, these core hole excited states are metastable, in that they may decay via emitting an electron in the process known as autoionization, into many final cation states. The accurate description of this decay, alone, not including other dynamics, is at the forefront of current methods. The dynamics of highly excited electronic states are also inherently high-dimensional, involving multiple active electrons, coupling between the electronic and the nuclear degrees of freedom, and ionization. The utility of Born-Oppenheimer eigenfunctions as a basis is thereby diminished, and the inclusion of the electronic continuum makes the use of such a basis truly problematic. Furthermore, the coupling of nuclear and electronic motion is often an important component of the physical process under study.

Thus there are three capabilities that a general numerical method for studying these problems must have:

• Multiple active electrons.
• Non-Born-Oppenheimer effects.
• Ionization.

My Implementation. Implementing each of these capabilities is a challenge on its own, but I have developed a code that includes all three. Over the last four years I have constructed an implementation of the Multiconfiguration Time-Dependent Hartree-Fock (MCTDHF) method [3-18] for calculating the electronic and nuclear dynamics of atoms and diatomic molecules subject to arbitrary laser pulses,
publishing preliminary work in Refs.[1,2]. My work follows several previous efforts to apply the algorithm to the molecular electronic problem that date to 2004 [4-10, 12-16]. These, in turn, follow the spectacular success of the method without permutation symmetry, MCTDH, in calculating nuclear dynamics on electronic potential energy surfaces [19]. The contrast between the state of the art in MCTDHF versus MCTDH is surprising but, as I will explain, reasonable given the nature of the electronic problem.

My implementation includes several innovations of mine that have, for the first time, opened the door to studies of electronic and nuclear dynamics relevant to current and next generation experiments. The three capabilities listed above, their implementation in the code, and their relevance is further described below. I began this project under my own impetus before I returned to the Atomic, Molecular, and Optical theory group at LBNL as a postdoc, and it has since become the core of the group’s activities.

1) Multiple active electrons

Multiple active electrons are required to treat the physics that results from inner shell excitation. For instance, Auger decay of a core excited state is described in terms of two-electron transitions, and results in a combination of final states having very different electronic configurations, with one or more outgoing correlated electrons. A single hole description of core-excited states is demonstrably deficient, overestimating the coherence time of the hole [20] in experiments with short pulses.

In the published calculations I have used full configuration interaction in representing the wave function. I have parallelized the resulting matrix-vector multiplications, and the code can distribute the propagation of the configuration coefficients among many processors. I propose formal and numerical extensions that will allow restricted configuration spaces to be used, and that will allow a greater number of orbitals. These capabilities are necessary to calculate dynamics of larger molecules, for which a full configuration interaction calculation is utterly impossible.

2) Non-Born-Oppenheimer effects

Non-Born-Oppenheimer effects underlie relevant phenomena. Charge localization, for instance, results from the coupling of electronic and nuclear motion that enables redistribution of energy from electronic to nuclear degrees of freedom. Nuclear motion is responsible for the decoherence of electronic excitations. Light induced potentials are a better description of the dynamics in strong fields [21], but even these display conical intersections and nonadiabatic effects [22].

Due to the importance of such nonadiabatic phenomena, it is crucial to develop methods that include coupled electronic and nuclear dynamics. My implementation sidesteps the Born-Oppenheimer approximation entirely, neither making the approximation nor using the corresponding eigenfunctions as a basis. The nonrelativistic Hamiltonian exact except for mass polarization is expressed in prolate spheroidal coordinates and the nuclear and electronic degrees of freedom are treated on the same footing.

However, there are problems inherent in the prolate spheroidal coordinate system that both poison the numerics and reduce the efficiency of the MCTDHF wave function ansatz. Therefore, I have not been able to calculate the nonadiabatic dynamics of many electron molecules, though benchmark nonadiabatic bound state energies were reported in Ref.[1]. I describe my proposal to implement an improvement to the prolate spheroidal coordinate system that will permit converged nonadiabatic calculations on many-electron diatomics. The long-range goal of this project is a nonadiabatic implementation for polyatomic molecules.

3) Ionization
Processes involving strong or energetic laser fields necessarily involve the ionization continuum. On one hand, ionization can serve as an impediment to an experiment, representing a loss process, for instance. On the other hand, ionized electrons can provide the experimental signal [23].

Applications of strong field ionization using isolated few-cycle IR pulses to probe electronic and nuclear dynamics [24-26] achieve resolution of less than a femtosecond, less than the period of the central frequency and the shortest available today; it and high harmonic generation are the tools currently used for imaging dynamics on the fastest timescale. The strong-field dynamics underlying this paradigm of attosecond physics involves the perturbation of valence and inner valence electrons, “requir[ing] an understanding of multielectronic excitations” [26]. More broadly, ultrafast 800nm IR lasers are used in various contexts to control and probe electronic and nuclear dynamics [27,28]. At higher frequencies, tunnel ionization may involve nonadiabatic effects [27].

With X-rays, one is interested in dynamics that result from core hole transitions – for instance, stimulated Raman. The relevant dipole matrix elements are small. Robustly creating a localized excitation requires short pulses. As a result, intense lasers are needed; below I show a calculation on NO using a $1.5\times10^{16}$ W cm$^{-2}$, 1 femtosecond pulse. At these intensities, numerous loss processes including ionization compete with the resonant transition, several photons may be absorbed, and time-dependent AC stark shifts cannot be ignored. All such effects are included in the ab initio MCTDHF algorithm, without any extra effort.

Soft and hard X-ray sources create core-electron excitations that affect the dynamics of electrons throughout the electronic shells of the molecule and that lead to autoionization. Molecular autoionization has many applications and consequences. It may provide an experimental probe of electronic and nuclear dynamics[29]. The process of interatomic Coulombic decay (ICD) is a form of autoionization with technological applications[30]. Autoionization affects the observed spectra via intrinsic linewidths and branching ratios. It poses a barrier to many applications of X-ray laser light, as it introduces a decay channel that competes with the desired process.

Thus, the accurate inclusion of ionization is a requirement for methods that seek to treat states that are highly excited and therefore metastable. A rigorous description of the electronic continuum may be obtained through the use of complex coordinate scaling[31-33], which treats the ionization continuum exactly. Complex scaling will yield energies, lifetimes, and branching ratios of metastable states, purely from the computed eigenvalues and eigenvectors, and is employed in my code.

**Multiconfiguration Time Dependent Hartree-Fock (MCTDHF) algorithm**

MCTDHF employs a time-dependent linear combination of Slater determinants constructed from time-dependent orbitals, and as such could be called time-dependent multiconfiguration self-consistent field. It is important to stress that the “Hartree-Fock” in MCTDHF is a misnomer, as the wave function is an expansion over many Slater determinants. Spin is omitted from the equations for clarity.

The wave function is thus expanded as a linear combination of Slater determinants, with coefficients $A$ and indexed by a vector $n$ of orbital indices. Each Slater determinant is an antisymmetrized product of orbitals. These are expanded as a linear combination of primitive basis functions $f$ with coefficients $c$. 

$$|\Psi(t)\rangle = \sum_n A_n(t)|\vec{n}(t)\rangle \quad |\vec{n}(t)\rangle = \mathcal{A}(\phi_{\vec{n},\alpha}(t)) \times \phi_{\vec{n},\alpha}(\vec{r}, t) = \sum_j c_{j\alpha}(t)f_j(\vec{r})$$

For dynamics including nonadiabatic motion in the nuclei, I make the ansatz that the wave function be expanded in a full basis in the nuclear coordinate(s), with orbitals for the electrons alone, in contrast to the treatment of Refs. [13,15]. The wave function is thus expanded in terms of a full set of primitive basis functions $\chi$ in the bond length $R$. 

\[
\langle R | \Psi(t) \rangle = \sum_{\vec{n}, \kappa} A_{\vec{n}, \kappa}(t) |\vec{n}(t; R)\rangle \chi_\kappa(R)
\]  

(2)

The parametric dependence of the configurations vector-\(n\) upon the bond length \(R\), as denoted above, is purely due to the parametric dependence of the coordinate system.

The choice of orbitals in the electronic coordinate and a larger, time-independent basis in \(R\) is motivated by two considerations. First, the de Broglie wavelength of nuclear motion is much smaller than that of electronic motion, and therefore many more orbitals are required to describe nuclear motion than are for the electronic part. This disparity will grow with the additional nuclear degrees of freedom in polyatomic molecules. Second, the choice allows efficient parallelization of the calculation over the nuclear degree(s) of freedom, reducing the amount of computation and communication. Separate grid points are distributed to each processor, which each calculate the corresponding contributions to the mean fields, etc. This ansatz therefore renders at least part of the algorithm easily parallelizable.

I emphasize that the expansion is in terms of a single set of orbitals that are used for all nuclear geometries, parametrically dependent upon the nuclear geometry. The prolate spheroidal coordinate system is optimal in that the electronic grid follows the nuclei. Therefore, only one orbital is required to describe the cusp in the wave function where an electron and a given nucleus coincide, for all nuclear geometries. I propose to generalize this framework, that of a single set of orbitals, parametrically dependent upon nuclear geometry, and used for all nuclear geometries, to polyatomic molecules. It yields a much more numerically compact representation, vastly enhancing the stability and speed of the integration of the equations of motion.

The coupled, nonlinear equations of motion for the orbital and configuration coefficients may be written as follows. All quantities are time dependent except for \(h\) in Eq.(4).

\[
i \frac{\partial}{\partial t} \vec{A} = \mathbf{H} \vec{A} \quad \text{with} \quad \mathbf{H}_{\vec{n}, \vec{n}'} = \langle \vec{n} | H | \vec{n}' \rangle
\]  

(3)

We have the time derivative of the \(A\)-vector, the configuration coefficients, given by the matrix \(\mathbf{H}\) comprised of matrix elements of the Hamiltonian over the time dependent configurations. This is the Schrödinger equation that one would use for a time dependent configuration interaction calculation with static orbitals. To this equation is coupled the equation for the time derivative of the orbitals,

\[
i \frac{\partial}{\partial t} \vec{c}_\alpha = (1 - \mathbf{P}) \sum_\beta \left[ h^{(1)} \delta_{\alpha \beta} + \sum_\gamma \rho_{\alpha \gamma} W^{\gamma \beta} \right] \vec{c}_\beta
\]  

(4)

The derivative of the vector of orbital coefficients is given in terms of a projector \(\mathbf{P}\) upon the occupied orbital space, the one body operator \(h\), the reduced one electron density matrix \(\rho\), and the mean field operator \(W\). These two equations, for orbitals and configurations, are tightly coupled; the quantities in the orbital equation depend upon the \(A\)-vector, and those in the \(A\)-vector equation depend upon the orbitals.

Directly integrating these coupled equations for a problem of any significant size using a standard method is hopeless. To address this problem I adopt the framework of Ref. [34] and split the two equations, that for the \(A\)-vector and that for the vector \(c\) of orbital coefficients, for short time steps, allowing the use of linear methods for the propagation of the \(A\)-vector, which is a crucial part of the algorithm. I have elaborated that method, which uses constant mean fields (CMF), to polynomial mean fields, with Magnus approximations for the \(A\)-vector propagation.
To calculate photoelectron kinetic energies I generalized the method of [35] to exterior complex scaling. Keith Lawler, who was a postdoc with us in the AMO theory group at LBNL, programmed the method. It involves a Fourier transform of a flux-flux correlation function in which matrix elements of the antihermitian component of the complex scaled Hamiltonian must be computed between wave functions at different times and with different orbitals:

\[
f(E) = \int_0^\infty dt \int_0^\infty dt' e^{iE(t-t')} \langle \Psi(t') | i[\hat{H} - \hat{H}^\dagger] | \Psi(t) \rangle
\]  

(5)

Because the orbitals are different for t and t’ all matrix elements of any operator with respect to the configurations at t and t’ are nonzero, except those zero by symmetry. This fact represents a potentially intractable barrier to the use of this method, and to other methods that may be used to analyze the wave function via such matrix elements. I conceived a method that enables the efficient computation of the above expression. It involves a transformation of the orbitals \( \phi \) at time t’ to a new basis \( \varphi \) such that \( \langle \phi_i | \phi_j \rangle = \delta_{ij} \)

\[
\langle \phi_i(t) | \phi_j(t') \rangle = s_{ij} \varphi_i(t') = \sum_j (s^{-1})_{ij} \phi_j(t') \quad \text{s.t.} \quad \langle \varphi_i | \varphi_j \rangle = \delta_{ij}
\]  

(6)

The wave function must remain unchanged by the orbital transformation and therefore the configuration coefficients must be transformed as well. The coefficients B of the transformed configurations vector-m must satisfy a linear equation involving the dense matrix S of overlaps of the original and transformed configurations at time t’.

\[
\Psi(t') = \sum_{\vec{n}} A_{\vec{n}|\vec{m}} \rightarrow \vec{A}(t') = S(t') \vec{B}(t') \quad \text{with} \quad S_{\vec{n}|\vec{m}} = \langle \vec{n}(t') | \vec{m}(t') \rangle
\]  

(7)

The solution of this equation, the middle one above, is performed by constructing a sparse matrix logarithm of S, and exponentiating to solve the linear equation.

\[
\vec{B} = \exp (-\ln S) \vec{A}
\]  

(8)

in which the operation of \( \ln S \) within the Krylov iterations (that provide the basis in which the exponential is represented) is performed by taking a matrix logarithm of s, and applying Slater’s rules.

The algorithms I just described are the nuts-and-bolts foundation that makes the solution and analysis of the MCTDHF equations tractable. The challenge in applying MCTDHF to the problem of electrons in molecules is not formal. The equations have been written long ago, and the method without permutation symmetry has been very successfully implemented for quantum nuclear dynamics by the group in Heidelberg [19]. The electronic problem presents its own challenges, including that of representing the cusp at the singularities of Coulomb potentials. The orbitals must be three-dimensional, because one-dimensional product functions will break degeneracies and mangle outgoing spherical waves. Due to the long-range nature of the Coulomb interaction, they also must extend far into the asymptotic region. The size of the primitive basis must then necessarily be much larger, which fact puts stringent requirements upon the representation of the operators. For an implementation that may be applied to larger molecules, the established methods of quantum chemistry cannot be used, due to their poor scalability.

The solution of the MCTDHF equations calls for the use of the most cutting-edge numerical methods, along with creative ways to solve the equations with good speed and accuracy. The algorithm will be further improved in both formal and numerical ways in order to treat larger polyatomic systems, using my ideas described below.
Examples of MCTDHF calculations

The figure at left shows a calculation on H\textsubscript{2} including nonadiabatic nuclear motion. A strong laser promoted population to the B state, which has moved to larger bond lengths. The algorithm uses one set of time dependent orbitals for all bond lengths. These orbitals are optimized to represent the wave function, ignoring bond lengths at which it is zero. The curves are Born-Oppenheimer eigenvalues calculated in the time-dependent, R-independent Slater determinant basis at each bond length; the corresponding time-dependent Born-Oppenheimer states are projected upon the nonadiabatic wave function to obtain the populations. The asymptotes are too high because the orbitals are not optimized to describe the states at larger bond lengths at this time.

The figure at left shows one photon single ionization of the HF molecule below the second ionization potential. Calculating this one photon process is an inappropriate use of MCTHDF, done only as a test of the description of metastable states, a Rydberg series of which accumulates below the second I.P at around 20eV. The MCTDHF results are blue lines, and are compared with results from ab initio complex Kohn scattering calculations, which are thin dotted lines. The agreement between the two is remarkable; the decay widths of the autoionizing states are correct, as are the Fano lineshapes; the decay of these states and the concomitant interference of resonant and background photoelectrons is accurately described.

The figure at left shows Rabi flopping in CN between the ground state with 1\textsigma\textpi\textSigma\textpi\textSigma configuration and the carbon 1s hole state 1\textsigma\textpi\textSigma\textpi\textSigma driven by a 280eV CW laser of intensity 10\textsuperscript{17} W cm\textsuperscript{-2}. These are populations in the length gauge. One can see that my algorithm stably integrates the equations of motion for this highly nonlinear process, and that the population decreases due to autoionization of the core hole state. The jagged substructure is gauge dependent.

The figures below describe a two-color core-hole stimulated Raman transition in the NO molecule driven by two concurrent laser pulses, 1.5 and 0.5 x 10\textsuperscript{16} W cm\textsuperscript{-2}. The goal is to produce a localized excitation on nitrogen, a linear combination of two valence states. The transition proceeds via two nearly isoenergetic core hole excited states. The population of the initial ground state is the black line; the intermediates, light orange and grey; the final states, thick blue and purple. The Fourier transform of the pulse is shown at right. Inclusion of nuclear motion will permit the description of the decoherence of the electronic excitation due to nuclear motion, which leads to the damping and perhaps revival of the oscillating dipole.
Proposed research
The goal of the project is to develop a polyatomic implementation of MCTDHF that will become the premier method for calculating ultrafast X-ray and strong-field molecular physics, and to apply the current and extended code to problems of interest. The polyatomic implementation will be developed over the course of the award and will employ several improvements to the algorithm.

Algorithmic and numerical improvements

1) Improvement of prolate spheroidal coordinates for nonadiabatic dynamics of diatomics

The prolate spheroidal coordinate system for two nuclei A and B with separation R, and one electron at radial distances \( r_A \) and \( r_B \), is

\[
\xi = \frac{r_A + r_B}{R} \quad \eta = \frac{r_A - r_B}{R}
\]

with \( \phi \) the azimuthal angle as in spherical polar coordinates. The set \( \{ \xi, \eta, \phi, R \} \) comprises a nonorthogonal coordinate system. An outgoing wave created by a scattering or ionization event is well approximated in the spherical polar radial coordinate system as a product of angular momentum functions in the angular coordinates and a wavepacket in the radial degree of freedom. The prolate spheroidal coordinates and their momenta, in contrast, do not correspond to the natural action-angle variables of the system. Outgoing waves will be better described as products of functions of R times functions of the radial distance of the electron, \( r \), than times functions of \( \xi \).

Furthermore, there are terms in the prolate spheroidal Hamiltonian whose magnitude grows without limit with increasing bond length, that inevitably will cause the breakdown of the numerical integration, and that introduce numerical error though the cancellation of large quantities. The term

\[
\left( \frac{1}{R} \frac{\partial}{\partial R} - \frac{1}{2R^2} \right) \left( \hat{Y} + \frac{3}{2} \right)
\]

in the prolate spheroidal Hamiltonian is a product of two first derivative operators, in R and the electronic coordinates \( \{ \xi, \eta \} \). The magnitude of the second factor, that in the electronic coordinates increases linearly with R given an outgoing electron with constant wave number. By the replacement of \( \xi \) with \( \xi' = R\xi/2 \) or \( \xi' = R(\xi^2-1)^{1/2}/2 \) this term will be well behaved; in the limit of \( r >> R \), we obtain the spherical polar coordinate system with \( \xi' = r, \eta = \cos \theta \), and the nonadiabatic couplings should go to zero instead of growing without limit.

2) Inclusion of rotation for diatomics

It is quite simple to include rotational motion for diatomics simply by combining those degrees of freedom with the bond coordinate as indexed in the code. I already have the operators necessary to construct the full Hamiltonian for electronic, rotational, and vibrational dynamics, including, for instance, the Coriolis coupling term (that is responsible, for instance, for the predissociation of a Sigma state by a Pi state). The only term omitted in the many-electron Hamiltonian so constructed is the negligible mass polarization term that occurs for more than one electron. As emphasized in the literature [22], it is quite often crucial to include rotation to accurately describe dynamics in strong field.

3) Algorithmic improvements for more orbitals and larger configuration spaces

At present the algorithm is certainly not scalable to very large systems, due to the large number of configurations and orbitals that are required. Several improvements will make this goal more reachable.
A) Restricted configuration spaces are required to treat systems with a large number of electrons. The term restricted configuration space means that not all Slater determinants that can be formed with \( n \) electrons in \( N \) orbitals are included in the calculation. If they are all included, it is called full configuration interaction (full CI). The working equations for MCTDHF have only been formulated for full CI. The use of the usual working equations with restricted configuration spaces introduces uncontrolled error and does not satisfy the underlying variational principle. Although one of the advantages of my implementation is that it can do full CI, which may describe complicated dynamics like Auger decay, the most compact representation of bound states is obtained through restricted configurations spaces like configuration interaction with single and double excitations (CISD). Furthermore, to scale the system to a large number of electrons and orbitals, restricted configuration spaces must be used; at least some electrons in the larger molecules must be spectators in the physical process. I will derive and implement the working equations for restricted configuration spaces that exactly satisfy the variational principle. I will also implement an approximate method in which the density matrix is block diagonal, with equivalent electrons combined in a block. Less occupied orbitals will occur in fewer Slater determinants used in the calculation. Intuitively, it would seem that this would produce the best representation of the wave function.

B) Splitting of the orbitals will greatly help the algorithm to be scaled to large systems. I split the propagation of the orbitals and configuration coefficients for short times. The propagation of the configuration coefficients is then easily parallelizable. I will employ a constraint upon the orbitals that does not alter the propagated wave function, which may allow a splitting of the propagation of the orbitals such that each may be propagated by a separate processor. If this is successful, it may allow the method to be scaled to arbitrarily large systems. The constraint is

\[
\left\langle \phi_i \left| \frac{\partial^2}{\partial t^2} \right| \phi_j \right\rangle = 0 \quad i \neq j
\]  

This constraint fixes the antihermitian matrix of first derivatives, \( \overline{g}_{ij} = \left\langle \phi_i \left| \frac{\partial}{\partial t} \right| \phi_j \right\rangle \) (adding a term to Eq.(4), which was given for the choice \( g = 0 \)). \( \overline{g}_{ij}(t) \) will be approximated by polynomials of increasing degree in a predictor-corrector fashion. To second order, it determines the off-diagonal couplings among the orbitals, is easily accounted for using exponential integration, and must only be recalculated at the end of a predictor/corrector iteration.

C) The following improvement will enhance the ability of the code to quickly and accurately calculate many-electron wave functions. If many orbitals \( \phi_i \) are included, the numerical significance of many of their coefficients becomes small and the integration becomes slow. I propose to derive new equations of motion in which the numerical significance of the coefficients will be comparable. Instead of MCTDHF orbitals \( \phi \) I propagate new orbitals \( \varphi \) defined as

\[
\varphi_i = \sum_j \left( \rho^{\frac{1}{2}} \right)_{ij} \phi_j
\]

In which \( \rho \) is the reduced one electron density matrix. The coefficients \( c \) with which the orbitals are expanded in terms of primitive basis functions will be small when the occupation number of the corresponding orbitals are small. Therefore, small errors in the propagation are not amplified and the method should show much greater stability when there are many orbitals with small occupations included in the calculation. A significant number of such orbitals would be necessary, for instance, to accurately describe the electron-electron correlation in double ionization.

4) Optional capabilities: Calculation of photon scattering, Floquet eigenvalues, and improved final state analysis
Scattered photons are not explicitly calculated in the code at this time. The most straightforward way to calculate high harmonic generation, or perhaps to calculate nonlinear susceptibilities for wave mixing experiments, would simply involve entail Fourier transforms of the dipole moment. This “dipole form” of the calculated spectrum is problematic for problems involving ionization and so, proper implementation of exact expressions [36] would be pursued. The stability of the method for calculating high harmonics is not guaranteed.

The calculation of Floquet eigenvalues may be performed with a small alteration of the code and would provide a means to describe dynamics in strong fields both nonadiabatically and via the construction of complex-valued light induced potentials. The bond length degree of freedom is simply replaced by or expanded with a discrete time coordinate, enforcing periodic boundary conditions over one oscillation of the fundamental frequency. I use an iterative method for calculating bound or metastable state eigenvectors and this would be straightforwardly applied to the Floquet problem.

Presently we must perform Fourier transforms to obtain kinetic energies for single ionization, as described above, necessitating long propagation times. For instance, in calculating single photoionization we use a half-femtosecond pulse, followed by a propagation of up to 100fs to resolve sharp features. However, the Fourier transform of the propagator is in fact the Green’s operator, so it is simpler, if possible, to simply operate with the Greens operator directly. This has been used in Ref. [37] in problems of double ionization and electron scattering.

Within MCTDHF, a filter diagonalization [38] representation of the outgoing Green’s operator may be implemented towards this end. As far as I am aware, this has not been described before. The Green’s operator is constructed using a basis of various Ψ(t), the propagated wave function evaluated at different times. As in filter diagonalization for eigenvalues and eigenvectors a set of filtered basis functions

$$\Phi(E_j) = \sum_i e^{iE_j t_i} \Psi(t_i)$$

are calculated for a set of E_j along a complex contour. The outgoing wave Green’s function is then simply constructed using this basis. It is hoped that good results may be obtained by propagating a wave function only until it has reached the complex scaled region of the grid – a few femtoseconds, perhaps, not one hundred.

**Generalization to polyatomic molecules**

The long-range goal of this research and the core of the present proposal is the extension of the method to treat electronic and nuclear dynamics in polyatomic molecules.

I will implement the working equations using a Cartesian grid upon which the orbitals are defined, with finer grids for the Cartesian coordinates of each nucleus. The treatment of problems involving breakup of the atomic centers will be more demanding, and there are many problems that simply involve local motions of the nuclei that redistribute energy among the electronic and nuclear degrees of freedom via non-Born-Oppenheimer effects. Thus the latter problems will be studied first.

At the end of the five-year duration of the award I expect to have a workable code for such problems involving 4 or 5 atomic centers. Conceivably, a meaningful if not completely accurate description of a problem involving nonadiabatic dynamics but only simple harmonic motion of the nuclei could include a small grid of 2x2x2=8 points for each nucleus, giving 8^5 = 32768 nuclear grid points for a five atom problem. Multiplied by a modest configuration basis of perhaps 300 Slater determinants, that could for instance describe single ionization into a variety of final cation states, we have ten million individual coefficients in the A-vector. As mentioned before, the propagation of the A-vector is easily parallelizable. Ten million configurations presents absolutely no problem.
Two versions will be tried: one in which the electronic grid moves with the nuclei, like the prolate coordinate system, and one in which it is fixed. Electronic calculations will be pursued, and the generalization of the diatomic methodology (enabled by a linearly-scaling number of two electron matrix elements) to nonadiabatic dynamics in polyatomics is in principle straightforward. For the fixed grid, the implementation is completely straightforward. A dynamic grid that allows electronic cusps in the orbitals to follow the nuclei, as in the prolate spheroidal coordinate system, introduces a complication: In general the orbitals may not comprise an orthonormal set at all geometries. By specifying the parametric dependence of the orbitals upon the nuclear geometry as expressed in Cartesian coordinates in a simple fashion, it is hoped that the overlap matrix of the Slater determinants will have a simple structure. It must be easy to operate with the overlap matrix in the configuration basis, because this is required for the Lanczos iterations that are performed in the propagator.

A basis of products of sinc functions on a Cartesian grid in x,y, and z is used to expand the orbitals. Potential energy matrix elements of these primitive functions are evaluated employing the discrete variable (DVR) approximation, as they are for atoms and diatoms, yielding very sparse matrices. This method, called the sinc DVR, was originally described in Ref.[39].

The prescription of the matrix elements of the one- and two-electron Coulomb potentials 1/|r-R| and 1/r_{12} using the Cartesian sine DVR basis presents a challenge. For atoms and diatoms I have applied a method described in [40,41] to the two-electron integrals, which involves the solution of Poisson’s equation with appropriate boundary conditions; the matrix elements of the one-electron operators, which are analytic functions in this coordinate system, are easily calculated. I conceived a generalization of this method to a three dimensional Cartesian grid. It is applied both to the two-electron operator and the one-body electron-nuclear repulsion. It can be called the optimal resolution of the identity approximation, in which there is no exterior basis.

The two-electron matrix element is expressed as follows.

\[
\langle \phi_i(1)\phi_j(2)|1/r_{12}|\phi_k(1)\phi_l(2)\rangle = \langle \phi_i(1)|y_{jl}(1)|\phi_k(1)\rangle \quad y_{jl}(r_i) = \langle \phi_j(2)|1/r_{12}|\phi_l(2)\rangle
\] (12)

such that the function \( y \) satisfies

\[
\nabla^2 y_{jl}(r_i) = -4\pi \langle \phi_j(2)|\delta^3(r_i - r_j)|\phi_l(2)\rangle = -4\pi \phi_j(r_i)\phi_l(r_i) \approx -4\pi \delta_{jl}\phi_j(r_i)\phi_j(r_i)
\] (13)

in which the far right hand side has been obtained via a resolution of the identity. This yields the approximation to the two-electron integral as

\[
\langle \phi_i(1)\phi_j(2)|1/r_{12}|\phi_k(1)\phi_l(2)\rangle = \delta_{ik}\delta_{jl} \left[ -4\pi \phi_i(r_i)\phi_j(r_j)(T^{-1})_{ij} + \text{b.c.} \right] \quad T_{ij} = \langle \phi_i|\nabla^2|\phi_j\rangle
\] (14)

with a boundary condition term that depends upon the three-dimensional representation. Notice that there are no off-diagonal matrix elements of the two-electron operator. In words, the two electron matrix element \( <ij|kl> \) is zero if \( i \neq k \) or \( j \neq l \), and otherwise, it is given in terms of the matrix element of the inverse of the one electron kinetic energy matrix between orbitals \( i \) and \( j \).

The numerically appropriate expression for the boundary condition term for a cubic Cartesian grid is not obvious. I will eliminate the need for a boundary condition term by defining the matrix elements for the sinc basis on a grid of infinite extent, and then truncating the basis. I must derive the expression for the inverse of the Laplacian matrix on this Cartesian grid of infinite extent. These matrix elements will be invariant with respect to translations, such that for a grid of \( n^3 \) points there are on the order of \( n^3 \) unique two electron matrix elements, easily stored in memory.
The derivation of the one-electron matrix element proceeds along the same lines as that of those of the two-electron, and as a function of the position of the hydrogen atom within the grid, vector \( r_H \), is

\[
\langle \varphi_i | \frac{1}{|r_i - r_H|} | \varphi_j \rangle = \delta_{ij} \left[ -4\pi \sum_k \varphi_k(r_H)(T^{-1})_{ik} + b.c. \right]
\]  

(15)

In this expression one can see that the \( 1/r \) operator is interpolated as a function of \( r_H \), and that the matrix elements are diagonal. I do not have the two electron matrix elements for the grid of infinite extent. Below I show the results using an ad hoc method in which I invert the Laplacian within a box and add a justifiable but somewhat arbitrary boundary condition term. I use a very large-spaced electronic grid, with an average spacing of approximately 0.2 bohr. With this spacing the sinc functions are nowhere close to describing the nuclear cusp.

Despite this fact, the Poisson solve method reproduces the hydrogenic energy to surprising accuracy, and more surprisingly, does not produce corrugations in the electronic energy as the position of the nucleus is varied, as seen to the left. The energy is convex, but this is the result of my inversion of the Laplacian on a finite grid. Given this behavior for the finite grid, I would not be surprised if the infinite grid gives electronic energies exactly constant with respect to variations in the nuclear geometry. (If so, it could probably be proven.) This lack of corrugations is very important because they can be responsible for unphysical scattering of the nuclear wave packet.

Barring the derivation of an analytic formula, a better numerical approximation can probably be implemented. One might find a numerical approximation to the translationally invariant inverse Laplacian matrix through a fitting procedure, for instance.

The implementation of the nonadiabatic polyatomic code will comprise the core of the work done in the 2nd to 5th years; its inception will not be immediate. There is a quicker way that will be tried first.

The quickest tractable way to implement a treatment of polyatomic molecules is to add hydrogen atoms to the prolate spheroidal grid on-axis making a linear tri- or tetraatomic. The most common such molecules are acetylene and hydrogen cyanide. The Coulomb potential energy terms involving these hydrogen atoms will be evaluated using the same Poisson technique described above. There have been many studies of these molecules using ultrafast, high-energy lasers [42-45].

\textbf{Applications}

I will focus on three directions of research.

1) Ultrafast pump-probe experiments using X-ray light and possibly attosecond few-cycle probes.
2) Modification of X-ray processes using strong fields.
3) Nonadiabatic processes in strong fields.

I also provide a list of extra projects that may or may not be pursued.

The implementation of the polyatomic code will progress over the five-year course of the award. Applications here involve atoms and diatoms, with some calculations including nonadiabatic nuclear motion, and possibly the addition of hydrogen atoms on the prolate grid, at one or both ends, restricted to linear geometry, the precursor to the Cartesian polyatomic code as described above.
High harmonic generation (HHG) has numerous applications including its use to probe electronic and nuclear dynamics [46-50]. Calculating HHG would be a powerful extension of the code and, if straightforward, a set of HHG calculations would have been proposed. However, I cannot guarantee its stability for such calculations. The problem is the incoming waves that are generated on the complex scaled part of the grid, which are amplified. The stability of the method depends upon the instantaneous spectra of the time-dependent Hamiltonian. The velocity gauge must be used and although one-dimensional calculations have shown promising stability, that of the MCTDHF equations is in question.

The MCTDHF ansatz is an explicit representation of an N-electron wave function. Its ionization into final cation states is resolved using the method described above. What it does not describe is the time-dependent dynamics of the cation states thereby produced, after the ionized electron is absorbed on the complex scaled grid. This restricts the processes that may be studied. For instance, a calculation of strong field ionization followed by X-ray probing of the cation, as in the pioneering experiment of Ref. [50], would not be possible. In general, the first step in the calculations here is excitation of the neutral.

To address this shortcoming one might extend the formalism such that to the MCTDHF wave function is coupled a reduced density matrix representation of the cation system, with possible recursion to higher charge states. I note that a reduced density matrix formalism [51] has been applied in several applications of X-rays to study ultrafast physics [50,52]. This coupled density matrix extension of the MCTDHF algorithm is a difficult project that is not proposed.

1) X-ray stimulated Raman pump–probe in NO or other molecules

First I will pursue calculations using an X-ray stimulated Raman pump with probing by X-rays or few-cycle attosecond pulses. The calculations below may all be performed on the NO molecule for which I showed a preliminary calculation of such an initial excitation above. A different transition in a different molecule may prove more appropriate for some of the applications but all of these may be read as applying to the NO molecule.

1A) The stimulated Raman electronic population transfer can be optimized with respect to intensity and frequency given a specified pulse duration. All effects like AC stark shifts are of course naturally included in this ab initio treatment. The reduced transition density operators, i.e., the partial traces of the transition density operator $\langle \Psi(t_0)|\Psi(t_1) \rangle$ over N-1 or N-2 electronic degrees of freedom, between the initial, unexcited, and final states will be calculated, and analysis of these operators may support or disprove the idea of a localized excitation, and determine the experimental parameters required to achieve one.

1B) Subsequently, I will explore X-ray probing of the electronic dynamics induced by an initial X-ray stimulated Raman transition. For NO, after simulated Raman via the nitrogen hole, I will add a probe pulse tuned to a near-edge or directly ionizing transition on the oxygen; this will represent a realistic proposal for a next generation experiment. The A and D Sigma states to which the initial Pi ground state is excited are separated by about 1-2 volts, making the beat frequency a few femtoseconds. This three-X ray-photon experiment is not possible with current pump-probe experiments, but will be accessible to next-generation technology.

1C) A similar calculation will be performed in which the use of a strong attosecond IR pulse, not an X-ray pulse, is used to probe the electronic dynamics subsequent to the stimulated Raman transition. As described in [46], such fields can provide resolutions at timescales shorter than the frequency of the IR laser. Thus this will be a simulated Raman pump, strong IR probe. The advantage of the strong IR probe is that it can selectively ionize the excited part of the wave function and not the ground state.
1D) The inclusion of nuclear motion will permit the description of the damping, and perhaps revival, of the oscillating dipole created by the localized excitation. It may offer the chance to explore elaborations on this experiment including IR fields that may improve the efficiency of the electronic excitation, but that also will affect vibrational and rotational motion.

2) Control of X-ray transitions using strong fields

Strong fields may be used to manipulate X-ray absorption in several ways that have applications in dynamics and spectroscopy. A simple effect of strong fields may be that of alignment, which allows an approximate determination of the resultant molecular-frame photoelectron angular distributions (MFPADs) that may be very sensitive probes of the evolving electronic and nuclear dynamics [23]. The MFPADs obtained for core hole ionization well above threshold may fairly be termed “electron diffraction images” [53] of the geometry of the molecule.

One of the most interesting applications of the combination of strong fields and X-ray light is in the manipulation of the decay channels of core-excited states [54]. In that work the ratio of singly to doubly charged final states was altered by varying the delay of femtosecond IR and X-ray pulses.

Along these lines I will study the decay of a particularly short-lived core hole state of a suitable atom as excited by a femtosecond X-ray pulse and modified by a strong IR pulse. I will attempt to modify the relative amounts of final cation states produced in this straightforward calculation. These numerical predictions will provide a motivation for the relatively simple next-generation experiment they represent.

Next, the same process in a diatom will be studied. Final cation states that dissociate would provide an experimental signal in a coincidence experiment in which the Auger electron and cation atomic fragment were measured, and such an experiment will be calculated. The addition of nonadiabatic rotation or vibration would determine the effect that these will have upon both the final states and the angular distribution and vector correlations of the fragments. I may also calculate the effect that the strong IR field has upon the distribution of final vibrational states caused by the modified Auger decay into a bound cation state. It would be interesting to design an experiment to produce a particular final vibrational wavepacket as this could conceivably find application.

Another interesting application of strong fields and X-ray pulses is the ability of the former to manipulate the absorption spectrum of the latter through nonlinear effects such as electromagnetically induced transparency (EIT) and line modification [55,56]. The fact that these spectral modifications may be studied as a function of the relative polarization directions of the strong and X-ray fields provides a means to study and manipulate the spatial symmetry, degeneracy, or number of states involved [57].

Such effects have not been quantitatively reproduced in calculations so far. Those in Ref.[57] indicated that a three state model of the process was insufficient. Indeed, the presence of the continuum means that it is inherently difficult to apply N-state models in these problems. The strong field may radically alter or even destroy the metastable state. I will demonstrate the calculation EIT and Autler-Townes splitting itself, in particular for Neon as studied in Ref.[57]. An Autler-Townes doublet or EIT feature may be calculated with a time-dependent propagation and I will do so with an atomic calculation. The optional implementation of the calculation of Floquet states would provide a direct and powerful alternate method to calculate EIT and Autler-Townes splitting. The complex-valued Floquet pseudoenergies give the location and width of the observed split or modified resonances.

Ultrafast experiments have demonstrated these effects [58,59] and the next step would be to calculate an atomic experiment analogous to that of Ref.[58], which was on Argon. The delay between a femtosecond
X-ray and an attosecond IR pulse will be varied, and the modification and splitting of the resulting absorption line will be quantitatively predicted.

3) Nonadiabatic processes in strong fields

The applications here center on nonadiabatic dynamics of molecules in strong fields. Femtosecond X-probes may be used to probe the resultant coupled nuclear and electronic dynamics that may result in dissociation. I do not discuss these possible X-ray probes and instead only describe the strong field dynamics that will be calculated with the nonadiabatic diatomic code.

As described above, the prolate coordinates will be improved and the addition of nonadiabatic rotational motion will enable calculations of nonadiabatic phenomena in strong fields, which are ubiquitous. With strong field coupling dependent upon vibration and rotation, two degrees of freedom, point conical intersections naturally arise in the light induced potentials (which do correspond to Floquet state pseudoenergies, when properly calculated in a sufficient basis). The significant consequences of the resultant nonadiabatic effects have been highlighted and explored in Refs.[22,60-63].

Ref.[60] treated the strong field spectrum of Na$_2$. With the optional implementation of the calculation of Floquet states, I could straightforwardly calculate spectra for more relevant molecules using MCTDHF, either as a demonstration or to provide input to a future experiment. The strong field rovibrational spectrum would be directly calculated, and the results interpreted via light induced potentials calculated with fixed nuclei. The easiest molecules to calculate and the ones most likely to display nonadiabatic effects will contain hydrogen, such as HF or OH.

These nonadiabatic effects were also shown [62] to have a significant effect in strong field orientation, such that the rigid rotor model is no longer accurate. The consequences of this for the laboratory frame angular distributions of core electrons ionized after a short orienting IR pulse – the “electron diffraction images” [53] – could be directly calculated, and the nonadiabatic effects quantified through fixed nuclei calculations or calculations in which either the angular or vibrational degree of freedom is fixed.

The experiments in Ref.[64] on strong field ionization of larger molecules show that the dynamics involves nonadiabatic physics. A diatomic will be chosen to see if this behavior can be also seen in smaller systems.

Strong fields may be used to manipulate dissociation dynamics: controlling the final electronic states in the fragments [65], or breaking a specific bond in preference to another [66-68]. Isotopomers of H$_2$ were the diatoms studied in Ref. [65]. I plan to calculate the manipulation of final electronic states by dissociation with strong lasers, in, again, most easily HF or OH. For these calculations I will not propagate the nonadiabatic wave function until dissociation. Subsequent to the strong pulse, the electronic state will be projected onto Born-Oppenheimer curves that will determine the asymptotic states.

Extra projects

1) I may demonstrate the calculation of light induced potentials using Floquet states. For instance, I could calculate the light induced potentials upon which the interpretation in Ref.[21] is based. Such light induced potentials give direct information about ionization rates. An extensive body of work on this subject is reviewed in [69].

2) With or without nuclear motion one could calculate the scattered IR radiation predicted by theory [70], by creating a core hole cation state by hand (annihilating a core hole electron, suitably defined) and propagating the resulting wave function.
3) Address the gauntlet that was thrown in Ref. [71], in which the strong-field ionization of Argon atoms was studied: “The complexity of the results defies easy model-dependent interpretations and invites full solutions to Schrodinger’s equation for these systems.”

4) A method has been proposed [72] for imaging electronic dynamics using strong field ionization with short pulses. It employs strong IR pulses and a measurement of the photoelectrons ionized in the backward direction. The idea is that by varying the intensity of an ultrafast IR pulse, one may extract electron-cation scattering differential cross sections as a function of energy, which are sensitive probes of dynamics. I may test this hypothesis for multielectron systems by comparing the electron scattering cross sections constructed with Lin’s method to those calculated via the complex Kohn variational principle.

5) I may study ionization stabilization, the phenomenon in which larger laser intensities may decrease the photoelectron yield [73,74]. The understanding of this process is largely based on single-active-electron models. Toy problems indicate that correlation among electrons will have a destabilizing effect [73] and it would be interesting to test this hypothesis by calculating ionization stabilization for actual molecules.

**Timetable**

**Year 1**
- Work on nitric oxide with fixed nuclei: creation and verification of localized excitations. Pump-probe studies involving core ionization of oxygen atom.
- Implementation of improved prolate coordinates.
- Initial calculations of strong field ionization

**Year 2**
- Implementation of rotation
- Derivation of Coulomb potential matrix elements for the polyatomic basis. If necessary, derivation and calculation of a numerical approximation.
- Implementation of hydrogen atoms on the diatomic grid for tri- and tetraatomics, with test calculations using fixed nuclei.
- Investigations into the strong field ionization and directed dissociation of diatomic molecules including nonadiabatic nuclear motion.
- Demonstration of the effect of nuclear motion upon the nitric oxide pump-probe experiment.

**Year 3**
- Calculations of EIT and Autler-Townes multiplets.
- Implementation of polyatomic basis within MCTDHF.
- Critical analysis of the performance of the polyatomic basis.
- Initial nonadiabatic calculations for tri- and tetraatomics.
- Further calculations of strong field ionization and directed dissociation.

**Year 4**
- Calculations of the effects of strong fields upon EIT and Autler-Townes multiplets.
- Further nonadiabatic calculations strong field ionization and directed dissociation of diatomics and linear tri- and tetraatomics.
- Preliminary implementation of nonadiabatic dynamics in polyatomic molecules using the Cartesian treatment.
- Further studies of ultrafast X-ray and strong field experiments.

**Year 5**
- Demonstration of nonadiabatic Cartesian polyatomic implementation.
- Further studies of ultrafast X-ray and strong field experiments.
Appendix I. Biographical Sketch

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Education

Ph.D. in Physical Chemistry
Dissertation title: “Dissociative Electron Attachment to Water”
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Research and Professional Experience

1/2011 – present:  Staff Scientist
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Publications

(1)  D. J. Haxton, K. V. Lawler, and C. W. McCurdy. Single photoionization of Be and HF using the


Synergistic Activities

Invited talk to High Dimensional Quantum Dynamics conference, Birmingham UK 2012, 4/13/2012 “Photoionization of atoms and diatoms as a diagnostic of the the MCTDH method”

Collaborators and Co-Editors

C.W. McCurdy, University of California, Davis and LBNL; T.N. Rescigno, LBNL; H.-D. Meyer, University of Heidelberg, Germany; Z. Zhang, Stanford; C.S. Trevisan, Cal State University, Maritime Academy; A.E. Orel, University of California, Davis; C.H. Greene, Purdue University, Boulder; S.A. Wrathmall, Durham University, UK; H. Lewandowski, JILA and the University of Colorado, Boulder; D.S Elliott, Purdue University; A. Belkacem, LBNL; H. Adaniya, LBNL; Th. Weber, LBNL; S. Lee, Villanova Preparatory School, California; T. Osipov, Stanford; R. Doerner, Frankfurt University, Germany; S. Miyabe, Stanford; K. Lawler, LBNL; D.S. Slaughter, LBNL; O. Kornilov, Max Born Institute, Germany; O. Buenemann, University of Goettingen, Germany; O. Gessner, LBNL; D. Neumark, LBNL; S. Leone, LBNL

Graduate and Postdoctoral Advisors and Advisees

Advisor Chris H. Greene, while at JILA, The University of Colorado, Boulder
Advisor C. William McCurdy, Lawrence Berkeley National Laboratory
Advisee Xuan Li, Lawrence Berkeley National Laboratory
Appendix II. Current and Pending Support

Current support

1) Project title: Proposal for an Integrated Ultrafast Science Laboratory at LBNL  
   Source of support: DOE  
   Period covered: 10/01/2012 – 9/30/2013  
   Annual funding: $150K  
   Level of effort: 50%  
   Scope of work: Calculation of ultrafast dynamics of atoms and diatoms; single and double ionization. (Co-PI with C.W. McCurdy)

2) Project title: Atomic, Molecular, and Optical Sciences  
   Source of support: DOE  
   Period covered: 10/01/2012 – 9/30/2013  
   Annual funding: $335K  
   Level of effort: 50%  
   Scope of work: To bridge the gap between development of ultrafast X-ray and XUV sources and their application to problems at the frontiers of the chemical, materials, and biological sciences. (Co-PI with C.W. McCurdy and T.N. Rescigno)
Appendix III. Bibliography and References Cited


[38] “Extraction, through filter-diagonalization, of general quantum eigenvalues or classical normal mode frequencies from a small number of residues or a short-time segment of a signal I.”


Appendix IV. Facilities and Other Resources

The research will be performed at Lawrence Berkeley National Laboratory using existing office space.