The intricate dance of electrons, photons, and ions when matter responds to light

Yusheng Dou and Roland E. Allen
Texas A&M University
This talk is based on papers at our web site, http://lightandmatter.net.

In the first 25 minutes, the model and algorithms will be described, and in the last 25 minutes some results will be presented.

The results for organic molecules show an elegant interdependence of the various electronic and vibrational degrees of freedom, with a simple physical and chemical interpretation.

Since our model is based on standard approximations, it is edifying to consider each of these approximations, and to discuss its potential problems, potential extensions, and relevance in the present context:

1. The atomic nuclei are treated as positive point charges.
2. The treatment is nonrelativistic.
3. The nuclear motion is treated classically.
4. The radiation field is treated classically.
5. The electrons are treated in a time-dependent mean-field picture, with many-body effects neglected.
6. Only the valence electrons are treated, with the inner electrons plus nucleus represented as an inert core.
7. The basis functions are atomic orbitals.
8. The spin-orbit interaction, exchange interaction, and other spin-dependent interactions are neglected.
9. The calculations are not explicitly self-consistent, and there is no explicit Coulomb repulsion.
10. The Hamiltonian matrix elements and core-core repulsion are determined from calculations involving pairs of atoms.
11. The Peierls substitution is used to couple the electrons to the radiation field.
12. The influence of a larger environment is not included.

For example, even with approximations 3 and 4 one still observes "n-photon" and "n-phonon" processes. On the other hand, approximation 3 implies difficulties that are, in a sense, related to the "Schrödinger cat" paradox.
Overview

• The response of matter to fast intense laser pulses is a current frontier of science.

• New discoveries often result from the ability to explore a new regime. Here one is exploring both short time scales (below one hundred femtoseconds) and high intensities (above one terawatt/cm$^2$).

• The standard approximations of theoretical physics and chemistry break down under these conditions, and both electrons and atoms exhibit new kinds of behavior.

• Computer simulations show processes in microscopic detail, and reveal properties that are experimentally inaccessible.
How the simulations are performed: ion and electron dynamics

Coupled dynamics of electrons and ions in matter subjected to an intense laser pulse

(1) Generalized Ehrenfest theorem for ion dynamics:

\[ M \ddot{X} = - \sum_j \Psi_j^\dagger \cdot \frac{\partial H}{\partial X} \cdot \Psi_j - \frac{\partial U}{\partial X} \quad (1) \]

(2) Time-dependent self-consistent field picture for electron dynamics:

\[ i\hbar \frac{\partial \Psi_j}{\partial t} = H(t) \cdot \Psi_j \quad (2) \]
How the simulations are performed: coupling of electrons to laser pulse

(3) Time-dependent Peierls substitution for coupling of electrons to radiation field:

\[ H_{\alpha\beta}(l, l') = H_{\alpha\beta}^0(l, l') \exp\left(\frac{ie}{\hbar c} \mathbf{A} \cdot (\mathbf{R}_l - \mathbf{R}_{l'})\right) \]  

where \( \mathbf{R}_l = \) position of \( l \)th ion and \( \alpha \) labels orbital

(4) Cayley algorithm for electron dynamics:

\[ \Psi_j(t + \Delta t) = (1 + iH\Delta t/2\hbar)^{-1} \cdot (1 - iH\Delta t/2\hbar) \cdot \Psi_j(t) \]
Approximation 1. The atomic nuclei are treated as positive point charges.

(a) Potential problems: The finite sizes and internal structure of the nuclei are essentially irrelevant for the phenomena considered in an ordinary chemical context, but the hyperfine interaction can be observable. Also, as is well known in the treatment of ortho- and para-hydrogen, symmetry implies a connection between the nuclear spin and rotational states of the molecule.

(b) Potential extensions: It is not difficult to add nuclear spin effects when they have any significance.

(c) Relevance in the present context: Nuclear spin is unimportant for the photochemical reactions considered here.
Approximation 2. The treatment is nonrelativistic.

(a) Potential problems: The inner core electrons are relativistic in heavy atoms. Even the valence electrons have tails extending into the region near the nucleus, so their energies will be slightly perturbed by relativistic effects in the case of heavy atoms.

(b) Potential extensions: The full machinery of relativistic field theory will never be required for the class of problems envisioned here. Any relativistic corrections can be handled with the Dirac equation (which only makes the method more complicated) or with the leading relativistic corrections obtained in the Foldy-Wouthuysen reduction.

(c) Relevance in the present context: Relativity is unimportant for the problems envisioned here.
Approximation 3. The nuclear motion is treated classically.

(a) Potential problems: The zero-point energy can be a significant part of the total energy for a molecule with light nuclei, like $\text{H}_2$. In addition, there is a more subtle problem when the nuclear wavefunction can evolve along multiple paths. Let $M$ and $X$ be any nuclear mass and coordinate, and let $P$ be the momentum conjugate to $X$. The Heisenberg equations of motion for the corresponding operators $\hat{X}$ and $\hat{P}$ simplify to $d\hat{X}/dt = \hat{P}/M$ and $d\hat{P}/dt = -\partial\hat{H}/\partial\hat{X}$, where $\mathcal{H}$ is the Hamiltonian for the complete system. It follows that $M d^2\langle \hat{X} \rangle/dt^2 = -\langle \partial\mathcal{H}/\partial\hat{X} \rangle$, and so one obtains Ehrenfest’s theorem

$$M \frac{d^2\langle \hat{X} \rangle}{dt^2} = -\left\langle \frac{\partial\mathcal{H}}{\partial\hat{X}} \right\rangle. \quad (1)$$

In a classical treatment, the nuclei are regarded as very massive, and the wavefunction for nuclear motion highly localized about each average position $\langle \hat{X} \rangle$, so that $\hat{X}$ can be replaced by a classical coordinate $X$. 
Approximation 3. The nuclear motion is treated classically.

This is an approximation, of course, and it will fail in those situations where the uncertainty in nuclear positions has a significant influence on the outcome. For example, suppose that a diatomic molecule is subjected to a laser pulse that promotes electrons from bonding to antibonding states. This raises the effective potential energy $V(r)$ associated with the relative coordinate $r$. If $V(r)$ becomes strongly repulsive for a long period of time, the molecule will dissociate with high probability, and quantum effects will not have a significant effect on the outcome. Also, if $V(r)$ remains strongly attractive, there will be a low probability of dissociation, and the outcome will again not be significantly influenced by quantum effects. On the other hand, if $V(r)$ is such that the molecule is very near the threshold for dissociation, then the evolution of the wavefunction for nuclear motion will produce two branches, corresponding to dissociation and no dissociation. This is precisely analogous to similar phenomena in elementary quantum mechanics, where the wavefunction of a particle incident on a barrier has amplitudes for both transmission and reflection, or the cat in Schrödinger’s famous thought experiment has amplitudes for being both alive and dead.
Approximation 3. The nuclear motion is treated classically.

(b) Potential extensions: For very simple systems, a quantum treatment of the nuclear motion is feasible, either by direct solution of the time-dependent Schrödinger equation or by some variation of Bohm’s formulation of quantum mechanics, in which

\[ M \frac{d^2 X_p}{dt^2} = - \frac{\partial U}{\partial X}, \quad U = V + V_Q \] (1)

for a one-dimensional problem. Here \( V \) is the actual potential, \( V_Q \) is Bohm’s quantum potential, and \( X_P \) is defined by

\[ \int_{X_P(t)}^{\infty} \rho(X, t) \, dX = P \] (2)

where \( \rho(X, t) \) is the probability density and \( P \) is any chosen probability between 0 and 1.
Approximation 3. The nuclear motion is treated classically.

(c) Relevance in the present context: A rough measure of the importance of quantum effects is provided by $\Delta E \Delta t \sim \hbar$, with $\Delta t \sim 100$ fs or more for the nuclei, so that $\Delta E \sim 0.01$ eV. When two outcomes are separated by $\sim 0.01$ eV, therefore, one expects that both may occur with comparable amplitudes, and that a classical treatment is not sufficient in this case. For the simulations reported here, however, the energy scales are typically two orders of magnitudes larger. (For example, see Fig. 14.) Alternatively, one might use the amplitude of the zero-point vibrations as a measure of the importance of quantum effects. In an Einstein model for the vibrations of a C atom, a rough estimate is $\langle (\Delta X)^2 \rangle^{1/2} \sim (\hbar / (M \omega_0))^{1/2} \sim 0.1$ Å, so the quantum motion of the principal atoms in an organic molecule is rather small under normal circumstances.

For these reasons, one expects that it is a quite good approximation to treat the nuclear motion classically in simulations like those of the present paper, where one is not concerned with subtleties like behavior very near threshold or other regimes where quantum effects are amplified.
Approximation 4. The radiation field is treated classically.

(a) Potential problems: With a classical treatment of the radiation field, there is no spontaneous emission.

(b) Potential extensions: If it were necessary, one might add random fluctuations of the radiation field to mimic the vacuum fluctuations that induce spontaneous emission.

(c) Relevance in the present context: Spontaneous emission, like other vacuum effects, is relatively weak and does not have a large effect on the times scales of interest in the present paper.

The present method treats both the nuclear motion and the electromagnetic field classically, so it is consistently a semiclassical method. Semiclassical treatments have the pleasant feature that they effectively include both \( n \)-photon and \( n \)-phonon processes. (Here we broaden the term “phonon” to include vibrational quanta in a molecule.) I.e., first-order time-dependent perturbation theory implies that the electrons gain or lose an energy \( \hbar \omega \) during absorption or stimulated emission, and \( n \)th-order perturbation theory implies that the change in energy is \( \pm n\hbar \omega \). Here \( \hbar \omega \) is either a photon or phonon energy, and there is a distribution of frequencies \( \omega \) in both the laser pulse and the molecular vibrations.
Approximation 5. The electrons are treated in a time-dependent mean-field picture, with many-body effects neglected.

(a) Potential problems: This is probably the most severe limitation of the method as it is currently formulated. It will eventually be necessary to extend the method by including some electron-electron correlation effects, in order to address a broader range of problems. Some examples of the importance of many-body effects are the following: (i) In either a molecule or an insulator, one-electron descriptions give HOMO-LUMO gaps that are typically too small. (ii) An admixture of two or more electronic configurations may be required to give the proper ordering of electronic energy levels in a molecule. (iii) In a semiconductor, electron-electron collisions lead to rapid equilibration of carriers (i.e., electrons promoted to the conduction band by laser excitation). (iv) Excitons, with electron and hole bound by the Coulomb attraction, are important for energy transport in many organic and biological systems.
Approximation 5. The electrons are treated in a time-dependent mean-field picture, with many-body effects neglected.

(b) Potential extensions: In physics, many-body effects are frequently addressed with techniques involving Green’s functions and self-energies. From this point of view, a proper treatment of nonequilibrium problems requires techniques like those introduced by Martin and Schwinger, Kadanoff and Baym, or Keldysh, which involve self-energies that are still more complicated than those encountered for systems in equilibrium. In chemistry, many-body effects are conventionally described by configuration interaction. One can imagine extending the present method via either approach, either by using a model self-energy or by including a small number of additional configurations. The method then becomes more complicated, but also more quantitative and broadly applicable.
Approximation 5. The electrons are treated in a time-dependent mean-field picture, with many-body effects neglected.

(c) Relevance in the present context: In the immediate context we are interested in the basic processes that occur during photoisomerization. Since our description of the excited states derives from density-functional theory, it is not precisely correct. In fact, for butadiene the density-functional HOMO-LUMO gap of 4.2 eV is about 2/3 of the measured gap, and we have scaled down the photon energy for the laser pulse accordingly. However, density-functional theory yields good results for the bonding, so the dynamics of the photoisomerization process following the laser pulse is reliable.
Approximation 6. Only the valence electrons are treated, with the inner electrons plus nucleus represented as an inert core.

(a) Potential problems: High energy processes can lead to core excitations. Core polarization can also have significant effects.

(b) Potential extensions: Inclusion of the core electrons merely leads to a larger computational problem.

(c) Relevance in the present context: The core electrons can be effectively replaced by a pseudopotential when one is concerned with chemical bonding and excitations of the order of a few eV.
Approximation 7. The basis functions are atomic orbitals.

(a) Potential problems: In practice, only a finite basis is used, with a correspondingly limited set of excited states. For example, the excited \(d\) states can be important even for atoms which have only \(s\) and \(p\) valence electrons: These \(d\) states hybridize with the \(s\) and \(p\) states, and tend to push the \(s\) and \(p\) excited states to lower energies through level repulsion. Also, of course, excitation to the \(d\) states themselves can be important. Furthermore, even if all the atomic orbitals could be included, the ionized states would still be missing, and ionization plays a critical role in many photochemical reactions. Finally, there is a more subtle effect associated with the fact that the basis functions are moving with the atoms: If a one-electron wavefunction \(\Psi_j\) is written in the form

\[
\Psi_j(x, t) = \sum_{\ell a} \Psi_j(\ell a, t) \phi_a(x - X_{\ell})
\]

(1)

where \(\phi_a(x - X_{\ell})\) is an atomic orbital on site \(X_{\ell}\), then \(\partial\Psi_j(x, t) / \partial t\) contains a contribution involving \(\dot{X}_\ell \cdot (\partial \phi_a(x - X_{\ell}) / \partial X_{\ell})\), due to motion of the atomic orbital, in addition to the usual contribution involving \(\partial\Psi_j(\ell a, t) / \partial t\).
Approximation 7. The basis functions are atomic orbitals.

(b) Potential extensions: By simply adding more atomic orbitals, one obtains a more complete description of the excited states. Ionization can be treated by either including the true ionized states or by modeling them as free-electron states. A numerically efficient method for treating ionization will be given elsewhere, where we will also present an approximate procedure for including $\dot{X} \cdot (\partial \phi_a (x - X) / \partial X)$ in the solution of the time-dependent Schrödinger equation.

(c) Relevance in the present context: In the immediate context of photoisomerization with a photon energy which just matches the HOMO-LUMO gap, it is a reasonable approximation to neglect the higher excited states and ionization. Also, we have carried out test calculations with our method for including the term with $\partial \phi_a (x - X) / \partial X$, and, in work that will be presented elsewhere, we find that it is a good approximation to neglect this term.
Approximation 8. The spin-orbit interaction, exchange interaction, and other spin-dependent interactions are neglected.

(a) Potential problems: The spin-orbit interaction is a fundamental part of the one-electron Hamiltonian, which follows from the Dirac equation and which is already important in the ground state of a free atom. In a molecule it can induce spin flips, or singlet-to-triplet and triplet-to-singlet transitions. The exchange interaction is an important consequence of the Pauli principle, which accounts for the electronic structure of transition metal and rare earth atoms, and for the magnetism of systems containing these atoms. The interaction of an electron with an external magnetic field is also spin-dependent.

(b) Potential extensions: By doubling the size of the basis set, one can include all of these spin-dependent interactions, at least with approximate or empirical models.

(c) Relevance in the present context: Spin-dependent interactions have only a weak effect for the specific problem addressed in the present paper.
Approximation 9. The calculations are not explicitly self-consistent, and there is no explicit Coulomb repulsion.

(a) Potential problems: During both bonding and excitation, the electronic charge is redistributed. Coulomb repulsion after charge redistribution plays an important role in determining even the geometry. There are also important processes, such as charge-transfer reactions, in which Coulomb interactions play a central role.

(b) Potential extensions: One can model these effects with simple extensions of the present approach, via the use of a Löwdin population analysis to determine the charge, the use of a Hubbard $U$ to shift the on-site Hamiltonian matrix elements, and explicit Coulomb interactions for ionic systems.

(c) Relevance in the present context: The main effects of self-consistency and Coulomb repulsion are implicitly included in the present model, because the parameters are determined in density-functional calculations.
Approximation 10. The Hamiltonian matrix elements and core-core repulsion are determined from calculations involving pairs of atoms.

(a) Potential problems: The exact Hamiltonian matrix is determined globally, by the whole system, rather than locally, by the bonding of pairs of atoms.

(b) Potential extensions: One might add environmental effects in the determination of the Hamiltonian matrix and repulsive interaction.

(c) Relevance in the present context: One expects the pairwise interactions to be of dominant importance, and for \( \text{C}_{60} \) the present model has proved to give a good description of bonding, vibrational frequencies, response to a laser pulse, and dissociation [30].
Approximation 11. The Peierls substitution is used to couple the electrons to the radiation field.

(a) Potential problems: The Peierls substitution does not yield intra-atomic excitations, since it involves \( \mathbf{R} - \mathbf{R}' \) for two different sites. Also, in the case of low-frequency radiation, the ion cores should be coupled to the field.

(b) Potential extensions: If intra-atomic excitations are of interest, one can add a term to the Hamiltonian containing the atomic dipole moment. Regarding the direct interaction with the ion cores, it is trivial to couple these to the radiation field via a force term \( q\mathbf{E} \).

(c) Relevance in the present context: The main features of the interaction of a molecule with a laser pulse are included through the Peierls substitution. It is the behavior of the molecule after application of the laser pulse that must be treated with more care. Also, for photon energies of order 2 eV, the period of oscillation is of order 2 fs. The radiation field then oscillates with a frequency that is two orders of magnitude too fast for the ion cores to show an appreciable response.
Approximation 12. The influence of a larger environment is not included.

(a) Potential problems: Much of chemistry and biology involves an environment. As one example, we mention the chromopore retinal within the protein rhodopsin, which itself lies within the cone cell of an eye. A simpler example is a molecule in a fluid.

(b) Potential extensions: The most important effects of the environment can often be modeled with a combination of molecular mechanics and electrostatic fields.

(c) Relevance in the present context: Here we are considering a free molecule on a time scale too short for collisions.
The primary process in vision is photoisomerization of retinal molecules in the eye. We have not yet performed a simulation for this molecule, but we have observed and extensively studied the similar photoisomerization of butadiene and stilbene. In this first butadiene simulation by Ben Torralva, the photon energy was 2.0 eV, the fluence 0.36 kJ/m², and the pulse duration 15 fs FWHM.

The more extensive results of Yusheng Dou will be shown later.
When a photon of light falls onto rhodopsin, the molecule absorbs the energy and the *cis*-double-bond between C-11 and C-12 in the retinal is temporarily converted into a single bond. This means the molecule can now rotate around this bond, which it does by swivelling through 180°. The double bond then reforms and locks the molecule back into position in a *trans* configuration. Thus the light has isomerised the molecule from *cis* to *trans*, and as it did so, it changed the shape of the retinal from curved to straight.

Whereas the 11-*cis*-retinal fitted into the opsin binding site perfectly, all-*trans*-retinal is the wrong shape. The Schiff base linkage becomes unstable, and the molecule undergoes a series of shape changes to try and better fit the binding site, before eventually breaking free of the opsin altogether. These rapid movements of the retinal are transferred to the protein, and from there into the lipid membrane and nerve cells to which it is attached. This generates nerve impulses which travel along the optic nerve to the brain, and we perceive them as visual signals - sight. The free all-*trans*-retinal is then converted back into the *cis* form by a series of enzyme-catalysed reactions, whereupon it reattaches to another opsin ready for the next photon to begin the process again.

In order to see color, we have 3 types of visual receptors, sensitive to red, green and blue light, but the primary molecule involved in all of these is still 11-*cis*-retinal. The different wavelength sensitivities are due to small variations in sidegroups attached to the opsin protein.

The above description is taken from http://www.ch.ic.ac.uk/vchemlib/mim/mim_project : Henry Rzepa, Wyn Locke (Imperial College), Karl Harrison (Oxford University), Paul May (Bristol University).
butadiene: structure and definition of some of the internal coordinates
excited state depopulation at avoided crossings

(a) Energy variations of HOMO, LUMO, and LUMO+1 orbitals of butadiene molecule with time. The molecule was coupled to a 75 fs FWHM laser pulse centered at 4.2 eV and with a fluence of 1.3 kJ/m².

(b) Electron occupation of LUMO and LUMO+1 orbitals of the butadiene molecule. The laser field coupled to the molecule is the same as in (a).
1-photon excitation from LUMO to LUMO+1

Expanded scale of previous figure from 0 to 150 fs.
(a) Changes in the torsion angles $\theta$, $\phi_1$, and $\phi_2$ of butadiene molecule during the simulation.

(b) Variations of $C_1 - C_2$ and $C_3 - C_4$ distances in the butadiene molecule with time.

(c) Variations of $C_2 - C_3$ distance.
Variations of carbon-hydrogen bond lengths in the butadiene molecule with time.
Variations of $C_1C_2C_3$ and $C_2C_3C_4$ bond angles of the butadiene molecule with time.
(a) Electronic energy variation with time.

(b) Kinetic energy variation with time.
cis-stilbene: structure and definition of some internal coordinates
Following a laser pulse, cis-stilbene is greatly distorted, but returns to the cis structure in this simulation.
(a) Changes in the torsion angles $\theta$, $\phi_1$, and $\phi_2$ of stilbene molecule during the simulation.

(b) Variation of $C_6 - C_9$ distance in the butadiene molecule with time.
(a) Energy variations of HOMO, LUMO and LUMO+1 orbitals of stilbene molecule with time. The molecule was coupled to a 150 fs FWHM laser pulse centered at 3.88 eV and with a fluence of 0.65 kJ/m².

(b) Electron occupation of LUMO orbital of the stilbene molecule. The laser field coupled to the molecule is the same as in (a).
(a) Variations of $C_7 - C_8$ bond length in the stilbene molecule with time.

(b) Variations of $C_6 - C_7$ and $C_8 - C_9$ bond lengths.
QuickTime™ and a GIF decompressor are needed to see this picture.
Photoisomerization: following a laser pulse, cis-stilbene converts to trans-stilbene in this simulation.
(a) Changes in the torsion angles $\theta$, $\phi_1$, and $\phi_2$ of stilbene molecule during the simulation.

(b) Variation of $C_6 - C_9$ distance in the butadiene molecule with time.
(a) Energy variations of HOMO, LUMO and LUMO+1 orbitals of stilbene molecule with time. The molecule was coupled to a 150 fs FWHM laser pulse centered at 3.88 eV and with a fluence of 0.65 kJ/m².

(b) Electron occupation of LUMO orbital of the stilbene molecule. The laser field coupled to the molecule is the same as in (a).
(a) Variations of $C_7 - C_8$ bond length in the stilbene molecule with time.

(b) Variations of $C_6 - C_7$ and $C_8 - C_9$ bond lengths.
QuickTime™ and a GIF decompressor are needed to see this picture.
CW from top left:  
John (Trey) Graves  
Traian Dumitrica  
Ben Torralva  
Yusheng Dou  

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