ELECTRONIC AND STRUCTURAL
RESPONSE OF SEMICONDUCTORS
TO ULTRA-INTENSE LASER PULSES

A Dissertation

by

JOHN STUDER GRAVES, III

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

August 1997

Major Subject: Physics
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August 1997

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ABSTRACT

Electronic and Structural Response of Semiconductors to Ultra-Intense Laser Pulses. (August 1997)

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Chair of Advisory Committee: Dr. Roland E. Allen

Motivated by recent experiments in which semiconductors have been subjected to intense laser pulses, as well as the desire to model excited state properties of semiconductors, we have performed simulations of the electron-ion dynamics of bulk semiconductors when subjected to intense subpicosecond laser pulses. We use a semi-empirical tight-binding Hamiltonian. The interaction of the radiation field with the material is treated through a time-dependent Peierls substitution which introduces no additional tight-binding parameters. The time-dependent Schrödinger equation is solved with an adapted Cayley algorithm which conserves probability. The atomic forces are determined by a generalized Hellmann-Feynman theorem which is valid for nonadiabatic processes. We find that the semiconductor undergoes band-gap collapse and structural deformation above an approximate threshold intensity which is consistent with that observed in the experiments. The imaginary part of the dielectric function, when evaluated as a function of time, further indicates the onset of metallic behavior in the semiconductor after a sufficiently intense laser pulse.
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I. INTRODUCTION

In the last two decades pump-probe spectroscopy has become an important tool for understanding ultra-fast processes in solids\textsuperscript{1-3}. As pulse durations become shorter and shorter, new phenomena are observed. The experiments of Glezer \textit{et al.}\textsuperscript{4,5}, and others\textsuperscript{6,7}, involving very intense subpicosecond pulses on gallium arsenide and silicon, are particularly important. The ultrashort, ultra-intense laser pulses used in these experiments are capable of causing structural instability on a time scale of less than half a picosecond, as discussed in Section II. This time scale of destabilization is too short to be attributed to a purely thermal mechanism; rather, the bonding has been disrupted, which in turn leads to an athermal "melting" of the lattice.

We have addressed this problem by considering the \textit{coupled} electron and ion dynamics. Our model is constructed from a semiempirical tight-binding Hamiltonian and an empirical potential, as explained in Section III. This framework can successfully describe the dominant bulk structural and electronic properties of semiconductors like gallium arsenide and silicon.

In Section IV, we describe in detail the technique of molecular (ion) dynamics. This technique allows us to solve for the motion of ions as the forces change at each successive instant of time. We also discuss the way in which the forces are determined. In particular, the electronic forces are determined from the Hellmann-Feynman theorem applied to the tight-binding Hamiltonian. A test case is first treated, in which the electrons are artificially promoted to excited states. The results indicate that loss of bonding can occur as electrons begin to occupy the antibonding states of the conduction band.

In order to construct a model which adequately describes the experiments of in-
terest, we need to include the electromagnetic field and solve for the resulting electron dynamics. These issues are discussed in Section V. A method is introduced for modifying the Hamiltonian in the presence of an electromagnetic field, incorporating the time-dependent vector potential in the tight-binding matrix elements. An approach is also introduced for solving the time-dependent Schrödinger equation while conserving probability. Finally, a generalized Hellmann-Feynman theorem is employed which is valid even when electrons are in excited states or undergoing transitions. We believe that all three of these elements are novel, and it will be seen that they permit practical calculations of the coupled dynamics of electrons and ions in the presence of a radiation field.

The methods of Section V are applied to real materials such as gallium arsenide and silicon in Section VI. The results indicate that for field strengths similar to those used in the experiments, the lattice does become unstable and the band gap collapses.

In the experiments of Glezer et al., the dielectric constant is measured at two frequencies for many hundreds of femtoseconds after the initial pump pulse. We have calculated the time evolution of the dielectric function in gallium arsenide and silicon as these materials are subjected to laser radiation. The experiments indicate that the band gap collapses and metallic behavior occurs at sufficiently high intensities. The results of our calculations, as detailed in Section VII, are in good general agreement with these observations.
II. MOTIVATIONS: EXPERIMENTAL AND THEORETICAL

A. Experimental Motivation

Ultrashort laser pulse experiments have been probing the dynamics of electrons and phonons in materials for the past two decades\textsuperscript{1–3}. These experiments subject a material to an initial pump laser pulse, then probe the affected material with other less intense laser pulses to observe changes in reflectivity or transmission. Optical studies of this kind have been conducted with varying intensities and pulse durations in order to examine different phenomena.

One class of experiments\textsuperscript{3,8–10} has studied the nonequilibrium, subpicosecond processes occurring when a semiconductor is in an excited state. These processes include diffusion of electrons, carrier-carrier scattering, electron-hole recombination, and band-gap renormalization. Pulse durations on the order of 100 fs are now routinely achieved. Pump fluences on the order of 0.1 kJ/m\textsuperscript{2} and less are only strong enough to create relatively weak electron plasmas, and thus only the carrier dynamics is studied. (The fluence is the amount of energy per unit area that is incident on the surface over the duration of the pulse. The carrier dynamics is essentially how electron plasmas in semiconductors behave after they have been created by laser pulses.) This class of experiments can also be used to study phonon dynamics\textsuperscript{11,12}.

Other experiments have been conducted with relatively long pump pulses on the order of several picoseconds, and with large intensities\textsuperscript{13,14}. One initial motivation was to understand the role which a laser pulse could play in the annealing process\textsuperscript{15}. Debate occurred as to the reason that subnanosecond laser pulses caused annealing in a semiconductor\textsuperscript{15–21}. Was the electronic energy transferred to the ions, thereby heating them and causing thermal melting? Or was the electronic structure changed in such a way that the bonding was disrupted?
The conclusion that was eventually settled upon was that a thermal mechanism was responsible for the disruption of the lattice in pulsed-laser annealing with nanosecond and picosecond pulses. The reason that the semiconductor is disrupted is very similar to ordinary thermal melting. It is the electrons which are initially excited by the pump pulse. However, the characteristic time for electron-phonon thermalization (i.e., heat exchange) is of the order of a few picoseconds, as indicated in time-resolved Raman scattering measurements. Thus, electrons are already beginning to transfer the energy they received from the field to the lattice, before the pulse has even ended. With a strong enough pulse, the ions gain enough energy for thermal melting.

On the other hand, recent experiments with both short and intense pulses have indicated that structural changes can occur on a subpicosecond time scale. These changes are too rapid to have a thermal mechanism; they occur in less than half a picosecond. Furthermore, it has been inferred from experiment that the band gap collapses; i.e., that the semiconductor becomes metallic. Many effects may be playing a role in the band gap collapse, such as screening, band gap renormalization, and structural deformation. Our calculations will address the role of structural deformation.

These recent experiments are clearly probing more than just the carrier dynamics. The higher intensities create large populations of excited carriers and cause structural modifications in the solid. The mechanism behind these structural changes can be interpreted as a loss of bonding, which results from the promotion of electrons from the valence band (bonding) states to the conduction band (antibonding) states. As the bonding is changed, the lattice loses its tetrahedral structure and becomes disrupted. The initial stages of this disruption occur on a very short time scale, of the order of a few hundred femtoseconds. This time scale is much shorter than that for thermal melting, which is characteristically of the order of tens of picoseconds.
FIG. 1. The behavior of the dielectric function in the Drude model.

The experiments are performed by subjecting GaAs and Si to intense laser pulses of 70-80 fs duration (full-width half-maximum) at 1.95-2.00 eV. In the GaAs experiments of Glezer et al., the fluence was varied from 0.0 up to 2.5 kJ/m². After the initial pump pulse, two less intense laser pulses, each at a different angle from the normal of the wafer, probe at successively later times. Two plane (p) polarized probes were used in order to unambiguously determine the imaginary and real parts of the dielectric function. With a knowledge of the p-polarized reflectivities \( R_p \) at two angles \( \theta_i \) \( (i = 1, 2) \), the two simultaneous Fresnel equations

\[
 r_p(\theta_i) = \frac{\epsilon_i \cos(\theta_i) - \sqrt{\epsilon_r \epsilon_i - \frac{\epsilon_i^2}{\epsilon_i^2} \sin^2(\theta_i)}}{\epsilon_i \cos(\theta_i) + \sqrt{\epsilon_r \epsilon_i - \frac{\epsilon_i^2}{\epsilon_i^2} \sin^2(\theta_i)}}
\]

(2.1)

could be numerically inverted to obtain the real and imaginary parts of the dielectric function \( \epsilon_r \) and \( \epsilon_i \). Here, \( r_p \) is the ratio of reflected and incident electric fields, so that
This is an important step in understanding what is occurring after the pump pulse. Ordinarily, the Drude model is used to interpret the dielectric constant. This model describes the excited carrier response to light for free, damped electrons (Fig. 1). Because the electrons are not bound, the Drude dielectric function does not exhibit a resonance in the imaginary part, along with a zero crossing in the real part; rather, one would expect a featureless rise as more electrons are promoted by higher and higher fluences. This is not, however, what was observed in the experiments of Ref. 4.

There is another way in which the semiconductor can contribute to the optical susceptibility, and that is through interband transitions. In an interband transition, photon absorption causes an electron to be promoted from the valence to the conduction band. There are some regions of reciprocal space where the valence and conduction bands are rather parallel. It follows that there are energies for which the joint density of states is high, and the imaginary part of the dielectric function consequently exhibits peaks. These peaks are shown for silicon in Fig. 2.

The dielectric function thus has two contributions, one from the Drude response of free carriers and another from the interband transitions:

$$\epsilon(\omega, t) = 1 + 4\pi (\chi_{\text{interband}}(\omega) + \chi_{\text{Drude}}(\omega)),$$ \hspace{1cm} (2.2)

Ordinarily the interband contribution is assumed to remain constant. Glezer et al., however, could only interpret their results understandably if the interband contributions were allowed to change. Their results indicated that the peaks seen in Fig. 2 were broadened, and that a low energy peak resulted.

As the fluences increased to 0.5 kJ/m$^2$ and higher, the Drude model did not adequately describe changes in the dielectric constant; rather, changes in interband transitions dominantly contributed to the change in optical susceptibility in this flu-
ence range. These interband transitions can be pictured in terms of electrons bound to the atoms, in contrast to more nearly free electrons in a metal (Fig. 3). This binding gives rise to a characteristic peak in the imaginary part of the dielectric constant and a corresponding zero in the real part. The peak corresponds to large absorption. In a real semiconductor like GaAs, the peak turns out to be due to transitions from the valence bands to the conduction bands, in regions of reciprocal space where the bands are more or less parallel and the joint density of states is consequently high.

The experimentalists cited above were able to infer that GaAs underwent band
gap collapse and structural deformation. These phenomena could be attributed to promotion of electrons to antibonding states, thereby lessening the bonding and leading to disruption of the lattice. Other mechanisms have been proposed, however. In the work of Kim et al., the possibility of band gap renormalization was addressed. This is an effect in which the charge transfer due to excitation causes a modification of the potential felt by the electrons.

Similar results were obtained by Sokolowski-Tinten et al. They performed single-angle time-resolved reflectivity measurements on both GaAs and Si after pump laser pulses similar to those of Glezer et al. They concluded that during the first 100 fs after the beginning of the 150 fs pulse, electronic excitation processes dominated changes in the optical measurements. Structural changes were seen on the order of 300 fs, along with a Drude-like metallic behavior for sufficiently intense pulses.

FIG. 3. The behavior of the dielectric function due to a single bound oscillator.
Second harmonic generation experiments have been performed by a number of groups\textsuperscript{5,6}. In these experiments, reflectivities at twice the probe frequency are measured. The second harmonic signal in a semiconductor like GaAs is nonzero in the ground state, because the crystal has no center of inversion\textsuperscript{1}. However, if the structural properties change significantly (through lattice disruption), the material can lose its original asymmetry and effectively gain a center of inversion, causing the second harmonic signal to drop. The second harmonic signal has been seen to vanish for GaAs\textsuperscript{5,6}, which suggests that the GaAs lattice has been disrupted. The same analysis cannot be performed on Si, since it is an elemental semiconductor with a center of inversion in the equilibrium structure.

As mentioned above, the dielectric constant in GaAs was originally measured only at 2.2 and 4.4 eV. Recent experiments\textsuperscript{26} are now able to measure the dielectric constant more or less continuously between 1.5 and 3.5 eV. These broadband experiments employ nonlinear optical techniques for dispersing the light, and corrective measures are taken to temporally shift the data at each frequency. These experiments are in full agreement with the 2.2 and 4.4 eV experiments. The measurements show that the optical response cannot be described by the Drude model alone; rather the imaginary part of the dielectric function shows a broadening and eventual low frequency peak for large enough intensities, thus indicating band gap collapse. On long time scales, the measurements of the dielectric function agree with the known dielectric function near the melting temperature. For short time scales, they do not agree, further indicating an athermal mechanism for instability.

As laser pulses become shorter and shorter, we are certain to gain new knowledge concerning the mechanisms of ultrafast processes. Understanding the interaction between these pulses and semiconductors could have a far-reaching impact on the electronic devices of the future. The pulses could play a role in annealing, or chemical
processes, or one could even imagine an ultrafast gate\textsuperscript{27}.

**B. Theoretical Motivation**

The present work was motivated not only by the state-of-the-art experiments just discussed, but also by the theoretical challenge of treating excited-state properties. In the past, most calculations and simulations for real materials have focused on only the ground state.

Excited-state materials science is now entering a phase in which experiments can be performed on a wide variety of materials and a variety of effects can be studied. Besides the radiation-induced structural phase transformations in GaAs and Si that were just described, it has been observed\textsuperscript{28} that PbTiO\textsubscript{3} undergoes a transition from tetragonal to rhombohedral when subjected to full-color picosecond light. Catalytic enhancement in TiO\textsubscript{2} is seen when subjected to light\textsuperscript{29}. Coherent oscillations in fullerenes (C\textsubscript{60}) are caused by application of intense laser pulses\textsuperscript{30}.

What these effects have in common is that the solids or molecules are subjected to electromagnetic radiation and electrons are promoted to excited states. We would like to have theoretical tools to describe these effects. In order to do this, one has to treat both the ion and the electron dynamics.

Ion dynamics (or molecular dynamics) is already a well-developed method which employs Newton’s equation of motion and derives forces from either potentials or the Hellmann-Feynman theorem. The electrons are governed by a different equation, the time-dependent Schrödinger equation. It has been shown\textsuperscript{31} that one can treat the electron dynamics through the time-dependent Schrödinger equation, and the ion dynamics through a generalized Hellmann-Feynman theorem, even when the electronic states are not eigenstates of the Hamiltonian. These two problems are clearly coupled in real materials.
Our model is intended to treat the first stages, during and immediately after an initial pump laser pulse. It does not describe how the electrons lose energy as a result of spontaneous emission, or how they diffuse because of chemical potential gradients. These processes occur over longer time scales. We will only be concerned with what occurs on a time scale of roughly 500 fs. Our model also does not contain any screening effects or electron-electron interactions, since we are focusing on the structural modifications and the one-electron states.

There has been some previous theoretical work related to this general phenomenon. First-principles molecular dynamics simulations have been performed, and the results indicated that covalent bonds can be weakened by the excitation of electrons to conduction bands. In another study, Stampfl and Bennemann determined, using an \textit{sp}^3 tight-binding model, that the transverse acoustic phonons become unstable for excitations of roughly about 10%. This was a result of the shear elastic constant becoming negative at high enough excitation. However, both of these treatments relied on thermodynamic arguments to estimate the population of excited electrons.

Our model goes further by treating both the ion \textit{and} electron dynamics, as electrons are promoted to excited states. The inclusion of the electromagnetic field is also critical. The model uses a tight-binding Hamiltonian to describe the electronic structure of GaAs and Si. The laser pulse is introduced by modifying the tight-binding matrix elements by a multiplicative factor. The time-evolution of the electronic states is solved by a norm-conserving algorithm for the time-dependent Schrödinger equation. This allows the electrons to be excited to conduction band states. The ionic forces are determined from a generalized Hellmann-Feynman theorem that is valid for excited states and nonadiabatic processes.
III. MODELING ELECTRONIC AND REPULSIVE INTERACTIONS

A. Tight-Binding Hamiltonian

Both structural and electronic modifications result from the application of an intense subpicosecond laser pulse to a semiconductor, so our model must properly incorporate both effects. The structural properties are determined by the chemical bonding of the atoms. A chemical bond is a feature of the electronic structure, however, so it is clear that the geometrical and electronic properties are coupled.

The structural properties can be treated through the method of molecular dynamics, in which forces on atoms are calculated at each time step, and their motion obtained as a function of time. There are three varieties of molecular dynamics techniques—empirical, tight-binding, and first-principles. Empirical methods rely solely on classical potentials to determine the forces each atom experiences as a simulation is performed. This approach requires an empirical fit for the parameters that enter the potential. Empirical potentials have been used to treat a wide variety of problems beginning with the noble gases, for which the Lennard-Jones potential\textsuperscript{37} gives accurate bond lengths and energies. Ionic, covalent, metallic, and hydrogen-bonded systems have also been treated with empirical techniques, yielding much information about structural, kinetic, and thermodynamic properties\textsuperscript{38}. This approach allows the simulation of thousands or even millions of atoms, because of the simple (usually pairwise) way in which interactions are included.

Empirical methods suffer from the drawback that they do not treat the electronic properties which are modified by the laser pulses, and which would in turn modify the empirical potentials. One could possibly construct a method which modifies the empirical potential after interaction with light, but this would be \textit{ad hoc} and poorly defined.
Because we cannot hope to realistically model the interaction with light using purely empirical models, we need another method which contains information about the electronic structure. This is especially important if we wish to understand an effect like band-gap collapse, which inherently requires that the electronic states be included.

First-principles methods give a very detailed description of a solid’s electronic structure. These methods solve the time-independent Schrödinger equation for the real-space wavefunctions. They typically represent the wavefunction as a sum over large plane wave basis sets. They have been successfully used to treat the ground state properties of many solid state and chemical systems. One disadvantage with first-principles calculations is that the required computational time would be prohibitive for the present calculations. The usual \textit{ab initio} methods are also inaccurate for some basic properties, like the size of the band gap. The local density approximation (LDA) within density functional theory predicts that Si has a band gap of less than 0.5 eV, whereas the gap is experimentally measured to be 1.1 eV. The LDA is especially unreliable for the excited state properties which we are interested in treating. There are methods, such as the GW approximation, that can come close to predicting correct band gaps, but these methods become enormously expensive in the amount of computation required.

Semiempirical tight-binding lies between empirical and first-principles methods. It provides a reasonably good description of the electronic structure (provided the parameters are fitted correctly) but is not computationally prohibitive. Semiempirical tight-binding has in the past been applied to ground-state properties. Examples include dimer switching and surface reconstruction. Here we will extend the approach to excited-state properties. In Section VII we will find that the imaginary part of the dielectric function is rather well described by the tight-binding model.
used here.

Tight-binding is the method of choice for the present simulations because it yields the correct band gap and energies of excited states, it is computationally efficient, and it can be used in the time-dependent Schrödinger equation to determine how the electrons respond to an electromagnetic field.

If we are to describe how the electrons are excited, we require a realistic treatment of the electronic structure. As electrons begin to occupy conduction bands, the bonding is different than when they occupy only the valence bands. Tight-binding very naturally describes the formation of bonding and antibonding states. As atomic wavefunctions overlap, the atomic energies broaden out into bands. In addition, there is an effective repulsion between the bonding and antibonding energy levels associated with the two atoms in a unit cell of a semiconductor like GaAs or Si, giving rise to a gap between the occupied valence-band states and the unoccupied conduction-band states. This causes semiconducting behavior, because the electrons are in rigid bonds and cannot move freely when a field is applied. In short, tight-binding accounts for the chemical bonding and related electronic properties.

In semiempirical tight-binding, matrix elements are represented by simple analytical expressions, and are fitted to the best available experimental and theoretical information; i.e., they are not evaluated from first principles wavefunctions in the coordinate representation. The accuracy of a tight-binding model depends on the choice of the basis functions and on the accuracy with which the parameters are fitted. With the proper choice of this input one can obtain a good description of many electronic properties like the density of states, band structure, and Fermi energy.

The orbitals used in the semiempirical approach are regarded as being localized on atomic sites. It is assumed that the overlap between orbitals on distant neighbors can be neglected. In the present materials, it is known that a basis set consisting
of a valence $s$ orbital and three valence $p$ orbitals provides a good description of the bonding valence band states when only nearest neighbor interactions are included. On the other hand, this minimal basis does not provide a completely adequate description of the conduction bands, and in particular fails to give an indirect gap in the case of silicon. For this reason, in the present calculations, the minimal basis set is augmented by a fictitious excited $s^*$ state which mimics the effect of the true excited $d$ states and other higher lying states, and has the effect of pushing down the conduction band to give a good representation of the band gaps for both gallium arsenide and silicon.

We are interested in finding the eigenstates of the electronic system. The tight-binding Hamiltonian $H_{\alpha,j}(\mathbf{k})$ as a function of crystal momentum (wavevector) $\mathbf{k}$ is

$$H_{\alpha,j}(\mathbf{k}) = \sum_L e^{i\mathbf{k}(\mathbf{R}_j - \mathbf{R}_i)} t_{\alpha,j}(\mathbf{R}_{j,L} - \mathbf{R}_i) + \epsilon_{\alpha} \delta_{\alpha,j}$$

where $\alpha$ and $\beta$ label orbitals on the atoms $i$ and $j$, respectively. The orbitals have symmetry related indices that characterize the state of an electron. As mentioned above, only orbitals with $s$ and $p$ symmetry are considered in our model. $\mathbf{R}_i$ is the position of the $i^{th}$ ion within the unit cell. In the molecular dynamics or electron-ion dynamics simulations to be discussed below, periodic boundary conditions are assumed, with a large unit cell within which the atoms are moving. $L$ denotes both the original unit cell and the other cells that are replicated with appropriate translations from the original unit cell. Then $\mathbf{R}_{j,L}$ is the position of the $j^{th}$ ion in either the original or a neighboring unit cell. The exponential factor, $e^{i\mathbf{k}(\mathbf{R}_j - \mathbf{R}_i)}$ results, as usual, from the fact that the eigenstates of the system satisfy Bloch’s theorem with the primitive unit cell replaced by a larger unit cell in the present simulations.

$t_{\alpha,j}(\mathbf{R}_{j,L} - \mathbf{R}_i)$ are the interatomic matrix elements; i.e., the off-diagonal elements of the Hamiltonian matrix. In Dirac notation, they represent overlap integrals involving a wavefunction on the site $\mathbf{R}_{j,L}$ with orbital symmetry $\beta$ and on the site $\mathbf{R}_i$. 

with orbital symmetry $\alpha$:

$$t_{\alpha,j\beta}(R_{j,L} - R_i) = \langle i\alpha \vert H \vert j\beta, L \rangle. \quad (3.2)$$

The diagonal elements $\epsilon_{\alpha}$ are interpreted as atomic energies within the solid.

$$\epsilon_{\alpha} = \langle i\alpha \vert H \vert i\alpha \rangle. \quad (3.3)$$

Once the Hamiltonian matrix has been constructed, it can be diagonalized to give both eigenvalues $\varepsilon_m$ and eigenvectors $\Phi_m$ as a functions of wave vector $k$ and band index $m$:

$$H(k)\Phi_m(k) = \varepsilon_m(k)\Phi_m(k). \quad (3.4)$$

B. Evaluation of the Matrix Elements

If one knew the best form for the one-electron Hamiltonian and the best forms for the one-electron wavefunctions in the coordinate representation, then one could in principle calculate the matrix elements of the Hamiltonian $t_{\alpha,j\beta}(R_{j,L} - R_i)$. This would be a computational very awkward problem for simulations for the kind that are reported here. Furthermore, the first-principles Hamiltonian and first-principles wavefunctions would not provide a good treatment of the excited states, because of the notorious difficulties of the LDA with respect to the band gaps and other excited state properties. In principle, one can treat the excited states using an energy dependent and nonlocal electronic self-energy, but this is a more formidable task than even first-principles calculations within the LDA, when one must solve the time-dependent Schrödinger equation using a 50 attosecond time step.

All of these difficulties can be finessed by the use of a semiempirical model which provides a good description of the chemical bonding and the excited states, both of which are essential in the present calculations.
Tight-binding can provide a good chemical description of materials when \(d\)-electrons and perhaps even \(f\)-electrons are included, but for the semiconductors considered here, only \(s\) and \(p\) orbitals are required. The off-site (hopping) matrix elements are given by:

\[
t_{is,jj} = \eta_{ss} \frac{\hbar^2}{m_e d^2}
\]

\[
t_{is,jp} = \eta_{sp} \frac{\hbar^2}{m_e d^2} = -t_{ip,jj}
\]

\[
t_{ip,jp} = \left[I_{\mu} I_{\nu} (\eta_{ppp} - \eta_{pp\sigma}) + \delta_{\mu\nu} I_{pp\sigma}\right] \frac{\hbar^2}{m_e d^2} = t_{ip,jj}
\]

where \(l_\mu = d_\mu/d\) is a direction cosine between sites \(i\) and \(j\) separated by a distance \(d\); i.e., if the vector from \(i\) to \(j\) is \(d = (x, y, z)\) with components \(x\), \(y\), and \(z\) (denoted by \(\mu\) and \(\nu\)), then \(l_x = x/d\) and similarly for \(l_y\) and \(l_z\). Also, \(m_e\) is the electron’s mass and the quantity \(\hbar^2/m_e\) is approximately \(7.62 \text{ eV}\cdot\text{Å}^2\).

These off-diagonal elements (3.5)–(3.7) scale according to Harrison\(^{12}\) as \(1/d^2\) where \(d\) is the distance between two atoms. The \(\eta\)’s are parameters which characterize the amount of overlap between two orbitals of particular symmetries. They are therefore responsible for the strength of the chemical bonds. They are empirically adjusted so as to correctly reproduce electronic properties such as the band gap. Some of these properties are obtained directly from experiment and others from first principles calculations. The values of the parameters used here are taken from Vogl \textit{et al.}\(^{17}\) They will be presented in Section III.C. They were determined by fitting to empirical pseudopotential bands, which were in turn fitted to reflectivity and photoemission data.

The subscripts \(\pi\) and \(\sigma\) represent the relative orientation of two orbitals. In the case of \(p\) orbitals, \(\pi\) indicates that they are pointing parallel to each other and \(\sigma\) that they are pointing toward each other. (See Fig. 4 for the case of a \(p\) and an \(s\) orbital.) The relative strength of the \(\pi\) and \(\sigma\) contributions will vary as the orientation of the
atoms is changed.

Our semiempirical model involves the two-center approximation\textsuperscript{48} for the off-diagonal matrix elements and the assumption that the atomic orbitals are actually orthogonal Wannier or Löwdin functions\textsuperscript{42,45}. In general, the off-diagonal elements of the Hamiltonian matrix involve a potential \( V(r - R_n) \), where \( R_n \) indicates the positions of all the atoms in the crystal. If the Wannier functions are represented by \( \phi_\alpha(r - R_i) \), then the Hamiltonian matrix element for sites \( i \) and \( j \) is given by the integrals

\[
\int \phi_\alpha^*(r - R_i) V(r - R_n) \phi_\beta(r - R_j) d^3r.
\]  

In the two center approximation, it is assumed that the potential is determined entirely by sites \( i \) and \( j \) themselves. The angular integrals in (3.8) can then be evaluated by rotating axes and transforming spherical harmonics. This leads to the relatively simple angular dependence of (3.5)-(3.7). These integrals can be understood from simple geometric arguments, however. For example, since \( s \) orbitals are isotropic, there is no dependence on the orientation of the two orbitals, so the resulting matrix element \( t_{is,j} \) has no angular dependence, as indicated by the form in Equation (3.5). This is, of course, not true for matrix elements involving \( p \) orbitals, which have lobes pointing along the axial directions. For example, as the orientation of an \( s \) and a \( p_x \) orbital is varied, the matrix elements change from being maximal (aligned) when the \( p_x \) and \( s \) orbitals are oriented along the \( x \) direction, and zero if the line joining the centers of these orbitals lies along the \( y \) or \( z \) direction. The result is zero in the second case because the lobes of the \( p_x \) orbital have opposite parity, thus canceling against the single parity of the \( s \) orbital (see Fig. 4). The slightly more complicated \( p-p \) interactions can be understood in a similar fashion.

There are, of course, other approximations in our simple semiempirical scheme. For example, the spin-orbit interaction is neglected, the influence of the environment
on the diagonal elements of the Hamiltonian is also neglected, and the fundamental starting point is the one-electron approximation in which the energy dependence and nonlocality of the self-energy are ignored. All of these approximations are rather good for the $sp$-bonded semiconductors considered here.

C. Tight-Binding with $sp^3s^*$ Orbitals

The covalent nature of group IV and III-V semiconductors is a result of the hybrid orbitals that are formed. As was first pointed out by Pauling, this hybridization results in the tetrahedral structure found for silicon, gallium arsenide, etc. By including one $s$ and three $p$ orbitals per atom, we automatically form linear combinations of these atomic-like orbitals that reproduce this covalent, tetrahedral bond.

Silicon has a two atom basis and a face centered cubic structure, as shown in Fig. 5. The band structure can be determined along symmetry lines of the Brillouin zone once a suitable set of parameters has been chosen. This is shown for an $sp^3$
FIG. 5. The crystal structure of GaAs. All atoms are equivalent in Si.

model of silicon in Fig. 6 with parameters indicated in Table I. Because there are two atoms and four electrons per atom, there are $4 \times 2 = 8$ bands, as can be seen in
TABLE I. Off-site and on-site parameters in the $sp^3$ tight-binding model for Si. Notice that $\eta_{ps\sigma} = -\eta_{sp\sigma}$. The $\epsilon$'s are measured in eV. The parameters are taken from Harrison.\(^{42}\).

<table>
<thead>
<tr>
<th></th>
<th>$\epsilon_s$</th>
<th>$\epsilon_p$</th>
<th>$\eta_{ss\sigma}$</th>
<th>$\eta_{sp\sigma}$</th>
<th>$\eta_{ps\sigma}$</th>
<th>$\eta_{pp\sigma}$</th>
<th>$\eta_{pp\pi}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>-4.050</td>
<td>2.980</td>
<td>-1.40</td>
<td>1.84</td>
<td>-1.84</td>
<td>3.24</td>
<td>-0.81</td>
</tr>
</tbody>
</table>

the figure. The Pauli exclusion principle implies that two electrons fill each orbital state in the valence bands. This, together with the fact that Si has four electrons per atom, implies that the lowest four bands in the figure are filled. The upper four bands and higher bands are empty in the ground state and are called the conduction bands. Application of a laser pulse will excite electrons from the bonding valence bands to the antibonding conduction bands.

Many of the ground state properties of group IV, III-V, and even II-VI semiconductors are well described by this minimal $sp^3$ model. Experiment verifies that the lowest valence band is in fact derived from the anion $s$ state and the higher valence bands are derived from the anion $p$ states. Furthermore, the dispersion of these valence bands is in rather good agreement with the experimental dispersion observed, for example, in photoemission. (There are discrepancies concerning some of the more subtle properties like effective masses which are not important in the present context.)

The worst shortcoming of the simple $sp^3$ model is that it does not yield the correct behavior for the conduction bands, especially those derived from the cation $p$ states. The bare $sp^3$ model predicts that all semiconductors have direct band gaps, from the anion $p$ state-derived valence band maximum at $\mathbf{k} = 0$ to the cation $s$ state-derived minimum, also at $\mathbf{k} = 0$. Many real semiconductors, however, have an indirect band gap, from the anion $p$ state valence band maximum at $\mathbf{k} = 0$ to a cation derived $p$ state minimum at some other wave vector $k_0$. This behavior results from an interaction of the cation $p$ state bands with other excited state bands at higher energies, in partic-
FIG. 6. Band structure of Si with $sp^3$ orbitals included. The symmetry points are those of the primitive unit cell. The indirect gap is not obtained with only $sp^3$ orbitals.

ular higher-lying $d$-states. As shown by Vogl et al., it is possible to mimic the effect of these excited states by representing them with a single excited $s$ state $s^*$ on each atom (anion and cation). The resulting $sp^3s^*$ model does give a good description of indirect band gap semiconductors, including silicon and gallium phosphide. Since it is imperative to have a proper representation of the conduction bands in the present simulations of excited-state dynamics, we will use the $sp^3s^*$ tight-binding model. The validity of this model will be demonstrated by our calculations of the dielectric function (reported in Section VII), which depend critically on the joint density of both valence band and conduction band states.

The essential effect of the $s^*$ states is to broaden the dispersion of the lowest conduction bands as a result of their interaction with these higher energy $s^*$ states. This pushes the lowest conduction bands down near the X and L points of the Brillouin
FIG. 7. Band structure of Si with $sp^3s^*$ orbitals included. The symmetry points are those of the primitive unit cell. The indirect gap is reproduced.

zone, as can be seen in Fig. 7. It should be mentioned that the only new interactions required in the $sp^3s^*$ model are the ones between a $p$ orbital and the fictitious $s^*$ orbital:

$$t_{is'js'} = 0 \quad (3.9)$$

$$t_{ip'u,js'} = \frac{\mu \eta_{ps^*} \pi^2}{m_e d^2} = -t_{is^*j_p} \quad (3.10)$$

$$t_{is^*js^*} = 0. \quad (3.11)$$

One nice feature of the $sp^3s^*$ model is that one does not have to include $d$ states. This is good for two reasons: (1) the angular factors are much more complicated for $d$ interactions and (2) the size of the matrix would be 9 orbitals per atom as opposed to 5 orbitals per atom with the $sp^3s^*$ model. Still another reason is economy of parameters.
TABLE II. Tight-binding parameters in the $sp^3s^*$ model for GaAs and Si. The $\epsilon$'s are measured in eV. Cation is denoted with a $c$ and anion with an $a$. These values are taken from Vogl et al.\textsuperscript{17}

<table>
<thead>
<tr>
<th></th>
<th>GaAs</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_{sa}$</td>
<td>-2.657</td>
<td>-4.200</td>
</tr>
<tr>
<td>$\epsilon_{pa}$</td>
<td>3.669</td>
<td>1.715</td>
</tr>
<tr>
<td>$\epsilon_{sa}$</td>
<td>6.739</td>
<td>6.685</td>
</tr>
<tr>
<td>$\epsilon_{sc}$</td>
<td>-8.343</td>
<td>-4.200</td>
</tr>
<tr>
<td>$\epsilon_{pc}$</td>
<td>1.041</td>
<td>1.715</td>
</tr>
<tr>
<td>$\epsilon_{sc}$</td>
<td>8.591</td>
<td>6.685</td>
</tr>
<tr>
<td>$\eta_{sa\sigma}$</td>
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<td>-1.504</td>
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<td>$\eta_{sa\sigma}$</td>
<td>1.529</td>
<td>1.798</td>
</tr>
<tr>
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<td>$\eta_{pa\sigma}$</td>
<td>2.386</td>
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<tr>
<td>$\eta_{pa\pi}$</td>
<td>-0.6153</td>
<td>-0.5182</td>
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<td>$\eta_{sa\sigma}$</td>
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<td>0.0</td>
</tr>
<tr>
<td>$\eta_{sa\sigma}$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\eta_{sa\pi}$</td>
<td>-1.640</td>
<td>-1.687</td>
</tr>
<tr>
<td>$\eta_{pa\sigma}$</td>
<td>1.652</td>
<td>1.687</td>
</tr>
<tr>
<td>$\eta_{sa\sigma}$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

The $sp^3s^*$ parameters for Si and GaAs are given in Table II, where $d$ is measured in Å, energies are measured in electron volts, and $\hbar^2/2m_e = 7.62$ eV·Å$^2$. The $sp^3s^*$ band structure of GaAs is shown in Fig. 8. Notice that GaAs is a direct gap semiconductor with a band gap of 1.5 eV, whereas Si is indirect with a gap of 1.1 eV. It is therefore quite appropriate to use laser pulses with photon energies of around 2.0 eV.
FIG. 8. Band structure of GaAs with $sp^3s^*$ orbitals included. The symmetry points are those of the primitive unit cell.

D. The Repulsive Potential

In a one-electron picture, the total energy is given by a sum of three terms: (1) the sum of the one-electron energy eigenvalues which are determined by the Hamiltonian described above; (2) the ion-ion repulsion; and (3) the negative of the electron-electron interaction which is doubly counted in the sum of the one-electron energies. The first of these terms gives rise to an attractive interaction between the atoms, because as the atoms come closer together, the occupied bonding states drop in energy, while the unoccupied antibonding states rise. The sum of the last two terms, on the other hand, gives rise to a repulsive interaction, as it must on physical grounds. In modeling the total energy and resulting forces for molecular dynamics simulations, it is conventional to represent the sum of the last two terms by a sum over repulsive two-body potentials.
TABLE III. Repulsive potential parameters for GaAs and Si. These values are appropriate when distances are measured in Å and energies in eV.

<table>
<thead>
<tr>
<th></th>
<th>α</th>
<th>β</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>263.7</td>
<td>-1227.5</td>
<td>3653.1</td>
</tr>
<tr>
<td>Si</td>
<td>263.2</td>
<td>-1027.0</td>
<td>2631.8</td>
</tr>
</tbody>
</table>

\[ \phi(d_{ij}) : \]

\[ U_{\text{rep}} = \sum_{i < j} \phi(d_{ij}). \]  

(3.12)

The distance between atoms \( i \) and \( j \) is denoted by \( d_{ij} \). The above sum is over all pairs of atoms.

The form of the potential that was used for both GaAs and Si is

\[ \phi(d) = \frac{\alpha}{d^4} + \frac{\beta}{d^6} + \frac{\gamma}{d^8} \]  

(3.13)

where \( d = d_{ij} \) and \( \alpha, \beta, \) and \( \gamma \) are adjustable parameters. Other forms involving different powers of \( d \) have been tested, as well as forms involving exponentials. Reasons for choosing the above form are given in more detail in Section III F.

The parameters \( \alpha, \beta, \) and \( \gamma \) are listed for GaAs and Si in Table III, with distances measured in Å and energies in eV. These parameters were adjusted to reproduce the most important properties in the ground state: the room temperature cohesive energy, interatomic distance, and bulk modulus. These three properties determine the three parameters of the potential, and they roughly correspond to the zeroth, first, and second derivatives of the total energy with respect to the interatomic distance. A description of the fitting procedure will be given in Section III F.

One advantage of the present semiempirical approach is that the true properties of the material are, in a sense, treated more accurately than in even the most sophisticated first-principles calculations. For example, the effect of electron correlations
(on the electronic structure) and the effect of the Pauli principle (on the repulsive interaction) are included in the experimental data which are used to determine the parameters of the present model. However, this model only includes the features that are of dominant physical importance in the present context. It omits other features; for example, the change in the repulsive potential and in the Hamiltonian matrix elements as electrons are promoted from bonding to antibonding states, with a consequent change in the distribution of charge.

**E. The Cutoff Function**

In principle, one could include the forces on atoms to second and even further neighbors. One problem with this scheme is that our tight-binding parameters are fitted only to nearest neighbors. Including second neighbor interactions would require fitting of new parameters, and would have questionable chemical and physical validity. For this reason we have introduced a smooth cutoff, which occurs close to the next nearest neighbor distance $d_{nnn}$. In the case of GaAs, this is the distance (4.00 Å) from one gallium atom to another gallium atom. For each atom in the large unit cell used in the molecular dynamics simulations, a search is done for all other atoms, including replicas of atoms in neighboring unit cells that are translated by a non-primitive lattice translation vector. If the distance between atoms is larger than $d_{nnn}$ then the interaction is omitted. A smooth cutoff is imposed inside the second neighbor distance, because a sudden cutoff would imply a theta function in the repulsive potential and Hamiltonian matrix element, and consequently a delta function or sudden impulse in the forces on atoms.

The cutoff is expressed as a multiplicative factor $C$ in both the tight-binding matrix elements and the repulsive potential:
\[ H_{\alpha,\beta}(k) = \sum_{L,|R_j - R_i| < d_{\text{nnn}}} e^{i k \cdot (R_j - R_i)} t_{\alpha,\beta}(R_j, R_i) C(R_j, R_i) + \epsilon_{\alpha,\beta} \delta_{\alpha,\beta} \]  

(3.14)

and

\[ U_{\text{rep}} = \frac{1}{2} \sum_{i,j} \phi(d_{ij}) C(d_{ij}). \]  

(3.15)

The above comments apply only to the Ga-As or As-Ga interactions which are of dominant importance in the initial stages of the simulations, or the corresponding nearest neighbor Si-Si interactions. Since next nearest neighbors played no role in the fitting of the Hamiltonian or repulsive potential parameters described above, a different prescription has been used in the case of these interactions. For example, Ga-Ga and As-As interactions in GaAs were taken to be zero unless the distance between atoms was less than the nearest neighbor distance. This means that these interactions are not being treated quantitatively, but they are not important in the regime that is of primary interest in the present simulations.

Let us now return to the smooth cutoff function that was used for the most important Ga-As or Si-Si interactions. Before giving the form that was actually used, let us consider another form which has been used previously:

\[ C(d) = \begin{cases} 
1 & : d \leq d_0 \\
\frac{1}{2} \left( \cos \left( \pi \frac{d-d_0}{d_{\text{nnn}}-d_0} \right) + 1 \right) & : d_0 \leq d < d_{\text{nnn}} \\
0 & : d \geq d_{\text{nnn}}.
\end{cases} \]  

(3.16)

We will now see that this form has some disadvantages. Letting \( d = \xi d_0 \) and taking the derivative with respect to \( \xi \), one gets

\[ \frac{\partial C(\xi)}{\partial \xi} = \begin{cases} 
0 & : d \leq d_0 \\
\frac{\pi d_0}{2(d_{\text{nnn}}-d_0)} \left( \sin \left( \pi \frac{\xi d_0 - d_0}{d_{\text{nnn}}-d_0} \right) \right) & : d_0 \leq d < d_{\text{nnn}} \\
0 & : d \geq d_{\text{nnn}}
\end{cases} \]  

(3.17)
and we see that the derivative of the cutoff function is smooth at $\xi = 1$ where we are matching one region to another. Continuing on to the second derivative we encounter a difficulty:

$$\frac{\partial^2 C(\xi)}{\partial \xi^2} = \begin{cases} 
0 & : d \leq d_0 \\
\frac{\pi^2 d_0^2}{2(d_{\text{nnn}} - d_0)^2} \left( \cos\left( \pi \frac{\xi d_0 - d_0}{d_{\text{nnn}} - d_0} \right) \right) & : d_0 \leq d < d_{\text{nnn}} \\
0 & : d \geq d_{\text{nnn}}.
\end{cases}$$

(3.18)

The second derivative can thus be seen to be discontinuous at $d = d_0$, or $\xi = 1$. The calculation of the bulk modulus (which involves the second derivative of the total energy with respect to volume) is therefore problematical.

The resulting discontinuity in the second derivative is apparent from Fig. 9. What is needed is a function that is continuous in the zeroth, first, and second derivatives, so that the contributions to the bulk modulus and other properties are not ambiguous. The required qualitative behavior is reminiscent of that for the Fermi function in statistical mechanics, which goes smoothly from one to zero with increasing values of
the argument. Let us therefore introduce a cutoff function which has the form of a Fermi function:

\[ C(d) = \frac{1}{\exp\left(\frac{d-d_c}{d_w}\right) + 1}. \]  

(3.19)

Here, \(d_w\) corresponds to the width of the falloff and \(d_c\) is the point at which \(C(d)\) is one-half its maximum value. To obtain good qualitative behavior near the equilibrium spacing \(d_0\), this point is taken to be halfway between \(1.2d_0\) and the equilibrium second neighbor distance \(d_{nnn}\); i.e.,

\[ d_c = 1.2d_0 + (d_{nnn} - 1.2d_0)/2. \]  

(3.20)

The width of the falloff of \(C(d)\) is chosen so that the \(1/d^2\) scaling is valid beyond the nearest neighbor distance.

We do not want the falloff to be too rapid because it then behaves as a theta function—exactly what we are trying to avoid. The value of \(d_w = 0.1\) Å satisfies both of the above requirements. The Fermi function cutoff with these values of \(d_c\) and \(d_w\) is plotted in Fig. 10. As can be seen in Fig. 11, the \(1/d^2\) scaling is still good to beyond 30% of the nearest neighbor distance.

The cutoff function of Fig. 10 is clearly continuous in all derivatives. One slight complication with this function is that it is not equal to unity at \(d_0\). Taking \(d_w = 0.1\) Å, and using the values for Si of \(d_0 = 2.35\) Å and \(d_{nnn} = 3.84\) Å we obtain \(C(d_0) = 0.995\). However, this small discrepancy of \(1/200\) does not lead to any error in the actual calculations, since we need only change the tight-binding parameters slightly to give the right results at \(d_0\). Also, \(C(d_{nnn}) = .005\), so we incur only a tiny error at even the next nearest neighbor distance.
FIG. 10. The Fermi function cutoff used in the present simulations. The horizontal axis is the distance between the atoms measured in Å. The values of $d_0 = 2.45$ Å and $d_{nnn} = 4.00$ Å are those of GaAs.

F. Fitting the Repulsive Potential Parameters

As mentioned in Section III D, the parameters $\alpha$, $\beta$, and $\gamma$ in the repulsive potential are fit to the cohesive energy, interatomic distance, and bulk modulus of the material. These correspond respectively to the zeroth, first, and second derivatives of the ground state total energy evaluated at the equilibrium lattice spacing $d_0$. It is not clear how accurate our model is over a wide range of interatomic distances, but the regime of greatest interest in the present simulations is $d \approx d_0$. This is because the central issue in the present simulations is the excitation of the electrons and disruption of the lattice immediately after the laser pulse.

Consider a Taylor series for the energy around the equilibrium separation $d_0$: 
FIG. 11. A comparison of $1/d^2$ and $C(d)/d^2$.

\[
E_{total}(d) = E_{total}(d_0) + \frac{\partial E_{total}}{\partial d} \bigg|_{d_0} (d - d_0) + \frac{1}{2} \frac{\partial^2 E_{total}}{\partial d^2} \bigg|_{d_0} (d - d_0)^2 + \ldots
\]

Given all terms, we would be able to describe the potential (and thus the forces) very well around the equilibrium distance. We cannot get this much data from experiment, but we can fit the first three. This is why we have chosen a parameterization (3.13) involving three parameters, since we will then be able to solve three simultaneous equations.

The cohesive energy $E_{coh}$ is defined as the energy required to separate the atoms to infinity from their equilibrium positions in the solid:


\[ E_{coh} = E_{total} \left|_{d=d_0} \right. - E_{total} \left|_{d=\infty} \right. \cdot \quad (3.22) \]

\( E_{total} \) is the sum of the repulsive and electronic energies. The interatomic distance \( d_0 \) is defined to be the distance at which the total energy is minimized:

\[ \frac{\partial E_{total}}{\partial d} \bigg|_{d=d_0} = 0. \quad (3.23) \]

(The temperature and pressure dependent contributions to the free energy are neglected.) The bulk modulus \( B \) is a second derivative property and therefore is related to the vibrational frequencies. It is defined as

\[ B = V \left( \frac{\partial^2 E_{total}}{\partial V^2} \right) \bigg|_{d=d_0} \quad (3.24) \]

where \( V \) is the volume, in this case the unit cell volume, since the total energy is that of the unit cell.

The total energy is the sum of the electronic and the repulsive energies:

\[ E_{total} = E_{elec} + U_{rep}. \quad (3.25) \]

Previous work\(^{33} \) has used hard core interactions such as \( \alpha/d_{ij}^\beta \). It was found that the optimum value of \( \beta \) was approximately 4 and additional parameters could be introduced, for example, through an exponential falloff:

\[ \Phi(d_{ij}) = \frac{\alpha}{d_{ij}^\beta} (1 - \exp (-\gamma(d_{ann} - d_{ij})^4)) \cdot \quad (3.26) \]

Here \( d_{nnn} \) is the next nearest neighbor distance, approximately about 4.00 Å in GaAs and slightly less in Si. Note that \( U_{rep} \) is zero at the next nearest neighbor distance with this potential. In order to avoid time-consuming and unphysical distant neighbor interactions, we impose the condition

\[ U_{rep} = 0 \text{ for } d > d_{nnn}. \quad (3.27) \]
FIG. 12. $E_{\text{total}}$, $E_{\text{elec}}$, and $E_{\text{rep}}$ per atom as a function of $d/d_0$ for GaAs.

FIG. 13. $E_{\text{total}}$, $E_{\text{rep}}$, and $E_{\text{elec}}$ as functions of $d/d_0$ for Si.
We have replaced the potential of (3.26) by that of (3.13), since the latter form is found to exhibit more stable and simpler behavior in the fitting of the parameters to the experimental properties. We use a cutoff function to bring all interactions (electronic and repulsive) to zero at the next nearest neighbor distance, \(d_{nnn}\). This smooth cutoff function \(C(d)\) has been discussed in detail in Section III E. The total energy along with the repulsive and electronic contributions is shown in Figures 12 and 13.

Let us now describe how to calculate the cohesive energy

\[
E_{coh} = E_{total} \bigg|_{d=d_0} - E_{total} \bigg|_{d=d_{nnn}}
\]

(3.28)

where we go out to \(d_{nnn}\) instead of infinity because of the cutoff function. The repulsive part at \(d = d_{nnn}\) is zero. The electronic part is not zero, but a simple expression for it can be obtained. As the cutoff function \(C(d)\) becomes zero at \(d_{nnn}\), the Hamiltonian matrix elements

\[
H_{\alpha\beta}(\mathbf{k}) = \sum_L e^{i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_i)} t_{\alpha\beta}(\mathbf{R}_j - \mathbf{R}_i) C(d_{ij}) + \epsilon_{\alpha} \delta_{\alpha\beta}
\]

(3.29)

become

\[
H_{\alpha\beta}(\mathbf{k}) = \epsilon_\alpha \delta_{\alpha\beta}.
\]

(3.30)

That is, the Hamiltonian is diagonal, with elements corresponding to the atomic energies \(\epsilon_\alpha\). The electronic energy (i.e., the first term in the total energy) is a sum over occupied states of the expectation value of the Hamiltonian:

\[
E_{elec} = \sum_k n_k \Phi_k^\dagger \cdot \mathbf{H} \cdot \Phi_k.
\]

(3.31)

Here \(n_k\) is the occupancy of the state labeled by \(k\), with \(k\) representing the wavevector \(\mathbf{k}\), the band index \(m\), and a spin index \(\sigma\). Therefore, the electronic energy at \(d = d_{nnn}\) is a sum over the occupied states of diagonal matrix elements:
Here \( f_{m,k} \) is the Fermi function for the energy eigenvalue \( \varepsilon_{m,k} \) which gives the occupancy of this state, and the factor of two is for spins. Thus, the total cohesive energy is given by

\[
E_{\text{coh}} = U_{\text{rep}}|_{d=d_0} + E_{\text{elec}}|_{d=d_0} - 2 \sum_{m,k} f_{m,k} \varepsilon_{m,k}.
\] (3.35)

Table IV gives the cohesive energy, as well as the lattice constant and bulk modulus for both GaAs and Si.

Next, we consider the equilibrium distance between atoms, which corresponds to minimizing the total energy. Let us insert a multiplicative scaling factor \( \xi \) into all lengths, corresponding to scaling of the lattice constant. This implies that every length in the repulsive potential or the Hamiltonian is multiplied by the factor \( \xi \). In the repulsive potential, for example, we have

\[
\Phi(\xi) = \sum_{l=4,6,8} \frac{\alpha}{(\xi d_0)^l} + \frac{\beta}{(\xi d_0)^6} + \frac{\gamma}{(\xi d_0)^8}
\] (3.36)

and taking the derivative with respect to \( \xi \) is easily accomplished.

The derivatives of the Hamiltonian can be simplified. The matrix elements (3.29) contain a phase \( e^{ik \cdot (R_j - R_k)} \) which gets a factor of \( \xi \) in the quantities involving position, but a compensating factor of \( 1/\xi \) in the wavevector \( \mathbf{k} \), so there is no contribution from the phase when taking the derivative with respect to \( \xi \).

The derivatives of the diagonal matrix elements are also zero since these elements are taken to be constant. The off-diagonal matrix elements have a \( 1/d^2 \) dependence, with the directional cosines remaining constant under scaling so that each off-diagonal element \( t \) can be replaced by \( t/\xi^2 \) after scaling, with a derivative of \( -2t/\xi^3 \).
TABLE IV. Comparison of the bulk modulus, lattice constant, and cohesive energy. The (2) and (8) are respectively the two atom (primitive) unit cell and the eight atom (conventional) unit cell. 10 inequivalent special points \(50\) were used in the two atom calculation and one special point \(\mathbf{k} = \frac{2\pi}{a}(\frac{1}{4}, \frac{3}{4}, \frac{3}{8})\) was used in the eight atom case. Values are compared with experiment (Exp), as given in Refs. 42 and 51.

<table>
<thead>
<tr>
<th>Material</th>
<th>(E_{coh}/\text{atom} \ [\text{eV}])</th>
<th>(d_0 \ [\text{Å}])</th>
<th>(B \ [\text{eV/Å}^3])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(2)</td>
<td>-4.64</td>
<td>2.36</td>
<td>0.604</td>
</tr>
<tr>
<td>Si(8)</td>
<td>-4.61</td>
<td>2.36</td>
<td>0.605</td>
</tr>
<tr>
<td>Si(Exp)</td>
<td>-4.64</td>
<td>2.35</td>
<td>0.617</td>
</tr>
<tr>
<td>GaAs(2)</td>
<td>-3.26</td>
<td>2.45</td>
<td>0.480</td>
</tr>
<tr>
<td>GaAs(8)</td>
<td>-3.24</td>
<td>2.45</td>
<td>0.480</td>
</tr>
<tr>
<td>GaAs(Exp)</td>
<td>-3.25</td>
<td>2.45</td>
<td>0.467</td>
</tr>
</tbody>
</table>

Taking advantage of the Hellmann-Feynman theorem (Section IV), which says that the derivatives of the state vectors do not contribute, we can evaluate the derivative of \(E_{elec}\). Substituting (3.29) into (3.31) and taking the derivative with respect to \(\xi\) gives

\[
\frac{\partial E_{elec}}{\partial \xi} \bigg|_{\xi=1} = \frac{\partial}{\partial \xi} \left[ \sum_k n_k \sum_{\langle i \alpha, j \beta \rangle} \Phi^*_{k,(i\alpha)} \right] (3.37)
\]

\[
\times \left( \sum_L e^{i \mathbf{k} \cdot (\mathbf{R}_{j,L} - \mathbf{R}_k)} \frac{1}{\xi^2} \epsilon_{i\alpha,j\beta}(\mathbf{R}_{j,L} - \mathbf{R}_k) C(\xi) + \epsilon_{i\alpha} \delta_{i\alpha,j\beta} \right) \Phi_{k,(j\beta)} \bigg|_{\xi=1}
\]

\[
= \left[ \sum_k n_k \sum_{\langle i \alpha, j \beta \rangle} \Phi^*_{k,(i\alpha)} \right] (3.38)
\]

\[
\times \left( \sum_L e^{i \mathbf{k} \cdot (\mathbf{R}_{j,L} - \mathbf{R}_k)} - \frac{2}{\xi^3} \epsilon_{i\alpha,j\beta}(\mathbf{R}_{j,L} - \mathbf{R}_k) C(\xi) \right) \Phi_{k,(j\beta)} \bigg|_{\xi=1}
\]

where we have left out a term involving the derivative of \(C(\xi)\) because (Section III E)

\[
\frac{\partial C}{\partial \xi} \bigg|_{\xi=1} \cong 0. (3.39)
\]

The diagonal elements \(\epsilon_{i\alpha} \delta_{i\alpha,j\beta}\) were lost in taking the derivatives, but they can be subtracted and added (with a factor of \(-2/\xi^3\)) in order to recover \(H_{i\alpha,j\beta}(\mathbf{k})\):
\[
\left. \frac{\partial E_{\text{elec}}}{\partial \xi} \right|_{\xi=1} = \left[ \sum_k n_k \sum_{(i\alpha)} \sum_{(j\beta)} \Phi_{k,(i\alpha)}^* \left( -\frac{2}{\varepsilon^3} H_{i\alpha,j\beta}(k) + \frac{2}{\varepsilon^3} \varepsilon_{i\alpha} \delta_{i\alpha,j\beta} \right) \Phi_{k,(j\beta)} \right]_{\xi=1} 
\]

Setting $\xi = 1$ at the equilibrium distance, we get:

\[
\left. \frac{\partial E_{\text{elec}}}{\partial \xi} \right|_{\xi=1} = 4 \sum_{m,k} f_{m,k} \left[ -\varepsilon_{m,k} + \sum_{(i\alpha)} \Phi_{m,(i\alpha)}^* (k) \varepsilon_{i\alpha} \Phi_{m,(i\alpha)} (k) \right]_{\xi=1} 
\]

where $\varepsilon_{m,k}$ are the eigenvalues and $\varepsilon_{i\alpha}$ are the diagonal matrix elements. The advantage of (3.41) is that we do not have to determine the derivative of $E_{\text{elec}}$ by an approximation such as

\[
\left. \frac{\partial E_{\text{elec}}}{\partial \xi} \right|_{\xi=1} \approx \frac{(E_{\text{elec}}(\xi + \Delta \xi) - E_{\text{elec}}(\xi - \Delta \xi))}{2 \Delta \xi}. 
\]

In practice, both methods were used, therefore providing a useful check. The second of the three simultaneous equations needed to solve for the parameters is thus

\[
\left. \frac{\partial E_{\text{elec}}}{\partial \xi} \right|_{\xi=1} + \left. \frac{\partial U_{\text{rep}}}{\partial \xi} \right|_{\xi=1} = 0. 
\]

As noted above, the bulk modulus $B$ is defined as

\[
B = V \left. \frac{\partial^2 E_{\text{total}}}{\partial V^2} \right|_{V=V_0} 
\]

where $V$ is the volume, in this case the unit cell volume. The volume of a primitive unit cell, with one Ga and one As, is one-fourth $a^3$, where $a$ is the conventional cube edge\textsuperscript{45,46}. Letting $a = \xi a_0$ and noting that $\sqrt[3]{3}a = 4d$, we find that the volume of a primitive cell is

\[
V = \frac{N_{\text{atoms}}}{8} a^3 = \frac{N_{\text{atoms}}}{8} (\xi a_0)^3
\]

where $N_{\text{atoms}}$ is the number of atoms in the unit cell (2 for the primitive cell and 8 for the cubical).

According to the chain rule, we can replace derivatives with respect to $V$ by derivatives with respect to $\xi$:
\[
\frac{\partial}{\partial V} = \frac{\partial \xi}{\partial V} \frac{\partial}{\partial \xi} = \frac{8}{3 N_{\text{atoms}} a_0^3} \frac{1}{\xi^2} \frac{\partial}{\partial \xi}
\]

so that

\[
B = V \left. \frac{\partial^2 E_{\text{total}}}{\partial V^2} \right|_{V=V_0} = \frac{8}{9 N_{\text{atoms}} a_0^3 \xi} \left( \frac{-2}{\xi} \frac{\partial E_{\text{total}}}{\partial \xi} + \frac{\partial^2 E_{\text{total}}}{\partial \xi^2} \right) \tag{3.49}
\]

The first derivative can be evaluated using (3.41). The second derivative may be evaluated by using

\[
\left. \frac{\partial^2 E_{\text{elec}}}{\partial \xi^2} \right|_{\xi=1} \approx \frac{E_{\text{elec}}(\xi + \Delta \xi) - E_{\text{elec}}(\xi - \Delta \xi)}{2\Delta \xi} \tag{3.50}
\]

or

\[
\left. \frac{\partial^2 E_{\text{elec}}}{\partial \xi^2} \right|_{\xi=1} \approx \frac{E_{\text{elec}}(\xi + \Delta \xi) - 2E_{\text{elec}}(\xi) + E_{\text{elec}}(\xi - \Delta \xi)}{2\Delta \xi} \tag{3.51}
\]

where the prime denotes the first derivative. We have evaluated the bulk modulus for both the primitive and cubical cells, as shown in Table IV using the appropriate value for \( N_{\text{atoms}} \). The 8-atom cubical cell is, of course, the one used in the simulations.

**G. Special Points**

Many electronic properties of crystals involve integrals over the first Brillouin zone of reciprocal space. Examples include the total energy and the dielectric function. Here we will particularly be interested in the Hellmann-Feynman forces, which are determined by the total energy and its dependence on the positions of the atoms.

We use the special points method of Chadi and Cohen\(^{50,52}\) where applicable whenever possible. The essential idea is to replace an integral over the Brillouin zone by
a summation over a small set of well-chosen points. For a simple cubic lattice the 
\( \mathbf{k} = 2\pi/a\left( \frac{1}{4}, \frac{1}{4}, \frac{1}{4} \right) \) point might be a good initial choice. Other larger sets of points can 
then be chosen as needed. The set of four points

\[
\begin{align*}
\mathbf{k}_1 &= \frac{2\pi}{a} \left( \frac{1}{8}, \frac{1}{8}, \frac{1}{8} \right) \\
\mathbf{k}_2 &= \frac{2\pi}{a} \left( \frac{3}{8}, \frac{3}{8}, \frac{3}{8} \right) \\
\mathbf{k}_3 &= \frac{2\pi}{a} \left( \frac{3}{8}, \frac{1}{8}, \frac{3}{8} \right) \\
\mathbf{k}_4 &= \frac{2\pi}{a} \left( \frac{3}{8}, \frac{3}{8}, \frac{1}{8} \right)
\end{align*}
\]

with corresponding weights

\[
w_1 = \frac{1}{8}, \ w_2 = \frac{3}{8}, \ w_3 = \frac{3}{8}, \ w_4 = \frac{1}{8}
\]

(3.53)

gives the next set of points which evaluate the periodic function. The weights are in 
proportion to the number of symmetry related points in the group.

Suppose, for example, that the total electronic energy is to be computed:

\[
E_{\text{elec}} = \sum_k n_k \mathbf{\Phi}^\dagger_k \cdot \mathbf{H} \cdot \mathbf{\Phi}_k
\]

(3.54)

\[
= 2 \sum_{m,k} f_{m,k} \varepsilon_{m,k}.
\]

(3.55)

Letting \( l \) label special points, we would sum over these four points so that

\[
E_{\text{elec}} = 2 \sum_{m,l} w_l f_{m,l} \varepsilon_{m,l}.
\]

(3.56)

The simulations were performed with an 8-atom cubical unit cell, using one special 
point, \( 2\pi/a\left( \frac{1}{8}, \frac{1}{8}, \frac{1}{8} \right) \), and the seven other points in the Brillouin zone that are 
obtained from this one through symmetry transformations. (All eight points must 
be included, because the original crystal symmetry is broken by both the polarization 
of the electromagnetic field and the motion of the atoms.) It is conventional in 
molecular dynamics simulations with a large unit cell to use only one sampling point
in the Brillouin zone (usually the $\Gamma$ or $k = 0$ point), so our use of eight is not a bad approximation. Larger sets of special points were used for parameter-fitting etc. with a 2-atom cell.

**H. Supercell and Periodic Boundary Conditions**

For the simulations we chose a unit cell containing eight atoms, which corresponds to the conventional cube for a face-centered cubic lattice. This cell was shown in Fig. 5. Each side of the cube ($a_0$) is 5.66 Å in the case of GaAs and 5.43 Å in the case of Si. The atoms in this large cell interact with those in neighboring cells; i.e., those translated by simple cubic lattice translation vectors. (The neighboring unit cells were labeled by $L$ in (3.1).) Periodic boundary conditions are imposed, and an atom passing out of the cell on one side is replaced by a replica entering from the other side.

Quantitatively, the replicated unit cells are given by the translations

$$T = n_1 a_1 + n_2 a_2 + n_3 a_3$$

where $a_1 = a_0 \hat{x}$, $a_2 = a_0 \hat{y}$, and $a_3 = a_0 \hat{z}$ are the translation lattice vectors. Consider an atom $i$ that has passed through the boundary and exited the cell in the $L = (n_1, n_2, n_3)$ direction. The position of this atom can then be written

$$R_i (n_1, n_2, n_3) = R_i (0, 0, 0) + T (n_1, n_2, n_3).$$

We therefore need only perform the operation

$$R_i (n_1, n_2, n_3) \to R_i (n_1, n_2, n_3) - T (n_1, n_2, n_3)$$

in order to bring it back into the central cell. This procedure is illustrated in Fig. 14. Although this is done in the program, we always keep track of where this atom would
have been if we had not performed the operation in (3.59). This is important if we are to measure quantities such as the average distance (Section IV B).

The next logical larger cell would be one containing 64 atoms, but to increase the size by a factor of eight would lead to a very large increase in computational expense. The required computer time increases rapidly with the number of atoms $N$, since matrix diagonalization scales as $N^3$. Recall that computational expense is a major issue in the present simulations, because they involve the solution of the time-dependent Schrödinger equation for the electrons with a 50 attosecond time step, in contrast to ordinary molecular dynamics calculations which require time steps of
the order of a femtosecond or more. We believe the size of simulation cell employed here is adequate for studying the phenomenon of primary interest, namely the initial stages of excitation and lattice instability when a laser pulse is applied.

Currently one simulation (with eight special points) takes about 90 minutes on an SGI Power Challenge XL after optimization for serial performance. Also, the Hamiltonian and its derivative fit into one megabyte of cache. A calculation for a 64 atom simulation cell would require hundreds of times more computer time and far more memory. With eight atoms per cell, and five orbitals per atom in an $sp^3s^*$ model, the Hamiltonian matrix is of size $40 \times 40$. The procedure we use for evaluating the Hamiltonian matrix is presented in Appendix D.
IV. ION DYNAMICS

A. Hellmann-Feynman Forces

The electronic forces on the individual ions are determined by the Hellmann-Feynman theorem. In 1985 it was pointed out independently by two groups that the Hellmann-Feynman theorem can be employed in both tight-binding molecular dynamics and first-principles molecular dynamics. More recently, the Hellmann-Feynman theorem has been generalized to apply to both excited states and nonadiabatic processes, as will be discussed in Section V D.

As mentioned previously (Section III D), the total energy consists of various contributions, with the first term obtained from the one-electron Hamiltonian \( H \) and the other terms represented by a repulsive potential. The first term, the electronic energy, is

\[
E_{\text{elec}} = \sum_k n_k \Phi_k^\dagger \cdot H \cdot \Phi_k. \tag{4.1}
\]

The \( n_k \) represents the occupancy of state \( k \). Applying the classical equations of motion to the electronic energy, we have

\[
M_i \ddot{R}_{i,\text{elec}} = -\sum_k n_k \Phi_k^\dagger \cdot \frac{\partial H(k)}{\partial R_i} \cdot \Phi_k \tag{4.2}
\]

\[
- \sum_k n_k \frac{\partial \Phi_k^\dagger}{\partial R_i} \cdot H(k) \cdot \Phi_k
\]

\[
- \sum_k n_k \Phi_k^\dagger \cdot H(k) \frac{\partial \Phi_k}{\partial R_i}.
\]

We have labeled the position of the \( i^{th} \) atom by \( R_i \) and its mass by \( M_i \). Equation (4.2) can be simplified in the special case that the one-electron states \( \Phi_k \) are eigenstates of the Hamiltonian:

\[
H \Phi_k = \varepsilon_k \Phi_k. \tag{4.3}
\]
We can then follow the usual proof of the standard Hellmann-Feynman theorem:

\[ M_i \ddot{R}_i, \text{elec} = - \sum_k n_k \Phi_k^\dagger \frac{\partial H(k)}{\partial \mathbf{R}_i} \cdot \Phi_k \]

\[ - \sum_k n_k \frac{\partial \Phi_k^\dagger}{\partial R_i} \cdot \varepsilon_k \Phi_k \]

\[ - \sum_k n_k \Phi_k^\dagger \varepsilon_k \cdot \frac{\partial \Phi_k}{\partial R_i} \]

\[ = - \sum_k n_k \Phi_k^\dagger \cdot \frac{\partial H(k)}{\partial \mathbf{R}_i} \cdot \Phi_k \]

\[ - \sum_k n_k \varepsilon_k \frac{\partial}{\partial R_i} \left( \Phi_k^\dagger \cdot \Phi_k \right). \]  

(4.4)

As mentioned above, the atomic orbitals in our tight-binding scheme are considered to be Löwdin-like or Wannier-like orbitals which are orthogonalized, so there is no overlap matrix in (4.3). The eigenvectors of the Hermitian matrix \( H \) can be taken to be orthonormal:

\[ \Phi_k^\dagger \cdot \Phi_{k'} = \delta_{k,k'}. \]  

(4.6)

The second term of (4.5) is then zero, because of the constant normalization as expressed in (4.6), and the total force on an ion \( i \) is just

\[ M_i \ddot{R}_i = - \sum_k n_k \Phi_k^\dagger \cdot \frac{\partial H(k)}{\partial \mathbf{R}_i} \cdot \Phi_k - \frac{\partial U_{\text{rep}}}{\partial \mathbf{R}_i}. \]

(4.7)

The factor of \( \frac{\partial H(k)}{\partial \mathbf{R}_i} \) implies that the derivative of each element in the Hamiltonian matrix must be found with respect to the coordinates of each ion in the unit cell. This procedure then yields a matrix of size 40x40x8x3. The evaluation of these matrix elements is discussed in D.

The Hellmann-Feynman theorem just discussed is valid for states \( \Phi_k \) which are eigenstates of the Hamiltonian. It is not immediately obvious that this theorem holds if the state \( \Phi_k \) is not an eigenstate, but rather a state evolved by the time-dependent Schrödinger equation. The generalization to excited states and nonadiabatic processes is discussed in Section VD.
An attractive feature of tight-binding molecular dynamics should be mentioned: In contrast to first-principles molecular dynamics using localized basis functions on the atoms, there are no Pulay corrections, i.e., there are no extra terms reflecting the motion of the basis functions with the atoms.

In the present treatment for heavy atoms (Ga, As, Si), the motion of the atoms is treated classically. Once the forces on each ion are determined, the velocity Verlet algorithm\textsuperscript{37,57} is used to integrate forward in time:

\begin{equation}
\mathbf{R}_i(t + \Delta t) = \mathbf{R}_i(t) + \dot{\mathbf{R}}_i(t) \Delta t + \frac{1}{2} \ddot{\mathbf{R}}_i(t) \Delta t^2
\end{equation}

\begin{equation}
\dot{\mathbf{R}}_i(t + \Delta t) = \dot{\mathbf{R}}_i(t) + \frac{1}{2} [\ddot{\mathbf{R}}_i(t + \Delta t) + \ddot{\mathbf{R}}_i(t)] \Delta t.
\end{equation}

The time step is denoted by $\Delta t$. Atomic vibrations are on a time scale of approximately 100 fs, so a time step shorter than this is required. For the atomic motion alone, a time step of about two femtoseconds was found to be sufficient to conserve energy to one part in $10^6$ during the entire simulation with the Hellmann-Feynman theorem of (4.7). On the other hand, when the electronic dynamics and the effect of the time-dependent electromagnetic field are included, a much shorter time step of 50 attoseconds is necessary for the time-dependent Schrödinger equation. (1 attosecond = $10^{-18}$ second = $10^{-3}$ femtosecond.) With a 50 attosecond time step, the energy is conserved to one part in $10^5$ during the whole simulation. This is, of course, for the case in which there is no applied field, since the energy is increased by excitation of electrons into the conduction bands. Even after the violent perturbation of the system by an intense laser pulse, however, the energy is conserved to about one part in $10^4$. (This result was obtained for the time $t = 200$ fs to $t = 450$ fs with $A_0 = 2.00$ gauss-cm, as in Fig. 19.) The reason that we have slightly poorer energy conservation in treating the electron dynamics is the numerical error in the algorithm for the time-dependent Schrödinger equation (see Section V C).
The ordinary Verlet algorithm,

\[ \mathbf{R}_i(t + \Delta t) = 2\mathbf{R}_i(t) - \mathbf{R}_i(t - \Delta t) + \ddot{\mathbf{R}}_i(t) \Delta t^2 \]  

(4.10)

has been used with good results, but numerically the velocity Verlet algorithm gives less round-off error. The velocity Verlet algorithm also is self-starting, while the ordinary Verlet algorithm requires another method to get from \( t = 0 \) to \( t = 0 + \Delta t \). Both the velocity and ordinary Verlet algorithms guarantee conservation of phase space.

The summation over electronic states involves a summation over both the states at a particular wave vector \( \mathbf{k} \) and over all wave vectors in the Brillouin zone. As discussed in Section III-G, the integration over the whole Brillouin zone is replaced by a summation over special points. In previous molecular dynamics simulations, it has been found that even the single \( \Gamma \) or \( \mathbf{k} = (0, 0, 0) \) point is adequate for a sizable simulation cell, but we prefer to use the \( \mathbf{k} = 2\pi/a(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}) \) point, (together with the points related to it through symmetry transformations), since it provides a better representation for the full Brillouin zone.

Let us now turn to the other part of the total energy, given by the repulsive potential. We must take the gradient of this potential for all atoms in the simulation to obtain the atomic forces:

\[ \mathbf{F}_{l, rep} = -\frac{\partial U_{rep}}{\partial \mathbf{R}_l}. \]  

(4.11)

We then need to evaluate

\[ \frac{1}{2} \sum_{i,j} \frac{\partial \phi}{\partial d} \frac{\partial d}{\partial \mathbf{R}_l} \]  

(4.12)

where \( d \) is the distance between atoms \( i \) and \( j \) and \( l \) denotes the atom which has a force acting on it. Since
\[
\frac{\partial d}{\partial \mathbf{R}_l} = \frac{\partial |\mathbf{R}_i - \mathbf{R}_j|}{\partial \mathbf{R}_l} = \frac{(\mathbf{R}_i - \mathbf{R}_j) \cdot \partial (\mathbf{R}_i - \mathbf{R}_j)}{d} = \frac{(\mathbf{R}_i - \mathbf{R}_j)}{d} (\delta_{il} - \delta_{jl}).
\] (4.13)

we then have

\[
\mathbf{F}_{\text{rep}} = -\frac{1}{2} \sum_{i,j} \frac{\partial \phi}{\partial d_{ij}} \frac{(\mathbf{R}_i - \mathbf{R}_j)}{d_{ij}} (\delta_{il} - \delta_{jl})
\] (4.16)

\[
= -\frac{1}{2} \sum_{j} \frac{\partial \phi}{\partial d_{ij}} \frac{(\mathbf{R}_i - \mathbf{R}_j)}{d_{ij}} - \frac{1}{2} \sum_{i} \frac{\partial \phi}{\partial d_{il}} \frac{(\mathbf{R}_i - \mathbf{R}_l)}{d_{il}}
\] (4.17)

\[
= -\frac{1}{2} \sum_{i} \frac{\partial \phi}{\partial d_{il}} \frac{(\mathbf{R}_i - \mathbf{R}_l)}{d_{il}} + \frac{1}{2} \sum_{i} \frac{\partial \phi}{\partial d_{ii}} \frac{(\mathbf{R}_i - \mathbf{R}_l)}{d_{ii}}
\] (4.18)

\[
= -\sum_{i} \frac{\partial \phi}{\partial d_{ii}} \frac{(\mathbf{R}_i - \mathbf{R}_l)}{d_{ii}}
\] (4.19)

which just states that the total force is the sum of the individual forces \(\frac{\partial \phi}{\partial d_{ii}}\) along the lines joining the pairs of atoms. The interacting atoms must be separated by a distance less than \(d_{nnn}\), as discussed in Section III E.

To begin a simulation, we must first give the atoms initial positions and velocities. We have chosen to let the initial positions be those corresponding to equilibrium in the tetrahedrally bonded (zincblende or diamond) structure. One could give the atoms random positions around equilibrium, but we instead give them random initial velocities. These velocities must satisfy two criteria: (1) the total initial momentum is zero and (2) the total kinetic energy must agree with the equipartition theorem

\[
\frac{1}{2} \sum_{i=1}^{N} M_i \dot{R}_i^2 = \frac{(3N - 3)}{2} kT.
\] (4.20)

\(N\) is the number of ions (each labeled by \(i\)), \(k\) is Boltzmann’s constant, and \(T\) is the temperature (which we here take to be room temperature). There are \(3N - 3\) degrees of freedom since 3 have been removed by keeping the center of mass constant.

Equation (4.20) is satisfied after the atoms have become equilibrated with an exchange of kinetic and potential energy. At the very beginning of the simulations,
the initial velocities are somewhat higher in order that the final temperature be 300K. During the process of equilibration over the first set of time steps, the velocities are adjusted up or down in order to satisfy (4.20) at the end of the equilibration process.

### B. Excited-State Molecular Dynamics

The idea that bonding is disrupted when the electrons are promoted from bonding to antibonding states can be tested by artificially promoting the electrons to excited states. (In the more physical simulations described later, the electrons are promoted by the interaction with the time-dependent vector potential in the applied electromagnetic field, i.e. the laser pulse.)

The Hellmann-Feynman theorem of Equation (4.2) involves a sum over occupied states. In the ground state,

\[
n_k = \begin{cases} 
1 & : n \leq N_F \\ 
0 & : n > N_F 
\end{cases}
\]  

(4.21)

where \(N_F\) is the highest occupied valence band state. Thus, the occupied orbital states are filled in pairs with the available number of electrons. For an eight atom supercell, the number of electrons is 32, hence \(N_F = 16\).

We have performed simulations in which the electrons are artificially excited into the conduction band. This requires modification of only \(n_k\). In promoting the electrons, the highest occupied states are emptied and the lowest conduction band states are filled. The number of electrons is conserved.

Figure 15 shows the average distance as calculated from

\[
R_{\text{avg}}(t) = \frac{1}{N} \sum_{i=1}^{N} |\mathbf{R}_i(t) - \mathbf{R}_i(0)|
\]  

(4.22)

for various levels of excitation in silicon. An equilibration period of 2000 fs is used to begin the simulation, but is not shown in the figure. As indicated in the figure, the
excitation occurs at a time of 50 fs, and for sufficient levels of promotion the lattice begins to exhibit disruption. We see that for excitations between 12.5\% (4/32) and 18.75\% (6/32) the lattice becomes unstable immediately at the point of excitation.

One can understand very simply the origin of the disruption by considering the change in the electronic energy as a function of excitation. This is illustrated in Fig. 16. Each time an electron is promoted from the valence band to the conduction band, an occupied bonding state is lost and an occupied antibonding state is gained,
FIG. 16. $E_{\text{total}}$ as a function of $d/d_0$ for the ground state and for four levels of artificial excitation. These correspond to the simulations for Si shown in Fig. 15.

with an antibonding state acting as the negative of a bonding state. This promotion therefore has a double effect in weakening the bonding and raising the electronic energy. Eventually the effective potential well is nearly lost and the effective equilibrium distance is increased.

Figure 17 shows the corresponding simulation for GaAs. Once again a sufficient excitation disrupts the lattice. In GaAs this occurs immediately after excitation for 6.25% (2/32) and 12.5% (4/32). The change in the potential energy well is very similar to that of Si.
FIG. 17. Average distance moved for GaAs atoms, excited-state molecular dynamics. This is shown as a function of time for varying excitation levels. 32 is the number of valence electrons.
V. ELECTRON-ION DYNAMICS

A. The Peierls Substitution

The inclusion of the interaction of an electromagnetic field with the electrons requires an appropriate modification of the Hamiltonian. One way that this could be accomplished is through an interaction Hamiltonian $H_{int}$ that is based on dipole matrix elements:

$$\langle \alpha, \mathbf{k} | \mathbf{p} \cdot \mathbf{A} | \beta, \mathbf{k}' \rangle.$$  \hspace{1cm} (5.1)

The new Hamiltonian would then be $H_0 + H_{int}$. The problem with this approach is that these matrix elements are not explicitly given in our original tight-binding Hamiltonian. The basis functions are in fact not even known in a tight-binding picture, so these matrix elements cannot be evaluated. One could assume Gaussian or other forms for the localized orbitals, and then evaluate the dipole matrix elements, but it is not at all clear that this would be consistent with the philosophy of semiempirical tight-binding. One could fit new parameters to experimental to data such as those obtained in photoemission and optical experiments. However, previous attempts at doing this have not had quantitative success\textsuperscript{59–61}. As a further reason for not trying this approach, the form (5.1) is valid only for small fields. With larger intensities, as in the case we are studying, a term involving

$$\langle \alpha, \mathbf{k} | \mathbf{A}^2 | \beta, \mathbf{k}' \rangle.$$  \hspace{1cm} (5.2)

would be necessary, further complicating the parameterization just described.

A better approach is to use a substitution due to Peierls which has been successful for time-independent electromagnetic fields, and has been generalized to time-dependent fields by Graf and Vogl\textsuperscript{36}. The starting point is the fact that in the fundamental Hamiltonian of quantum mechanics for electrons, the inclusion of the
vector potential \( \mathbf{A} \) associated with an electromagnetic field is given by the fundamental minimal coupling substitution \( \mathbf{p} \rightarrow \mathbf{p} - \frac{e}{c} \mathbf{A} \), where \( e \) is the charge of an electron. (In this notation, \( e \) is negative.) The corresponding substitution in a tight-binding representation is a replacement of the interatomic matrix element \( t_{i\alpha,j\beta}(\mathbf{R}_{j,L} - \mathbf{R}_i) \) by new matrix elements which incorporate \( \mathbf{A} \). This substitution reflects the gauge invariance of the time-dependent Schrödinger equation.

The procedure is outlined by Graf and Vogl\(^{36}\) and begins with

\[
H(\mathbf{r}, \mathbf{p} - \frac{e}{c} \mathbf{A}(\mathbf{r}, t)) = \exp\left[ -\frac{i e}{\hbar c} \int_{\mathbf{r}} A(s, t) \cdot ds \right] \times H(\mathbf{r}, \mathbf{p}) \exp\left[ \frac{i e}{\hbar c} \int_{\mathbf{r}} A(s, t) \cdot ds \right].
\]  

(5.3)

Here \( ds \) is a line element. \( H(\mathbf{r}, \mathbf{p}) \) denotes the Hamiltonian as a function of canonical variables \( \mathbf{r} \) and \( \mathbf{p} \); i.e., this is the one-electron Hamiltonian that results from applying a variational technique to the total Hartree or Hartree-Fock (H-F) energy of the system\(^6\). Written explicitly,

\[
H(\mathbf{r}, \mathbf{p}) = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{\text{exchange}}(\mathbf{r}).
\]  

(5.4)

It is the Hartree term in the above one-electron Hamiltonian that leads to the double-counting of the total electronic energy, as discussed in Section III D. The transformed Hamiltonian is therefore

\[
H(\mathbf{r}, \mathbf{p} - \frac{e}{c} \mathbf{A}(\mathbf{r}, t)) = \frac{(\mathbf{p} - \frac{e}{c} \mathbf{A}(\mathbf{r}, t))^2}{2m} + V(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{\text{exchange}}(\mathbf{r}).
\]  

(5.5)

The one-electron potential \( V(\mathbf{r}) \), Hartree, and exchange terms are all functions of \( \mathbf{r} \) and not of \( \mathbf{p} \). They therefore are unaffected by the minimal coupling substitution. Formula (5.3) is directly verified by substituting (5.4) into (5.3) to obtain (5.5).

To employ the formula (5.3) in a tight-binding scheme, we recognize that matrix elements with (5.3) are the same as matrix elements obtained from the unperturbed Hamiltonian (5.4) but with the localized basis functions multiplied by \( \frac{ie}{\hbar c} \int_{\mathbf{r}} \mathbf{A} \cdot ds \),
which we approximate by \( \frac{-ie}{\hbar c} \int_{\mathbf{R}_{i,L}}^{\mathbf{R}_{j,L}} \mathbf{A} \cdot d\mathbf{s} \). The result is that the new interatomic matrix element \( t_{i\alpha,j\beta}(\mathbf{R}_{j,L} - \mathbf{R}_{i}) \) is given by the old matrix element \( t_{i\alpha,j\beta}^{0}(\mathbf{R}_{j,L} - \mathbf{R}_{i}) \) times a multiplicative factor:

\[
t_{i\alpha,j\beta}(\mathbf{R}_{j,L} - \mathbf{R}_{i}) = t_{i\alpha,j\beta}^{0}(\mathbf{R}_{j,L} - \mathbf{R}_{i}) \\
\times \exp \left[ -\frac{ie}{\hbar c} (\mathbf{R}_{j,L} - \mathbf{R}_{i}) \cdot \mathbf{A}(t) \right]
\]

We have used the fact that \( \mathbf{A}(t) \) is nearly constant over an interatomic spacing \( d \sim 1 \) Å, since \( \lambda \sim 5000 \) Å for the fields considered here. This method allows us to couple the electrons to the time-dependent electromagnetic field without the addition of any new parameters. We call this approach the time-dependent Peierls substitution\(^{36,63-65}\), since Sir Rudolf Peierls applied it to tight-binding in the early years of quantum mechanics.

B. The Vector Potential

The vector potential consists of an oscillating wave modulated by an envelope. We use a cosine form for the envelope as well as the oscillating part. The explicit form is

\[
\mathbf{A}(t) = A_0 \cos \left( \frac{\pi (t - t_0/2)}{t_0} \right) \cos (\omega t)
\]

where \( t_0 \) is the total time of the pulse (about 140 fs in the experiments of Ref. 4) and \( \omega \) is the angular frequency of the light. The \( \cos \left( \frac{\pi (t - t_0/2)}{t_0} \right) \) factor serves several purposes: (1) it clips the pulse to zero at the beginning and end of the pulse; (2) it gives us a full-width half-maximum of exactly half the pulse length for the intensity, which we will see goes as the square of the vector potential in Appendix A; (3) its square resembles the shape of a Gaussian as shown in Fig. 18 and (4) the slope of \( \cos^2 \left( \frac{\pi (t - t_0/2)}{t_0} \right) \) is zero at the beginning and end of the pulse. The oscillatory nature of light is included with the \( \cos(\omega t) \) term.
FIG. 18. A comparison of two forms for the square of the vector potential. The $\cos^2$ form fits the Gaussian well during most of the pulse, and is naturally clipped. The vertical axis is in arbitrary units.

The most useful gauge to describe an electromagnetic wave is the Coulomb gauge, also called the radiation gauge, in which $\mathbf{A}$ and $\Phi$ satisfy

$$\nabla \cdot \mathbf{A} = 0$$  \hspace{1cm} (5.8)

and

$$\nabla^2 \Phi = -4\pi \rho = 0.$$  \hspace{1cm} (5.9)

Equation (5.9) is Laplace's equation, and therefore the scalar potential has a solution
Far away from the source $\rho$ (or when no source is present), the potential $\Phi$ is zero.

The vector potential $A$ must satisfy the homogeneous wave equation

\begin{equation}
\nabla^2 A - \frac{1}{c^2} \frac{\partial^2 A}{\partial t^2} = 0.
\end{equation}

A solution is provided by

\begin{equation}
A(t, \mathbf{r}) = A_e \left( \frac{\pi}{t_0} \left( t - \frac{\hat{k} \cdot \mathbf{r}}{c} \right) \right) \cos \left( \omega \left( t - \frac{\hat{k} \cdot \mathbf{r}}{c} \right) \right)
\end{equation}

where the specific form of the envelope $A_e$ is left out; it is only important that it is a function of time and distance like $\cos \left( \omega \left( t - \frac{\hat{k} \cdot \mathbf{r}}{c} \right) \right)$ (but with a different inverse period $\pi/t_0$). The form (5.7) satisfies (5.12). In the Peierls substitution, we are only interested in the time variation, so we may drop the spatial part. As mentioned, this was due to the wavelength of the laser pulse being much longer than the size of the unit cell.

This form satisfies the requirements for the Coulomb gauge provided that $A_0 \cdot \mathbf{k} = 0$. This is the condition that the polarization be transverse to the direction of propagation.

C. The Schrödinger Equation

So far we have discussed only the ion dynamics. Though the motion of the atoms (or ions) is an essential part of understanding what occurs in the experiments we are considering, the electrons play an even more crucial role. The movement of the ions affects the states of the electrons, and the electronic states determine the forces on the ions.

To treat the electron dynamics, one must solve the time-dependent Schrödinger equation. This equation can be regarded as resulting from an empirical Lagrangian$^{31}$:
This Lagrangian satisfies Lagrange’s equations of motion for the canonical variables \( R_l, \Psi_k^\dagger, \) and \( \Psi_k \):

\[
\frac{\partial}{\partial t} \frac{\partial L}{\partial \Psi_k^\dagger} = \frac{\partial L}{\partial \Psi_k}.
\] (5.14)

This equation results from the application of a variational principle to (5.13). We then have

\[
i\hbar \frac{\partial \Psi_k^\dagger}{\partial t} = \Psi_k^\dagger \mathbf{H}(t).
\] (5.15)

Taking the adjoint of this equation and using \( \mathbf{H} = \mathbf{H}^\dagger \), one gets the time-dependent Schrödinger equation:

\[
i\hbar \partial \Psi_k / \partial t = \mathbf{H}(t)\Psi_k.
\] (5.16)

The state vector of the \( k^{th} \) electron is labeled \( \Psi_k \). The Hellmann-Feynman theorem applied to excited, nonadiabatic states can also be derived from this empirical Lagrangian (Section V D).

This equation must be solved numerically with a time step \( \Delta t \). The conventional difference equation obtained by letting partials become differences

\[
\Psi_k(t + \Delta t) = -i/\hbar \mathbf{H}(t)\Psi_k(t)
\] (5.17)

does not conserve probability. We therefore need a different method which conserves the norm of the eigenvectors \( \Psi_k^\dagger \cdot \Psi_{k'} = \delta_{k,k'} \). (I.e., we need a method which, like the time-dependent Schrödinger equation, is unitary.) Consider the formal solution to the time-dependent Schrödinger equation

\[
\Psi_k(t + \Delta t) = e^{-i\mathbf{H}(t)\Delta t/\hbar}\Psi_k(t).
\] (5.18)

One way to achieve a norm-preserving algorithm is to use the Cayley form for the exponential[^6]
\[ e^{-i\Delta} \approx \frac{(1 - i\Delta)}{(1 + i\Delta)}. \]  
\text{(5.19)}

This can be derived by simply splitting the exponential of (5.19) into two parts:

\[
\Psi_k(t + \Delta t) = e^{-\frac{iH\Delta t}{\hbar}} \Psi_k(t)
\]
\[
= e^{-\frac{iH\Delta t}{2\hbar}} e^{-\frac{iH\Delta t}{2\hbar}} \Psi_k(t)
\]
\text{(5.20)}

which implies that

\[
e^{-\frac{iH\Delta t}{2\hbar}} \Psi_k(t + \Delta t) = e^{-\frac{iH\Delta t}{2\hbar}} \Psi_k(t).
\]
\text{(5.21)}

Now approximate the exponential by its first two terms

\[
(1 + \frac{iH\Delta t}{2\hbar}) \Psi_k(t + \Delta t) = (1 - \frac{iH\Delta t}{2\hbar}) \Psi_k(t).
\]
\text{(5.22)}

Here \(1\) is the identity matrix. In order to solve for \(\Psi_k(t + \Delta t)\), we must find the inverse of \(1 + \frac{iH\Delta t}{2\hbar}\). With this strategy, we conserve probability to one part in \(3 \times 10^6\) during the whole simulation. In verifying that this algorithm is indeed unitary, we should check to make sure that the eigenvectors remain orthogonal as well as normalized. Orthogonality plays a major role in many aspects of the calculation, including the use of the Hellmann-Feynman theorem.

First, write the adjoint of equation (5.23):

\[
\Psi_{k'}^\dagger(t + \Delta t)(1 - \frac{iH\Delta t}{2\hbar}) = \Psi_{k'}^\dagger(t)(1 + \frac{iH\Delta t}{2\hbar})
\]
\text{(5.24)}

where we have used \(H = H^\dagger\) for the Hermitian matrix \(H\). Multiply (5.23) from the left by (5.24) to obtain

\[
\Psi_{k'}^\dagger(t + \Delta t)(1 - \frac{iH\Delta t}{2\hbar})(1 + \frac{iH\Delta t}{2\hbar}) \Psi_k(t + \Delta t) = \Psi_{k'}^\dagger(t)(1 + \frac{iH\Delta t}{2\hbar})(1 - \frac{iH\Delta t}{2\hbar}) \Psi_k(t)
\]
\text{(5.25)}

which can be simplified to
\[
\Psi_k^\dagger (t + \Delta t) \cdot \Psi_k(t + \Delta t) = \Psi_k^\dagger (t) \cdot \Psi_k(t) + \frac{\Psi_k^\dagger (t) \cdot \mathbf{H}^2 \Delta t^2 \cdot \Psi_k(t)}{4\hbar^2} - \frac{\Psi_k^\dagger (t + \Delta t) \cdot \mathbf{H}^2 \Delta t^2 \cdot \Psi_k(t + \Delta t)}{4\hbar^2}.
\] (5.26)

Thus, the algorithm is good to second order in \(\Delta t\). During the simulations reported below, probability and orthogonality were found to be well preserved with the use of the algorithm (5.23) for \(\Psi_k^\dagger (t + \Delta t)\).

The time step \(\Delta t\) in a simulation must be considerably smaller than the characteristic time scale for the dynamics. The vibrational period associated with atomic motion is of the order of 0.1 picosecond, or 100 femtoseconds\(^{42}\). The corresponding time scale associated with the vibrations of the electromagnetic field in the electron dynamics is of the order of 2 femtoseconds. Thus, unless the time-dependent Schrödinger equation can be integrated analytically over that time period\(^{31}\), one must use a time step which is much smaller than one femtosecond. We have found that a value of 50 attoseconds is sufficient. The reliability of this value can be checked by lowering the time step and seeing if the results remain unchanged.

Higher order algorithms are available. For example, one could write down the next term in the expansion as

\[
e^{-i\Delta} \sim \frac{1 - i\Delta/2 - \Delta^2/8}{1 + i\Delta/2 - \Delta^2/8}.
\] (5.27)

This is accurate to order \((\Delta t)^3\). However, it adds another matrix multiplication, and such multiplication may result in roundoff error as well as computational expense. Fourth-order Runge-Kutta algorithms also exist for solving first-order differential equations like the time-dependent Schrödinger equation\(^{66}\).
D. A Hellmann-Feynman Theorem Appropriate for Nonadiabatic Processes

In Section IV A we showed that interatomic forces could be determined from the Hellmann-Feynman theorem. This theorem is appropriate for both ground and excited states. However, in proving the theorem, the assumption that the state vector $\Phi_k$ is an eigenstate of the electronic Hamiltonian $H$ was used. If we are to solve for the time-evolution of state vectors via the time-dependent Schrödinger equation, then the states will no longer be guaranteed to be eigenstates of the system. The question arises as to whether the Hellmann-Feynman theorem is still valid when the electrons are in excited states and undergoing transitions.

In Ref. 31, the Hellmann-Feynman theorem was generalized to apply to both excited states and nonadiabatic processes$^{31}$. This is actually a consequence of Ehrenfest’s theorem$^{67}$:

$$\frac{d}{dt} \langle \mathbf{p} \rangle = -\langle \nabla V \rangle. \quad (5.28)$$

Ehrenfest’s theorem expresses the correspondence between classical dynamics and the expectation values in quantum dynamics. If one removes the angular brackets in (5.28), one has in fact the usual statement of Newton’s second law of motion. As mentioned above, the atomic orbitals in our tight-binding scheme are considered to be Löwdin-like or Wannier-like orbitals which are orthogonalized, so that the overlap between neighboring wavefunctions is zero. Then the force on ion $i$ is

$$M_i \ddot{\mathbf{R}}_i = -\sum_k \Psi_k^* \cdot \frac{\partial H(k)}{\partial \mathbf{R}_i} \cdot \Psi_k - \frac{\partial U_{rep}}{\partial \mathbf{R}_i}. \quad (5.29)$$

where $M_i$ and $\ddot{\mathbf{R}}_i$ are the mass and acceleration of the this ion. The $n_k$ is left out, because an electronic state $\Psi_k$ has been chosen to represent each electron $k$.

Use of the empirical Lagrangian of Section V C will give the result (5.29). This is accomplished by using the canonical variables $\mathbf{R}_i$ and $\ddot{\mathbf{R}}_i$ in the Lagrangian equations.
of motion. The original proof of Ref. 31 was given in a first-principles context, but yields a result equivalent to (5.29).

E. Electron Occupancy

Electrons are excited to conduction band states when the electromagnetic field is applied. They are assumed to occupy the lowest lying states initially. In a time-dependent self-consistent field picture, each electron is regarded as having its own quantum state $\Psi_l$. Each of these time-dependent states evolves according to the time-dependent Schrödinger equation. On the other hand, one can define $\Phi_m$ to be an eigenvector of the time-dependent Hamiltonian. As the electrons are promoted to excited states via the application of an electromagnetic pulse, we are interested in seeing how the occupancy of the bands changes. This is determined by projecting the time-dependent electron wavefunction $\Psi_l$ onto the eigenstates $\Phi_m$. As usual, the probability that electron $l$ is in an eigenstate $m$ is given by the square of the probability amplitude $\Psi_l^*(t) \cdot \Phi_m(t)$. The total occupation for the electrons to be in the valence bands, for example, is the sum of over all of the electrons $l$ of this probability amplitude squared and a sum over all valence band states $m$.

To determine the occupancy of the $m^{th}$ band $n_m(t)$, therefore, we calculate

$$n_m(t) = \sum_l |\Psi_l^*(t) \cdot \Phi_m(t)|^2.$$  \hspace{1cm} (5.30)

To review the ideas of the proceeding paragraph, the term $\Psi_l^*(t) \cdot \Phi_m(t)$ is the probability amplitude that an electron (labeled by $l$) is in the $m^{th}$ band, $\Phi_m(t)$ is an eigenvector of the Hamiltonian at time $t$, and $\Psi_l(t)$ is the electron state vector which has been integrated forward in time via the time-dependent Schrödinger equation. The probability is given by the modulus squared, and summing this probability over all the electrons gives the total probability occupying the $m^{th}$ band. With this no-
tation, \( l \) and \( m \) contain a wavevector index. Explicitly indicating the dependence on the wavevector \( \mathbf{k} \), we have

\[
n(m, \mathbf{k}) = \sum_l |\Psi_l^1(\mathbf{k}, t) \cdot \Phi_m(\mathbf{k}, t)|^2.
\] (5.31)

We will be interested in knowing how many electrons have been excited to the conduction band at a given special point \( \mathbf{k} \). If this occupancy is denoted by \( n^{c,b}(\mathbf{k}) \), it can be calculated from

\[
n^{c,b}(\mathbf{k}) = \sum_{m>N_F} \sum_l |\Psi_l^1(\mathbf{k}, t) \cdot \Phi_m(\mathbf{k}, t)|^2
\] (5.32)

where the summation extends over the bands \( m \) from the level just above the Fermi level \( N_F \) to the highest band. The total excited electron occupancy \( n^{c,b} \) is given by the sum over these \( \mathbf{k} \)-points with their appropriate weightings:

\[
n^{c,b} = \sum_{\mathbf{k}} w(\mathbf{k}) n^{c,b}(\mathbf{k}).
\] (5.33)

For the molecular dynamics simulations of primary interest, eight special points were used, as discussed in Section III G. The excitations cited in Section VI are all average occupations as in (5.33).
VI. SEMICONDUCTORS UNDER INTENSE LASER EXCITATION

In this section, we apply the methods discussed in Section V to the interaction of ultra-intense, ultrashort laser pulses with semiconductors. We have attempted to use laser pulses, shapes, strengths, durations, and frequencies similar to those used in the experiments of Glezer et al. and Sokolowski-Tinten et al. The duration of these pulses was 140 fs in GaAs for the experiments of Glezer et al. and 150 fs in the experiments of Sokolowski-Tinten et al. for Si and GaAs.

Each simulation began with an equilibration run of 2000 fs using the ordinary Hellmann-Feynman theorem of Equation (4.7). This assures that the ion motion is randomized and that the average kinetic energy corresponds to room temperature. In the plots to be shown below, the clock is reset in the sense that the origin of time is taken to be the end of the initial equilibration run. At a time of 50 fs after the equilibration has been concluded, the lowest occupied eigenvectors are selected as the initial electron state vectors $\Psi_k$. These state vectors are then allowed to evolve via the time-dependent Schrödinger equation. The electromagnetic pulse is applied at this time of 50 fs, and the dynamics is obtained for the following 400 fs. As mentioned earlier (Section III), the interactions between nearest neighbor atoms (gallium-arsenic, or silicon-silicon) are treated with a smooth cutoff function. On the other hand, the less physically meaningful second neighbor interactions (e.g., Ga-Ga or As-As) are treated with a theta function cutoff, so that these interactions do not come into play until the original second neighbor atoms have moved through a relative distance of 1.5 Å starting at their equilibrium positions.

In the simulations it is necessary to use the special point $(2\pi/a)(1/4, 1/4, 1/4)$ and seven equivalent points in the remainder of the Brillouin zone. These other symmetry-related special points are needed because the symmetry of the Hamiltonian is broken by the application of the electromagnetic field and the motion of the atoms. It should
be mentioned that only the usual set of special points (in the irreducible wedge of the first Brillouin zone) was needed in the fitting of the repulsive potential parameters, because there the size of the cell was changed isotropically.

A time step of 50 attoseconds was used in treating both the electron and the ion dynamics, even though a longer time step would be sufficient for the ions. To test the adequacy of this time step we performed simulations at shorter and shorter time steps. The results for steps smaller than 50 attoseconds were within 3% of the 50 attosecond results for the average distance and occupation. This is within the accuracy that is required for the present simulations.

A. GaAs

Figure 19 shows the average distance that the atoms moved, starting from their equilibrium positions, as calculated from

\[ R_{\text{avg}}(t) = \frac{1}{N} \sum_{i=1}^{N} |\mathbf{R}_i(t) - \mathbf{R}_i(0)| \]  

for various pump intensities in the case of GaAs. The unit of distance is 1 Å, and the equilibrium nearest neighbor distance for GaAs is 2.45 Å. As is conventional in molecular dynamics simulations, periodic boundary conditions are imposed at the edges of the cube containing eight atoms (4 As and 4 Ga). In computing the average of (6.1), an atom is followed even if it leaves its original unit cell. (It is replaced by a replica that emerges from the opposite side of the cell, as discussed in Section III H). The pulse is indicated by a thin solid line, indicating the duration over which it occurs. The factors \( A_0 \) are chosen so that the fluence (which goes as \( A_0^2 \)) increases linearly. That is, \( A_0 = \{0.00, 1.00, 1.41, 1.73, 2.00, 2.45, 2.83\} \) gauss-cm correspond to fluences \( F \propto \{0.00, 1.00, 2.00, 3.00, 4.00, 6.00, 8.00\} \) kJ/m\(^2\). The precise correspondence is given by Eq. (A22) of Appendix A, with, e.g., \( A_0 = 2 \) gauss-cm corresponding to \( F = 3.26 \) kJ/m\(^2\) for the fluence inside the crystal.
For no applied field ($A_0 = 0.00$ gauss·cm) and pulse strengths of $A_0 = 1.00$ gauss·cm and $A_0 = 1.41$ gauss·cm, the material is stable and shows normal equilibrium oscillations. In Fig. 20, the number of electrons excited by the pulse is plotted for various intensities, as calculated from (5.32). The fact that no electrons are excited when no field is applied is a useful check of the algorithm and computer code. An applied field corresponding to $A_0 = 1.00$ gauss·cm leads to an excitation population.
FIG. 20. Electronic excitation for GaAs, as a percentage of valence electrons. This is shown as a function of time for varying pulse intensities. The pulse is indicated by a solid line.

of roughly 1%. (Once again, this is a test of the model, algorithm, and computer program, since we do see electronic excitation as a result of applying an oscillating electromagnetic field using the Peierls substitution described in Section V A.)

As the intensity is increased to $A_0 = 1.73$ gauss·cm, the material exhibits larger oscillations. The graph of the average position in Fig. 19 does not make it clear
whether or not the material has become unstable at this intensity, but this will become more clear when the results are discussed for the pair correlation function below. (It will be found, in fact, that the lattice is stable at this intensity.) The level of excitation is now 5%; i.e., about 5% of the electrons have been excited from the valence bands to the conduction bands. Notice that this excitation amount is less than the threshold excitation of roughly 10% that was obtained in the case of an artificial promotion of electrons, as discussed in Section IV B.

The excitation has increased to 10% and 12% for an intensities of \( A_0 = 2.00 \) gauss-cm and \( A_0 = 2.45 \) gauss-cm. In Fig. 19 it can be seen that the GaAs lattice has become slightly unstable for these intensities. The bumps in the curves at these intensities correspond to Ga-Ga and As-As (i.e., second neighbor) interactions after the atoms have left their equilibrium positions and moved a considerable distance. This is a strong signature that the material has lost its crystalline structure.

At the largest intensity of \( A_0 = 2.83 \) gauss-cm shown in Fig. 19, even the Ga-Ga and As-As interactions are not sufficient to prevent diffusion on a relatively short time of a few hundred femtoseconds. Our model was constructed to provide a realistic description of the behavior of electrons and ions during and immediately after the application of the laser pulse, so the validity of the model on much longer time scales is questionable. However, it is not unreasonable that at large intensities enough energy has been absorbed to cause a melting and diffusive motion of the atoms. Although we believe the present model is adequate in the regime of primary interest, namely on a relatively short time scale of approximately 300 femtoseconds starting at the beginning of the laser pulse, there are a number of effects on longer time scales that are not incorporated in the model. For example, in Fig. 20 it can be seen that the occupancy of the excited states remains constant after the pulse has been turned off. In reality there are various mechanisms which would cause a relaxation
FIG. 21. Electronic energy eigenvalues at the \((2\pi/a)(1/4,1/4,1/4)\) point as a function of time with \(A_0 = 0.00\) gauss-cm for GaAs.

of the excited state electron distribution. These include spontaneous emission due to vacuum fluctuations (the treatment of which would require second quantization of the electromagnetic field), electron-electron interactions (associated with many-body effects), and the emission of phonons (which are associated with quantization of the atomic motion). In addition, the present model does not include electron-hole recombination and carrier diffusion in any realistic sense.

Figure 21 shows the electronic energy eigenvalues at the \(\mathbf{k} = (2\pi/a)(1/4,1/4,1/4)\) point of the Brillouin zone as a function of time. These are the eigenvalues of the time dependent Hamiltonian. There is a clearly recognizable band gap at this wavevector \(\mathbf{k}\), between about -0.5 eV to 2.0 eV. This is not the fundamental band gap of GaAs at the \(\Gamma\) point (\(\mathbf{k} = 0\)) which extends from 0.0 eV to 1.5 eV. Oscillations in Figure 21 on a time scale of roughly 100 fs are observed. These result from the atomic motion, which
FIG. 22. Electronic energy eigenvalues at the \((2\pi/a)(1/4,1/4,1/4)\) point as a function of time with \(A_0 = 1.00 \text{ gauss-cm}\) for GaAs.

FIG. 23. Electronic energy eigenvalues at the \((2\pi/a)(1/4,1/4,1/4)\) point as a function of time with \(A_0 = 1.41 \text{ gauss-cm}\) for GaAs.
FIG. 24. Electronic energy eigenvalues at the \((2\pi/a)(1/4,1/4,1/4)\) point as a function of time with \(A_0 = 1.73\) gauss·cm for GaAs.

has a characteristic vibrational period of roughly 100 fs. These atomic vibrations cause only small modulation of the band structure, on the order of 0.2 eV.

Now let us turn from the case of no applied field to cases of fields with a strength of \(A_0 = 1.00\) gauss·cm to \(A_0 = 1.73\) gauss·cm, as shown in Fig. 22 through Fig. 24. The slower oscillations discussed immediately above for the case of no field are still present, but there are now some very rapid oscillations between 50 and 150 fs. These are, of course, due to the applied electromagnetic pulse. We have chosen to diagonalize the full time-dependent Hamiltonian, i.e., the Hamiltonian with the Peierls factor included. The rapid oscillations simply correspond to the period of oscillation of roughly two femtoseconds, corresponding to a photon energy of roughly 2.0 eV.

The energy gap between valence and conduction band states has begun to diminish for an intensity of \(A_0 = 2.00\) gauss·cm, as shown in Fig. 25. As the pulse intensity
FIG. 25. Electronic energy eigenvalues at the \((2\pi/a)(1/4,1/4,1/4)\) point as a function of time with \(A_0 = 2.00\) gauss-cm for GaAs.

FIG. 26. Electronic energy eigenvalues at the \((2\pi/a)(1/4,1/4,1/4)\) point as a function of time with \(A_0 = 2.45\) gauss-cm for GaAs.
is further increased to $A_0 = 2.45$ gauss-cm (Fig. 26), there is a clear change in the qualitative behavior of the bands. In Fig. 27 the band gap has closed up, corresponding to metallic behavior as the tetrahedral lattice has become quite unstable. We thus see that band gap collapse occurs due to purely structural effects.

The motivation of the present work is to determine whether lattice destabilization and band gap collapse can be explained through the excitation of the electrons. As seen above, this answer has a positive answer. We have omitted other effects which can additionally lead to band gap collapse. These include band gap renormalization (due to the change in the potential felt by the electrons), screening (due to carriers in the conduction band), and the effects of exchange and correlation. These effects are sure to play some role, but the results of our calculations indicate that the dominant role is played by structural changes due to the changes in the chemical bonding as
electrons are excited. It should be mentioned that the experiments of Ref. 4 indicate that screening cannot account for all of the band gap collapse in the material.

We have determined the fluence that these pulse strengths \( A_0 \) correspond to for the case of a vacuum. This is discussed in Appendix A. We realize that this is only a first approximation, however, the full treatment would require knowledge of the boundary conditions as a function of time, which is even in principle a difficult task. The estimate for the relation between the vector potential strength and the fluence \( F \) is found to be:

\[
F [\text{kJ/m}^2] = 0.815 (A_0 [\text{gauss \cdot cm}])^2
\]

where the brackets denote units. When \( A_0 = 2.00 \text{ gauss \cdot cm} \), which we have seen to be roughly where the disruption occurs, we get a fluence of \( F = 3.26 \text{ kJ/m}^2 \). This is comparable to the values seen in the experiments: \( 1.0 \text{ kJ/m}^2 \) in Ref. 4 and \( 1.7 \text{ kJ/m}^2 \) in Ref. 6.

The average Ga-As bond length is shown in Fig. 28. This bond length is \( 2.45 \text{ Å} \) in the equilibrium structure. For stable runs, the bond length fluctuates by only a small amount. However, once the lattice loses its stability, the bond length increases rapidly. This is an indication that the lattice is unstable for intensities greater than about \( A_0 = 2.0 \text{ gauss \cdot cm} \).

It is difficult to determine from the average distance moved whether the material is losing its crystal structure as the intensity is increased. For this reason we have calculated the pair correlation function as it evolves during the simulation. We define the pair correlation function using the normalized number of atoms within particular distance ranges. Specifically, a search is made by: (1) choosing an atom in the unit cell; (2) finding the distances to all other atoms both inside and outside the central cell; (3) counting how many of these other atoms are in each distance range, with increments of \( 0.25 \text{ Å} \); (4) repeating steps (1), (2), and (3) for all other atoms in the
FIG. 28. Average bond length in GaAs as a function of time, for varying pulse intensities. As in the preceding figures, the pulse is indicated by the solid line between 50 and 200 fs.

unit cell; and (5) normalizing by dividing by the number of atoms in the unit cell, which is 8 in the present simulations.

In the equilibrium structure, we should see peaks and at the first, second, third, etc. nearest neighbors. As shown in Fig. 29, for the case of no applied field, there are four nearest neighbors \((0.75 + 3.25)\) near \(2.5\) Å. There are then 12 neighbors at the next nearest neighbor distance of \(4.00\) Å, and another 12 neighbors at the third
FIG. 29. The pair correlation function for GaAs at a time of 75 fs in the case of no applied field. The impulses indicate the number of neighbors in bins of size 0.25 Å at distances from 0.0 to 5.0 Å.

nearest neighbor distance. We have purposely not smoothed the pair correlation function, in order to indicate that we are dealing with a finite number of atoms in the unit cell.

In Fig. 30, we show the time evolution of the pair correlation function over the duration of the simulation. There are only very minor modifications as the ions move about their equilibrium lattice positions. The same is true for intensities from $A_0 = 1.00$ gauss·cm to $A_0 = 1.73$ gauss·cm, as illustrated in Figs. 31, 32, and 33.

As the intensity is increased further, to $A_0 = 2.00$ gauss·cm (Fig. 34), the peaks at the second and third nearest neighbors have decreased and broadened. This is
FIG. 30. Time evolution of the pair correlation function for GaAs at a field intensity of $A_0 = 0.00$ gauss-cm.

FIG. 31. Time evolution of the pair correlation function for GaAs at a field intensity of $A_0 = 1.00$ gauss-cm.
FIG. 32. Time evolution of the pair correlation function for GaAs at a field intensity of $A_0 = 1.41$ gauss-cm.

FIG. 33. Time evolution of the pair correlation function for GaAs at a field intensity of $A_0 = 1.73$ gauss-cm.
FIG. 34. Time evolution of the pair correlation function for GaAs at a field intensity of $A_0 = 2.00$ gauss-cm.

FIG. 35. Time evolution of the pair correlation function for GaAs at a field intensity of $A_0 = 2.45$ gauss-cm.
FIG. 36. Time evolution of the pair correlation function for GaAs at a field intensity of
$A_0 = 2.83$ gauss·cm.

also seen for $A_0 = 2.45$ gauss·cm in Fig. 35. For the intensity of $A_0 = 2.83$ gauss·cm,
which we saw previously to show diffusive behavior, the first to second neighbor valley
has been completely filled in (Fig. 36). There is certainly no new crystal structure,
as there are no new valleys that have opened up.

B. Si

The results for silicon are very similar to those for gallium arsenide, as first in-
dicated by Fig. 37. We have subjected both to pulses of exactly the same strength,
duration, and polarization. The principal difference between the results is that Si
undergoes a structural instability at slightly lower intensities than GaAs. This at
first seems counterintuitive, because Si is a smaller atom with stronger bonding than
GaAs. (Ga and As lie in the same row of the periodic table as germanium, and the
bonding strength increases as one goes up in the periodic table from larger atoms to smaller atoms in the sequence Pb, Sn, Ge, Si, C, with the strongest bonds of all in the diamond structure. However, the band gap is smaller for Si than for GaAs, 1.1 eV as opposed to 1.5 eV, because of the homopolar as opposed to heteropolar character of the bonding, and one expects larger excitation and greater disruption for a smaller
FIG. 38. Electronic excitation for Si, as a percentage of valence electrons. This is shown as a function of time for varying pulse intensities. The pulse is indicated by a solid line.

This is borne out by a comparison of the occupancy of excited states in Figures 20 and 38. For example, for $A_0 = 2.00$ gauss·cm, one can see that about 10% of the electrons are excited in the case of GaAs (Fig. 20), and about 15% in the case of Si (Fig. 38).

Figure 39 summarizes the results for the population of electrons in excited states,
FIG. 39. The degree of excitation with increasing values of the fluence (or $A_0^2$) for GaAs and Si.

in the cases of both GaAs and Si. At low fluences the amount of excitation is not linear. As the fluence is increased, a linear dependence is approximately approached. What is most apparent is that, for the same intensity, Si is more excited than is GaAs.

Silicon begins exhibit disruption at about the same intensity of $A_0 = 2.00$ gauss·cm as gallium arsenide. It has been seen in the experiments that GaAs and Si show permanent damage at the same intensities. The reason for this seems to be that, although the bonding is stronger in Si, the band gap is smaller and the joint density of states is larger, leading to stronger excitation levels for the same electromagnetic field, which in turn leads to greater loss of the initial bonding.

Once again, disruption at an intensity of $A_0 = 2.00$ gauss·cm is further indicated by a plot of the average bond length. This is shown in Fig. 40. Although the
average bond length increases by almost 30%, this is what might be expected from a consideration of how the total energy as a function of distance behaves as electrons are promoted. (See Fig. 16.) Our tight-binding model naturally changes the interatomic forces as excitation occurs.

The band structure as a function of time for Si is similar to that of GaAs, as seen in Figs. 41-47. The atomic vibrations are more rapid than for GaAs (because of
FIG. 41. Electronic energy eigenvalues at the \((2\pi/a)(1/4,1/4,1/4)\) point as a function of time with \(A_0 = 0.00\) gauss-cm for Si.

FIG. 42. Electronic energy eigenvalues at the \((2\pi/a)(1/4,1/4,1/4)\) point as a function of time with \(A_0 = 1.00\) gauss-cm for Si.
FIG. 43. Electronic energy eigenvalues at the \((2\pi/a)(1/4, 1/4, 1/4)\) point as a function of time with \(A_0 = 1.41\) gauss-cm for Si.


the smaller atomic mass and stronger bonding), and the band gap begins to collapse for slightly lower intensities. This is because silicon reaches the diffusive regime at a slightly lower intensity of \(A_0 = 2.45\) gauss-cm as opposed to \(A_0 = 2.83\) gauss-cm in GaAs. As discussed earlier, we find that these structural disruptions are primarily responsible for the band gap collapse. We mention that there appears to be a small exception to the constancy of the electron occupancy after the pulse, at the higher intensities in Fig. 38. This is due to the onset of a metallic band structure. As shown in Fig. 47, the conduction and valence bands in fact overlap after the laser pulse. Notice that the first overlap occurs at about 260 fs. This is exactly where the first wiggle appears in Fig. 38 for an intensity of \(A_0 = 2.45\) gauss-cm. We can understand the wiggles in the electron excitation percentage as resulting from the bands keeping the same orbital character as they cross each other, and from our classification of


FIG. 44. Electronic energy eigenvalues at the $(2\pi/a)(1/4,1/4,1/4)$ point as a function of time with $A_0 = 1.73 \text{ gauss-cm}$ for Si.

“excited” states as being those derived from the original conduction bands.

The pair correlation function shows similar features to those seen for GaAs (Figs. 48-54). As the lattice begins to show disruption at $A_0 = 2.00 \text{ gauss-cm}$, the valley between the first and second neighbor distances begins to fill in. For smaller intensities, this valley is unaffected. For larger intensities, the second and third neighbor peaks broaden out.
FIG. 45. Electronic energy eigenvalues at the $(2\pi/a)(1/4,1/4,1/4)$ point as a function of time with $A_0 = 2.00$ gauss-cm for Si.

FIG. 46. Electronic energy eigenvalues at the $(2\pi/a)(1/4,1/4,1/4)$ point as a function of time with $A_0 = 2.24$ gauss-cm for Si.
FIG. 47. Electronic energy eigenvalues at the \((2\pi/\alpha)(1/4, 1/4, 1/4)\) point as a function of time with \(A_0 = 2.45\) gauss-cm for Si.

FIG. 48. Time evolution of the pair correlation function for Si at a field intensity of \(A_0 = 0.00\) gauss-cm.
FIG. 49. Time evolution of the pair correlation function for Si at a field intensity of $A_0 = 1.00$ gauss-cm.

FIG. 50. Time evolution of the pair correlation function for Si at a field intensity of $A_0 = 1.41$ gauss-cm.
FIG. 51. Time evolution of the pair correlation function for Si at a field intensity of $A_0 = 1.73$ gauss·cm.

FIG. 52. Time evolution of the pair correlation function for Si at a field intensity of $A_0 = 2.00$ gauss·cm.
FIG. 53. Time evolution of the pair correlation function for Si at a field intensity of $A_0 = 2.24$ gauss-cm.

FIG. 54. Time evolution of the pair correlation function for Si at a field intensity of $A_0 = 2.45$ gauss-cm.
VII. DIELECTRIC FUNCTION

In the experiments of Glezer et al., both the real and imaginary parts of the dielectric function were measured at 2.2 and 4.4 eV. Through probing at successive times after the initial pulse, the time evolution of the dielectric function could be determined, but only at these two energies. The results of the experiments indicated that the dielectric function changes were due to interband contributions to the optical susceptibility. This is in contrast to the usual interpretation that free carriers (which have been excited by the pump) are responsible for the optical changes. That is, the Drude model assumes that the interband contributions remain constant. It is clearly of great interest to see whether our model can describe the observed changes in the dielectric function due to intense laser excitation.

It is not a priori obvious whether one can perform reliable calculations of the dielectric function as a function of frequency (or photon energy) using a tight-binding formalism. We will now show, however, that good results can be obtained for this quantity using the proper formulation.

Let the imaginary part of the dielectric function be denoted \( \text{Im}[\varepsilon(\omega, t)] \). The resulting expression for the imaginary part of the dielectric function is\(^{36}\):

\[
\text{Im} \varepsilon(\omega) \propto \frac{1}{\omega^2} \sum_{n,m,k} \left[ f_n(k) - f_m(k) \right] \\
\times p_{nm}(k) \cdot p_{mn}(k) \delta(\omega - \omega_{mn}(k))
\]

where

\[
p_{nm}(k) \propto \sum_{i,\alpha,j,\beta} \phi_{\alpha\beta}^{i}(n,k) \sum_{L} i(R_{j\beta,L} - R_{i\alpha}) \\
\times e^{i(k \cdot (R_{\beta,L} - R_{\alpha}))} \delta_{i,\alpha,j,\beta}(R_{j,L} - R_{i}) \phi_{j\beta}(mk).
\]

In these equations, \( \omega \) is the angular frequency, \( f_n(k) \) is the occupancy of the state with band index \( n \) and wavevector \( k \), \( \delta(\omega - \omega_{mn}) \) is the Dirac delta function, and
\[ \omega_{mn} = \omega_m - \omega_n. \]

As before, \( \alpha \) and \( \beta \) are orbital indices. The result (7.1) is the standard self-consistent field dielectric function that comes from linear response theory, except applied to the tight-binding Hamiltonian. We have chosen only to evaluate the imaginary part of the dielectric function in arbitrary units. The authors of Ref. 36 have determined the complete quantity, and their results agree with experiment to within a factor of two.

This formula includes the joint density of states \( 1/\omega^2 \sum_{n,m}[f_n(k) - f_m(k)]\delta(\omega - \omega_{mn}(k)) \). Notice also that matrix element effects are included through the matrices.
The occupation difference \( [f_n(k) - f_m(k)] \) is approximated by averaging over the special point \( k_0 = \frac{2\pi}{a} (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}) \) and its seven symmetry related points, since these are the points at which the time-dependent Schrödinger equation is solved. The delta function in (7.1) must additionally be approximated. We use a Gaussian

\[
\delta(\omega) \approx \frac{1}{\sqrt{\pi}} \frac{e^{-\left(\frac{n\omega}{\epsilon}\right)^2}}{\epsilon}
\]  

(7.3)

with width \( \epsilon = 0.3 \) eV. We also calculate the dielectric function at 0.1 eV intervals.

Our results for the imaginary part of the dielectric function are shown in Fig. 55 and are compared with experiment\(^{24}\). The characteristic absorption peaks occur in the right locations, although the relative magnitude of these peaks is not precisely correct. It should be mentioned that these results are considerably better than those obtained using only the joint density of states and without including proper matrix elements effects.

When determining the imaginary part of the dielectric function during the simulation, we use 512 points in reciprocal space. Even and odd permutations are used, as it is not obvious whether or not the result (7.1) changes sign under inversion, especially when the atoms are not in their equilibrium positions. Still, these points probably have some redundancy. We have opted for the brute force method, as the computational expense required to calculate the dielectric function is not the major factor in the present simulations. The points are:

\[
k_{n_1, n_2, n_3} = \frac{1}{16}(n_1, n_2, n_3)
\]

(7.4)

where

\[
n_1, n_2, n_3 = \pm 1, \pm 3, \pm 5, \pm 7.
\]

(7.5)

Using this explicit method, every point has the same weight. This method is certainly highly redundant when the material is in the equilibrium structure.
Our calculations for the imaginary part of the dielectric function in Si are shown in Fig. 56. When compared with experimental results\textsuperscript{24}, agreement is even better than for GaAs. Not only do the characteristic absorption peaks occur in the right locations, their relative magnitudes are correct.

Figure 57 shows the time evolution of the dielectric function for the case of no applied field over an energy range of 1.5 to 6.0 eV. The time is given by the axis pointing out of the page. Nothing remarkable is seen, and the dielectric function remains constant. The same is true when the intensity of the applied electromagnetic field is
FIG. 57. Time evolution of $\text{Im}(\epsilon(E))$ with GaAs for a field intensity of $A_0 = 0.00$ gauss-cm. The vertical axis represents the dielectric function in arbitrary units.

FIG. 58. Time evolution of $\text{Im}(\epsilon(E))$ with GaAs for a field intensity of $A_0 = 1.00$ gauss-cm. The vertical axis represents the dielectric function in arbitrary units.
FIG. 59. Time evolution of $\text{Im}(\epsilon(E))$ with GaAs for a field intensity of $A_0 = 1.41$ gauss·cm. The vertical axis represents the dielectric function in arbitrary units.

given by $A_0 = 1.00$ gauss·cm (Fig. 58), $A_0 = 1.41$ gauss·cm (Fig. 59), and $A_0 = 1.73$ gauss·cm (Fig. 60). For low intensities therefore, the tetrahedral lattice structure remains intact and only thermal oscillations are observed in the time-dependent behavior of the dielectric function.

In Figure 61, it can be seen that for a higher intensity corresponding to $A_0 = 2.00$ gauss·cm, the structural features (peaks and troughs) are largely lost as time progresses. However, the imaginary part of the dielectric function is still nearly equal to zero at low energies (up to nearly 2.0 eV), indicating the presence of a semiconducting band gap. It should be mentioned that the strong features in the joint density of states, and therefore in $\text{Im}[\epsilon(\omega, t)]$, are associated with the anion (As) and cation (Ga) $p$-states. The top of the valence band exhibits a high density of states, and is associated with the As $p$-states. The bottom of the conduction band,
FIG. 60. Time evolution of $\text{Im}(\epsilon(E))$ with GaAs for a field intensity of $A_0 = 1.73$ gauss·cm. The vertical axis represents the dielectric function in arbitrary units.

FIG. 61. Time evolution of $\text{Im}(\epsilon(E))$ with GaAs for a field intensity of $A_0 = 2.00$ gauss·cm. The vertical axis represents the dielectric function in arbitrary units.
FIG. 62. Time evolution of Im($\epsilon(E)$) with GaAs for a field intensity of $A_0 = 2.45$ gauss-cm. The vertical axis represents the dielectric function in arbitrary units.

on the other hand, is associated with highly-dispersed $s$-bands, and has a low density of one-electron states. It is only at somewhat higher energy, somewhere between 1.5 eV and 2.0 eV above the valence band maximum, that one encounters a high density of states, associated with the Ga $p$-states. In the perfect zincblende structure for GaAs, therefore, there is no absorption of radiation for photon energies between 0.0 and 1.5 eV, and only low absorption until one reaches an energy near 2.0 eV. (The band gap of GaAs is 1.5 eV at 0 K, and 1.4 eV at room temperature.) To review, at low intensities there is no modification of the prominent features in the dielectric function seen below $A_0 = 2.00$ gauss-cm, but at a somewhat higher intensity the incipient structural rearrangement due to the applied radiation has caused these features to be washed out, even though the band gap is still present at low energies below 2.0 eV.
FIG. 63. Time evolution of $\text{Im}(\epsilon(E))$ with GaAs for a field intensity of $A_0 = 2.83$ gauss·cm. The vertical axis represents the dielectric function in arbitrary units.

Figures 62 and 63 show the even stronger perturbations of the electronic structure and dielectric function when more intense fields are applied. Notice that there is now substantial absorption at low energies, well below 2.0 eV, and that the absorption for the highest intensity shown in Fig. 63 at low energies is almost Drude-like. The dielectric functions at these two highest intensities, therefore, clearly show band gap collapse and metallic rather than semiconducting behavior.

The time evolution of the dielectric function in Si shows many similarities to GaAs (Figs. 64-70), as would be expected from the results of Section VI. For $A_0 = 1.41$ gauss·cm or less, normal modifications due to oscillations are observed. It is barely apparent in Fig. 67, that for the stable case of $A_0 = 1.73$ gauss·cm, a slight low frequency peak occurs. This is not due to the change in band structure (the $\delta(\omega - \omega_{mn}(k))$ in equation (7.1)), but rather from the change in occupation (the
FIG. 64. Time evolution of \( \text{Im}(\epsilon(E)) \) with Si for a field intensity of \( A_0 = 0.00 \) gauss\-cm. The vertical axis represents the dielectric function in arbitrary units.

FIG. 65. Time evolution of \( \text{Im}(\epsilon(E)) \) with Si for a field intensity of \( A_0 = 1.00 \) gauss\-cm. The vertical axis represents the dielectric function in arbitrary units.
FIG. 66. Time evolution of $\text{Im}(\epsilon(E))$ with Si for a field intensity of $A_0 = 1.41$ gauss-cm. The vertical axis represents the dielectric function in arbitrary units.

$[f_n(k) - f_m(k)]$ in equation (7.1)). That is, this factor can give contributions to the dielectric function from valence band $m$ to valence band $n$ if $f_m \neq f_n \neq 1$.

For intensities of $A_0 = 2.00$ gauss-cm and greater, a strong low frequency peak is present. We therefore see metallic behavior resulting in Si after sufficiently intense laser pulses.
FIG. 67. Time evolution of $\text{Im}(\varepsilon(E))$ with Si for a field intensity of $A_0 = 1.73$ gauss-cm.

The vertical axis represents the dielectric function in arbitrary units.

FIG. 68. Time evolution of $\text{Im}(\varepsilon(E))$ with Si for a field intensity of $A_0 = 2.00$ gauss-cm.

The vertical axis represents the dielectric function in arbitrary units.
FIG. 69. Time evolution of $\text{Im}(\epsilon(E))$ with Si for a field intensity of $A_0 = 2.24$ gauss·cm.

The vertical axis represents the dielectric function in arbitrary units.

FIG. 70. Time evolution of $\text{Im}(\epsilon(E))$ with Si for a field intensity of $A_0 = 2.45$ gauss·cm.

The vertical axis represents the dielectric function in arbitrary units.
VIII. CONCLUSIONS

The recent availability of ultrashort and ultra-intense laser pulses has provided new techniques for studying the electronic and structural properties of both molecules and materials. In the work described here, we were concerned with two materials of great technological and scientific importance, gallium arsenide and silicon. (GaAs is the most important and best studied of the compound semiconductors, with applications in solid state lasers and light emitting diodes, for example. Si is the most important and best studied of the elemental semiconductors and is used in virtually all applications in modern electronics.) During the last several years, two groups have examined the response of these two semiconductors to laser pulses with frequencies of about 2.0 eV, fluences of about 1.0 kJ/m², and durations of about 100 fs. Motivated by these experiments, we have performed simulations of the coupled electron and atomic dynamics when the material is subjected to an intense electromagnetic pulse on a short time scale. We in fact used frequencies, fluences, and pulse shapes and durations that were comparable to those used in the experiments. Our principal goal in these microscopic simulations was to determine whether a structural instability and band gap collapse could be induced by such pulses. This is not a trivial issue, since other mechanisms have been invoked to explain the observations: for example, screening of the electron-electron interactions and thermal melting of the lattice. Our principal conclusion is that, for both GaAs and Si, lattice destabilization and band gap collapse do occur for laser intensities above an approximate threshold intensity that is comparable to that observed in the experiments. Our model has been constructed to be realistic in the regime of greatest interest — namely the time during which the pulse is being applied and a time of about 100–200 femtoseconds after the termination of the pulse. During this relevant period of time, we find that there is an athermal disruption of the lattice due to the promotion of electrons from the bonding, valence-band
states to the antibonding, conduction-band states. We also find that the effect at a fixed photon energy of 2.0 eV is greater in the case of Si, even though the chemical bonding is stronger, because the joint density of states corresponding to this energy is larger in the case of Si, producing a higher occupancy in the excited conduction band states. This qualitative conclusion, like the other qualitative conclusions above, is fully consistent with the experimental observations.
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APPENDIX A: 
DETERMINING THE FLUENCE

The most common measure of pulse intensity used by experimental groups is the fluence\textsuperscript{4-6}, which is defined to be the total energy per unit area that the incident pulse beam carries over the duration of the pulse. As described in Section VA, we have included the pulse by incorporating the vector potential into the tight-binding Hamiltonian. In this appendix we use ideas from electrodynamics to relate the vector potential strength to the fluence.

The Poynting vector $S$ is defined as the amount of energy per unit area per unit time and is therefore a measure of energy flow. By knowing $S$ as a function of time, we can determine the fluence $F$ by integrating over the duration of the pulse $t_0$:

$$ F = \int_{0}^{t_0} dt S(t). \quad (A1) $$

We vary the pulse strength through the proportionality constant $A_0$ (see Section VB). It is this factor $A_0$ that we ultimately will be interested in relating to the fluence. We will also relate the fluence to the energy (frequency) of the electromagnetic pulse and the duration of the pulse $t_0$.

We will consider only the case of free space; i.e., we will not take into account that the material is a semiconductor with an index of refraction different from unity, that the laser pulse impinges on the surface at 63\textdegree from the normal (as in the experiments of Ref. 4), that the laser is not perfectly monochromatic, etc. I.e., the correspondence between the fluence and the vector potential that is given here holds within the material, and would have to corrected in order to allow for reflectivity, etc., in order to make a quantitative comparison with the experimental fluence outside the material.

The definition of the Poynting vector $S$ is\textsuperscript{70}

$$ S = \frac{c}{4\pi}(\mathbf{E} \times \mathbf{H}) \quad (A2) $$
where the magnetic permeability is equal to unity in free space, so that \( B = H \). The electric and magnetic fields are related to the scalar and vector potentials by

\[
E = -\nabla \Phi - \frac{1}{c} \dot{A}
\]  \hspace{1cm} (A3)

and

\[
B = \nabla \times A.
\]  \hspace{1cm} (A4)

Because the scalar potential can be set to zero in the radiation gauge (see Section V B) the electric and magnetic fields are now found from the following equations:

\[
E = -\frac{1}{c} \dot{A}
\]  \hspace{1cm} (A5)

\[
B = \nabla \times A.
\]  \hspace{1cm} (A6)

In Section V B we included both the time \textit{and} spatial dependences of the vector potential:

\[
A(t, \mathbf{r}) = A_e \left( \frac{\pi}{t_0} (t - \frac{\hat{k} \cdot \mathbf{r}}{c}) \right) \cos \left( \omega \left( t - \frac{\hat{k} \cdot \mathbf{r}}{c} \right) \right).
\]  \hspace{1cm} (A7)

The period of oscillation of light \( 2\pi/\omega \) is much shorter than the characteristic time over which the pulse changes appreciably. Likewise, the spatial length of the envelope \( A_e(\frac{\pi}{t_0} (t - \frac{k \cdot r}{c})) \) is much longer than the wavelength. We can therefore consider the envelope to be constant. Substituting this form (Equation A7) into equations A5 and A6, and dropping the spacial dependence afterwards leaves

\[
E = (\omega/c) \dot{A}_e(t) \sin(\omega t)
\]  \hspace{1cm} (A8)

\[
B = (\omega/c) \hat{k} \times \dot{A}_e(t) \sin(\omega t).
\]  \hspace{1cm} (A9)

Taking the time derivative or the curl of \( A_e(t, \mathbf{r}) \), would have led to another term of order \( (\omega t_0)^{-1} \) smaller than the derivative from \( \cos(\omega \left( t - \frac{\hat{k} \cdot \mathbf{r}}{c} \right)) \). We dropped the \( \mathbf{r} \) dependence because the wavelength is much longer than the size of the unit cell. The
E and B fields have the same magnitude, and are perpendicular to each other, and perpendicular to the direction of propagation since \( \mathbf{A}_e \cdot \mathbf{k} = 0 \) (Section VB). The Poynting vector is:

\[
S = \frac{c}{4\pi} E^2 = \frac{c}{4\pi} \left( \frac{\omega}{c} A_e(t) \sin(\omega t) \right)^2
\]
\[
= \frac{\omega^2}{4\pi c} A_e^2(t) \sin^2(\omega t). \tag{A10}
\]

We may now average over one period of oscillation, again assuming that the envelope is constant. Using

\[(1/T) \int_0^T \sin^2(\omega t) dt = 1/2 \tag{A12}\]

we have a time-averaged Poynting flux given by:

\[S = \frac{\omega^2}{8\pi c} A_e(t)^2. \tag{A13}\]

The specific form we use for \( A_e \) is that of a cosine (Equation 5.7) so that

\[S = \frac{\omega^2 A_0^2}{8\pi c} \cos^2 \left( \frac{\pi (t - t_0/2)}{t_0} \right). \tag{A14}\]

The fluence becomes

\[F = \int_0^{t_0} dt S(t) = \frac{\omega^2 A_0^2}{8\pi c} \int_0^{t_0} dt \cos^2 \left( \frac{\pi (t - t_0/2)}{t_0} \right) \tag{A15}\]
\[= \frac{\omega^2 A_0^2}{8\pi c} \frac{t_0}{2} \cos^2 \left( \frac{\pi (t - t_0/2)}{t_0} \right) \tag{A16}\]
\[= \frac{\omega^2 A_0^2 t_0}{16\pi c} \tag{A17}\]

and hence

\[F = \frac{\omega^2 A_0^2 t_0}{16\pi c}. \tag{A18}\]

Up to now we have been working in Gaussian units. It would be convenient to convert this to MKSA\(^7\) so that we can determine the fluence in kJ/m\(^2\), as commonly quoted in experiment. Consulting the conversion table in Ref. 70, we see that
\[ E \to \sqrt{4\pi \epsilon_0} E \quad \text{(A19)} \]
\[ H \to \sqrt{4\pi \epsilon_0} H \]

and

\[ c \to (\mu_0 \epsilon_0)^{-1/2} \]

where we must use \( H \) instead of \( B \) because \( S = \frac{c}{4\pi} (E \times H) \).

We have chosen the units of the vector potential in the Peierls factor (Section VA) to be gauss-cm. We also choose to work with energy \( \mathcal{E} \) in electron volts, where \( \mathcal{E} = \hbar \omega \). A convenient unit of time is femtoseconds. Using brackets to denote the desired units, we then have

\[ F[kJ/m^2] = \frac{1}{4\hbar^2 \mu_0} \left( \mathcal{E}[eV]\right)^2 \left( A_0[\text{gauss \cdot cm}]\right)^2 t_0[\text{fs}] \quad \text{(A20)} \]

Hence, we need to express \( \frac{1}{4\hbar^2 \mu_0} \) in units of kJ/m² (eV gauss-cm)⁻² fs⁻¹. The result is that

\[ \frac{1}{4\hbar^2 \mu_0} = 1.53 \times 10^{-3} \text{kJ/m}^2(\text{eV gauss \cdot cm})^{-2}\text{fs}^{-1}. \quad \text{(A21)} \]

Letting \( \mathcal{E} = 1.95 \text{eV} \) and \( t_0 = 140 \text{fs} \) as in Ref. 4, we have that

\[ F[kJ/m^2] = 0.815(A_0[\text{gauss \cdot cm}])^2 \quad \text{(A22)} \]

Finally, with \( A_0 = 2.0 \text{ gauss-cm} \) we get a fluence \( F = 3.26 \text{kJ/m}^2 \).
APPENDIX B:
CONVERTING QUANTITIES TO MICROSCOPIC UNITS

The Hamiltonian matrix elements are computed with energies in electron volts (eV), distances in Angstroms (Å), and masses in atomic mass units (amu). This choice requires that care be taken when calculating some quantities; e.g., time. Consider the position in the Verlet algorithm (4.8):

\[ \mathbf{R}_i(t + \Delta t) = \mathbf{R}_i(t) + \dot{\mathbf{R}}_i(t) \Delta t + \frac{1}{2} \ddot{\mathbf{R}}_i(t) \Delta t^2. \] (B1)

The acceleration is found from the Hellmann-Feynman theorem (4.7):

\[ M_i \ddot{\mathbf{R}}_i = - \sum_k n_k \Phi_k \cdot \frac{\partial \mathbf{H}(k)}{\partial \mathbf{R}_i} \cdot \Phi_k - \frac{\partial U_{\text{rep}}}{\partial \mathbf{R}_i}. \] (B2)

Denoting the units with brackets, we have

\[ M_i [\text{amu}] \ddot{\mathbf{R}}_i [\text{eV}/(\text{Å amu})] = - \sum_k n_k \Phi_k \cdot \frac{\partial \mathbf{H}(k)}{\partial \mathbf{R}_i} [\text{eV}/\text{Å}] \cdot \Phi_k - \frac{\partial U_{\text{rep}}}{\partial \mathbf{R}_i} [\text{eV}/\text{Å}]. \] (B3)

That is, \( \ddot{\mathbf{R}}_i \) must have units of eV/(Å amu) as a result of the Hamiltonian and repulsive potential having units of eV, the units of mass being amu, and the units of distance being Å. Therefore time, as can be seen from (B1), must have units of Å/(amu/eV)\(^{1/2}\). A convenient unit of time for the current simulations is femtoseconds.

We must therefore convert Å/(amu/eV)\(^{1/2}\) to fs:

\[ \text{Å} \left( \frac{\text{amu}}{\text{eV}} \right)^{1/2} = \frac{\text{Å}}{c} \left( \frac{931 \text{ MeV}/c^2}{\text{eV}} \right)^{1/2} \] (B4)

\[ = \frac{\text{Å}}{c} \left( \frac{931 \times 10^6 \text{ eV}}{\text{eV}} \right)^{1/2} \] (B5)

\[ = \frac{\text{Å}}{3.00 \times 10^{8+10-15} \text{ Å/fs}} \left( \frac{931 \times 10^6 \text{ eV}}{\text{eV}} \right)^{1/2} \] (B6)

\[ = 10.2 \text{ fs}. \] (B7)

(This number is more precisely 10.18051). Thus, if we use femtoseconds as the units of the time step in the Verlet algorithm, we must convert it to Å/(amu/eV)\(^{1/2}\). This
requires that we divide by 10.2 in the Verlet algorithm if the appropriate quantities in the Hellmann-Feynman theorem are measured in Å, eV, and amu.
APPENDIX C:
CALCULATING THE HELLMANN-FEYNMAN FORCES

The Hellmann-Feynman theorem, as discussed in Section IV A and Section V D, involves two matrix-vector multiplications. Each is, in principle, a multiplication involving all the elements of the derivatives of the Hamiltonian matrix. However, almost half the elements of the derivative of the electronic Hamiltonian are zero when only nearest neighbor interactions are included for a two atom cell. To see this, consider the two atom primitive cell. If only Ga-As and As-Ga interactions are allowed, then there is no contribution to the matrix elements for Ga-Ga and As-As, except for the diagonal elements, which are just the atomic energies. This is also true for the eight atom supercell if only nearest neighbor interactions are allowed.

With almost half the elements in the matrix being zero, the two matrix multiplications can be simplified so that only about 1/4 of the full matrix-vector computation is performed. Recall that the Hellmann-Feynman theorem is given by (4.2),

\[ M_i \vec{R}_d = - \sum_k n_k \Phi_k^\dagger \cdot \frac{\partial H}{\partial \vec{R}_d} \cdot \Phi_k - \frac{\partial U_{\text{rep}}}{\partial \vec{R}_d}. \]  

We will now denote the \( i \)th component of the \( k \)th eigenvector \( \Phi_k \) (or statevector \( \Psi_k \)) as \((\Phi_k)_i\) \((((\Psi_k)_i)\)\), so that the electronic contribution is

\[ - \sum_{i=1}^{N_{\text{orb}}} \sum_{j=1}^{N_{\text{states}}} \sum_{k=1}^{N_{\text{orb}}} n_k (\Phi_k^*)_i \partial_k H_{i,j} (\Phi_k)_j \]  

(C2)

Here, \( \partial_k H_{i,j} \) is the derivative of \( H_{i,j} \) with respect to \( \vec{R}_d \). Note that this \( l \) indexes the components of every atom in the unit cell. We have indicated the number of orbitals by \( N_{\text{orb}} \) and the number of states by \( N_{\text{states}} \). Each sum in \( i \) and \( j \) in the term above can be written as two half sums:

\[ - \sum_{k=1}^{N_{\text{states}}} \left( \sum_{i=1}^{N_{\text{orb}}/2} + \sum_{i=N_{\text{orb}}/2+1}^{N_{\text{orb}}} \right) \left( \sum_{j=1}^{N_{\text{orb}}/2} + \sum_{j=N_{\text{orb}}/2+1}^{N_{\text{orb}}} \right) n_k (\Phi_k^*)_i \partial_k H_{i,j} (\Phi_k)_j \]  

(C3)

which expands to
This can be simplified. First switch the indices:

\[
- \sum_{k=1}^{N_{\text{states}}} \left( \sum_{i=1}^{N_{\text{orb}}/2} \sum_{j=1}^{N_{\text{orb}}/2} + \sum_{i=N_{\text{orb}}/2+1}^{N_{\text{orb}}} \sum_{j=1}^{N_{\text{orb}}/2+1} \right) n_k (\Phi_k^*)_i \partial_k H_{i,j} (\Phi_k)_j \tag{C4}
\]

If there are no nonzero Ga-Ga or As-As matrix elements (i.e., if we do not include Ga-Ga and As-As interactions), then the matrix \(H_{i,j}\) is block off-diagonal, except for the diagonal elements, which are just constants so that their derivatives are zero.

Hence \(\partial_k H_{i,j}\) is totally block off-diagonal. In mathematical terms:

\[
\partial_k H_{i,j} = \begin{cases} 
0 & : 1 \leq i, j \leq \frac{N_{\text{orb}}}{2} \\
0 & : \frac{N_{\text{orb}}}{2} + 1 \leq i, j \leq N_{\text{orb}} \\
\neq 0 & : \text{otherwise}.
\end{cases} \tag{C5}
\]

Thus, \(\partial_k H_{i,j}\) is zero for the first and last of the four terms involving the sums over \(i\) and \(j\) in (C4). We are left with

\[
- \sum_{k=1}^{N_{\text{states}}} \left( \sum_{i=1}^{N_{\text{orb}}/2} \sum_{j=N_{\text{orb}}/2+1}^{N_{\text{orb}}} + \sum_{i=N_{\text{orb}}/2+1}^{N_{\text{orb}}} \sum_{j=1}^{N_{\text{orb}}/2+1} \right) n_k (\Phi_k^*)_i \partial_k H_{i,j} (\Phi_k)_j \tag{C6}
\]

This can be simplified. First switch the indices:

\[
- \sum_{k=1}^{N_{\text{states}}} n_k \left( \sum_{i=1}^{N_{\text{orb}}/2} \sum_{j=N_{\text{orb}}/2+1}^{N_{\text{orb}}} (\Phi_k^*)_i \partial_k H_{i,j} (\Phi_k)_j + \right)
\]

\[
- \sum_{j=N_{\text{orb}}/2+1}^{N_{\text{orb}}} \sum_{i=1}^{N_{\text{orb}}/2} (\Phi_k^*)_j \partial_k H_{j,i} (\Phi_k)_i \right) \tag{C7}
\]

\[
= - \sum_{k=1}^{N_{\text{states}}} n_k \left( \sum_{i=1}^{N_{\text{orb}}/2} \sum_{j=N_{\text{orb}}/2+1}^{N_{\text{orb}}} (\Phi_k^*)_i \partial_k H_{i,j} (\Phi_k)_j + (\Phi_k^*)_j \partial_k H_{i,j} (\Phi_k)_i \right) \tag{C8}
\]

\[
= - \sum_{k=1}^{N_{\text{states}}} n_k \left( \sum_{i=1}^{N_{\text{orb}}/2} \sum_{j=N_{\text{orb}}/2+1}^{N_{\text{orb}}} (\Phi_k^*)_i \partial_k H_{i,j} (\Phi_k)_j + (\Phi_k^*)_j \partial_k H_{i,j} (\Phi_k)_i \right) \tag{C9}
\]

\[
= - \sum_{k=1}^{N_{\text{states}}} n_k \left( \sum_{i=1}^{N_{\text{orb}}/2} \sum_{j=N_{\text{orb}}/2+1}^{N_{\text{orb}}} (\Phi_k^*)_i \partial_k H_{i,j} (\Phi_k)_j + (\Phi_k^*)_j \partial_k H_{i,j} (\Phi_k)_i \right) \tag{C10}
\]

\[
= - \sum_{k=1}^{N_{\text{states}}} n_k \left( \sum_{i=1}^{N_{\text{orb}}/2} \sum_{j=N_{\text{orb}}/2+1}^{N_{\text{orb}}} (\Phi_k^*)_i \partial_k H_{i,j} (\Phi_k)_j + (\Phi_k^*)_j \partial_k H_{i,j} (\Phi_k)_i \right) \tag{C11}
\]

\[
= - \sum_{k=1}^{N_{\text{states}}} n_k \left( \sum_{i=1}^{N_{\text{orb}}/2} \sum_{j=N_{\text{orb}}/2+1}^{N_{\text{orb}}} 2 \text{Re} \left[ (\Phi_k^*)_i \partial_k H_{i,j} (\Phi_k)_j \right] \right) \tag{C12}
\]
where we have denoted the complex conjugate by $c.c$. We have made use of the Hermiticity of $H_{i,j}$ in going from (C8) to (C9). Before the above simplification there were $N_{arb}^2$ terms. This has now been reduced to $(N_{arb}/2)^2$ terms, decreasing the required computation by a factor of 4.
APPENDIX D:
CALCULATING THE HAMILTONIAN MATRIX ELEMENTS

The Hamiltonian matrix elements may be determined using a variety of methods. We have used an approach which results in the least amount of redundancy. To illustrate the procedure we use, consider a brute force method for determining the matrix elements. In the following code, $t_{iajb}$ are the interatomic matrix elements $t_{iajb} (R_j - R_i); l, m, and n$ are the direction cosines; and usssig, uspsig, etc. correspond to $\eta_{ssa} \hbar^2 / m_e d^2$ and $\eta_{sps} \hbar^2 / m_e d^2$, as detailed in Section III. In the 2nd and 4th indices of $t_{iajb}$, 1 corresponds to an $s$ orbital, 2–4 correspond to the $p_{x}$, $p_{y}$, and $p_{z}$ orbitals, respectively, and 5 corresponds to an $s^*$ orbital.

\[
\begin{align*}
    t_{iajb}(i,1,j,1) &= \text{usssig} \\
    t_{iajb}(i,1,j,2) &= (1*\text{uspsig}) \\
    t_{iajb}(i,1,j,3) &= (m*\text{uspsig}) \\
    t_{iajb}(i,1,j,4) &= (n*\text{uspsig}) \\
    t_{iajb}(i,1,j,5) &= \text{ustsig} \\
    t_{iajb}(i,2,j,1) &= (1*\text{upssig}) \\
    t_{iajb}(i,2,j,2) &= (1**2*\text{uppsig}+(1.d0-1**2)*\text{upppi}) \\
    t_{iajb}(i,2,j,3) &= (1*m*\text{uppsig}-1*m*\text{upppi}) \\
    t_{iajb}(i,2,j,4) &= (1*n*\text{uppsig}-1*n*\text{upppi}) \\
    t_{iajb}(i,2,j,5) &= (1*\text{uptsig}) \\
    t_{iajb}(i,3,j,1) &= (m*\text{upssig}) \\
    t_{iajb}(i,3,j,2) &= (1*m*\text{uppsig}-1*m*\text{upppi}) \\
    t_{iajb}(i,3,j,3) &= (m**2*\text{uppsig}+(1.d0-m**2)*\text{upppi}) \\
    t_{iajb}(i,3,j,4) &= (m*n*\text{uppsig}-m*n*\text{upppi}) \\
    t_{iajb}(i,3,j,5) &= (m*\text{uptsig}) \\
    t_{iajb}(i,4,j,1) &= (n*\text{upssig}) \\
    t_{iajb}(i,4,j,2) &= (1*n*\text{uppsig}-1*n*\text{upppi}) \\
    t_{iajb}(i,4,j,3) &= (m*n*\text{uppsig}-m*n*\text{upppi}) \\
    t_{iajb}(i,4,j,4) &= (n**2*\text{uppsig}+(1.d0-n**2)*\text{upppi}) \\
    t_{iajb}(i,4,j,5) &= (n*\text{uptsig}) \\
    t_{iajb}(i,5,j,1) &= \text{utssig} \\
    t_{iajb}(i,5,j,2) &= (1*\text{utpsig}) \\
    t_{iajb}(i,5,j,3) &= (m*\text{utpsig}) \\
    t_{iajb}(i,5,j,4) &= (n*\text{utpsig})
\end{align*}
\]
The redundancy is apparent; e.g., $t_{iajb}(i,2,j,2)$ is the same as $t_{iajb}(i,3,j,3)$ but with the direction cosine $m$ replaced by $n$. Furthermore, when the derivatives of the matrix elements must be found, as in the the Hellmann-Feynman theorem of Section V D, we must find three times as many equations. It is simple matter to find all of these derivatives, especially with the aid of a symbolic mathematical package. But even with a symbolic package this is tedious, mainly because the Fortran code has to be modified in order to be read by the package, and then it must be converted back to Fortran after the derivatives are found. Furthermore, there is increased danger of programming error when dealing with this many equations.

We have found another method which (1) reduces the amount of redundancy, (2) is simpler to understand, and (3) easily evaluates only one triangle of the Hermitian matrix $H_{ia,jb}(k)$, leaving the other elements to be found by taking the adjoint. This method uses function calls, each of which corresponds uniquely to $t_{is,js}$, $t_{ip,jp}$, $t_{is,js}$, etc. Thus, we make calls to the following routines, as incorporated into this Fortran 90 module:

```fortran
module matrix_elements


use numbers, only : double ! double <= real*8

! The following is a key to the variables within this module:
! me: matrix element
```

$t_{iajb}(i,5,j,5) = uttsig$
contains

!!!!!!!!!!!!  Matrix Elements  !!!!!!!!!!!!!
function ss (sig,d) result (me) ! t_isjs matrix element
  implicit none
  real(double) :: me
  real(double) :: sig,d
  me = sig/(d**2)
end function ss

function sp (sig,l,d) result (me) ! t_isjp matrix elements
  implicit none
  real(double) :: me
  real(double) :: sig,l,d
  me = sig*l/(d**2)
end function sp

function pp (sig,pi,T,kdelta,d) result (me)
  ! t_ipjp matrix elements
  implicit none
  real(double) :: me
  real(double) :: sig,pi,T,d,kdelta
  me = (T*(sig - pi) + kdelta*pi)/(d**2)
end function pp

!!!!!!!!!!!!  Derivatives of Matrix Elements  !!!!!!!!!!!!!
function dss (sig,d,l) result (me)
  ! derivatives of the t_isjs matrix elements
  implicit none
  real(double) :: me(3)
  real(double) :: sig,d,l(3)
  me(:) = -2.0*l(:)*sig/(d**3)
  ! The colon denotes vector subscripts.
  ! All three components of me are evaluated.
end function dss
function dsp (sig,T,kdelta,i,d) result (me)
  ! derivatives of the t_isjp matrix elements
  implicit none
  integer :: i,j
  real(double) :: me(3)
  real(double) :: sig,T(3,3),kdelta(3,3),d

  do j = 1,3
    me(j) = sig*(- 3.0*T(i,j) + kdelta(i,j))/d**3
  end do

end function dsp

function dpp (sig,pi,T,kdelta,l,i,j,d) result (me)
  ! derivatives of the t_ipjp matrix elements
  implicit none
  integer :: i,j,k
  real(double) :: me(3)
  real(double) :: sig,pi,l(3),d,kdelta(3,3),T(3,3)

  do k = 1,3
    me(k) = ( &
      &   ( kdelta(i,k)*l(j) + kdelta(j,k)*l(i) - &
      &           4*T(i,j)*l(k)*pi &
      &           - 2* kdelta(i,j)*l(k)*pi &
      &     )/d**3
    &   )
  end do

end function dpp

end module matrix_elements

One can see the ease with which the derivatives can be determined. A symbolic package is not necessary. This method is robust enough to extend to calculating matrix elements involving d orbitals. Of course, this method is not complete without a routine to call these functions. These routines, as well as others, are available from the author.
VITA

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