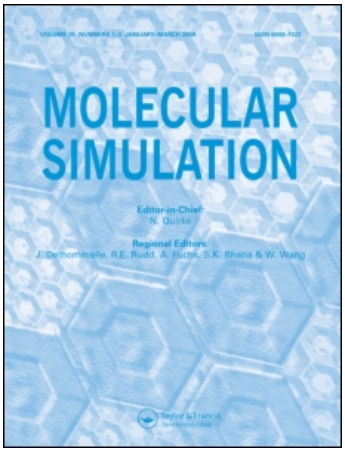

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Ab Initio Materials Science and Engineering using the Molecular Dynamics Method for Total Energy Pseudopotential Calculations

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AB INITIO MATERIALS SCIENCE AND ENGINEERING USING THE MOLECULAR DYNAMICS METHOD FOR TOTAL ENERGY PSEUDOPOTENTIAL CALCULATIONS

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A description of the total energy pseudopotential technique and of Car and Parrinello's molecular dynamics method is given. A detailed investigation of the extent to which the electronic degrees of freedom in the molecular dynamics method should be regarded as classical degrees of freedom is presented. It is shown that a cancellation of the errors in the Hellmann-Feynman forces occurs when the molecular dynamics equations of motion are used to evolve the electronic degrees of freedom during a dynamical simulation of the ionic system. Applications of the molecular dynamics method to study surface reconstructions and grain boundaries in germanium and defects in arsenic tri-selenide are briefly described and the possibility of using ab-initio methods to study problems in materials science and engineering is discussed.

KEY WORDS: Total energy, pseudopotential

INTRODUCTION

The ultimate goal of all techniques for studying static and dynamical properties of materials should be the use of ab initio interatomic potentials rather than empirical potentials. Only then can the results of the study be taken as describing a real material rather than a fictitious substance whose interatomic interactions are those described by the empirical potential. Empirical potentials work well in a region of phase space but it is very difficult to assess how large this region of phase space is and when the system has moved outside this region. Until very recently ab-initio methods could only be applied to study the static properties of systems containing fewer than ten atoms in the unit cell and it may have appeared that it would never be possible to apply ab initio methods to realistic systems. However, the molecular dynamics method introduced by Car and Parrinello [1] has increased the power of the ab initio total energy pseudopotential technique to the point where systems containing a hundred atoms can be routinely studied and so the difference between the sizes of systems that can be studied using ab initio and empirical techniques has been considerably reduced. The ability to use very large plane wave basis sets using Car-Parrinello methods has lead to another development in the pseudopotential technique. At one time it was assumed that transition metals and first row elements such as oxygen could not be represented by pseudopotentials. However, recent work has

shown that pseudopotentials can be used to represent these atoms provided that an extremely large basis set is used [2, 3]. Therefore, the Car-Parrinello scheme not only allows a larger number of atoms to be included in the unit cell but it also allows the total energy pseudopotential technique to be applied to systems which at one time were believed to be beyond the scope of the method.

The total energy pseudopotential technique is described in the next section and the Car-Parrinello method is reviewed in section 3. In section 4 the extent to which the Car-Parrinello scheme should be described as molecular dynamics is examined and in section 5 it is shown that the scheme has some significant advantages over alternative iterative matrix diagonalisation techniques when performing dynamical simulations of the ionic system. A number of calculations performed using the Car-Parrinello method are very briefly reviewed in section 6. This section is included to show the size of system that is presently accessible to total energy pseudopotential calculations and the information that can be obtained from the calculations. In the final section the future development of the total energy pseudopotential method is considered and the prospects for using such calculations for engineering and materials science applications are reviewed.

2. THE TOTAL ENERGY PSEUDOPOTENTIAL METHOD

The simplifications and approximations that are needed to perform total energy pseudopotential calculations for a bulk system are briefly described in this section. More detailed descriptions of the total energy pseudopotential method can be found in references 4 and 5. The first problem is to reduce the infinite bulk system to a finite system. This is achieved by performing calculations on a periodic supercell. The infinite number of electrons in the system are now represented by an infinite number of k-points in the Brillouin zone with a finite number of occupied electronic states at each k-point. The equations for the electronic wavefunctions can be solved independently at each point. If the charge density and the contribution to the total energy due to the electronic states in a region of the Brillouin zone can be represented by the electronic states at a single k-point then the charge density and total energy of the infinite bulk system can be calculated by computing the electronic states at a finite number of k-points.

The periodicity of the system introduced by using a supercell allows a discrete plane wave basis set to be used to expand the electronic wavefunctions and if the basis set is truncated by retaining only the plane waves which have kinetic energies below a particular cut-off energy the basis set becomes finite. Plane waves are not very well suited to describing electronic wavefunctions because a very large number are required to describe the wavefunctions of the core electrons and to describe the oscillations of the valence electrons in the core region. If the full ionic potential is replaced by a pseudopotential the core electron states are no longer included in the calculation. The valence wavefunctions are relatively smooth in the pseudopotential and so they can be expanded using a reasonably small number of plane wave basis states.

The most difficult problem in any electronic structure calculation is taking account of the electron-electron interaction. Hohenberg and Kohn showed that the exchange-correlation energy is a unique functional of the groundstate electronic density [6]. Kohn and Sham showed that the system of interacting electrons could be mapped into a system of non-interacting electrons moving in effective potential V_{XC}, the exchange-

correlation potential, which takes account of the effects of exchange and correlation exactly [7]. The non-interacting states are the solutions to the Kohn-Sham equations [7].

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + \mathbf{V}_{ion}(\mathbf{r}) + \mathbf{V}_H(\mathbf{r}) + \mathbf{V}_{xc}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \lambda_i \psi_i(\mathbf{r}) \tag{1}$$

where $\mathbf{V}_{ion}$ is the ionic potential and $\mathbf{V}_H$ is the Hartree potential given by

$$\mathbf{V}_H(\mathbf{r}) = \frac{e^2}{4\pi\varepsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \tag{2}$$

where $n(\mathbf{r})$ is the electronic charge density.

The exchange-correlation potential $\mathbf{V}_{XC}$ is given by

$$\mathbf{V}_{XC}(\mathbf{r}) = \frac{\delta\varepsilon[n(\mathbf{r})]}{\delta n(\mathbf{r})} \tag{3}$$

where $\varepsilon[n(\mathbf{r})]$ is the exchange-correlation energy functional. This mapping is exact and the resulting potential $\mathbf{V}_{XC}$ takes account of the electron-electron interactions exactly. However, as the exchange-correlation energy functional is not known an approximation to it has to be made so that in practice exchange and correlation can only approximately be taken into account in density functional calculations. The most common approximation used to construct $\mathbf{V}_{XC}$ is to assume that the exchange-correlation energy density at point $\mathbf{r}$ in the electron gas is the same as that in a homogeneous electron gas whose density is the same as that of the electron gas at $\mathbf{r}$. This is called the local density approximation and it is the only uncontrolled approximation in a total energy pseudopotential calculation.

The Kohn-Sham equations must be solved self-consistently so that the single-particle states generate the charge density that was used to construct the electronic potentials in the original equations. This is usually achieved by using an iterative method in which the charge density used to construct the Hartree and exchange-correlation potentials in the Kohn-Sham equations for the next iteration is taken to be a mixture of the charge densities generated by the solutions of the Kohn-Sham equations from the present and previous iterations.

It may appear that so many approximations and simplifications are required to perform a total energy pseudopotential calculation that the results will have no relevance to real systems. However, total energy pseudopotential calculations have been remarkably successful in obtaining agreement with experimental results for a wide range of properties such as lattice constants, bulk moduli, phase transition pressures and temperatures [8, 9]. The agreement with experiment is achieved without any variable parameters. The pseudopotential is calculated for an isolated atom and this pseudopotential is subsequently used to represent the ion irrespective of the nature of the system or the detailed atomic environment. The exchange-correlation potential is constructed from the results of calculations of the exchange-correlation energy of free-electron gases of varying densities. The success of the total energy pseudopotential method in obtaining agreement with existing experimental results has produced sufficient confidence in the method that it is now common to use the method to make predictions for structures or properties of materials that are not known experimentally.

3. THE CAR-PARRINELLO METHOD

The most time consuming step in a total energy pseudopotential calculation is the solution of the Kohn-Sham equations to determine the single particle eigenstates. Even though a pseudopotential is much weaker than the full ionic potential a large number of plane waves are still required to expand the electronic wavefunctions. A system that contains only atoms which have weak pseudopotentials might require 100 plane waves per atom to expand the electronic wavefunctions but this number has to be increased considerably if the system contains any ion that has a strong pseudopotential. The size of system that can be studied is severely restricted if conventional matrix diagonalisation techniques are used to calculate the Kohn-Sham eigenstates. A number of people had started to use iterative matrix diagonalisation techniques to solve for the Kohn-Sham eigenstates before the introduction of the Car-Parrinello method but the use of an iterative matrix diagonalisation technique is only one of a number of features of the method which together have lead to the significant increase in the power of the total energy pseudopotential technique. Car and Parrinello formulated their method in the language of molecular dynamics and this language will be used in the description of the method in this section. In the following section the extent to which the Car-Parrinello scheme is molecular dynamics will be examined.

In the Car-Parrinello scheme the electronic degrees of freedom are treated as dynamical variables. The system is described by the following Lagrangian

$$\mathscr{L} = \sum_i \mu \langle \dot{\psi}_i | \dot{\psi}_i \rangle + \sum_I \tfrac{1}{2} M_I |\dot{\mathbf{R}}_I|^2 + \sum_\nu \tfrac{1}{2}\beta \dot{\alpha}_\nu^2 - E[\{\psi_i\}, \{\mathbf{R}_I\}, \{\alpha_\nu\}] \tag{4}$$

where μ is a fictitious mass associated with the dynamics of the electronic states, $\{\psi_i\}$ is the set of electronic wavefunctions, $\mathbf{R}_I$ is the position of ion $\mathbf{I}$ and M_I is its mass, β is a fictitious mass associated with the constraints on the system, $\{\alpha_\nu\}$ is the set of constraints on the system such as the size and shape of the periodic supercell and E is the Kohn-Sham energy functional.

The first term in equation (4) is the fictitious kinetic energy associated with the dynamics of the electronic degrees of freedom, the second term is the kinetic energy of the ions and the third term is the fictitious kinetic energy associated with the motions of the constraints on the system. The final term in equation (4) is the Kohn-Sham energy functional which replaces the potential energy term of a conventional Lagrangian formulation. The Lagrangian gives the following equations of motion for the electronic degrees of freedom.

$$\mu \ddot{\psi}_i = - H\psi_i + \sum_j \Lambda_{ij} \psi_j \tag{5}$$

where H is the Kohn-Sham Hamiltonian given by the terms in the square brackets in equation (1) and Λ_{ij} are Lagrange multipliers for the constraints of orthogonality and normalisation of the electronic wavefunctions.

A system in which the positions of the ions and the size and shape of the periodic supercell are kept fixed will be considered first. It will be assumed that the wavefunctions are expanded in terms of a basis set $\{\phi\}$

$$\psi_i = \sum_n c_{i,n} \phi_n \tag{6}$$

If the equations of motion for the electronic states are integrated without any damping the excess energy in the electronic system will be distributed equally amongst all the electronic degrees of freedom. There are two degrees of freedom associated with each coefficient $\mathbf{c}_{i,n}$: the kinetic energy due to the motion of the coefficient and the potential energy that arises because the value of the coefficient differs from the value that minimises the Kohn-Sham energy functional. If some form of damping is applied to the motions of the coefficients then energy will be continuously removed from the electronic degrees of freedom until the velocities of the coefficients have been reduced to zero and the system is in the configuration which has the minimum potential energy. It can be seen from (5) that when the wavefunctions are orthogonal and the accelerations are zero the wavefunctions are solutions to the Kohn-Sham equations so the Car-Parrinello scheme provides a method for calculating the Kohn-Sham eigenstates.

The problem of finding self-consistent Kohn-Sham eigenstates has been ignored so far. If the electronic potential is recalculated at each step of the electron dynamics the stationary wavefunctions are automatically self-consistent because the electronic potential in the Hamiltonian is generated by these wavefunctions. Therefore the processes of solving for the Kohn-Sham eigenstates and of obtaining self-consistency are performed simultaneously in the Car-Parrinello scheme.

The molecular dynamics Lagrangian gives two further sets of equations of motion. The first set for the motion of the ions

$$M_I \ddot{\mathbf{R}}_I = -\frac{\partial E}{\partial \mathbf{R}_I} \tag{7}$$

which simply relates the acceleration of each ion to the force acting on it and the second set for the constraints on the system

$$\beta \ddot{\alpha}_\upsilon = -\frac{\partial E}{\partial \alpha_\upsilon} \tag{8}$$

In the case of the constraints of the size on shape of the unit cell these equations relate the accelerations of the lengths of the edges of the unit cell to the integrals of the diagonal components of the stress tensor and the accelerations of the angles between the unit cell vectors to the integrals of the off-diagonal components of the stress tensor.

Writing the Kohn-Sham energy functional as a sum of the Ewald energy of the ionic system and the electronic energy

$$\mathbf{E} = \mathbf{E}^{\text{ion}} + \langle \Psi | \mathbf{H} | \Psi \rangle \tag{9}$$

where Ψ is the many-electron wavefunction.

Substituting (9) into (7) the equations of motion for the ions become

$$M_I \ddot{\mathbf{R}}_I = -\frac{\partial E^{\text{ion}}}{\partial \mathbf{R}_I} - \langle \frac{\partial \Psi}{\partial \mathbf{R}_I} | \mathbf{H} | \Psi \rangle - \langle \Psi | \frac{\partial \mathbf{H}}{\partial \mathbf{R}_I} | \Psi \rangle - \langle \Psi | \mathbf{H} | \frac{\partial \Psi}{\partial \mathbf{R}_I} \rangle \tag{10}$$

The first and third terms in (10) can be evaluated without great difficulty but the second and final terms in (10) involve the implicit dependence of the electronic

wavefunction on the positions of the ions. These implicit dependences are very difficult to calculate. However Hellmann and Feynman have show that the second and final terms in (10) sum to zero when the electronic wavefunction is an eigenstate of the Hamiltonian [10, 11], a result commonly referred to as the Hellmann-Feynman theorem. In practice the electronic wavefunction will never be an exact eigenstate and the neglect of the implicit dependence of the force on the electronic wavefunction will produce an error in the value of the computed force. If the ionic system is to be relaxed to its equilibrium geometry the errors in the Hellmann-Feynman forces must be smaller than the actual forces or moving the ions in the directions of the Hellmann-Feynman forces will not reduce the total energy of the system and so the electronic configuration must be relaxed closer and closer to its groundstate configuration as the ions move towards their equilibrium positions. In a dynamical simulation of the ionic system errors in the Hellmann-Feynman forces will destroy the accuracy of the constant energy evolution of the ionic configuration. The error in the Hellmann-Feynman force is first order with respect to the error in the electronic wavefunction and this might be expected to produce severe difficulties for such dynamical simulations. In section 4 it will be shown that there is a tendency for the errors in the Hellmann-Feynman forces to cancel when the molecular dynamics equations of motion are used to evolve the electronic configuration and this permits dynamical simulations to be performed using the Car-Parrinello scheme.

The final feature of the Car-Parrinello method is the use of real and reciprocal space to compute the product of the Hamiltonian and the electronic wavefunction required to determine the accelerations of the wavefunction given by (5). The kinetic energy operator is diagonal in reciprocal space and with a local pseudopotential the potential energy operator is diagonal in real space so the multiplication of the wavefunction by the Hamiltonian can be achieved in NlnN operations where N is the number of plane wave basis states by using fast Fourier transforms to transform the wavefunction between real and reciprocal space. This contrasts to the N^2 operations required for a conventional matrix multiplication and represents a considerable saving in computational time.

The unusual formulation of the Car-Parrinello method means that it is not immediately obvious what benefits the scheme possesses. The scheme is essentially an iterative matrix diagonalisation technique in which the multiplication of the wavefunction by the Hamiltonian is performed partially in real space and partially in reciprocal space. The processes of obtaining self-consistency in the electronic potential and of relaxing the ionic configuration to equilibrium or moving the ions in a dynamical simulation are performed at the same time as solving for the Kohn-Sham eigenstates thus producing a further increase in the computational speed. Any iterative matrix diagonalisation scheme can exploit the features of the Car-Parrinello scheme to maximise the computational speed and it is not clear whether an alternative equation of motion to (5) or a different iterative matrix diagonalisation scheme will be superior.

4. IS THE CAR-PARRINELLO SCHEME MOLECULAR DYNAMICS?

In the previous section it was shown that the electronic configuration will evolve to the groundstate if damping is applied to the motions of the wavefunctions as they evolve under the molecular dynamics equations of motion. It will now be shown that

the constraint of normalisation of the wavefunctions damps the motions of the coefficients so that the electronic configuration will relax to its groundstate even in even if there is no damping explicitly applied in the equations of motion. From now on the electronic configuration will be represented by a single many-particle wavefunction ψ and the fictitious mass μ will be set equal to unity. The unconstrained equation of motion for ψ can be written

$$\ddot{\psi} = -[H - \lambda]\psi \tag{11}$$

where λ is an arbitrary energy shift. The eigenstates of the Hamiltonian are given by

$$H\zeta_n = \lambda_n\zeta_n \tag{12}$$

Expanding ψ in terms of the eigenstates ζ_n gives

$$\psi = \sum_n c_n\zeta_n \tag{13}$$

Substituting (13) in the equation of motion for ψ gives

$$\ddot{c}_n = -[\lambda_n - \lambda]c_n \tag{14}$$

Integrating the equations of motion for the coefficients c_n gives

$$\begin{aligned} c_n(t) &= c_n(O)\cos[(\lambda_n - \lambda)^{1/2}t] \quad \lambda_n > \lambda \\ c_n(t) &= c_n(O)\cosh[|\lambda_n - \lambda|^{1/2}t] \quad \lambda_n < \lambda \end{aligned} \tag{15}$$

It is possible for the wavefunction $\psi(t)$ to remain normalised if the value of λ is chosen to be smaller than the lowest energy eigenstate of H. In this case the amplitude of each coefficient c_n does not change with time and the wavefunction $\psi(t)$ will depend on the initial trial wavefunction irrespective of the value of t. This wavefunction would never give the correct total energy of the system or the correct forces on the ions. If the value of λ is chosen to be larger than the groundstate eigenvalue and if the initial electronic wavefunction spans the groundstate then the magnitude of the electronic wavefunction will grow with time due to the exponential increase of the coefficient c_0. Applying the constraint of normalisation reduces the magnitudes and velocities of all the coefficients and thus damps the motions of the coefficients. Therefore, the electronic configuration will relax to the groundstate even when there is no damping applied explicitly in the molecular dynamics equations of motion. If λ is chosen to be the expectation value of the energy of ψ this ensures that the electronic configuration converges to the groundstate and it is the exact Lagrange multiplier for normalisation when ψ is the groundstate wavefunction. From here on it will be assumed that λ is taken to have this value.

In a dynamical simulation of the ionic system it is necessary for the electronic configuration to continuously evolve to the new instantaneous groundstate. It has just been shown that the constraint of normalisation continuously removes energy from the electronic degrees of freedom. If energy is continuously removed by the constraint of normalisation then the coefficients can continue to change only if energy is continuously supplied to them. This energy cannot be taken from the ionic degrees of freedom since this would produce a severe damping of the motions of the ionic degrees of freedom yet it appears that there are no other sources of energy in the system. The solution to this problem is quite subtle. The forces on the ions are calculated when the electronic system is close to its instantaneous groundstate configuration and it is

assumed that the forces vary slowly along the path of the ion. However if the forces on the ions were recalculated after displacing the ions but before the electronic configuration is allowed to relax to the new groundstate it would be found that the value of the force had changed considerably. There are thus two values that could be assigned to the work done by each ion during its displacement. One is the work done against the forces generated when the electronic configuration is in the instantaneous groundstate configuration at each point along the path. The other is the work that would be done against the forces generated by the fixed electronic configuration. The difference between the two values for the work done is equal to the excitation energy in the electronic system after the ions have been displaced. This excess energy provides the kinetic energy needed to evolve the electronic configuration to its new instantaneous groundstate and the energy is eventually removed from the electronic degrees of freedom by damping either due to a damping force explicitly applied to the equations of motion or due to the damping produced by the constraint of normalisation.

It can be seen that it is not correct to describe the motion of the electronic degrees of freedom in the Car-Parrinello scheme as a constant energy molecular dynamics. Energy is continuously supplied to the electronic degrees of freedom and subsequently removed by damping. The idea that these degrees of freedom are undergoing a classical molecular dynamics is completely untenable. In a typical total energy pseudopotential calculation there are 10^4 times as many degrees of freedom in the electronic system as in the ionic system. If all these degrees of freedom formed a classical molecular dynamics system equipartition would occur so that the majority of the energy of the system would appear in the electronic degrees of freedom and the electronic degrees of freedom would act as a heat bath for the ionic system so that the energy of each ion would follow a Boltzmann distribution and the total energy evolution of the ionic system would be completely destroyed by fluctuations of energy between the electronic and ionic systems. Only by maintaining a delicate balance between supplying energy to the electronic degrees of freedom and removing the energy by damping can the electronic degrees of freedom move between the instantaneous groundstate configurations without fluctuations of energy between the electronic and ionic systems destroying the accuracy of the ionic trajectories.

5. ERROR-CANCELLATION IN THE CAR-PARRINELLO SCHEME

In this section it will be shown that the errors in the Hellmann-Feynman forces tend to cancel in a dynamical simulation of the ionic system when the molecular dynamics equations of motion are used to evolve the electronic configuration. If the ions move between positions $\mathbf{R}_i$ and $\mathbf{R}_i'$ in a time T then assuming that the self-consistent potential varies linearly between these two configurations the Hamiltonian at time t can be written

$$H(t) = H(\{\mathbf{R}_i'\}) - \left[1 - \frac{t}{T}\right] \Delta \mathbf{V}_{sc} \tag{16}$$

where $H(\{\mathbf{R}_i'\})$ is the Hamiltonian for the ions in positions $\mathbf{R}_i'$, and $\Delta \mathbf{V}_{sc}$ is the change in the self-consistent potential on moving the ions from positions $\mathbf{R}_i$ to $\mathbf{R}_i'$. The actual Hamiltonian at time t will differ from this expression if the electronic wavefunction at time t is not the instantaneous groundstate wavefunction because the potential

generated by the electronic states will not be the self-consistent electronic potential. If the electronic configuration moves too far from the instantaneous groundstate configuration the evolution of the electronic configuration becomes unstable.

The groundstate wavefunction at time t, $\psi_0(t)$, to first order in perturbation theory is

$$\psi_0(\mathbf{t}) = \chi_0 - \left[1 - \frac{t}{T}\right] \sum_{n \neq 0} \frac{\langle \chi_n | \Delta v V_{sc} | \chi_0 \rangle}{\varepsilon_0 - \varepsilon_n} \chi_n \tag{17}$$

where $\{\chi\}$ are the eigenstates of Hamiltonian $H(\{\mathbf{R}_I'\})$ given by

$$H(\{\mathbf{R}_I'\})\chi_n = \varepsilon_n \chi_n \tag{18}$$

The electronic configuration is in the groundstate of Hamiltonian H(t) at $t = 0$. It will be assumed that the electronic configuration is stationary at this time but this assumption does not affect the following analysis because the error cancellation in the Hellmann-Feynman forces is independent of the initial velocities of the electronic degrees of freedom. During the time $0 \leqslant t \leqslant T$ the electronic configuration evolves according to the molecular dynamics equation of motion

$$\ddot{\psi}(t) = -[H(t) - \varepsilon(t)]\psi(t) \tag{19}$$

where $\varepsilon(t) = \langle \psi(t)|H(t)|\psi(t)\rangle$.

The contribution to the calculated Hellmann-Feynman force exerted on ion I at time t due to the electrons is given by

$$\mathbf{f}_I'(t) = -\langle \psi(t)|\nabla_I \mathbf{V}_I(\mathbf{r} - \mathbf{R}_I(t)|\psi(t)\rangle \tag{20}$$

where $\mathbf{v}_I$ is the pseudopotential of ion I.

The correct contribution to the Hellmann-Feynman force is

$$\mathbf{f}_I(t) = -\langle \psi_0(t)|\nabla_I \mathbf{V}_I(\mathbf{r} - \mathbf{R}_I(t))|\psi_0(t)\rangle \tag{21}$$

The operator $\nabla_I \mathbf{V}_I(\mathbf{r} - \mathbf{R}_I)$ is not diagonal so the error in the Hellmann-Feynman force is first order with respect to the error in the wavefunctions, as mentioned previously.

Expanding the wavefunction $\psi(t)$ in terms of the basis set $\{\chi\}$

$$\psi(t) = \sum_n \mathbf{c}_n(t)\chi_n \tag{22}$$

and substituting this expression into the molecular dynamics equation of motion gives the following equations of motion for the coefficients $\mathbf{c}_n$

$$\ddot{\mathbf{c}}_n(t) = -[\varepsilon_n - \varepsilon(t)]\mathbf{c}_n(t) + \sum_m \left[1 - \frac{t}{T}\right]\langle \chi_n|\Delta \mathbf{V}_{sc}|\chi_m\rangle \mathbf{c}_m(t) \tag{23}$$

To first order in the self-consistent potential the coefficient c_0 remains equal to 1 during the interval $0 \leqslant t \leqslant T$, all the other coefficients remain of order $\Delta \mathbf{V}_{sc}$ and $\varepsilon(t)$ is equal to

$$\varepsilon(t) = \varepsilon_0 - \left[1 - \frac{t}{T}\right]\langle \chi_0|\Delta \mathbf{V}_{sc}|\chi_0\rangle \tag{24}$$

If $\langle \chi_0|\Delta \mathbf{V}_{sc}|\chi_0\rangle$ is much smaller than any of the differences between the eigenvalue ε_0 and the eigenvalues ε_n the equations of motion for the coefficients are approximately given by

$$\ddot{\mathbf{c}}_n(t) = -[\varepsilon_n - \varepsilon_0]\mathbf{c}_n(t) + \left[1 - \frac{t}{T}\right]\langle\chi_n|\Delta\mathbf{V}_{sc}|\chi_0\rangle \; n \neq 0 \tag{25}$$

These equations can be integrated to give the wavefunction at time t as

$$\psi(t) = \chi_0 - \sum_{n\neq 0}\left\{\left[1 - \frac{t}{T}\right]\frac{\langle\chi_n|\Delta\mathbf{V}_{sc}|\chi_0\rangle}{\varepsilon_0 - \varepsilon_n}\right\}\chi_n + \sum_{n\neq 0}\left\{\frac{\langle\chi_n|\Delta\mathbf{V}_{sc}|\chi_0\rangle}{(\varepsilon_n - \varepsilon_0)^{3/2}T}\sin[(\varepsilon_n - \varepsilon_0)^{1/2}t]\chi_n\right\} \tag{26}$$

The first two terms in (26) are equivalent to the instantaneous groundstate wavefunction $\phi_0(t)$ so the final term in (26) represents the error in the wavefunction at time t. It can be seen that the error in the wavefunction is oscillatory in time. Hence the errors in the Hellmann-Feynman force exerted on a single ion will be oscillatory in time and the errors will tend to cancel when averaged along the trajectory of the ion so that there will not be a continuous transfer of energy from the ions to the electronic degrees of freedom.

To show that the error cancellation does not take place if a different equation of motion is used to evolve the electronic configuration a first order equation of motion will now be considered. With the approximations introduced above the first order equations of motion for the evolution of the coefficients $\mathbf{c}_n$ are

$$\dot{\mathbf{c}}_n(t) = -[\varepsilon_n - \varepsilon_0]\mathbf{c}_n(t) + \left[1 - \frac{t}{T}\right]\langle\chi_n|\Delta\mathbf{V}_{sc}|\chi_0\rangle \; n \neq 0 \tag{27}$$

Solving for the wavefunction at time t gives

$$\psi(t) = \chi_0 - \sum_{n\neq 0}\left\{\left[1 - \frac{t}{T}\right]\frac{\langle\chi_n|\Delta\mathbf{V}_{sc}|\chi_0\rangle}{\varepsilon_0 - \varepsilon_n}\right\}\chi_n + \sum_{n\neq 0}\left\{\frac{\langle\chi_n|\Delta\mathbf{V}_{sc}|\chi_0\rangle}{T(\varepsilon_n - \varepsilon_0)^2}(1 - exp\,[-(\varepsilon_n - \varepsilon_0)t])\,\chi_n\right\} \tag{27}$$

It can be seen that the error in this wavefunction is single-signed and that the error in the wavefunction tends to a constant at large times. The error in the Hellmann-Feynman force exerted on a single ion will always be in the same direction and the error in the force will not average to zero when integrated along the path of the ion so that there will be a continuous transfer of energy from the ions to the electronic degrees of freedom when a first order equation of motion is used to evolve the electronic degrees of freedom.

The loss of energy from the ionic system becomes second order with respect to the error in the electronic wavefunction when the molecular dynamics equations of motion are used to evolve the electronic degrees of freedom but it is first order with respect to error in the wavefunction when a first order equation of motion is used to evolve the electronic degrees of freedom. To obtain the most accurate ionic trajectories in a dynamical simulation the electronic degrees of freedom should, therefore, be evolved using the molecular dynamics equations of motion.

The magnitude of the error in the electronic wavefunction is proportional to $\Delta\mathbf{V}_{sc}/T$ when either the first or second order equations of motion are used to evolve the electronic degrees of freedom so the error in the wavefunction is proportional to the velocity of the ions. Hence, the magnitude of the error in the electronic wavefunction

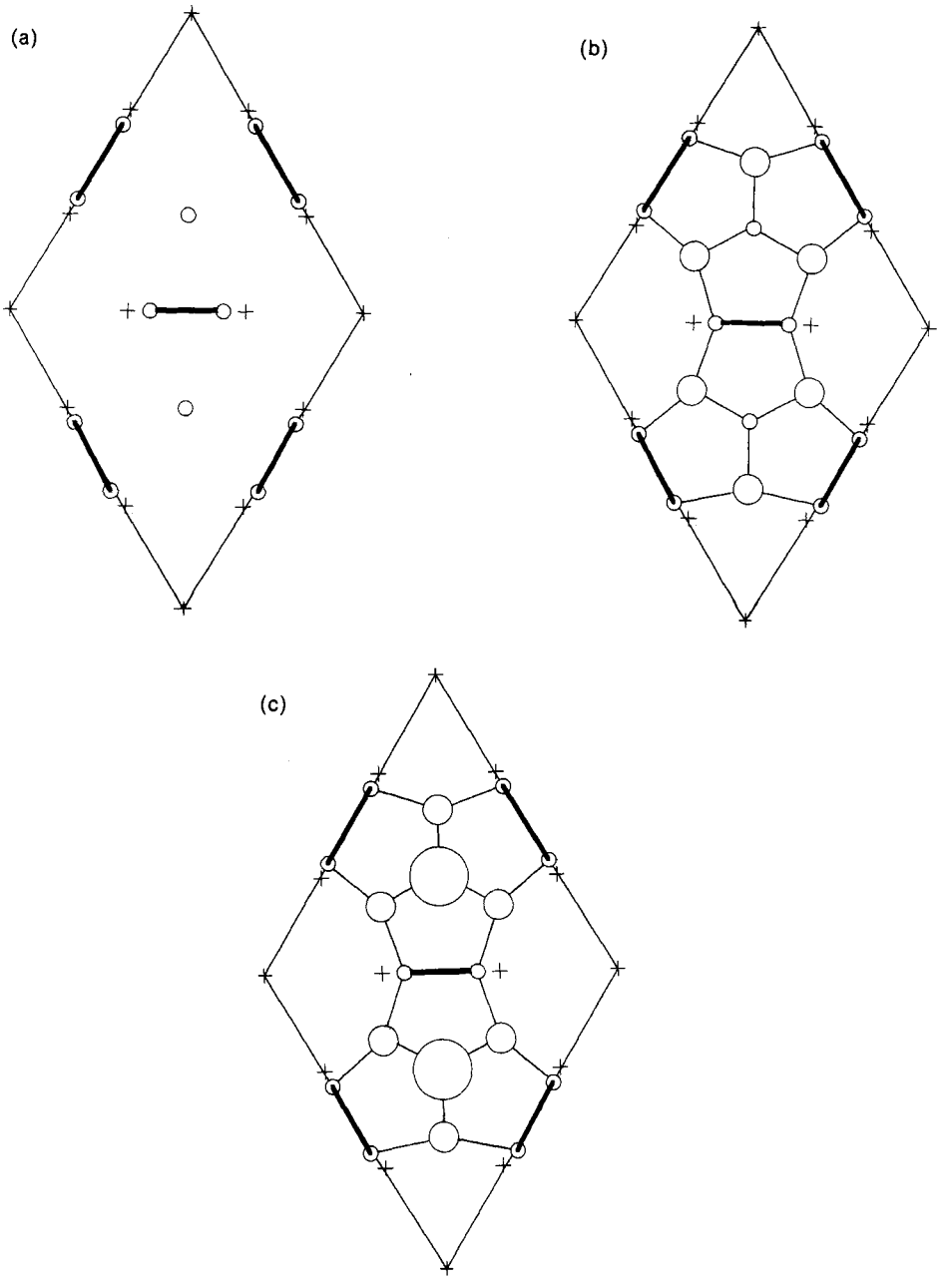

Figure 1 (a) The positions of the atoms in the second layer of the (3 × 3) Takayanagi reconstruction. The crosses show the positions of the atoms in the unreconstructed surface and the thick lines show the dimer bonds. (b) As (a) but showing the first and second layers. (c) As (a) but showing the adatoms and the first and second layers.

can be decreased by increasing the masses of the ions with respect to the fictitious mass of the electronic degrees of freedom so that the ions move more slowly with respect to the electronic degrees of freedom.

6. APPLICATIONS OF THE MOLECULAR DYNAMICS METHOD

In this section we briefly describe three systems to which the molecular dynamics method has been applied. The examples give some idea of the range of problems to which the total energy pseudopotential technique can be applied and the size of system that can presently be studied using Car-Parrinello methods. Examples of the use of the Car-Parrinello method to perform dynamical simulations of ionic systems can be found in references 12–14.

i. The Takayanagi Reconstruction

The Takayanagi reconstruction is observed on the (111) surfaces of silicon and strained germanium after annealing. The Takayanagi structure describes a family of reconstructions that can be formed in $(2m + 1) \times (2m + 1)$ unit cells where m is an integer. The reconstruction consists of dimer bonds and missing atoms in the second layer of atoms, stacking faults separating the first and second layers of atoms and adatoms. The (3×3) reconstruction is illustrated schematically in figure 1. The stability of the reconstruction is rather puzzling since the Takayanagi structure does not minimise the density of dangling bonds or the density of defects on the surface. By calculating the energy of the Takayanagi structure and of sub-elements of the structure it has been shown that the reconstruction is stabilised by a direct strain interaction between the dimers in the second layer of atoms and the adatoms [15].

ii. Negative Hubbard U Defects in Arsenic Tri-Selenide

It has been suggested that defects in chalcogenide systems would have a negative Hubbard U which implies that it is energetically favourable for two neutral defects to convert into a negatively charged and a positively charged pair of defects [16, 17]. The presence of defects in arsenic tri-selenide which have negative Hubbard U has been confirmed experimentally [18] but the nature of the defect was not known. By calculating the energies of selenium antisite defects in the neutral, positive and negative charge states it has been shown that this defect in arsenic tri-selenide has a negative Hubbard U of -0.3eV [19].

iii. The Structure of $\Sigma = 5$ [001] twist boundary in germanium

The $\Sigma = 5$ [001] twist boundary in germanium is formed by rotating one half of an infinite crystal bounded by an (001) plane by either 36.9 or 53.1° around an [001] axis. The boundary is free to translate both in and normal to the interfacial (001) plane and the boundary will adopt the translation state that has the lowest energy. By performing calculations in which the translation state in the plane of the interface is fixed and the positions of the ions are allowed to relax to equilibrium and the translation state perpendicular to the boundary is allowed to vary the energy surface of the boundary can be obtained and from this the lowest energy translation state can be deduced.

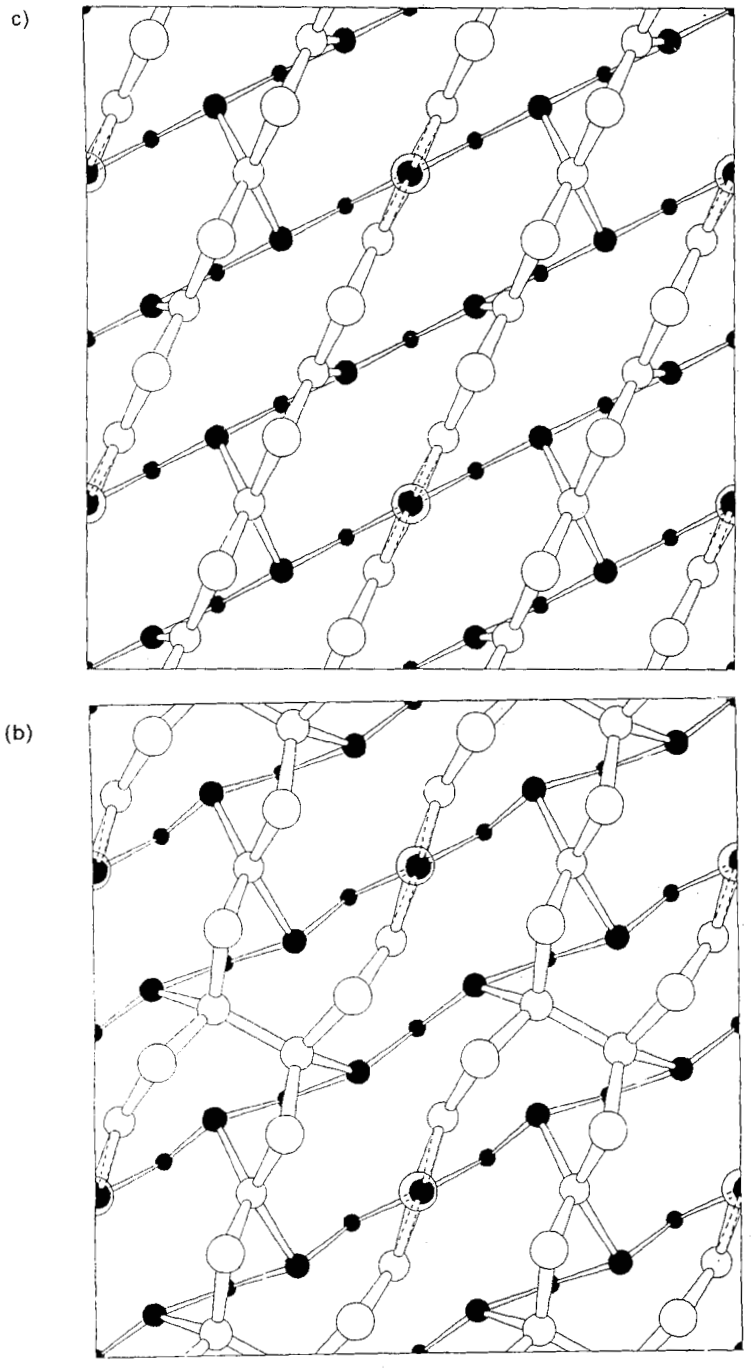

Figure 2 Atomic positions in planes normal to the [001] direction for two layers above (open circles) and below (filled circles) a $\sum = 5$ [001] twist boundary in germanium. (a) Unrelaxed CSL. (b) Relaxed CSL. (c) Unrelaxed 1/20 ⟨210⟩ state. (d) Relaxed 1/20 ⟨210⟩ state.

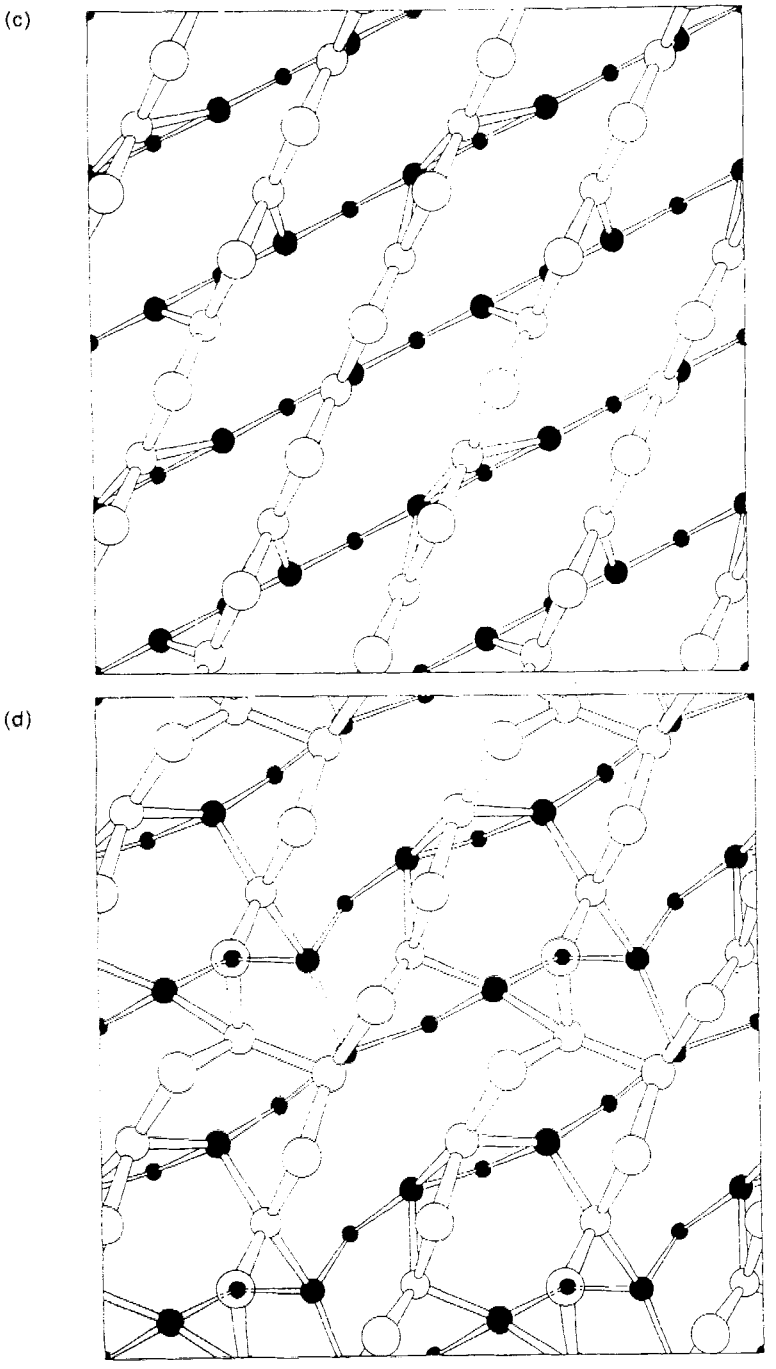

Figure 2 Atomic positions in planes normal to the [001] direction for two layers above (open circles) and below (filled circles) a $\sum = 5$ [001] twist boundary in germanium. (a) Unrelaxed CSL. (b) Relaxed CSL. (c) Unrelaxed 1 20 $\langle 210 \rangle$ state. (d) Relaxed 1 20 $\langle 210 \rangle$ state.

Typical structures found before and after relaxation are shown in figure 2. Figures 2(a) and 2(b) show the unrelaxed and relaxed structures of the concident site lattice (CSL) geometry where the upper crystal has been rotated about an axis passing through an atom adjacent to the interface. Figures 2(c) and 2(d) show the unrelaxed and relaxed structures of a boundary formed by translating the upper crystal through a displacement of 1/20 ⟨210⟩ from the CSL geometry.

The calculations described in this section used between 40 and 70 atoms in the unit cell and as many as 11,000 plane wave basis states were used to expand the electronic wavefunctions. Structural relaxation plays a crucial role in all of these systems so these problems can only be studied using a technique that allows the forces on the ions to be calculated accurately. Almost all of the calculations were on systems for which the microscopic structure is not known exactly and relaxing the system to equilibrium was an essential first step in each study. The ability to perform calculations and obtain detailed information about complex systems for which the microscopic structures are not known is unique to the total energy pseudopotential technique.

7. AB-INITIO MATERIALS SCIENCE AND ENGINEERING?

The purpose of this meeting is to consider computer modelling of new materials. The pseudopotential technique has the advantage of allowing reliable forces to be computed and the technique is a prime candidate for ab-initio studies of new materials. The Car-Parrinello scheme has increased the size and the range of systems that can be studied using the total energy pseudopotential technique. The application of the pseudopotential technique is basically limited by the size of system that can be studied. At present up to a hundred 'simple' atoms can be included in the unit cell. Relaxing the positions of the atoms to equilibrium and calculating the total energy for a system of this size may require up to 10 hours on a CRAY X-MP. Dynamical simulations of a system containing a hundred atoms for several thousand timesteps would require up to 100 hours on a CRAY X-MP. Computer speeds will increase significantly in the next few years mainly as a result of moving to parallel architectures. Car-Parrinello methods are ideally suited to parallel machines and so it should be possible to take full advantage of the new machines. However, ab-initio methods will always be intensely computationally demanding and they should always be applied with some degree of caution. Total energy pseudopotential methods will always be too expensive to allow them to be used to perform calculations on macroscopic systems but this does not mean that phenomena that occur in macroscopic systems cannot be studied using *ab-initio* techniques. *Ab-initio* techniques can be used to calculate the parameters in an effective Hamiltonian that describes the macroscopic system. Phase transition temperatures have been successfully calculated using this method [9, 20] which avoids the problems associated with finite size simulations and with critical slowing near the transition temperature. The path to success in using ab-initio calculations in engineering and in materials science is to isolate the parts of the problem where the microscopic behaviour of the system plays a critical role. For instance the microscopic structure of a crack tip plays a critical role in the propagation of the crack. However the structure of the crack tip is not the only parameter of relevance to crack propagation (for a review see references 21). The stress fields around a crack tip can activate dislocations sources in regions away from the crack tip. To model the entire system would require a calculation of a large region containing the crack tip and the

dislocation source which would be prohibitively costly. However, the crack tip and the dislocation source can be modelled separately and elasticity theory can be used to calculate the stress fields in the entire system to link the two regions. This would provide a realistic totally *ab-initio* method (if the elastic constants were calculated using *ab-initio* methods) to study crack propagation.

The Car-Parrinello method has taken the total energy pseudopotential method a long way towards the point where simple materials science problems are accessible to *ab-initio* techniques. Increases in computer power and algorithmic developments which have been notably lacking in the Car Parrinello scheme to date should enable relatively complex problems to be addressed using *ab-initio* methods.

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