

# AB FERE INITIO EQUATIONS OF STATE FOR SOLIDS

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A scheme is under development for predicting the equation of state of solid materials in shock-wave scenarios using a minimum of experimental data. Typically, the only experimental input is a pressure correction to match the ambient density. The equation of state is split as usual into components from the ground state of the electrons in a frozen-ion lattice, the electronic specific heat capacity and the thermal energy of the lattice. The electron ground state is calculated by a quantum-mechanical simulation of a lattice cell. The electron-thermal contribution is calculated from the band structure. The thermal energy of the lattice is found from its phonon modes. These are calculated from the forces acting on an atom displaced from its equilibrium position, e.g. by perturbing the position of atoms in the ground-state calculation. Anharmonic terms may be included. Results are presented for aluminium and silicon.

## INTRODUCTION

Theoretical methods are approaching the point where they can be used to deduce the equation of state (EOS) of a substance from first principles. This work is an evaluation of completely *ab initio* techniques, and a minimal normalisation to experiment. The EOS are evaluated in the context of high pressures.

## CONSTRUCTION

Completely *ab initio* EOS were generated, and then adjusted slightly to match experimental measurements. The specific internal energy  $e$  was split into contributions from the ground state, lattice-thermal and electron-thermal energies. Thermodynamic relations were used to deduce the pressure  $p$ .

The EOS were generated as rectangular tables of  $e$  and  $p$  as functions of density  $\rho$  and temperature  $T$ . Bilinear or quadratic interpolation was used in finding  $p$  and  $e$  at states between the ordinates of  $\rho$  and  $T$ .

### Ground state

The variation of ground state energy with density was calculated in the frozen-ion approximation using *ab initio* pseudopotential techniques. A non-local ( $l$ -dependent) reciprocal ( $k$ )-space pseu-

dopotential was obtained which had been fitted to reproduce the theoretical scattering effects of the core electrons in an isolated atom. Schrödinger's equation was solved to predict the ground state energy  $e_g$  of the outer electrons as a function of compression.(1) The electron band structure and Fermi energy were also predicted.

For aluminium, the use of the pseudopotential meant that only three outer electrons from each atom had to be considered. Calculations were made of fcc, hcp and bcc structures. The results agreed with the experimental observation that fcc is the stable phase up to several hundred GPa. For silicon, four outer electrons were considered from each atom. Calculations were made of the diamond structure – other phases are in progress.

These calculations used the local density approximation(2) and generalised gradient correction(3) to model the exchange-correlation effect. The outer electron wavefunctions were expanded in a plane-wave basis set. Plane waves with energies of up to a few hundred eV, were necessary for a converged ground state energy. The wavefunctions were evaluated at a finite number of points in  $k$  space, evenly distributed throughout the reciprocal lattice cell. Using 1000 points distributed uniformly throughout the Brillouin zone, the

ground state energy had converged to better than 1 GPa. The symmetry of the lattice was used to identify a smaller set of unique  $k$ -points, increasing the speed of the ground state calculations.

### Lattice-thermal energy

To predict the lattice-thermal energy, the harmonic modes of lattice vibration were determined and a density of phonon states deduced. The phonon modes were populated using Bose-Einstein statistics to obtain the lattice-thermal energy as a function of temperature, at each density.

Lattice modes can be calculated quite efficiently if the atoms can be treated as if they were interacting through an analytic potential. Empirical interatomic potentials were fitted to the frozen-ion cold curve in aluminium, and the resulting density of states compared with experimental data. Radial pair potentials of the inverse power type gave a poor match to the density of states. Morse potentials(4) gave a better match. Multi-body potentials of the Finnis-Sinclair type(5) gave the most promising match, but these potentials contained too many degrees of freedom to be fitted only to the cold curve – most of the lattice modes were unstable.

It is not appropriate to represent interatomic interactions in silicon using radial or Finnis-Sinclair potentials. Elements of the dynamical matrix of the lattice were found by perturbing atoms in the ground state calculations, and making use of the relation

$$\frac{\partial^2 \Phi}{\partial [\vec{u}_i]_\alpha \partial [\vec{u}_j]_\beta} \simeq \frac{\partial \Phi([\vec{u}_i]_\alpha)}{\partial [\vec{u}_j]_\beta} \frac{1}{[\vec{u}_i]_\alpha} \quad (1)$$

where  $\vec{u}_i$  is the displacement of atom  $i$  from its equilibrium position,  $\Phi$  is the total potential energy, and square brackets denote components of a vector.  $\frac{\partial \Phi([\vec{u}_i]_\alpha)}{\partial [\vec{u}_j]_\beta}$  is the force component  $[\vec{f}_j]_\beta$  on atom  $j$  when atom  $i$  is displaced in the  $\alpha$ -direction – a quantity readily obtained from the ground state calculation. Symmetry operations were used to reduce the number of calculations required. For silicon, only a single displacement was necessary of one atom in one direction at each density. The diamond structure is not centrosymmetric, so an iterative scheme had to be used to enforce the sym-

metry of the dynamical matrix.(6) Calculations were made with displacements of different magnitudes, in order to estimate the anharmonic effects. These seemed small in silicon. The perturbations were made in a periodic 8-atom diamond cell, so the atomic forces were obtained out to second nearest neighbours.

Similar calculations were made for aluminium, using a periodic array of  $2 \times 2 \times 2$  fcc cells. The atomic forces were estimated to third nearest neighbours. The fcc lattice is centrosymmetric, so the symmetry of the dynamical matrix can be enforced by altering the components on the main diagonal.(6) The density of states was closer to experiment than the results obtained using a radial pair potential. The remaining deficiency probably reflects the slower convergence of forces with iterations towards the ground state, compared with the convergence rate of the total energy.

Estimates were made of anharmonic corrections in aluminium using a Morse potential in Monte-Carlo simulations of the lattice. Initial results show some anharmonicity, but more work is needed before the correction can be added reliably to the EOS.

### Electron-thermal energy

The density of electron energy levels was estimated from the band structure, and populated using Fermi-Dirac statistics, varying the chemical potential to constrain the total number of electrons.(7) As expected for a simple metal such as aluminium, the resulting electron-thermal energy was very close to estimates made with the free electron model(8) in the range of states considered here. The electron-thermal energy was ignored in silicon.

### Completing the equation of state

Given the total specific energy  $e(T)$  along each isochore, the specific entropy  $s$  was found by integration:

$$s(T) = \int_0^T \frac{dT'}{T'} \frac{\partial e}{\partial T'}. \quad (2)$$

The specific free energy  $f$  was then calculated simply from  $f = e - Ts$ . The pressure  $p$  was obtained from  $p = -(\partial f / \partial v)_T$ .

### Improving the accuracy

It was found that the *ab initio* EOS overpredicted the density at  $p = 0$ . To retain as much *ab initio* character as possible, a minimal normalisation was made, offsetting the ground state pressure by a constant amount  $\Delta p_g$ . This resulted in a tilt in ground state energy,  $\Delta e_g = -v\Delta p_g$ . The almost first-principles ('*ab fere initio*') EOS were then calculated as before, but starting from this new ground state energy. A pressure offset of 2 to 5 GPa was required in practice.

### EVALUATION

Since the EOS derived from this work are intended for use in shock wave simulations, they were evaluated against measurements for  $\rho \geq \rho_0$ .

### Normal density

Table 1 shows the *ab initio* predictions of normal densities at 293 K compared with experiment. The *ab initio* EOS produced densities which were somewhat too large. In the *ab fere initio* EOS, this discrepancy was corrected to arbitrary accuracy.

**TABLE 1.** Normal densities ( $\text{Mg}/\text{m}^3$ ).

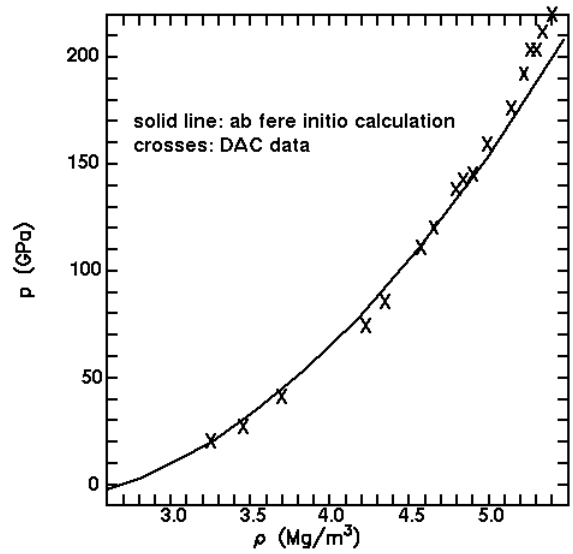
	experiment	calculation
aluminium	2.70	2.76
silicon	2.33	2.42

### Ambient isotherm

Diamond anvil measurements have been made of the isotherm of aluminium at room temperature to 220 GPa.(9) The *ab fere initio* EOS matched the data very closely up to about 100 GPa, then fell below it. (Fig. 1.) The pseudopotential model breaks down at high compressions, when the inner electron states change appreciably. This is the likely cause of the discrepancy.

### Shock Hugoniot

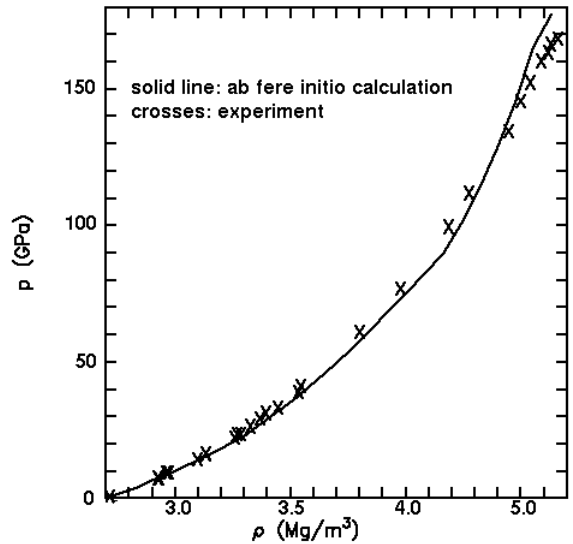
The principal shock Hugoniot was calculated using the EOS to close the Rankine-Hugoniot form of the hydrodynamic conservation equations.(10) This was compared with data on aluminium alloys 1100 and 6061,(11,12) whose composition and equilibrium density are close to that of the element.



**FIGURE 1.** Ambient isotherm of aluminium.

The effects of non-isotropic stress (e.g. material strength) were ignored in this analysis.

The *ab fere initio* EOS was a reasonable match to the data over its full range. The undulations evident in the density – pressure graph are caused by the use of bilinear interpolation on a relatively coarse density grid. (Figures 2 and 3.)



**FIGURE 2.** Aluminium Hugoniot: pressure and density.

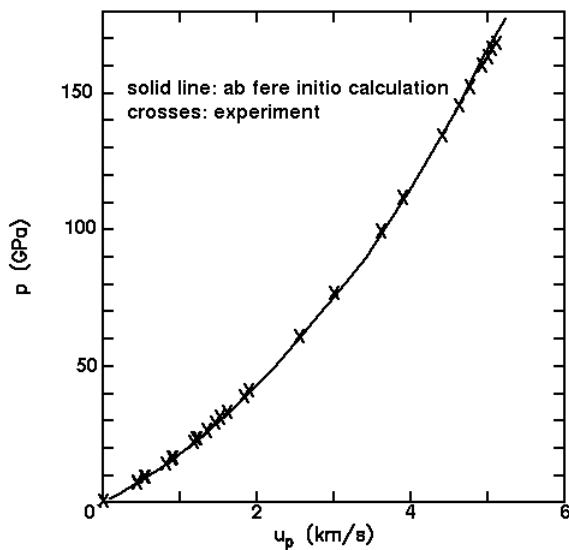


FIGURE 3. Aluminium Hugoniot: pressure and particle speed.

In silicon, the *ab fere initio* EOS was a good match to the data(13) up to the first phase transition. (Fig. 4.)

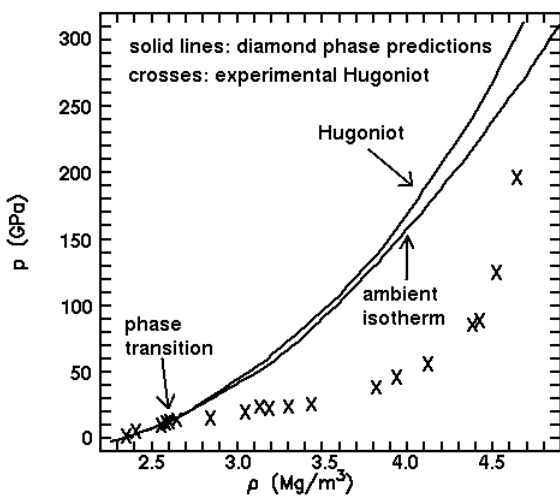


FIGURE 4. Silicon: pressure and density.

## CONCLUSIONS

This study demonstrates that completely *ab initio* methods based on non-local pseudopotentials and the quasiharmonic approximation, with

minimal fitting to experimental data, can reproduce the compression equation of state of aluminium to over 50 GPa and that of silicon to the first phase transition. The equation of state was adjusted by adding a pressure offset to give the correct normal density.

The scheme described has considerable attractions as a method of generating equations of state. It can be applied to any substance which can be represented by a reasonably small number of atoms in a repeating lattice. The method can be checked against results from other types of experiment, such as the density of phonon states.

## ACKNOWLEDGEMENTS

This work would not have been possible without the help of Graeme Ackland, Stewart Clark, Michele Warren (University of Edinburgh) and Mike Payne (University of Cambridge) for theory and algorithms, and Art Ruoff (Cornell University), Bill Nellis and David Young (Lawrence Livermore National Laboratory) for experimental data.

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