WHY LINEAR BIRCH AND U_3 - U_0 EXPANSIONS WORK

R. GROVER

Physics Department, University of California, Lawrence Livermore National Laboratory,
P.O. Box 808, Livermore, California 94550*

The equivalence of the Birch-Murnaghan equation to a linear U_3 - U_0 equation was illustrated in the previous paper. Here we show in a direct manner how the virial theorem and the effect of core exclusion on valence electron kinetic energy changes lead to the convergence of the Eulerian strain expansion about the zero-pressure state.

1. INTRODUCTION

As in the case of the velocity expansion of shock compression data, the Eulerian finite strain expression for isothermal pressure-density data on solids appears to converge so well that even in the best circumstances it shows little or no evidence for quadratic strain terms.^{1,2} Since it is both systematic and convergent, the Eulerian strain expansion seems, therefore, to represent an optimum way of characterizing the static lattice equation of state of all types of solids over extended ranges of compression. However, a general physical explanation of this situation has unfortunately not been reported, although the consistency of shock compression data with standard, phenomenological pseudo-potential and pair-potential models has previously been discussed.³

Here we present a semiquantitative explanation of the convergence of the Eulerian strain expansion from the self-consistent electron band theory of solids in the local density approximation for exchange and correlation. This theory has provided a basis for nearly exact calculations of equation of state properties for a great variety of solids.

Several static lattice calculations for simpler metals have in fact been found to be well represented by nearly linear strain expansions out to compressions of 3.² We find that the virial theorem can be used with this theory to relate the bulk modulus and its higher derivatives to electron kinetic energy changes during compression. McMahon⁴ has already identified the latter as an important factor in changes of phase and electron bonding at high pressure. The necessary kinetic energy properties for convergence are then derived in a semiquantitative way from several appropriate models.

2. VIRIAL THEOREM APPLICATION TO BIRCH EQUATION

The virial theorem for Coulombic systems relates the kinetic energy t and potential energy ϕ components of the internal energy E to the pressure P

$$E = t + \phi \quad (1)$$

$$VP \equiv dE/d\ln\rho = \frac{2t}{3} + \frac{\phi}{3} \quad (2)$$

If we separate first order energy changes into scaling, σ , and distortion, γ , components such as

$$dt = d_\sigma t + d_\gamma t \quad (3)$$

then in Hartree-Fock theory $d_\gamma \phi = -d_\gamma t$ so that

* Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

MASTER

$d_g E = 0$. In taking higher derivatives of Eq. (2) to study higher compression moduli the same cancellation is not complete and more complicated expressions result.

It is known that additional small terms must be added to the pressure Eq. (2) in the local density approximation. A rough estimate of the correction for the Hedin-Lundquist model for exchange-correlation is $< 20\%$ of the correlation energy. Looking ahead we will find that the desired properties depend on changes in the much larger electron kinetic energies, permitting us to drop this and other correlation corrections from further consideration.

Thus we estimate bulk moduli and their high pressure derivatives from differentiations of (2) with respect to density, replacing ϕ by $E - t$ and $dE/d\ln\rho$ by VP to get equations in terms of electron kinetic energies and P . For instance the bulk modulus K and its first pressure derivative K' , the Murnaghan parameter, are then given at zero pressure simply by

$$3V K_0 = dt/d\ln\rho \equiv t' \quad (4)$$

$$K_0' - 7/3 = d^2t/d\ln\rho^2 \equiv \tau \quad (5)$$

in terms of two convenient kinetic energy parameters t' and τ .

The linear Birch-Murnaghan equation of state is completely determined by these quantities, the pressure being scaled to K_0 and the coefficient of the linear strain term, A_1 by K_0'

$$A_1 = 3/2 (K_0' - 4) \quad (6)$$

The convergence of the strain expansion in the range of presently available compression data is then adequately evaluated by looking at the next two higher strain coefficients A_2 and A_3 which involve the next two pressure derivatives of K_0 . By differentiating (2) twice more and with the use of (4) and (5) we may write these pressure derivatives at zero pressure in dimensionless form as

$$K_0 K_0'' = -K_0' + \mathcal{O}[(1 - \tau/3 + d\tau/d\ln\rho) \quad (7)$$

$$K_0^2 K_0''' = -2K_0' K_0 K_0'' + \mathcal{O}[(\tau - 1/3) d\tau/d\ln\rho + d^2\tau/d(\ln\rho)^2]. \quad (8)$$

Empirically the K_0' is a large number in the range 3.5-6 for all solids of interest. The virial theorem then allows this to be done with smaller values of τ in the range 1-3, according to (5), which values we justify in the next section in terms of the behavior of electron kinetic energy in compression. Here we argue, mainly because of the large size of K_0' , that the last terms in (7) and (8) are relatively small as indicated by the nomenclature. Dropping them, we may show the smallness of A_2 and A_3 , starting from their expressions in terms of K_0 , K_0' , etc.,

$$A_2 = 3/2 [K_0 K_0'' + K_0' + (K_0' - 11/3)(K_0' - 13/3)] \quad (9)$$

$$A_3 = 9/8 (K_0^2 K_0''') + 4K_0 K_0' (K_0' - 8/3) + (K_0' - 16/3) [(K_0' - 8/3)^2 + 6] \quad (10)$$

Calculations of A_2 and A_3 in the indicated approximations (7) and (8) are shown in Table 1 to demonstrate their smallness.

Table 1

K_0'	3.5	4	5	5.5
A_2	.21	-.17	1.33	3.21
A_3	0.63	0.33	-0.54	0.57

Together with smallness of the Eulerian strain variable $(-\Delta R/R)$ in the range of compression data (< 5) the conditions (7) and (8) assure very small non-linear strain contributions to the equation of state² below compressions of 2.

3. MODEL CALCULATIONS OF τ

Here we can only qualitatively describe and summarize our calculations of electron kinetic energy changes during compression. We use for this purpose the quantity t' defined by (4) which represents a characteristic amount of kinetic energy increase under infinitesimal

amounts of compression. According to (3) we may divide this into distortional and scaling contributions,

$$t' = t'_Y + t'_\sigma \equiv \frac{d t_Y}{d \ln p} + \frac{d t_\sigma}{d \ln p} \quad (11)$$

For example in the high density, uniform electron gas model $t' \rightarrow t'_\sigma = 2t/3$ and $\tau \rightarrow 2/3$. The logarithmic derivatives of t' given by τ and its density derivatives then determine the convergence of the Birch-Murnaghan equation as indicated in Eqs. (5)-(10).

For normal atoms contributions to kinetic energy changes, t' , are essentially localized to the outer, more polarizable layers of the atom, as the higher energy valence electrons gradually become excluded from a rigid ion core. Such properties are readily seen in the electronic charge or potential distribution given by the Thomas-Fermi (TF) model, which model provides a realistic average model for equation of state. Table 2 presents some direct calculations of the kinetic parameter τ , (5), with the TF model over a wide range of interatomic radii (Z scaled).

Table 2. Kinetic energy parameter in Thomas-Fermi theory

$Z^{1/3}R$	=	100	25	10	5	0
τ_{TF}	?	.45	.57	.65	1.0	$\rightarrow 2/3$

Thus in a TF gas model of compressibilities at normal densities, ranging over $2 < Z^{1/3}R_0 < 20$, or from metallic H to C_6 , kinetic energy changes raise values of K_0' to about 2/3 of normal values according to (5) and, because of the slow variation of τ with density, are also consistent with the higher order approximations in Eqs. (7) & (8).

Boundary localization effects play a stronger role however in full electron-band theory calculations of energy changes around normal solid densities. Here electrons find

themselves in band states of definite angular momentum & (approximately) which are confined to a region outside of a fixed ion core, increasing the sensitivity of their kinetic energy to compression of the atomic cell. Volume independent core exclusion can arise both from the centrifugal potential in non-zero l states and from orthogonalization to much lower states of the same l in non-threshold cases. These features are indeed built into the concept of electron pseudo-potentials and can be treated in a perturbation theory for the simpler metals. Here we try to crudely model kinetic energy effects in a non-perturbative way so as to approximate their properties in any correct band theory calculation.

We may first of all approximate enhancement of τ by a simple, one-dimensional gas model for radial kinetic energies in which electrons are confined between the Wigner-Seitz and inner core radii of R and R_c where

$$R_c = K_c R. \quad (12)$$

In this case t refers to valence kinetic energies only and we can introduce a related quantity λ according to

$$\lambda = \frac{d t_Y}{d \ln p}, \quad \tau = \lambda + \frac{d \lambda}{d \ln p} \quad (13)$$

Then simple calculations for this excluded core potential v_{cx} gives the large, realistic values of τ , when K_c is not small, shown in Table 3.

Table 3. Core size dependence of kinetic energy for v_{cx} model

K_c	1/3	1/2	2/3	3/4
λv	1	4/3	2	8/3
τv	7/6	5/3	8/3	11/3
$d\tau_Y/d\ln p$	1/4	2/3	(2)	(4)
$d^2\tau_Y/d(\ln p)^2$	1/6	2/3	(7/8)	(28/3)

The large values of the higher derivatives at the largest K_c are taken to be upper limits

due to model deficiencies (see below). How this model comes to have the essential features of the kinetic energy changes is made clear in a semiclassical treatment of electron band states of different λ .

The two main questions which are discussed here are what values of K_C are to be used and the adequacy of the uniform Fermi-gas approximation for the electron bandstates. We use a Thomas-Fermi model at the appropriate atomic volume for the electrostatic part of the electron potential v_{TF} in different λ states. Thus band eigenstates are obtained in the lowest semiclassical approximation from the radial 'phase' integral $\chi(\epsilon) = \int_{-}^{+} k(r, \epsilon) dr \equiv n_{\lambda} \pi$ where $k = [\epsilon - v_{TF} - (\lambda+1/2)^2 / 2r^2]^{1/2}$ and the kinetic energy of a valence electron ϵ_{λ} is primarily determined by its radial quantum number n_{λ} and the corresponding density of states $n_{\lambda, \epsilon} = dn_{\lambda} / d\epsilon$

$$\epsilon_{\lambda} = v_{TF} / n_{\lambda, \epsilon}, \quad n_{\lambda, \epsilon} = \frac{1}{\pi} \int_{-}^{+} \frac{dr}{k_{\lambda}} \quad (14)$$

It is well known that valence electron states are largely excluded from core states because of overlap with lower energy bound states of the same λ or because of the centrifugal potential for 'threshold' cases where no bound state exist. If we represent this by an empty-core electron pseudopotential we may obtain a realistic estimate of R_C (and K_C) by requiring $n_{\lambda} = 1/2$ for electrons at the Fermi energy. Such estimates agree closely with electron potentials in metals calculated by electron band theory methods.⁷ Representative examples are given in Table (4) calculated with Thomas Fermi potentials. Carbon is an example of a threshold λ -state (i.e., a p-state) with a typical small core, but in most cases solids with p-state bonding experience large phase transitions on compression and are not of interest here. Rb has a large 4s

orthogonalization core and in Ag the 4s core K_C is especially large because of its high density due to strong resonance bonding of the 4d electrons. Experimental values of K_0 also increase dramatically from C to Ag consistent with the increase in their K_C 's.

Table 4. Semiclassical calculations of τ in Thomas-Fermi potential

Element	$2^{1/3} R_0$	v_{TF}	K_C	γ_0	γ_1
C	3.82	> 1	~.2	—	~1.0
Rb	19.0	~.6	~.35	~1.7	—
Ag	11.0	~.65	~.65	—	—

Semiclassical values of λ_{λ} from Eq. (14) for particular band states in a fixed v_{TF} are also shown in Table 4 and they imply a τ equal to or greater than values in Table 3 at the corresponding K_C . Additional calculations including the effect of self-consistency as well as band averaging will be presented in a later, more complete publication.

REFERENCES

1. R. Jeanloz and R. Grover (previous article this volume).
2. R. Grover, Birch Expansions Beyond 2-Fold Compression, Lawrence Livermore Nat. Lab. UCL-95388 (1986).
3. A.L. Ruoff, J. Applied Phys. 38 (1967) 4976
S.P. Singh, Phys. Rev. B, 9 (1973) 3313
K.-J. Dunn, Phys. Rev. B, 12 (1975) 3497.
4. A.K. McHahan, Physica 139 & 140 B (1986) 31.
5. D.J. Steinberg, J. Phys. Chem. Solids 43 (1982) 1173.
6. Note the smallness of A_2 and A_3 in Table 1 arise from Eq. (7), requiring that roots of A_2 be $11/3$ and $13/3$ and Eq. (8), that A_3 's roots are $(11 \pm \sqrt{3})/3$ and $16/3$.
7. V.L. Moruzzi, J.F. Janak, A.R. Williams, Calculated Electronic Properties of Metals, (Pergamon Press Inc., New York, 1978).

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.