Ab initio calculations of bulk moduli and comparison with experiment

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Bulk moduli appear readily accessible in electronic structure calculations, but the calculated values are often substantially greater than experimental bulk moduli. This discrepancy is the result of an unfair comparison of calculated and experimental results: many workers ignored the zero-point and finite-temperature effects that are present in experiments but absent from most calculations. These effects can alter bulk moduli by up to 20%. We show how good approximations to the required corrections may be obtained with little effort. We also deal with the statistical errors and biases in quantities derived from the noisy energy-volume curves produced by quantum Monte Carlo simulations.

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I. INTRODUCTION

Calculations of bulk moduli are often used to test *ab initio* electronic structure techniques such as Hartree-Fock theory, Hohenberg-Kohn-Sham density-functional theory[1] (DFT) within the local density or generalized gradient approximation (LDA or GGA), and variational and diffusion quantum Monte Carlo[2] (VMC and DMC) methods. Only a handful of publications,[3–5] however, have taken proper account of subtleties that cannot be ignored. The results of zero-temperature ground-state electronic structure calculations are not directly comparable with experimental measurements that include zero-point phonon effects, and are often taken at room temperature. The temperature and phonon effects can modify the calculated bulk modulus by up to 20% (see Table I), invalidating any comparison of theory and experiment that does not take them into account, and explaining the frequently reported overestimation of bulk moduli.[6–9] Although these effects are known and have been evaluated satisfactorily,[3–5] they are still frequently overlooked.

One of the two main aims of this paper is to show how, by generalizing the work of Ref. 10, one can deal adequately with these issues in an approximate way, without having to calculate the volume dependent phonon spectrum, as necessary when using the quasiharmonic approximation (QHA).[3–5] Our approach uses measured quantities to adjust the experimental bulk modulus B, isolating the underlying value B_0. Stripped of zero-point and finite-temperature effects, B_0 is directly comparable to the results of *ab initio* ground-state calculations with frozen ions, such as the QMC method. This methodology becomes useful whenever the QHA is not feasible (i.e., in complex systems or when using QMC methods) or where the extra effort required to implement the QHA is not warranted.

The second aim of this paper is to address the difficulties that arise from the anharmonicity of the equation of state (EOS), and, in the case of VMC and DMC calculations, from statistical errors in the data. Previous QMC calculations of bulk moduli did not take adequate account of these issues, and consequently their results are of dubious value. Throughout this paper, we refer to our own LDA and VMC calculations of bulk aluminum.[11]

II. BULK MODULUS

Most DFT and quantum Monte Carlo (QMC) calculations assume that the nuclei are frozen and hence that the total energy is the quantum-mechanical energy of the electrons plus the Coulomb energy of the fixed lattice of the atom cores. Phonon zero-point and thermal effects, usually present in experimental data, are absent.

Additional difficulties arise because the energy versus volume curve is quadratic only very close to the minimum. In DFT calculations, this problem is commonly dealt with by using a more flexible fitting function such as a quartic polynomial or the Murnaghan EOS.[12] In QMC calculations, where the data are noisy, the choice of fitting function becomes even more important. Furthermore, the variances and

TABLE I. This table shows the experimental bulk modulus B (10^{11} Nm^{-2}), its pressure derivative B' (dimensionless), and the equilibrium lattice parameter a (Å), of a selection of solids. After the removal of finite-temperature and zero-point effects (see the text), the experimental bulk modulus and lattice parameter reduce to the values B_0 and a_0. The results of first-principles, ground-state calculations are directly comparable to B_0 and a_0, and are therefore presented in the same column. The experimental values of B' are not adjusted and are not directly comparable with the theoretical values. Note that the VMC-4 result is within a standard deviation of B_0.

	B	B'	a	B_0	a_0
Experiment					
Al	0.759	4.27	4.050	0.813	4.022
Li	0.121	3.39	3.51	0.145	3.44
Ni	1.86	2.90	3.52	1.91	3.51
Pb	0.448	2.58	4.95	0.473	4.91
Theory					
Al:LDA	-	[4.83]	-	0.802	3.960
Al:VMC-4	-	[6.9(1.1)]	-	0.65(17)	3.970(14)
Al:VMC-2	-	[-1]	-	0.72(7)	4.034(15)
Li:LDA	-	-	-	0.151	3.37
Ni:GGA	-	-	-	1.92	3.53
Pb:LDA	-	[5.32]	-	0.487	4.99

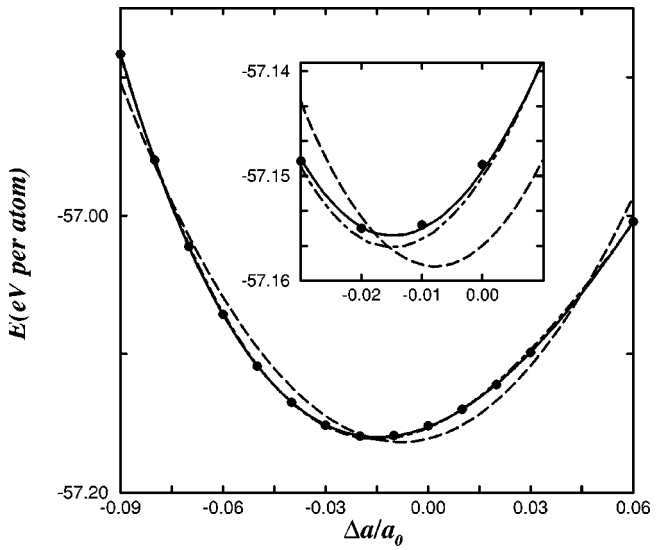

FIG. 1. The energy as a function of the fractional change in the lattice constant relative to the experimental equilibrium value. The dots are the LDA data points. The solid line is a quartic fit, the dot-dashed line is a cubic fit, and the dashed line is a quadratic fit.

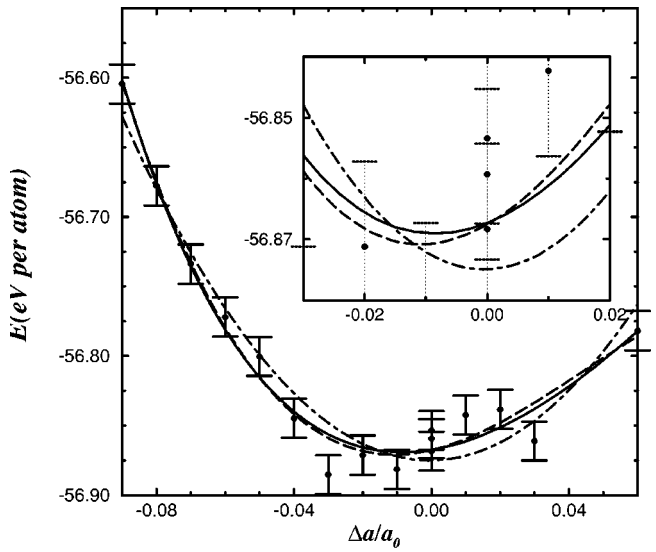

FIG. 2. The dots with error bars are VMC energies and errors. The solid line is a fit to the Murnaghan equation, the dashed line is a quartic fit, and the dot-dashed line is a quadratic fit. Note that the Murnaghan and quartic fits, despite their similarity, give bulk moduli differing by 10%.

biases of bulk moduli and other physical quantities obtained from the fitted EOS can be large and need careful statistical analysis.

A. Equation of state

The bulk modulus B is defined by the equation

$$B = V\frac{\partial^2 E}{\partial V^2} = -V\frac{\partial P}{\partial V}, \tag{2.1}$$

where $E(V)$ is the total ground-state energy as a function of volume, P is the pressure, and B is evaluated at the minimum of $E(V)$.

Although the bulk modulus is essentially the curvature of $E(V)$ at the equilibrium volume, it is customary, but not universal,[13,14] to go beyond a simple quadratic fit. In fact, if E is assumed to be a quadratic function of V (or of the lattice parameter a), the pressure derivative $B' = dB/dP$ is equal to -1 (or 1). In most real solids, B' lies between 3 and 5 (see Table I). Better fitting functions are higher-order polynomials, the Murnaghan equation of state[12] (which is based on the assumption of constant B'), or generalizations thereof.

Figure 1 shows the anharmonicity of the EOS of aluminum as calculated within the LDA. When the EOS is calculated using QMC methods, it is necessary to take data over a wide range of lattice parameters in order to discern the underlying shape of the curve above the noise. A simple quadratic fit to such data may ''look'' acceptable (see Fig. 2), but produces very inaccurate numerical results. These difficulties may be demonstrated by fitting the almost noise-free LDA EOS over a similarly wide range of lattice parameters. Quartic polynomial and Murnaghan equation fits (not shown) work well and produce nearly indistinguishable results, while cubic and quadratic polynomial fits show serious discrepancies (see Fig. 1) that are worse when fitting to $E(V)$ than to $E(a)$. In addition, we find that the variance of the distribution of VMC data points around a second- or third-order polynomial fit is greater than the QMC error, implying that the fitting function is insufficiently flexible. By contrast, if we use polynomials of order greater than 6, we may find that we are fitting the noise. In practice, we prefer a quartic fit, because, unlike the Murnaghan equation, it is linear in the parameters, aiding the statistical analysis.

Although the quadratic fit (Fig. 2 and VMC-2 in Table I) to the noisy VMC EOS of aluminum is numerically unsatisfactory, it appears to give better results than the more realistic quartic fit (VMC-4). The bulk modulus obtained from the more trustworthy quartic fit is not very accurate, but nevertheless lies within one standard deviation of the experimental value.

B. Approximate adjustment

A good way to account for the zero-point and finite-temperature effects is to evaluate the phonon spectrum and its volume dependence in conjuction with the QHA,[3–5] which, however, goes well beyond a ground-state electronic structure calculation. Instead, we aim for a method whereby we use experimental data to extrapolate the measured value of B to zero temperature and then subtract the zero-point contribution, yielding a value that is directly comparable to calculated *ab initio* results. One might equally well choose to adjust the computational results,[15] but our approach has the advantage of maintaining a clear division between experimental data and computational results derived from first principles.

The following analysis is based on the work of Dacorogna *et al.*[10] on adjusting bulk moduli for the effect of the zero-point motion of the ions. We extend Dacoragna's analysis to include the effects of finite temperature. This is necessary if

zero-temperature data is not available, if it is too unreliable, or if the material of interest does not exist at 0 K (e.g., bcc lithium).

The measured fractional volume change[16] $\Delta V/V$ that occurs on heating from 0 K to room temperature can be viewed as having been brought about by applying a small negative pressure P_t, which we can estimate by virtue of $\Delta V/V = -P_t/B$. We can then use data on the pressure or volume dependence of the bulk modulus to translate the temperature-induced volume change into a predicted change in bulk modulus. The zero-point motion, which also increases the volume of the unit cell, acts as another source of negative pressure P_z, which can be treated analogously.

The phonon energies are related to the elastic constants, one of which is the bulk modulus. Since the frequency of any harmonic oscillator scales as the square root of the spring constant, we deduce[10] that the phonon zero-point energy ζ_z, which in the Debye theory is equal to $\frac{9}{8}k_B\Theta_D$, where Θ_D is the Debye temperature, scales as $\sqrt{B}$. The effective pressure required to mimic the effect of the zero-point energy is thus

$$P_z = \frac{\partial \zeta_z}{\partial V} = \frac{\zeta_z}{2B}\frac{\partial B}{\partial P}\frac{\partial P}{\partial V} = -\frac{\zeta_z}{2V}B'. \tag{2.2}$$

The increase in the lattice constant caused by the zero-point motion may be obtained from P_z as follows:

$$\frac{\Delta V}{V} = -\frac{P_z}{B_0} = \frac{\zeta_z B'}{2VB_0}. \tag{2.3}$$

Finite-temperature and zero-point motion effects push the ions apart, so P_t and P_z are both negative. Using $\Delta B = B'(P_t + P_z)$, we find the change in B induced by these effects. Since $\Delta B < 0$, the underlying electronic bulk modulus is larger than the experimental one.

Table I shows adjusted and unadjusted experimental data for several different materials (fcc aluminum, nickel, lead, and bcc lithium), as well as computational results. The experimental bulk moduli are room-temperature values extracted from the single-crystal elastic constants[17] given in the *CRC Handbook of Chemistry and Physics*; B' is estimated using Gschneider's[18] data; and all other input variables are taken from Ref. 16. The DFT/LDA and VMC results for Al are taken from Gaudoin *et al.*,[11] the DFT/GGA results for Ni from Cho *et al.*,[19] the DFT/LDA results for Li from Sigalas *et al.*,[21] and the DFT/LDA for lead were generated using ABINIT.[20] Entries marked VMC-2 or VMC-4 are obtained using a quadratic fit to the VMC data for $E(V)$ or a quartic fit to the VMC data for $E(a)$, respectively. The results emphasize that calculations appearing out of step with experimental data may turn out to be quite accurate once zero-point and finite-temperature corrections have been applied.

Note that many substances, including bcc lithium, change crystal structure as they are cooled. In such cases, the adjusted experimental data ought to be compared with the results of zero-temperature electronic structure calculations for the room-temperature crystal structure. Also note that despite not being *ab initio*, the scheme presented here is sound and easy to apply.

C. Statistical analysis of Monte Carlo data

Since QMC data for $E(V)$ is noisy, estimates of the bulk modulus obtained are bound to be noisy and biased too. Due to frequent neglect of the statistical analysis of QMC data we quickly present what we think is an adequate analysis when the fitting function is linear in the parameters.

A general least-squares fit minimizes the quantity $d = \langle E - f(\boldsymbol{\alpha}) | E - f(\boldsymbol{\alpha}) \rangle$ with respect to the fitting parameters $\boldsymbol{\alpha}$, where E is the energy per unit cell, $\langle x|y\rangle := \Sigma_i [x(a_i)y(a_i)/\sigma_i^2]$, and the sum is over the set of lattice parameters a_i. We write the fitting function as a linear combination of basis functions $b_j(a)$, which might be low-order polynomials: $f(a,\boldsymbol{\alpha}) = \Sigma_j \alpha_j b_j(a)$. The implicit assumptions are that there exist parameter values α_j^0 that capture the underlying phenomenon, and that the measured quantities are noisy realizations of $f(a_i,\boldsymbol{\alpha}^0)$. It follows that $E(a_i) = f(a_i,\boldsymbol{\alpha}^0) + \eta_i(0,\sigma_i^2)$, $\eta_i(0,\sigma_i^2)$ being independent Gaussian random variables with mean 0 and variance σ_i^2. If the σ_i^2's are unknown they may be set to 1, as a least-squares fit does not depend on a constant scaling factor in the errors. However, the statistical analysis presented below does depend on the magnitude of σ^2, which can be estimated *post hoc* from the distribution of data points relative to the fitted curve. As a consistency check, it is advisable to perform such an estimate in any case. In Fig. 2 for example, as expected, five of the 16 data points lie more than one error bar from the fitted curve.

In order to simplify the statistical analysis, we use a modified Gram-Schmidt method to generate linear combinations $\tilde{b}_i$ of the original b_i's such that $\langle \tilde{b}_i | \tilde{b}_j \rangle = \delta_{i,j}$. Any basis function that turns out to be (nearly) linearly dependent on the others should be discarded (cf. the singular value decomposition[22]). The parameters are now simple projections, $\alpha_i = \langle \tilde{b}_i | E \rangle$, and the fitted parameters have particularly simple statistics: $\overline{\Delta\alpha_i} = 0$ and $\overline{\Delta\alpha_i \Delta\alpha_j} = \delta_{i,j}$ with $\Delta\alpha_i = \alpha_i - \alpha_i^0$.

The fitted bulk modulus is a function of the parameters α_j and may be expanded as follows:

$$B(\boldsymbol{\alpha}) = B(\boldsymbol{\alpha}^0) + \sum_k \left.\frac{\partial B}{\partial \alpha_k}\right|_{\boldsymbol{\alpha}^0} \Delta\alpha_k + \frac{1}{2}\sum_{k,l} \left.\frac{\partial^2 B}{\partial \alpha_k \partial \alpha_l}\right|_{\boldsymbol{\alpha}^0} \Delta\alpha_k \Delta\alpha_l + \cdots. \tag{2.4}$$

After averaging, this yields an expression for the leading-order contribution to the bias: $\Delta B = \overline{B(\boldsymbol{\alpha}) - B(\boldsymbol{\alpha}^0)} = \frac{1}{2}\Sigma_k (\partial^2 B/\partial\alpha_k^2)|_{\boldsymbol{\alpha}^0}$. As $\boldsymbol{\alpha}^0$ is unknown, the derivatives have to be evaluated at $\boldsymbol{\alpha}$, giving $\Delta B = \frac{1}{2}\Sigma_k (\partial^2 B/\partial\alpha_k^2)|_{\boldsymbol{\alpha}}$ to leading order. Similarly, for the variance, we get $\mathrm{var}\, B = \overline{[B(\boldsymbol{\alpha}) - B(\boldsymbol{\alpha}^0)]^2} = \Sigma_k [(\partial B/\partial\alpha_k)|_{\boldsymbol{\alpha}}]^2$. Averaging over 10^6 random samples using typical QMC values has shown that the second-order expansion [Eq. (2.4)] is sufficient.

Given the implicit definition of the minimum a_m,

$$0 = f'(a_m,\boldsymbol{\alpha}) = \sum_j \alpha_j \tilde{b}_j'(a_m), \tag{2.5}$$

where the primes signify differentiation with respect to the a, it is possible to derive statistics for a_m. That is, differentiating Eq. (2.5), with respect to α_k, yields $\partial a_m/\partial \alpha_k$. Other derivatives can be obtained similarly.

A note of caution: In order to obtain the statistics of the bulk modulus, one might consider taking the calculated energies $E(a_i)$ and adding additional random errors of variance σ_i^2 to each of them (cf. Yao *et al.*[14]), thus producing many ''dummy'' data sets from the original data set. This procedure, however, adds another bias term to already biased data, therefore doubling the bias.

III. CONCLUSIONS

When using QMC simulations, where the statistical errors force the use of a wide range of lattice parameters, it is necessary to go beyond a quadratic fitting function for the EOS and to perform a rigorous statistical analysis. We have included a brief account of how to analyze the statistical errors and biases that arise when the values of the energy as a function of lattice parameter are noisy.

We have also shown how simple but adequate estimates of the finite-temperature and zero-point corrections required to align experimental and computational values of B may be obtained by extending Dacorogna's[10] method. This avoids more elaborate calculations,[3–5] which may not always be feasible or warranted.

We apply this methodology to a calculation of the bulk moduli of several materials, and find that our results agree well with more elaborate calculations.[3–5] Zero-point and finite-temperature contributions to bulk moduli can be as large as 20%, explaining the discrepancy in many reported DFT calculations.[6–9] Our work provides a simple and yet effective method for estimating these frequently overlooked corrections.

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