Theory for structure and bulk-modulus determination

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A new method for direct evaluation of both crystalline structure, bulk modulus $B_0$, and bulk-modulus pressure derivative $B'_0$ of solid materials with complex crystal structures is presented. The explicit and exact results presented here permit a multidimensional polynomial fit of the total energy as a function of all relevant structure parameters to simultaneously determine the equilibrium configuration and the elastic properties. The method allows for inclusion of general (internal) structure parameters, e.g., bond lengths and angles within the unit cell, on an equal footing with the unit-cell lattice parameters. The method is illustrated by the calculation of $B_0$ and $B'_0$ for a few selected materials with multiple structure parameters for which data is obtained by using first-principles density functional theory.

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I. INTRODUCTION

Calculations of the bulk structure and the bulk elastic properties play an important role in the physics of condensed matter. Bulk calculations help us understand, characterize, and predict mechanical properties of materials in our surroundings, under extreme conditions, as in geological formations and setting and for industrial applications. Crystalline materials come in many different structures and, in contrast to isotropic materials, the structure description of crystalline materials may in general need multiple lattice parameters and an atomic basis. In this paper we discuss how to determine the equilibrium structure of a (multiparameter) crystalline material while, at the same time, directly determining the bulk modulus and the bulk modulus pressure derivative. We argue and show that for theoretical structure calculations of multiparameter systems this is simpler and more exact than fitting to (semi-)empirical equations of state (EOS) such as, e.g., the Murnaghan or Birch EOS. In particular, with our direct method there is no need to first determine the hydrostatic path of the system. We further discuss how to include the atomic basis in this process in a natural way.

In crystalline materials described by a single lattice parameter (e.g., monatomic cubic phases) the lattice parameter is a simple function of the unit-cell volume, and the equilibrium volume thus uniquely determines the equilibrium structure, i.e., the value of the lattice parameter. This is not the case when multiple lattice parameters characterize the system and a whole range of lattice-parameter values can form the same unit-cell volume. The equilibrium structure of the material must then be found by fitting and minimizing the free energy within the multidimensional space of lattice parameters. Relevant variables describing the atomic basis (e.g., bond lengths or binding angles) may be included among the parameters, and the full set of lattice parameters and internal (atomic basis) parameters are collected into the vector $x$, scaled to dimensionless form. The volume of the unit cell $V(x)$ depends in a simple way on the values of the lattice parameters describing the unit cell, but not on the internal atomic configuration. Nevertheless, we here treat the external and internal parameters on an equal footing.

From theory bulk calculations the total energy (per unit cell) $E(x)$ is found for a number of structures $x$. The elastic response of typical hard crystalline materials corresponds to small deviations $\delta x = x - x^{(0)}$ of the structural parameters from the equilibrium structure $x^{(0)}$. The observation that the total energy forms a natural potential (hyper-)surface in the parameter space of lattice and internal parameters $x$, combined with the accuracy of present-day bulk-calculation methods (such as density functional theory, embedded atom methods, or effective medium theory), then makes it possible to fit the corresponding total-energy variation through the multidimensional fit

$$E(x) = k + \frac{1}{2} M_{ij} \delta x_i \delta x_j + \frac{1}{3!} \gamma_{ijkl} \delta x_i \delta x_j \delta x_k + O(\delta x^4),$$

(1)

at controlled accuracy. Here $k$, $M_{ij}$, and $\gamma_{ijkl}$ denote zeroth, second, and third-rank tensors of fitting constants. An additional set of fitting constants are the $x^{(0)}$ hidden in $\delta x = x - x^{(0)}$. The polynomial fit gives a transparent description of the materials-structure energy variation and directly determines the equilibrium structure $x^{(0)}$.

In this paper we exploit and use the structure calculation, i.e., the multidimensional polynomial fit of the total energy for an additional and direct determination of the zero-pressure bulk modulus $B_0 = -V(x^{(0)})/(\partial p/\partial V)|_{x=x^{(0)}}$ and its pressure derivative, $B'_0 = -\partial V(\partial p/\partial V)|_{x=x^{(0)}}$ at zero temperature.

For a general set of structure parameters, $x$, we expand the volume around the equilibrium configuration $x^{(0)}$ using the gradient $g = \nabla V(x)|_{x=x^{(0)}}$ and the Hessian $H = \{\partial^2 V(x)/(\partial x_i \partial x_j)\}_{ij}^{x=x^{(0)}}$ of the volume. We note that derivatives of the volume with respect to the internal parameters vanish, by definition. By providing a systematic treatment of the struc-
tural changes induced by the pressure $p = -\partial E/\partial V$ we extract from the minimum of the zero-temperature enthalpy

$$\mathcal{H}(x, p) = E(x) + pV(x)$$

both the bulk modulus

$$B_0 = \frac{V(x^{(0)})}{g^TM^{-1}g}$$

and the bulk-modulus pressure derivative

$$B'_0 = V(x^{(0)}) \frac{3g^TM^{-1}HM^{-1}g - \gamma_{ijkl} (M^{-1}g)_i (M^{-1}g)_j (M^{-1}g)_l}{(g^TM^{-1}g)^2} - 1.$$  

The algorithm outlined above can also be applied to the corresponding direct determinations of general harmonic and anharmonic elastic properties.

Our results both enhance the theory understanding of the crystalline mechanical properties and simplify the desired testing of theory calculations as they combine the formal determination of the crystalline structure [Eq. (1)] and of the elastic properties [Eqs. (3) and (4)]. For example, from Eqs. (1) and (2), we can directly identify which (internal) structure parameters softens the bulk modulus and we may, in turn, strengthen the materials by suitable chemical or structural modification.

For cases like graphite, where the state-of-the-art DFT based on the generalized gradient approximation (GGA) fails to describe the weak physical interlayer binding, the polynomial fit highlights the intrinsic theory challenges: the total energy has no minimum in the space of lattice parameters, the too soft dependence of the total energy on the graphite-layer separation is quite apparent in the fit. At the same time, for strongly bonded crystalline materials the fit produces usable estimates of the equilibrium crystalline structure and shows the strength of GGA-DFT. The equilibrium volume, the crystallographic parameters, and the bulk modulus, describing the material’s resistance to hydrostatic stress, provide simple experimental tests against which we can compare and calibrate our calculations.

Besides the direct relevance of our results for the description of complex materials our calculations of bulk structure and bulk modulus calculations are also of interest for development of pseudo-potential-based density-functional theory (DFT) methods and for methods using empirical parameters. There, a first and critical test of the pseudopotential or the empirical parameters is whether the calculations predict a correct materials structure, binding, and elastic properties for the relevant equilibrium configuration. Present DFT scripts can automate some pseudopotential testing for simple materials and symmetries, our formal results generalize such testing of theory accuracy to cases when multiple structural parameters determine the elastic properties.

The outline of this paper is as follows. In Section II we discuss the traditional methods of determining the bulk modulus for single- and multiparameter systems. In Section III we derive our expressions for the bulk modulus and the bulk modulus derivative, Eqs. (3) and (4), for the simple one-parameter problem (e.g., mono-atomic fcc or bcc structures), easily generalized to the $n$-parameter problem. In Section IV we proceed to illustrate and test the algorithm on a number of mono- and di-atomic materials based on first-principle DFT calculations and comparison to experiments. Comparisons of $B_0$ and $B'_0$ together with the test of the lattice and structure parameters themselves, represent the typical test of materials-theory accuracy. Section V contains the conclusion.

## II. BACKGROUND

A theory determination of the zero-temperature bulk modulus based on either traditional methods or our formal result is straightforward when one single structural parameter (e.g., the lattice parameter $a$) defines the crystalline state. This situation applies for monatomic crystals with simple cubic (sc), face-centered cubic (fcc) and body-centered cubic (bcc) symmetries. Here, the unit-cell volume $V(a) = qa^3$ uniquely determines the lattice parameter $a$ through a dimensionless number $q$ which depends on the crystal symmetry ($q = 1$, $q = 1/4$, and $q = 1/2$ for sc, fcc, and bcc lattices, respectively). All which is required are theory calculations of total energies for a range of $a$ values to determine both the equilibrium structure $a_0$ and the equilibrium volume $V^{(0)}$. The total energy per unit cell, $E(a)$ (as in Eq. (1)), can then be expressed as a function of the unit-cell volume, $E(V)$.

The general approach is illustrated by the example in Figure which shows the total energy as a function of the lattice parameter $a$ for the zinc-blende phase of SiC...
and Birch’s equations (5) and (6) the quantities
nomial fit and are not shown separately. In Murnaghan’s
yield, to the eye, curves identical to the fourth-order poly-

tation of the lattice parameter
FIG. 1: The total energy per unit cell (two atoms) as a func-
Solid line: Fourth-order polynomial fit as used for the values
Dashed line: Second-order polynomial fit to the
other equations of state traditionally used are
The values of the equilibrium lattice parameter
of $B_0$ and $B'_0$ obtained from Eqs. (5) and (6) and from
the Murnaghan and Birch fits are included in Table I. For
systems described by one lattice parameter Eqs. (5)
and (6) give bulk moduli and bulk-modulus derivatives
in close agreement with our present direct approach, Eqs. (3)
and (4).

We would like to stress that the moduli $B_0$ and $B'_0$
are formally defined as zero-pressure quantities, and in
no way depend on finite-pressure behavior beyond the
pressure gradient at $p = 0$. If we are able to sample
our theory system in a sufficiently dense grid around the
zero-pressure structure the values of $V_0$, $B_0$, and $B'_0$ in (3)
and (4) are exact and can be related to the correspond-
ing exact determination of the elastic constants. Fits to
empirical EOS may yield results of $V_0$, $B_0$, and $B'_0$ that
are in good agreement with experimental observations,
but they do not necessarily constitute the exact quadratic
response.

For materials with multiple structure parameters, the
procedure of the traditional approaches further becomes
quite awkward as it must be supplemented by a separate
discussion of how the experimental conditions define the
relevant structural constraint at a given volume, the
hydrostatic path $x = x(V)$. Moreover, cross-correlations
on the $n$-dimensional energy surface are ignored in tradi-
tional fitting procedures. These procedures are basi-
cally a one-dimensional fit in the $n$-dimensional space
and they are thus more subject to numerical noise in the
data points than our approaches based on the multi-
dimensional least-squares polynomial fit (1).

A simple multi-parameter case illustrates this point.
Figure 2 both describes the energy surface, Eq. (1), fit-
ted through DFT calculations for Co, and emphasizes
the general advantages of our direct approach (Eqs. (3)
and (4)).

FIG. 2: Contour plot of the fourth-order polynomial fit to the
Co hcp total energy, including the hydrostatic path. The hcp
unit cell is given by the two independent lattice parameters
$a$ and $c/a$. The contour step is 0.025 eV per unit cell (two
atoms).
TABLE I: Bulk properties calculated from DFT data obtained directly from Eqs. (3) and (4) via a fourth-order polynomial fit ("Present approach"), available experimental values, and values from fits to Murnaghan’s and Birch’s equations (5) and (6). For the internal parameter in 2H-SiC we find the following value: Si-C distance along the c-direction $u(\text{Si-C})=0.3752\text{\AA}$ or bondlength $\ell_{\text{bond}}=1.9031\text{\AA}$. (Experiments find $u(\text{Si-C})_{\text{exp}}=0.3760\text{\AA}$, $\ell_{\text{bond}}_{\text{exp}}=1.8998\text{\AA}$.) For 4H-SiC we find $u(\text{Si-C})_1=0.1880\text{\AA}$, $u(\text{Si-C})_2=0.1874\text{\AA}$, $u(\text{Si-Si})=0.2500\text{\AA}$, in good agreement with other theoretical results. 

|              | Present approach | Experiment | Murnaghan | Birch |
|--------------|------------------|------------|-----------|-------|
|              | $a_0$ [\AA] | $c/a$ | $B_0$ [GPa] | $B_0'$ | $a_0$ [\AA] | $c/a$ | $B_0$ [GPa] | $B_0'$ | $a_0$ [\AA] | $c/a$ | $B_0$ [GPa] | $B_0'$ |
| Co           | fcc             | 3.531 | 218 | 4.80 | 214 | 4.47 | 216 | 4.65 |
|              | bcc             | 2.817 | 206 | 5.09 | 199.4 | 4.90 | 205 | 4.95 |
|              | hcp             | 2.500 | 1.617 | 2.470 | 1.622$^a$ | 191.4$^a$ | 5.07$^b$ | 217 | 4.52 | 219 | 4.61 |
| SiC          | 3C              | 4.376 | 213 | 3.93 | 4.359$^c$ | 224$^d$ | 4.0$^e$ | 212 | 3.87 | 213 | 3.91 |
|              | 2H              | 3.092 | 2.274 | 2.221 | 2.973$^f$ | 223$^g$ | 3.271$^h$ | 208 | 3.74 | 211 | 3.86 |
|              | 4H              | 3.092 | 2.724 | 2.721 | 2.737$^i$ | 223$^g$ | 3.271$^h$ | 212 | 3.78 | 213 | 3.89 |
| C            | diam            | 3.565 | 436 | 3.71 | 3.567$^j$ | 443$^a$ | 4.07$^a$ | 432 | 3.72 | 435 | 3.70 |
| Si           | diam            | 5.466 | 88.7 | 4.35 | 5.430$^k$ | 98.8$^a$ | 4.09$^a$ | 87.7 | 4.20 | 88.3 | 4.28 |

$a$Ref. 12, $b$Ref. 13, $c$Ref. 14, $d$Ref. 22, $e$Ref. 21, $f$Ref. 16, $g$Ref. 20, $h$Ref. 17, $i$Ref. 23, $j$Ref. 24, $k$Ref. 24.

and [4] compared with the traditional bulk-modulus determinations.\textsuperscript{13,14} Materials like Co, which has a non-ideal hexagonal close-packed (hcp) structure, graphite with its layered structure, or the polytypes of SiC\textsuperscript{6} or alumina\textsuperscript{6} have multiple lattice parameters (plus relevant internal degrees of freedom) which are, of course, no longer uniquely specified by the volume but depend on the general materials conditions. The hydrostatic path defines the system when subject to uniform pressure (as relevant for the bulk-modulus measurements). The hydrostatic path is identified in Fig. 1. The traditional approach\textsuperscript{13,14} proceed by implementing this complex constraint in the equation of state, Eq. 1 or 2, to fit the bulk modulus and its derivative. Instead, we present an explicit determination, Eqs. 3 and 4, based directly on the equation of state 1, expressed as a function of the underlying crystalline structural parameters.

III. DERIVATION

Our direct bulk-modulus evaluations, Eqs. 3 and 4, are the results of using the pressure (instead of the volume) in a formal identification of the hydrostatic path and then invoking a systematic expansion in small pressure for an explicit specification of $B_0$ and $B_0'$. Today DFT and other materials-theory bulk-calculations are done with high accuracy, and we need only to vary the lattice parameters values slightly around the optimal structure to approximate the total-energy curve by an accurate polynomial fit, Eq. 4. The minimum of the corresponding (zero-temperature) enthalpy 4 can thus be used to directly specify the physically correct structural configuration at any given pressure $p$. The set of these optimal structure-parameter values, $x_{\text{hydro}}(p)$, trace out the hydrostatic path which, when parameterized by $p$, is obtained by simply solving the equation

$$\nabla H(x, p) = \nabla E(x) + p \nabla V(x) = 0. \quad (7)$$

We obtain a formal expression for the general (pressure dependent) bulk modulus by taking the derivative along this hydrostatic path

$$B = -V(x_{\text{hydro}}(p)) \left( \frac{\partial V(x_{\text{hydro}}(p))}{\partial p} \right)^{-1}, \quad (8)$$

and finally we extract the explicit results for the zero-pressure bulk-modulus $B_0$ and for its pressure derivative, $B_0'$. We illustrate the general derivation by focusing on a one-dimensional parameter space $x$, e.g., for the fcc or bcc one-atomic structure. Then the total energy can be fitted by the polynomial

$$E(x) = k + \frac{1}{2} M (x-x^{(0)})^2 + \frac{1}{3} \gamma (x-x^{(0)})^3 + f(x-x^{(0)})^4$$

where $f(x-x^{(0)})=O(x-x^{(0)})^4$ contains higher order terms. The coefficients $k$, $M$, $\gamma$, the coefficients of $f(x-x^{(0)})$, as well as the optimal value of the lattice parameter at zero pressure, $x^{(0)}$, are the fitting parameters to be specified, for example, by a set of accurate underlying DFT calculations.
At small pressures, i.e., for lattice and internal parameter values close to the zero-pressure optimal values, the $pV$ term in the enthalpy is small and can be regarded as a perturbation of the system. To proceed we introduce a small, non-dimensional and real parameter $\lambda$ such that we can write the small pressure as $p = \lambda p^{(1)}$ and the lattice-parameter variable as $x = x^{(0)} + \lambda x^{(1)} + \lambda^2 x^{(2)} + \mathcal{O}(\lambda^3)$. The variables $x^{(1)}$, $x^{(2)}$, ... are unknown, are functions of the pressure and must be found in the following.

The bulk modulus expression requires calculation of the volume $V(x)$ and its pressure derivative. We write the volume in a Taylor-expansion around the zero-pressure solution $x^{(0)}$ as

$$V(x) = V(x^{(0)}) + \lambda g x^{(1)} + \lambda^2 \left( x^{(2)} g + \frac{1}{2!} \left( x^{(1)} \right)^2 H \right) + \mathcal{O}(\lambda^3) \quad (10)$$

with $g = dV/dx|_{x=x^{(0)}}$ and $H = d^2V/dx^2|_{x=x^{(0)}}$. Here, the pressure dependence enters through the variables $x^{(1)}$, $x^{(2)}$, .... The pressure derivative of the volume is thus

$$\frac{\partial V(x)}{\partial p} = g \frac{\partial x^{(1)}}{\partial p^{(1)}} + \lambda \left( g \frac{\partial x^{(2)}}{\partial p^{(1)}} + \frac{\partial x^{(1)}}{\partial p^{(1)}} H x^{(1)} \right) + \mathcal{O}(\lambda^3) \quad (11)$$

and we determine the variables $x^{(1)}$, $x^{(2)}$, ... by solving the condition on the enthalpy given by (7)

$$0 = \lambda \left( M x^{(1)} + p^{(1)} g \right) + \lambda^2 \left( M x^{(2)} + \frac{1}{2} \gamma \left( x^{(1)} \right)^2 + p^{(1)} H x^{(1)} \right) + \mathcal{O}(\lambda^3). \quad (12)$$

The identity (12) must hold for every order and we thus obtain a formal pressure dependence of the lattice parameter

$$x^{(1)} = -p^{(1)} M^{-1} g \quad (13)$$

$$x^{(2)} = \left( p^{(1)} \right)^2 \left\{ M^{-1} H M^{-1} g - \frac{1}{2} M^{-1} \gamma M^{-1} g M^{-1} g \right\}. \quad (14)$$

Finally, introducing these solutions into (11) we find for $\lambda = 0$ the isothermal zero-pressure bulk modulus

$$B_0 = -V(x^{(0)}) \left( \frac{\partial V}{\partial p} \right)^{-1}_{x=x^{(0)}} = \frac{V(x^{(0)})}{g M^{-1} g} \quad (15)$$

and taking the derivative of $-V(\partial V/\partial p)^{-1}$ with respect to $p = \lambda p^{(1)}$ we find at $\lambda = 0$

$$B'_0 = V(x^{(0)}) \frac{3 g M^{-1} H M^{-1} g - \gamma M^{-1} g M^{-1} g M^{-1} g}{(g M^{-1} g)^2} - 1 \quad (16)$$

in the case when one (lattice) parameter suffices to describe the unit cell and its atom basis.

The above derivation is straightforwardly generalized to materials systems in which $n$ independent lattice and internal parameters determine the structure and the bulk moduli Eqs. (3) and (4), which is our main result. We stress that $B_0$ and $B'_0$ are evaluated at zero pressure and thus the results are exact in spite of the perturbation. $B_0$ and $B'_0$ depend directly on the second order, respectively on the second and third order, coefficients of the energy fit ($M$ and $\gamma$). We observe that the coefficients of $f(x-x^{(0)})$ do not enter the expression for the bulk modulus (3) or the pressure derivative of the bulk modulus (4). However, their presence may improve the fit (9), and thereby affect also the coefficients $M$, and $\gamma$, and thus $B_0$ and $B'_0$. Internal parameters, which describe the positions of the atoms within the unit cell, naturally do not enter the expression of the volume, and thus not the volume derivatives $g$ and $H$ either, but do affect $B_0$ and $B'_0$ through $M^{-1}$.

Higher pressure derivatives of the bulk modulus may be found by taking into account the higher orders of $\lambda$ in the Taylor expansions of $x$ and the volume. The pressure derivatives will depend on successively higher orders in the polynomial fit. The derivation is straightforward if somewhat tedious.

### IV. EXAMPLES OF APPLICATIONS

As an example of the use of the algorithm for determining $B_0$ and $B'_0$, evaluate the structure and bulk modulus of a selection of one and two-species materials. We fit data obtained from DFT calculations, described in further detail below, to fourth-order polynomials of the form (11) in $n$-dimensional space, where $n = 1, 2, 3, or 5$.

The pseudopotentials used in DFT calculations may be optimized for various purposes, but should generally yield consistent and transferable accuracy and results. Here, we have used some of the pre-defined pseudopotentials of the open-source DFT program DACapo. The values that we find for the lattice constants, for $B_0$, and for $B'_0$, are collected in Table I. For reference, the experimental values are also included, as well as the bulk moduli from a Murnaghan and Birch fit along the hydrostatic path.

We have calculated the structure and bulk modulus for three multiparameter systems, as well as for a number of related one-parameter systems: the two-parameter hcp phase of Co, the three-parameter (one internal) wurtzite phase of SiC (2H), the five-parameter (three internal parameters) hexagonal 4H-polytype of SiC, and the one-parameter bcc and fcc phases of Co, the zinc-blende (3C) phase of SiC and the diamond phases of C and Si.

For the DFT calculations we used the plane-wave DACapo code with GGA. For the calculations of the 2H and 4H-polytype of SiC we used $8 \times 8 \times 8$ and $8 \times 8 \times 4$ $k$-points, respectively, to describe the Brillouin zone. For all other calculations $10 \times 10 \times 10$ $k$-points were used.
A uniform energy cut-off of 400 eV, and a conservative choice of fast-Fourier transform (FFT) grid was used. For each evaluation of the optimal structure we calculated by DFT a number of data points for the lattice parameter(s) approximately within ±10% from the expected optimal value(s) of the lattice parameter(s). In the one-parameter systems we calculated 20-30 data points, for the Co hcp-structure 120 data points, for the 2H-polytype of SiC 140 data points, and for 4H-SiC we calculated 7500 data points. The Co calculations were spin-polarized, yielding realistic values of the spin polarization over the range of lattice parameter values considered here.

The possibility of treating the external and internal parameters collectively is important. For example, the variation of internal bond length with pressure might be as important for the total energy as the change in (external) lattice parameters. Often, relaxation of the internal parameters is done with a steepest-descent (or similar) search minimizing the Hellmann-Feynman forces to a certain cut-off at fixed lattice parameters. Although in practice the atomic relaxation will often be a convenient way of obtaining the optimal position of the atoms within the unit cell, the approach has two shortcomings: it introduces a random residual lattice strain, which in turn affects the total energy, and further, the Hellmann-Feynman forces have a non-trivial dependence on the pressure acting on the unit cell and therefore a constant cut-off on the force will not correspond to a constant accuracy of the total energy with varying pressure. Thus a better accuracy — and a consistent choice of accuracy — can be obtained by treating the lattice and internal parameters on an equal footing. This is here done for the 2H and the 4H polytype of SiC. The results are shown in Table I. For the Murnaghan and Birch values of \( B_0 \) and \( B'_0 \) we need to explicitly calculate the hydrostatic path \([a, c/a, u]\) and \([a, c/a, u_1, u_2, u_3]\) space before obtaining the fit. In contrast, we stress that when using (3) and (4) there is no need to explicitly calculate the hydrostatic path. This is here done purely for illustrational purposes.

V. CONCLUSION

In summary, we have presented a new direct algorithm for a combined determination of structure and bulk moduli \( B_0 \) and \( B'_0 \). The lattice constants of a multiparameter system are best found in a least-squares polynomial fit, as previously noticed for the SiC hexagonal polytypes.\(^2\) We show (a) how to exploit this polynomial fit for a direct determination of the zero-pressure bulk modulus \( B_0 \) and its pressure derivative \( B'_0 \), avoiding the calculation of the hydrostatic path and the subsequent one-dimensional fit to this path. We further show (b) how to consistently include internal parameters, such as bond lengths or bonding angles, in the formalism along with the external lattice parameters. In addition, we have evaluated these formal results in explicit cases within our approach, based on DFT calculations.

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