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Modified Moments for Harmonic Solids*

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Appropriately defined modified moments of the frequency distribution provide a powerful new tool for studying the properties of solids in the harmonic approximation. They can be calculated much more easily than power moments and stably determine the thermal and dynamic properties of harmonic solids with great accuracy. We define a set of modified moments appropriate for harmonic solids and show how they can be computed directly from the dynamical matrix by algebraic techniques. As an illustration of the method, forty exact modified moments are given for the cubic close-packed solid with nearest-neighbor interactions. The method is stable for the computation of approximate modified moments for models where exact computation is not feasible. In contrast to approximate power moments, approximate modified moments contain sufficient information about the frequency distribution to determine thermal and dynamic properties of harmonic solids.

The harmonic approximation to crystalline solids occupies a central role in solid-state physics.[1] When the temperature is sufficiently low, the harmonic approximation may itself be quite accurate, and , in addition, more sophisticated treatments often rely upon it as a starting point. In spite of the fundamental and relatively simple nature of the harmonic model, the vibrational frequency spectrum is known exactly for only a few very special cases,[2] and approximate methods must be used to investigate the properties of most examples, even some of the simplest.

Power moments have often been used to characterize the vibrational frequency spectrum of harmonic crystals.[3-12] Recently considerable progress has been made in the calculation of these moments and in determining other properties of the crystals from them. Numerical[7,8] and algebraic[9,10] procedures have been used to compute substantial numbers of power moments for a variety of crystal structures, both with nearest-neighbor and with longer- (but finite) ranged forces. Wheeler and Gordon[11,12] have shown that Gaussian quadrature methods can be used to determine the thermodynamic properties of harmonic solids extremely accurately from the moments.

A serious limitation to these promising developments arises because the power moments are only sensitive to the high-frequency portion of the vibrational spectrum. As a consequence, the determination of quadrature formulas from power moments is numerically unstable. This severely limits the number of moments which can be used in practice, both because the moments themselves must be known exactly (or to extremely high precision) in order to convey accurate information about the frequency spectrum, and because increasingly high precision must be used to obtain reliable quadrature formulas from the moments.

In this paper we show how both of these difficulties can be surmounted. Sack and Donovan[13] and Gautschi[14] have observed that suitably chosen *modified moments* determine Gaussian quadrature rules for classical weight functions far more stably than do the power moments. This suggests that modified moments may be useful in the study of harmonic solids. We have found that the vibrational spectrum of a harmonic solid can be characterized by modified moments which are more sensitive to the spectrum than are the power moments, which determine the quadrature rules extremely stably, and which are easier to calculate than the power moments themselves.

The even-power moments μ_n are defined as the average of the $2n$th power of the frequency ω:

$$\mu_n = \int_0^{\omega_{\max}} \omega^{2n} \rho(\omega)\, d\omega \; , \qquad (1)$$

where $\rho(\omega)$ is the spectral density. Modified moments ν_n may be defined analogously by

$$\nu_n = \int_0^{\omega_{\max}} p_n(\omega^2) \rho(\omega)\, d\omega \; , \qquad (2)$$

where the p_n are polynomials of degree n satisfying a three-term recursion relation:

$$p_{n+1}(x) = (x - a_n)\, p_n(x) - b_n p_{n-1}(x), \qquad (p_{-1} = 0, \quad p_0 = 1) \qquad (3)$$

We have found that shifted Chebyshev polynomials of the second kind, for which

$$a_n = (\tfrac{1}{2}\,\omega_{\max}), \qquad b_n = (\tfrac{1}{4}\,\omega_{\max})^2 \qquad (4)$$

TABLE I. Modified moments for cubic-close-packed (ccp) harmonic solid with nearest-neighbor force constants.

V_n	n	V_n	n	V_n	n
1	0	-68 29568	14	73712 63908 39104	28
0	1	520 45376	15	-4 92533 33515 58272	29
0	2	673 12688	16	-8 14268 52621 47072	30
16	3	-3196 09600	17	-21 67008 84312 01408	31
-16	4	7641 84192	18	-175 38890 18068 00336	32
-224	5	34034 97088	19	-27 96440 30025 99168	33
-192	6	- 56314 76864	20	2543 82675 14633 40672	34
224	7	-1 09849 81632	21	15906 29907 90698 98880	35
1840	8	-7 88549 90592	22	25323 53678 24822 91072	36
19200	9	-16 48872 57984	23	-2 56292 86511 44264 91648	37
40384	10	-123 31867 07040	24	-5 09307 10414 23939 47648	38
12224	11	-2126 28733 06624	25	32 96814 56460 62732 52096	39
-3 46592	12	1695 19035 22688	26		
-45 36000	13	63096 40354 68672	27		

independently of n, are particularly appropriate for the harmonic solid.

Isenberg[9] has shown that the dynamical matrix for a simple harmonic crystal with finite-ranged force constants can be manipulated algebraically to obtain the even power moments of the vibrational spectrum. The elements of the dynamical matrix $\underline{D}$ can be expressed as finite multinomials in formal parameters x, y, z, and their inverses, x^{-1}, y^{-1}, and z^{-1}. The powers of $\underline{D}$ are obtained algebraically as functions of the formal parameters, and the nth even power moment is given by the term independent of the parameters x, y, and z in the trace of the nth power of $\underline{D}$.

This method can be adapted to obtain modified moments. We define a sequence of matrices $\underline{P}_n$ by the recursion relation

$$\underline{P}_{n+1} = (\underline{D} - a_n I)\underline{P}_n - b_n \underline{P}_{n-1}$$

$$\underline{P}_0 = I, \quad \underline{P}_{-1} = 0. \tag{5}$$

The elements of $\underline{D}$ are formed in terms of the formal parameters x, y, and z, as above, and the a_n and b_n are the recursion coefficients of the p_n in Eqs. (3) and (4). The modified moment ν_n is then just the term independent of x, y, and z in the trace of $\underline{P}_n$.

Exact modified moments clearly contain precisely the same information as exact power moments. The modified moments, however, enjoy significant advantages over the power moments.

First, the exact computation of modified moments is easier than the exact computation of power moments because the modified moments are much smaller and many more can be calculated before special multilength arithmetic procedures must be employed. As an illustration, we have computed the first 40 even modified moments for the cubic-close-packed (ccp) crystal with nearest-neighbor central-force interactions. (This is more than twice the number of exact power moments previously reported.) These modified moments are presented in Table I in terms of the dimensionless variables $v_n = 16^n \nu_n / \omega_{\max}^{2n}$. (When the problem is formulated in terms of these variables, the coefficients in $\underline{D}$ are integers and the a_n and b_n of Eq. (3) become the integers 8 and 16, respectively.) The power moments, which can be calculated from the modified moments by use of Eq. (3), grow much more rapidly than do the modified moments. For example, $\mu_{20}/\nu_{20} \approx 5\times 10^{12}$ and $\mu_{39}/\nu_{39} \approx 3\times 10^{23}$. The computation of 40 modified moments required only standard double precision arithmetic, whereas direct computation of the same number of power moments is unfeasible because of the multiple precision arithmetic required.

A second and more important advantage of the modified moments is that they need to be known only approximately to reliably determine the properties of the solid. Approximate modified moments determine quadrature formulas very stably. There was no detectable buildup of error when the 40 modified moments given above were used with single precision arithmetic to determine the quadrature formulas used by Wheeler and Gordon. In contrast, the quadrature formulas could not be determined at all from 40 power moments, even with double precision arithmetic, because of the exponential growth of rounding errors. Details of these calculations as well as some procedures for the manipulation of modified moments and methods for the very accurate determination of thermal and dynamic properties will be presented in a more extensive paper.

In view of the utility of approximate modified moments, it is of interest to determine the stability of the procedure for computing them. This is particularly important because, in all but the simplest models, the coefficients of the formal parameters in the dynamical matrix are functions of force constant ratios and cannot be represented as integers. (The moments can be found exactly as functions of the force constant ratios, but this is very cumbersome.[7,10]) An investigation of the ccp model with both nearest- and next-nearest-neighbor central-force interactions indicates that the computation of approximate modified moments is very stable. It is therefore possible to carry out the entire computation of accurate thermodynamic properties of a complex solid, from the dynamical matrix, through modified moments, to quadrature formulas, within single precision arithmetic.

We believe that modified moments provide a powerful new tool for the study of harmonic solids. Moment techniques have the advantage over root-sampling procedures that thermal and dynamic properties can be expressed by simple quadrature formulas which involve only a few numbers and which provide error bounds. Modified moments enjoy the additional important advantage that they determine these properties stably even when they are known only approximately, and can themselves be computed stably with limited precision arithmetic. More complex models, long-ranged forces and other procedures for computation are being investigated.

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Perturbation Treatment of High-Energy-Electron Diffraction from Imperfect Crystals*

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A modified-Bloch-wave expansion is used to develop a theory of high-energy-electron diffraction from imperfect crystals. To compute these new Bloch waves one must solve a linear hyperbolic system in n unknowns. Scattering among the Bloch waves is controlled by the matrix elements of the perturbing potential, and various approximations to this scattering are discussed. The hyperbolic system is transformed to normal form; in making this transformation, the unknown functions become the plane-wave amplitudes of the Darwin representation. The normal form reveals the region of determinacy of the system: a cone generated by the diffracted beams. The contraction of this cone to a line (the column approximation) is discussed in terms of the Bloch-wave scattering.

I. INTRODUCTION

In the analysis of high-energy-electron diffraction from crystal defects, one never loses sight of the periodicity of the perfect crystal. This motivates one to begin with one of the well-understood representations for the perfect-crystal wave function, and then modify it in such a fashion as to render theoretical calculations and experimental analysis tractable.

The two common representations for the wave functions are the Bloch representation and the Darwin representation. In the Bloch representation, the wave function ψ is expressed as a linear combination of the eigenfunctions of the perfect-crystal Hamiltonian, which is always of the form $F_k(\vec{r})e^{i\vec{k}\cdot\vec{r}}$, where $F_k(\vec{r})$ is a periodic function of the crystal lattice. In the Darwin representation, one expands ψ as a summation of plane waves, with spatially varying amplitudes, traveling in the various diffraction directions as specified by Bragg's law.

Surprisingly, the modification of these representations to include nonperiodic distortions associated with crystal defects has been almost exclusively directed toward the Darwin representation.[1,2] In order to complement these approaches, we shall here begin with a modified Bloch representation in which the amplitudes to excite various Bloch states are changed from the constants θ^j of the perfect crystal to slowly varying functions of position $\theta^j(\vec{r})$ in the defect crystal. Wilkens[3] and later Howie and Basinski[2] have considered expansions with modified Bloch waves, but either initially (Howie and Basinski) or early in the derivation (Wilkens) they restrict the variation in $\theta^j(\vec{r})$ to z dependence, where z is a coordinate parallel to the zone axis of the diffracting planes. These treatments involve