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1990 J. Phys. A: Math. Gen. 23 567

(http://iopscience.iop.org/0305-4470/23/4/025)

J. Phys. A: Math. Gen. 23 (1990) 567-573. Printed in the UK

Lattice dynamics shell model as a constrained Hamiltonian system

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Received 22 May 1989

Abstract. We show that the shell model, currently used in the lattice dynamics study of ionic crystals, is a singular system. The model is treated as a constrained Hamiltonian system. The use of the Dirac generalised Hamiltonian formalism for constrained systems permits us to solve the difficulties which appear in quantum mechanics and statistical mechanics formulations.

The constraints, first-class Hamiltonian and Dirac bracket are obtained. The general expression for the partition function of the quantum statistical mechanics is defined.

Finally some considerations about the perturbative and non-perturbative methods are performed.

1. Introduction

For the lattice dynamics study of ionic crystals the so-called shell model was used with considerable success [1]. The outer electrons of the ions are represented in this model by a spherically symmetric massless charge shell. In this way polarisable effects are incorporated, and much better agreement than that predicted for the rigid ion model can be obtained for the dispersion curves of phonons as well as other properties measured for several materials [2].

In a harmonic approximation the usual treatment is to find the shell coordinate from their equations of motion (adiabatic condition), and then substitute in order to give an effective potential for the motion of the cores (nuclei) [1]. However there exist various cases in which the harmonic approximation can become inadequate, for example at high temperatures when the atomic displacements are large, or when we are near a structural phase transition. Therefore an anharmonic part in the potential must be incorporated [3].

Now, in an anharmonic situation the shell coordinate cannot be obtained exactly from the adiabatic condition. Thus the formulation of the dynamics and statistical mechanics of the shell model with a general potential of interaction is a question that cannot be solved immediately. This difficulty should be overcome by assigning a finite mass to the shell but this fact leads to the introduction of undesirable degrees of freedom which cannot be eliminated later (i.e. in the thermodynamic properties) [4].

A more recent result in the treatment of an anharmonic model is a perturbative method using a self-consistent phonon approximation as a generalisation of the harmonic model [5]. On the other hand, a formal expression for the partition function

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of classical statistical mechanics was obtained [6]. However it can be useful to give a general expression for the partition function in which the perturbative and non-perturbative effects can be incorporated. As is well known, to take into account the non-perturbative effects is essential near a structural phase transition [7].

The purpose of the present paper is to consider the shell model and show that it can be treated as a constrained Hamiltonian system [8], where all the constraints are of second class.

Since the pioneering work of Dirac, the theory of singular systems (constrained Hamiltonian systems) has been the subject of considerable interest. This formalism is the one currently used in field theories and the connection between constraint and invariance properties (i.e. gauge symmetry) of theory is well established. The incorporation of the constraints in the notion of a Feynman path integral was formulated by Fadeev [9]. His work treated only systems with first class constraints. Senjanovic generalised it to systems with second class constraints [10].

The present paper is organised as follows. In section 2 the model is presented and their difficulties are discussed. We show that the model corresponds to a singular Lagrangian system. In section 3 by using the theory of constrained Hamiltonian systems the model is studied. In section 4 the quantification problem and the statistical mechanics of the model are treated. An expression for quantum partition function is found. Finally in section 5 conclusions are given.

2. Preliminaries of the model

In the usual lattice dynamics the interaction between the nuclei, including the effects of the electron clouds, can be taken into account in a potential $\Phi(\boldsymbol{u})$ (where $\boldsymbol{u}$ is the displacement of the cores). The normal approach is to treat the electrons adiabatically [11] by first solving an equation for the electron motion, assuming that the nuclei are fixed, and then using these solutions to supply the potential $\Phi(\boldsymbol{u})$ for the motion of the cores. This approximation is a good one as the electron mass is small.

Instead of solving the electron motion explicitly, it has been found that a good form in which to treat the electrons is as massless shells, with an empirical potential between the shells themselves, and between cores and shells.

Having this in mind, the equations of motion of the lattice dynamics of systems which are described through a shell model can be obtained from the Lagrangian:

$$L(\boldsymbol{u}, \boldsymbol{u}, \boldsymbol{v}) = \tfrac{1}{2}\dot{\boldsymbol{u}}^{+}\boldsymbol{M}\dot{\boldsymbol{u}} - \Phi(\boldsymbol{u}, \boldsymbol{v}) \tag{2.1}$$

where the vectors $\boldsymbol{u}$ and $\boldsymbol{v}$ describe the core and shell displacements, respectively. These vectors have elements corresponding to the cartesian component of the ion in their respective unit cell. $\boldsymbol{M}$ is the mass matrix, $\Phi(\boldsymbol{u}, \boldsymbol{v})$ is a general potential.

The Euler–Lagrange equations are

$$\boldsymbol{M}\ddot{\boldsymbol{u}} + \frac{\partial\Phi}{\partial\boldsymbol{u}} = 0 \tag{2.2a}$$

$$\frac{\partial\Phi}{\partial v} = 0. \tag{2.2b}$$

Equation (2.2b) is the so-called adiabatic condition. Because (2.2b) is in general nonlinear in $\boldsymbol{v}$, we do not know the functional relation $\boldsymbol{v}(\boldsymbol{u})$.

As is well known the Hamiltonian is essential for the statistical and quantum formulations. Now the Legendre transformation involved in passing from the Lagrangian (2.1) to the corresponding Hamiltonian is singular. This is because

$$p_v \equiv \frac{\partial L}{\partial \dot{v}} = 0. \tag{2.3}$$

The previous considerations show us that we are in the presence of a constrained Hamiltonian system [8].

3. Constraints and first-class Hamiltonian

Then the Hamiltonian formulation of the shell model requires the introduction of the following primary constraints:

$$p_v \approx 0. \tag{3.1}$$

Equation (3.1) is a weak one. (For the meaning of the symbol $\approx$ see [8].) As the Hamiltonian is not univocally determined, we can define a total Hamiltonian as follows:

$$H_{\mathrm{T}} \equiv H + \boldsymbol{F}^{+}\boldsymbol{p}_v \tag{3.2}$$

where H is the naive Hamiltonian:

$$H = \tfrac{1}{2}\boldsymbol{p}_u^{+}\boldsymbol{M}^{-1}\boldsymbol{p}_u + \Phi(\boldsymbol{u}, \boldsymbol{v}). \tag{3.3}$$

In (3.2), the components of the vector $\boldsymbol{F}$ are general functions of the coordinates and momenta. These functions can be interpreted as the shell velocities, because

$$\dot{\boldsymbol{v}} \approx \{\boldsymbol{v}, H_{\mathrm{T}}\}_{\mathrm{PB}} = \boldsymbol{F} \tag{3.4}$$

where we have used (3.1)-(3.3) and the fundamental Poisson brackets (PB).

The consistency conditions of the theory requires the preservation in time of the constraints (3.1). This leads us to the equation

$$\dot{\boldsymbol{p}}_v \approx \{\boldsymbol{p}_v, H_{\mathrm{T}}\}_{\mathrm{PB}} = \{\boldsymbol{p}_v, \Phi(\boldsymbol{u}, \boldsymbol{v})\}_{\mathrm{PB}} = -\frac{\partial \Phi}{\partial \boldsymbol{v}}(\boldsymbol{u}, \boldsymbol{v}). \tag{3.5}$$

This introduces a new set of constraints:

$$-\frac{\partial \Phi}{\partial \boldsymbol{v}} \equiv \chi(\boldsymbol{u}, \boldsymbol{v}) \approx 0. \tag{3.6}$$

Then the adiabatic condition appears in the theory as a secondary constraint. If we further proceed to examine the consistency relations, we find

$$\{\chi(\boldsymbol{u}, \boldsymbol{v}), H_{\mathrm{T}}\} \approx -\boldsymbol{T}^{+}(\boldsymbol{u}, \boldsymbol{v})\boldsymbol{M}^{-1}\boldsymbol{p}_v - \boldsymbol{S}(\boldsymbol{u}, \boldsymbol{v})\boldsymbol{F} = 0 \tag{3.7}$$

where we have introduced the following matrix notation:

$$\boldsymbol{T}(\boldsymbol{u}, \boldsymbol{v}) = \frac{\partial^2 \Phi}{\partial \boldsymbol{u} \partial \boldsymbol{v}} \tag{3.8a}$$

$$\boldsymbol{S}(\boldsymbol{u}, \boldsymbol{v}) = \frac{\partial^2 \Phi}{\partial \boldsymbol{v} \partial \boldsymbol{v}}. \tag{3.8b}$$

In the harmonic case, these are force constant matrices of the model. For a general potential of interaction Φ these matrices are functions of $\boldsymbol{u}$ and $\boldsymbol{v}$. It will be shown that $\boldsymbol{S}(\boldsymbol{u}, \boldsymbol{v})$ must be a non-singular matrix (this is well known in lattice dynamics theory in the harmonic approximation) and therefore all the $\boldsymbol{F}$ components are determined and these can be formally expressed as

$$\boldsymbol{F} = -\boldsymbol{S}^{-1}\boldsymbol{T}^{+}\boldsymbol{M}^{-1}\boldsymbol{p}_u. \tag{3.9}$$

Therefore the first-class Hamiltonian (3.2) becomes

$$H_{\mathrm{T}} = \tfrac{1}{2}\boldsymbol{p}_u^{+}\boldsymbol{M}^{-1}\boldsymbol{p}_u + \Phi(\boldsymbol{u}, \boldsymbol{v}) - \boldsymbol{p}_u^{+}\boldsymbol{M}^{-1}\boldsymbol{T}\boldsymbol{S}^{-1}\boldsymbol{p}_v. \tag{3.10}$$

In summary, we have a theory which is defined by the first-class Hamiltonian (3.10) without arbitrary coefficients, unlike gauge theory [12]. This is because all the constraints (3.1) and (3.6) are of second class. The existence of these second-class constraints reveals the existence of degrees of freedom which are not physically relevant. In the harmonic case these degrees of freedom can be discarded as we have mentioned, and this constitutes the usual approach.

In the present case we have a general interaction potential. Then the nonlinearity of the adiabatic condition makes impossible the elimination of these degrees of freedom. However, the identification of our system as a constraint system allows us to continue with the treatment of the dynamics of the model.

4. Quantisation and statistical mechanics

The second-class constraints may be eliminated by means of a Dirac bracket (DB). Any two quantities A and B have a Dirac bracket defined by

$$\{A, B\}_{\mathrm{DB}} \equiv \{A, B\}_{\mathrm{PB}} - \{A, \phi^a\}\Delta^{ab}\{\phi^b, B\} \tag{4.1}$$

where ϕ^a are the components of the constraint vector:

$$\boldsymbol{\phi} = \begin{pmatrix} \boldsymbol{p}_v \\ \boldsymbol{\chi}(\boldsymbol{u}, \boldsymbol{v}) \end{pmatrix} \tag{4.2}$$

and $\Delta^{ab}\{\phi^b, \phi^c\}_{\mathrm{PB}} = \delta^{ac}$. The explicit form of the $\boldsymbol{\Delta}$ is

$$\boldsymbol{\Delta} \equiv \begin{pmatrix} 0 & -\boldsymbol{S}^{-1} \\ \boldsymbol{S}^{-1} & 0 \end{pmatrix}. \tag{4.3}$$

From the Dirac theory we can see that det $\boldsymbol{\Delta}^{-1}$ is different from zero and this implies that $\boldsymbol{S}$ is an invertible matrix, as we have mentioned in section 3.

The equations of motion are valid for both Dirac brackets or Poisson brackets, because H_{T} is first class. This equations are equivalent to the Euler–Lagrange equations (2.2) together with the equations for the shell velocities.

Now, as is usual in this treatment, we have a quantisation method for our formalism. For this purpose we must take the conmutation relation corresponding to the Dirac bracket (4.1) and consider the constraints as strong equations between operators. This canonical procedure for quantisation of the shell model might be hard to use in a particular model.

The quantisation in terms of path integrals becomes a more powerful method and allows us to extend the results to quantum statistical mechanics. The probability amplitude of the system which was at $\boldsymbol{u}_0 \cdot \boldsymbol{v}_0$ will be at $\boldsymbol{u}_1 \cdot \boldsymbol{v}_1$ at time T can be written as a path integral for a constrained system [10]. In this case the general expression takes the form

$$\langle \boldsymbol{u}, \boldsymbol{v} \mid \boldsymbol{u}_0 \boldsymbol{v}_0 \rangle = \int \mathscr{D}\boldsymbol{u}\mathscr{D}\boldsymbol{v}\mathscr{D}\boldsymbol{p}_u\mathscr{D}\boldsymbol{p}_v (\det \boldsymbol{\Delta}^{-1})^{1/2} \delta(\boldsymbol{p}_v)\delta(\boldsymbol{\chi}) \exp\left(\frac{\mathrm{i}}{\hbar}\int_0^T \mathrm{d}t[\boldsymbol{p}_u^+\dot{\boldsymbol{u}} + \boldsymbol{p}_v^+\dot{\boldsymbol{v}} - H_\mathrm{T}]\right). \tag{4.4}$$

Using the expression (4.3) for $\boldsymbol{\Delta}$ and by integrating $\boldsymbol{p}_u$ and $\boldsymbol{p}_v$ we have

$$\langle \boldsymbol{u}_1 \boldsymbol{v}_1 \mid \boldsymbol{u}_0 \boldsymbol{v}_0 \rangle = \int \mathscr{D}\boldsymbol{u}\mathscr{D}\boldsymbol{v} \det \boldsymbol{S}\delta(\boldsymbol{x}) \exp\left(\frac{\mathrm{i}}{\hbar}\int_0^T \mathrm{d}t[\tfrac{1}{2}\dot{\boldsymbol{u}}^+ \boldsymbol{M}\dot{\boldsymbol{u}} - \Phi(\boldsymbol{u}, \boldsymbol{v})]\right). \tag{4.5}$$

In this expression the variables $\boldsymbol{u}$ and $\boldsymbol{v}$ are present. To arrive at the partition function, we must carry out the integration over all periodic paths and to make the change of variable $\mathrm{i}t = \tau$ [13]. Thus we have

$$Z = \int_{\text{periodic}} \mathscr{D}\boldsymbol{u}\mathscr{D}\boldsymbol{v} \det \boldsymbol{S}\delta(\boldsymbol{\chi}) \exp\left(-\frac{\mathrm{i}}{\hbar} S_\mathrm{E}(\boldsymbol{u}, \boldsymbol{v})\right) \tag{4.6}$$

where

$$S_\mathrm{E}(\boldsymbol{u}, \boldsymbol{v}) = \int_0^{\beta\hbar} \mathrm{d}\tau \left[\frac{1}{2}\left(\frac{\mathrm{d}\boldsymbol{u}}{\mathrm{d}\tau}\right)^+ \boldsymbol{M}\left(\frac{\mathrm{d}\boldsymbol{u}}{\mathrm{d}\tau}\right) + \Phi(\boldsymbol{u}, \boldsymbol{v})\right]. \tag{4.7}$$

The expression (4.6) can be obtained in a straightforward manner as we show in the appendix.

We can write the extra factors in the measure of expression (4.6) in analogy with the gauge theories [12] and therefore we find

$$Z = \int \mathscr{D}\boldsymbol{u}\mathscr{D}\boldsymbol{v}\mathscr{D}\boldsymbol{\eta}\mathscr{D}\boldsymbol{\eta}^+\mathscr{D}\boldsymbol{\lambda} \exp\left(-\frac{\mathrm{i}}{\hbar} S_\mathrm{E}^\mathrm{eff}[\boldsymbol{u}, \boldsymbol{v}, \boldsymbol{\eta}, \boldsymbol{\eta}^+, \boldsymbol{\lambda}]\right) \tag{4.8}$$

with

$$S_\mathrm{E}^\mathrm{eff}[\boldsymbol{u}, \boldsymbol{v}, \boldsymbol{\eta}, \boldsymbol{\eta}^+, \boldsymbol{\lambda}] = S_\mathrm{E}[\boldsymbol{u}, \boldsymbol{v}] + \int_0^{\beta\hbar} \mathrm{d}\tau[\boldsymbol{\lambda}^+\boldsymbol{\chi}(\boldsymbol{u}, \boldsymbol{v}) + \boldsymbol{\eta}^+\boldsymbol{S}(\boldsymbol{u}, \boldsymbol{v})\boldsymbol{\eta}]. \tag{4.9}$$

The $\boldsymbol{\lambda}$ field was introduced when δ function integral representation is used. On the other hand the det $\boldsymbol{S}$ can be written as a path integral over Grassmann numbers. This fact leads to the introduction of $\boldsymbol{\eta}$ fields. These fields are equivalent to Faddeev–Popov ghosts which appear in gauge theories.

5. Conclusions

We show that the shell model for lattice dynamics is a constrained Hamiltonian system. This fact allows us to solve the difficulties which exist in the model. This was made without any artificial approximation, i.e. to assign finite mass to the shells.

We have obtained a general expression for the partition function (4.8) which can be evaluated in both cases, perturbative and non-perturbative, and this is an important result of our method. The expression (4.8) can be taken as a starting point for constructing the Feynman rules for the perturbative treatment.

Our system has only second-class constraints and the incorporation of them in a path integral must be done by using the Senjanovick method [10]. This is rather different from using the Faddeev-Popov method [14] as was suggested in [5], because this method has been used for Yang-Mills theories which are systems where all the constraints are first class.

Finally, in a recent work [6] we show that it is possible to incorporate the nonlinear effects in the classical partition function of a particular shell model. By similar arguments we think that the nonlinear effects in quantum statistical mechanics, in a semiclassical approximation [15], can be incorporated. These arguments are under consideration.

Appendix

In an equivalent way to [6] for the classical statistical case, the formal expression for the quantum partition function is given by

$$Z = \int_{\text{periodic}} \mathscr{D}\boldsymbol{u} \exp\left(-\frac{\mathrm{i}}{\hbar} S_{\mathrm{E}}(\boldsymbol{u}, \boldsymbol{v}(\boldsymbol{u}))\right) \tag{A1}$$

with

$$S_{\mathrm{E}}(\boldsymbol{u}, \boldsymbol{v}(\boldsymbol{u})) = \int_0^{\beta\hbar} \mathrm{d}\tau \left[\frac{1}{2}\left(\frac{\mathrm{d}\boldsymbol{u}}{\mathrm{d}\tau}\right)^{+} \boldsymbol{M} \left(\frac{\mathrm{d}\boldsymbol{u}}{\mathrm{d}\tau}\right) + \Phi(\boldsymbol{u}, \boldsymbol{v}(\boldsymbol{u}))\right] \tag{A2}$$

where $\boldsymbol{v}(\boldsymbol{u})$ must be considered as implicit functions of $\boldsymbol{u}$ through the adiabatic condition

$$\chi[\boldsymbol{u}, \boldsymbol{v}] = -\frac{\partial\Phi}{\partial\boldsymbol{v}}(\boldsymbol{u}, \boldsymbol{v}). \tag{A3}$$

We rewrite the measure of the integral (A1) as follows:

$$\mathscr{D}\boldsymbol{u} = \mathscr{D}\boldsymbol{u}\mathscr{D}\boldsymbol{v}\delta(\boldsymbol{v} - \boldsymbol{v}(\boldsymbol{u})) \tag{A4}$$

where δ is the functional Dirac delta [16].

Then the expression (A1) takes the form:

$$Z = \int \mathscr{D}\boldsymbol{u}\mathscr{D}\boldsymbol{v} \det\left[\frac{\partial\chi(\boldsymbol{u}, \boldsymbol{v})}{\partial\boldsymbol{v}}\right] \delta(\chi(\boldsymbol{u}, \boldsymbol{v})) \exp\left\{-\frac{\mathrm{i}}{\hbar} S_{\mathrm{E}}(\boldsymbol{u}, \boldsymbol{v})\right\} \tag{A5}$$

where we have written

$$\delta(\boldsymbol{v} - \boldsymbol{v}(\boldsymbol{u})) = \delta(\chi(\boldsymbol{u}, \boldsymbol{v})) \det\left[\frac{\partial\chi(\boldsymbol{u}, \boldsymbol{v})}{\partial\boldsymbol{v}}\right]. \tag{A6}$$

Equation (A5) is the same as (4.6). Although this form is more straightforward than the one obtained in this paper, it does not show us the constrained nature of the shell model which is non-trivial.

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