J. Condensed Matter Nucl. Sci. 12 (2013) 69–104

Research Article

Born–Oppenheimer and Fixed-point Models for Second-order Phonon Exchange in a Metal

Peter L. Hagelstein *

Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

Irfan U. Chaudhary

Department of Computer Science and Engineering, University of Engineering and Technology. Lahore, Pakistan

Abstract

We have been interested in the development of a model for anomalies in condensed matter nuclear science, and over the past few years we have developed new models that describe coherent phonon exchange between a highly-excited vibrational mode and nuclei under conditions of fractionation. When we modeled collimated X-ray emission in the Karabut experiment, we found that the conditions required by the model did not match the conditions of the experiment. One possible reason for this might be the neglect of phonon fluctuations due to coupling with conduction electrons. We would like to add a description of this effect to our phonon–nuclear model; however, models normally used for electron–phonon interactions in metals are based on the Bloch picture, and we were concerned that it may not be well suited to the problem. This has motivated us to develop a new model for phonon fluctuations in a metal that is based on the Born–Oppenheimer picture, within the context of a Brillouin–Wigner formulation. The Born–Oppenheimer results are complicated, so we have reduced them in a simpler fixed-point picture (which is based on a Taylor series expansion of the Born–Oppenheimer approximation around fixed nuclear equilibrium points). In order to verify the resulting formalism, we constructed a simplified model for the monatomic crystal phonon dispersion relation, which is well known in the Bloch picture literature. From this model we are able to extract the longitudinal dielectric constant. We find that the fixed-point dielectric constant at second order is more accurate than the Bloch picture equivalent, and that it includes dynamic corrections that match the result from field theory up to $O(\omega^2)$. This model is used in a subsequent paper for the development of phonon fluctuation models, where it is found that the Bloch picture is appropriate when the metal sample is micron scale or larger, and that the Born–Oppenheimer picture is appropriate for nano-scale samples.
 ISSN 2227-3123

Keywords: Phonon theory, Born-Oppenheimer approximation, phonon fluctuations, fractionation

*E-mail: plh@mit.edu

© 2013 ISCMNS. All rights reserved. ISSN 2227-3123

1. Introduction

We remain interested in the theoretical problem associated with how excess heat in the Fleischmann–Pons experiment [1–4] works. The key problem for us is the absence of energetic nuclear radiation in amounts commensurate with the energy produced [5], in experiments where the origin of the energy is thought to be nuclear. More than a decade ago we found that coherent energy exchange between two-level systems and a highly excited oscillator could occur efficiently when the characteristic energies were highly mismatched [6], in the lossy spin-boson boson model. In this case, energy conservation required that an (odd) integer number of oscillator quanta were needed to make up a large two-level system quantum. Coherent energy exchange in this situation in the spin-boson model is a very weak effect [7,8]; but when the model is augmented with loss, the destructive interference which hinders energy exchange can be eliminated, resulting in efficient coherent energy exchange in the lossy version of the spin–boson model [9–15].

More recently, we have developed a new physical model that is closely related to the lossy spin–boson model [16–18], and which implements the same mechanism for efficient coherent energy exchange under conditions where a large quantum is fractionated. In a sense, the new model is just the direct generalization of the nonrelativistic solid state Hamiltonian to include a relativistic description of nuclei as relativistic composite particles. In the relativistic version of the problem there is a strong coupling between the lattice vibrations and the internal nuclear degrees of freedom. Under conventional conditions, a generalized Foldy–Wouthuysen transformation rotates out this strong first-order coupling, resulting in a relativistic model not very different from the nonrelativistic one (in which the coupling between vibrations and internal nuclear degrees of freedom is very weak). The situation is very much analogous to the spin–boson model, where the first-order coupling between the oscillator and two-level systems can be removed with a Foldy–Wouthuysen type of transformation. However, when the loss is sufficiently strong to modify the occupation of the off-resonant states, then the transformation becomes unhelpful, and the model is best analyzed by brute force in the unrotated frame. The relativistic generalization of the condensed matter Hamiltonian is closely related, so when loss becomes important we propose that the Foldy–Wouthuysen transformation similarly becomes unhelpful. In this case the strong first-order coupling is available to mediate coherent dynamics on low-loss transitions. This in our view is the origin of the anomalies in condensed matter nuclear science [18].

Over the past year or two we have accumulated some experience with this new physical model. It is very interesting, in that it seems to predict anomalies very much like those seen in experiment (at least qualitatively). Since this model is capable of fractionating large quanta, it can be used to model coherent deuteron-deuteron reactions going to ^{4}He, with energy going into vibrations. Low-level gamma emission, and also transmutation effects, follow naturally as a result of coupling to internal nuclear excited state [19,20]. In our view, the simplest of the anomalies is direct vibrationally induced nuclear excitation [17], which we have proposed as responsible for collimated X-ray emission in the Karabut experiment [21–26]; this effect is also predicted by the new model. However, for all of its good things about the new theory that we have enumerated here, it is offset by the difficulty that the theory, particular model, and interpretation of the Karabut experiment are not in agreement yet quantitatively [18]. Our conclusion given this situation is that we are "close;" but some issue remains either with the theory, the model, or the interpretation.

The motivation for this work is the possibility that the theory is deficient in the case of metals generally, because coupling between vibrations and conduction electrons has not been included. We are interested in developing a model for phonon fluctuations due to this coupling to see whether it impacts, and perhaps increases, the ability of the coupled phonon–nuclear system to fractionate a large quantum.

The argument is subtle, and perhaps worth some thought here. In the lossy spin–boson model, the coupling between the two-level systems and oscillator produces a mixing between states that are far apart in energy. This coupling with off-resonant states produces a second-order indirect coupling between neighboring phonon basis states with the same two-level excitation, but different by two phonons. In the lossy spin–boson model it is this second-order interaction that determines how fast coherent energy exchange occurs under conditions of fractionation. It is no accident that

the relevant dimensionless coupling strength for coherent energy exchange goes like $g/\Delta n^2$, since the second-order indirect coupling between phonon states different by two is what produces this coupling strength [13].

Consequently, we might expect that the lossy spin–boson model will be sensitive to the addition of mechanisms which produce a coupling between neighboring phonon states. And because the new physical model is so closely related to the lossy spin–boson model, we would expect the same to be true for it as well. The coupling between vibrations and conduction electrons in a metal results ultimately in fluctuations in the phonon distribution. These fluctuations cause a spreading of the phonon distribution, caused by indirect coupling between phonon states different by two phonons, very similar to the indirect coupling resulting from the phonon–nuclear interaction. Consequently, we would expect the rate at which energy exchange occurs between phonons and nuclei under conditions of fractionation would depend on the amount of fluctuations induced in the phonon system by coupling to conduction electrons.

If so, then all that remains is to include phonon fluctuations due to phonon–electron coupling into the model. Our goal seems clear, and one might expect that all we need to do is to apply some analysis to the problem and we should be able to obtain a resolution. After all, electron–phonon coupling in metals is one problem that has been worked on a great deal over many decades. There is more than enough literature available to make clear the models and approaches available. However, amazingly enough some technical issues arise which are subtle, and these have motivated us to review the formulation of the problem.

The issue concerns two different physical pictures that appear in the literature to model phonon exchange. The leading formalism is of course the Bloch picture [27,28], which is based on periodic Bloch electron waves, and their interaction with phonons. The great majority of all calculations involve electron–phonon coupling has been done in the Bloch picture. A different approach altogether is available in the Born–Oppenheimer picture [29,30]. In this case, electrons are described using more general adiabatic wavefunctions, and phonon exchange is computed using the non-adiabatic terms in the Born–Oppenheimer Hamiltonian. Now, one might hope that the same physics is described in both cases. Most of the calculations that involve the electron–phonon interaction in metals is centered on the problem of electron screening. A much smaller number of papers are concerned with phonon decay rates resulting from resonant absorption by conduction electrons. For these problems, good answers are obtained in the Bloch picture.

But in our model, we are concerned with the coupled phonon–nuclear problem, in which states that are very much off of resonance are important. In this case it is important for us to work with a formulation that is well suited to the problem (and also which we can understand intuitively). For example, it can be shown that the phonon exchange matrix element in the Bloch picture and in the Born–Oppenheimer picture coincide when the phonon energy matches the difference in the electron energies [29]. However, we are interested in phonon fluctuations induced by the coupling with electrons, which involves off-resonant interactions. In this case, it seems we should want to use the Born–Oppenheimer picture (since there are no issues for off-resonant states). Unfortunately, we were not aware of anyone pursuing this kind of problem in a Born–Oppenheimer picture previously when we started (the formal development given by Sham and Ziman [27] covers many of the issues); so when we began it wasn't clear that a suitable foundation was available in the literature that we could use for phonon fluctuations. It seems in the literature that the two pictures are considered to be essentially equivalent, and results known so far are essentially the same in both (we will pursue this question in a following work).

Consequently, one task will be to examine the development of a suitable formulation for electron–phonon interactions in a metal that we can use to evaluation phonon fluctuations. In principle the starting place for our model is pretty clear. There is a strong electron–phonon interaction present initially, which we would like to rotate out in order to recover a model for dressed phonons that don't interact at first order. Unfortunately we do not have available an exact transformation that can do this. So instead we will work with an algebraic Brillouin–Wigner type of formulation which is well adapted to second-order models of this type, and which is also consistent with our formulation of the coupled phonon–nuclear problem. We can use it to obtain a version of the rotated problem that is good to second order, and which we could improve further later on if we wished.

With a suitable starting place and approach to follow, there is no particular difficulty in the development that follows. Unfortunately, since the Born–Oppenheimer picture describes very general configurations, the resulting formulas are quite complicated. We are able to develop a reduced version of this model in which we expand the Born–Oppenheimer wavefunctions around equilibrium positions; the model that results is a fixed-point approximation. We might consider this fixed-point model as constituting an important picture in its own right; it might be thought of as a Born–Oppenheimer version of the Bloch picture.

The development involves a fair number of pages and lots of formulas, so some effort is needed to determine whether we might have confidence in the results. For example, we would like to be able to make a connection with some known problem where the answer is available from previous work. In this case we can extract a result from the longitudinal dielectric constant directly from the model, and compare it with known results from the Bloch picture. We find that our second-order formulation results in a model for the longitudinal dielectric constant which includes frequency-dependent terms up to second order in ω, and which we are able to verify is in agreement with literature results.

In the end, we have a Born–Oppenheimer based model that allows us to specify the coupling matrix elements that describe phonon fluctuations due to coupling with conduction electrons. These matrix elements can be evaluated then in order to develop a model for phonon–nuclear coupling that includes fluctuations due to phonon–electron coupling. Such a model is analyzed in a following paper.

2. Basic Model and Sector Decomposition

The tasks that lie before us are at the same time easy (since the basic problem of electrons and nuclei is well known, and since the Born–Oppenheimer formalism is also well known) and hard (since there are some subtleties, a great many issues, and since the Brillouin–Wigner formalism is not as well known in the literature as it might otherwise be). Unfortunately, the path forward in the development that follows is not linear. Linear steps that are well motivated in each case are preferred, but in what follows we consider two independent paths that converge only after a fair amount of development and discussion.

The headache is that the separation of the phonon and electron degrees of freedom that we desire can be done effectively within the Brillouin–Wigner formalism; but sadly, the Brillouin–Wigner formalism requires a fair amount of structure within the model in order to make use of it. In particular, we need a definition of the phonon modes in order to make sense of the Brillouin–Wigner construction; but the relevant phonon mode structure can only be determined after we have made use of the Brillouin–Wigner construction.

On the other hand, electron–phonon coupling in metals is a very well known problem that has been worked over in the literature for more than 80 years. Given this, we know from earlier work that there are phonons; there are conduction electrons; they couple together; phonon exchange occurs; there is screening by conduction electrons; and we could make use of previous work to write down already a constraint for the phonon modes that would be quite close to what we will eventually arrive at. Because of this, working with a development that is not linear in what follows will cause us very little difficulty. We already know pretty much how things work and what to expect. At issue here then are the interactions that produce phonon fluctuations within the Born–Oppenheimer formalism; and the construction of the machinery that we need to describe the problem generally, and to carry out detailed calculations in particular.

This motivates us here to focus on the two ares that make up our two starting places. One is the basic physical model, which basically involves a metal lattice with interacting electrons and nuclei. The other is the basic Brillouin–Wigner separation of phonon and electron degrees of freedom.

2.1. Basic physical model

Our starting place is the specification of a model for nuclei and electrons in a metal lattice with Coulomb interactions

$$\hat{H} = \hat{H}_{\rm N} + \hat{H}_{\rm e} + \hat{V}_{\rm eN}. \tag{1}$$

The nuclear Hamiltonian is

$$\hat{H}_{\rm N} = \sum_j \frac{|\hat{\mathbf{P}}_j|^2}{2M_j} + \sum_{j<k} \frac{Z_j Z_k e^2}{4\pi\epsilon_0 |\mathbf{R}_k - \mathbf{R}_j|} \tag{2}$$

and the Hamiltonian for the electrons is

$$\hat{H}_{\rm e} = \sum_\alpha \frac{|\hat{\mathbf{p}}_\alpha|^2}{2m} + \sum_{\alpha<\beta} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_\beta - \mathbf{r}_\alpha|}. \tag{3}$$

Coupling between electrons and the nuclei is described by

$$\hat{V}_{\rm eN} = -\sum_{j,\alpha} \frac{Z_j e^2}{4\pi\epsilon_0 |\mathbf{R}_j - \mathbf{r}_\alpha|}. \tag{4}$$

This Hamiltonian describes the same basic model as has been used in the literature for many decades (see e.g. Eq. (3.1) in [27]), and as such is well known. Our interest ultimately is in a somewhat more sophisticated model that will involve phonon–nuclear coupling, so our intention then is to take the results that we obtain for the simpler problem considered in this paper, and adapt them to the phonon–nuclear problem in a following paper.

2.2. Sector decomposition

There are a variety of mathematical techniques that are available to us to analyze this problem, along with a vast literature since our starting place is so general. In what follows we will make use of a sector decomposition approach, which is not so often used in the modern literature. It offers a number of advantages for our purposes here: the approach is relatively simple; it is easy to develop approximations in which different degrees of freedom are separated; we can work with resonant and off-resonant situations in a straightforward way; we can develop results for loss mechanisms simply; and the approach is consistent generally with the formulation that we are using for the phonon–nuclear models. It has the disadvantage of being relatively unfamiliar in this day and age, and it involves intermediate steps which are easy to specify formally but which imply projection operator constructions that are inconvenient.

In a sector decomposition generally we split the relevant Hilbert space into different pieces (which are the sectors), and then carry out our analysis on the individual sectors subsequently (this approach was used in times past in nuclear physics [31], and is discussed briefly in Appendix A of [9]). We are ultimately interested in working with a lattice in which a single-phonon mode is highly excited, so that the different sectors will correspond to the number of phonons in the highly excited mode. However, initially we will be working with more general vibrational states similar to the vibrational states of a molecule. Nevertheless, even in this case of a complicated molecule with many vibrational modes, it may be that one of the modes in particular is highly excited, so that the basic notion underlying our sector decomposition can be well defined. To accomplish this we write

$$\Psi = \Psi_0 + \Psi_1 + \Psi_2 + \cdots, \tag{5}$$

where Ψ_n is the sector that contains n phonons in the highly excited mode.

As remarked upon above, we are able to specify sectors here in the formalism which at this point in the analysis are inconvenient to specify since as yet we do not even have a specification of what constitutes a vibrational mode. Since a great deal of work has preceded our effort, much is known about the problem generally, and we know that there are vibrational modes in molecules, metals, and semiconductors. After further analysis we will be able to develop a constraint within the formalism that will determine the vibrational modes.

2.3. Sector eigenvalue equations

We are interested in the coupling of the vibrational degrees of freedom with the electronic degrees of freedom, and once again based on previous work we know that in a metal the electron–phonon coupling is dominated by single-phonon exchange interactions. If we start with the time-independent Schrödinger equation for the electrons and nuclei

$$E\Psi = \hat{H}\Psi \tag{6}$$

then we can develop coupled sector equations generally of the form

$$E\Psi_n = \hat{H}_{n,n}\Psi_n + \hat{H}_{n,n-1}\Psi_{n-1} + \hat{H}_{n,n+1}\Psi_{n+1}, \tag{7}$$

where the off-diagonal terms describe single-phonon exchange.

2.4. Second-order sector equations

It is possible to eliminate the first-order coupling by solving formally for the intermediate sectors; for example, in the case of one such intermediate sector we may write

$$\Psi_n = \left[E - \hat{H}_{n,n}\right]^{-1}\left(\hat{H}_{n,n-1}\Psi_{n-1} + \hat{H}_{n,n+1}\Psi_{n+1}\right). \tag{8}$$

Upon substituting back we obtain coupled second-order sector equations of the form

$$\begin{aligned} E\Psi_n =& \hat{H}_{n,n}\Psi_n + \hat{H}_{n,n-1}\left[E - \hat{H}_{n-1,n-1}\right]^{-1}\hat{H}_{n-1,n-2}\Psi_{n-2} \\ &+ \hat{H}_{n,n-1}\left[E - \hat{H}_{n-1,n-1}\right]^{-1}\hat{H}_{n-1,n}\Psi_n + \hat{H}_{n,n+1}\left[E - \hat{H}_{n+1,n+1}\right]^{-1}\hat{H}_{n+1,n}\Psi_n \\ &+ \hat{H}_{n,n+1}\left[E - \hat{H}_{n+1,n+1}\right]^{-1}\hat{H}_{n+1,n+2}\Psi_{n+2}. \end{aligned} \tag{9}$$

Even though the implementation of the required projection operators needed for these equations at this point remains formidable, we have achieved a suitable starting place for our investigations. We see that when first-order interactions are eliminated, we end up with diagonal and off-diagonal second-order interaction terms as a direct consequence of the basic assumptions that we have made so far (that phonons will exist in the system, and the first-order interactions are dominant).

3. Born–Oppenheimer Approximation and Phonon Exchange

Phonon exchange in metals is usually described within the framework of a Bloch picture, rather than within the framework of a Born–Oppenheimer picture. It will be useful here to pursue the development within the context of the more general Born–Oppenheimer picture here for the reasons already mentioned: the Bloch picture is thought to work well for resonant single-phonon exchange, but there are issues when we consider virtual processes; there is a close connection between the Born–Oppenheimer formulation and the Bloch formulation that will help to guide us in the development; and in process we will have developed a more general formulation (than the Bloch picture) that we can use if we like later on in connection with non-periodic systems.

Within the Born–Oppenheimer both adiabatic and non-adiabatic contributions to the Hamiltonian are recognized. For most problems the adiabatic Hamiltonian is sufficient, and the non-adiabatic Hamiltonian discarded because the associated effects are small. However, it is the non-adiabatic terms which mediate phonon exchange, so we will keep them and make use of them in what follows.

3.1. The Born–Oppenheimer approximation

In the Born–Oppenheimer approximation we separate the wavefunction into electronic and nuclear pieces [27]

$$\Psi(\{\mathbf{r}\},\{\mathbf{R}\}) = \Psi(\{\mathbf{R}\})\Phi(\{\mathbf{r}\};\{\mathbf{R}\}). \tag{10}$$

The idea is that the electronic motion is much faster than the ion motion, so the electronic wavefunction is defined assuming fixed nuclei according to

$$E_{\rm e}(\{\mathbf{R}\})\Phi(\{\mathbf{r}\};\{\mathbf{R}\}) = \left[\hat{H}_{\rm e} + \hat{V}_{\rm eN}\right]\Phi(\{\mathbf{r}\};\{\mathbf{R}\}). \tag{11}$$

The nuclear wavefunction in the adiabatic approximation is determined from

$$E\Psi(\{\mathbf{R}\}) = \left[\hat{H}_{\rm N} + E_{\rm e}(\{\mathbf{R}\})\right]\Psi(\{\mathbf{R}\}). \tag{12}$$

3.2. Isolation of the vibrational degrees of freedom

We can isolate the vibrational degrees of freedom by taking advantage of the Brillouin–Wigner formalism. To proceed we write the sector wavefunction in the form

$$\Psi_n(\{\mathbf{r}\},\{\mathbf{R}\}) = \Psi_n(\{\mathbf{R}\})\Phi_0(\{\mathbf{r}\};\{\mathbf{R}\}). \tag{13}$$

In writing this we are requiring the electronic wavefunction to be the same in the different vibrational sectors that we work with, which means that no electronic excitation is allowed in the model in association to transitions between neighboring sectors. Electronic excitation is possible in the intermediate sectors; and since electronic excitation is not permitted in the sectors that we keep we see that the part of the Hilbert space is then eliminated from further consideration (which simplifies the problem, but which we recognize is an approximation that we make). In this case, all of the outlying sectors that we do keep for our analysis will be off resonance; a situation which is consistent with the phonon–nuclear coupling problem (which is why we are interested in it), but qualitatively different from normal molecular or solid state problems (which tend to focus on the on-resonance part of the problem).

We project out the electronic degrees of freedom formally to obtain

$$\begin{aligned} E\Psi_n(\{\mathbf{R}\}) =& \langle\Phi_0|\hat{H}_{n,n}|\Phi_0\rangle\Psi_n(\{\mathbf{R}\}) \\ &+ \left\langle \Phi_0 \middle| \hat{H}_{n,n-1}\left[E - \hat{H}_{n-1,n-1}\right]^{-1}\hat{H}_{n-1,n-2}\middle|\Phi_0\right\rangle \Psi_{n-2}(\{\mathbf{R}\}) \\ &+ \left\langle \Phi_0 \middle| \hat{H}_{n,n-1}\left[E - \hat{H}_{n-1,n-1}\right]^{-1}\hat{H}_{n-1,n}\middle|\Phi_0\right\rangle \Psi_{n}(\{\mathbf{R}\}) \\ &+ \left\langle \Phi_0 \middle| \hat{H}_{n,n+1}\left[E - \hat{H}_{n+1,n+1}\right]^{-1}\hat{H}_{n+1,n}\middle|\Phi_0\right\rangle \Psi_{n}(\{\mathbf{R}\}) \\ &+ \left\langle \Phi_0 \middle| \hat{H}_{n,n+1}\left[E - \hat{H}_{n+1,n+1}\right]^{-1}\hat{H}_{n+1,n+2}\middle|\Phi_0\right\rangle \Psi_{n+2}(\{\mathbf{R}\}). \end{aligned} \tag{14}$$

By isolating the vibrational degrees of freedom, we are now much closer to being able to specify the phonon modes, and to being able to implement the projection operators implied by the formalism.

We might have reason to be concerned with not including the possibility of additional electronic excitation within this restricted version of the problem that we have kept. We note that the strong first-order phonon–electron coupling has been removed in the formalism, so that in a sense we are now dealing with phonon states which act as "dressed" (as if we had succeeded in rotating out the first-order interaction). The residual interactions are much weaker, and these are often neglected in conventional models for phonon dynamics. There is no obvious effect in the problems of interest to us that would suggest that it would not be reasonable to neglect electronic excitation in connection with phonon fluctuations. Should we wish, we could add electronic excitation as a loss later on.

Note however that we are keeping some of the second-order interactions to describe indirect coupling between phonon states differing by two; these will give rise to phonon fluctuations that are of interest for including electron–phonon coupling effects in the phonon–nuclear model.

3.3. Diagonal electronic matrix element

Within the Born–Oppenheimer approximation we can write for the expectation value of the Hamiltonian over the electronic degrees of freedom

$$\begin{aligned} \langle\Phi_0|\hat{H}|\Phi_0\rangle &= \langle\Phi_0|\hat{H}_{\rm N} + \hat{H}_{\rm e} + \hat{V}_{\rm eN}|\Phi_0\rangle \\ &= \sum_j \frac{|\hat{\mathbf{P}}_j|^2}{2M_j} + \sum_{j<k}\frac{Z_j Z_k e^2}{4\pi\epsilon_0|\mathbf{R}_k - \mathbf{R}_j|} + E_e(\{\mathbf{R}\}) \\ &\quad \sum_j \frac{1}{2M_j}\left(\langle\Phi_0|\ |\hat{\mathbf{P}}_j|^2|\Phi_0\rangle - |\hat{\mathbf{P}}_j|^2\right). \end{aligned} \tag{15}$$

We recognize adiabatic (second line) and non-adiabatic (third line) terms arising from electronic matrix elements of the Hamiltonian.

We can use this to isolate the lowest-order contribution to the diagonal sector Hamiltonian

$$\langle\Phi_0|\hat{H}_{n,n}|\Phi_0\rangle = \left|n\right\rangle\left\langle n\middle|\langle\Phi_0|\hat{H}|\Phi_0\rangle\middle|n\right\rangle\left\langle n\right|. \tag{16}$$

In this notation we will use the large $|n\rangle$ notation to refer to the complicated Born–Oppenheimer vibrational states with n phonons in the highly excited mode (the details of the rest of the vibrational wavefunction is not focused on, other than we presume that it remains unchanged in this model). In doing so, we have made our first significant connection between the Born–Oppenheimer part of the problem, and our Brillouin–Wigner formalism.

3.4. The first-order non-adiabatic term

The electronic matrix elements of the non-adiabatic part of the Born–Oppenheimer Hamiltonian can be thought of as being made up of first-order and second-order contributions. If the initial and final electronic states are different, then the non-adiabatic terms can be evaluated as

$$\langle \Phi_X | \, |\hat{\mathbf{P}}_j|^2 |\Phi_Y\rangle = 2\langle \Phi_X | (\hat{\mathbf{P}}_j \Phi_Y)\rangle \cdot \hat{\mathbf{P}}_j + \langle \Phi_X | (|\hat{\mathbf{P}}_j|^2 \Phi_Y)\rangle. \tag{17}$$

The first term on the RHS is expected to be dominated by single-phonon exchange, while the second is dominated by two-phonon exchange interactions.

It is possible to develop an estimate for the first-order non-adiabatic contribution by following an argument similar to that of Ziman [29]; this will lead to a slight generalization of Ziman's formula, which is a connection between the first-order non-adiabatic interaction and the gradient of the nuclear Coulomb potential. We recall that the electronic wavefunction in the Born–Oppenheimer approximation is determined from

$$E_Y(\{\mathbf{R}\})\Phi_Y(\{\mathbf{r}\};\{\mathbf{R}\}) = \left[\hat{H}_{\rm e} + \hat{V}_{\rm eN}\right]\Phi_Y(\{\mathbf{r}\};\{\mathbf{R}\}). \tag{18}$$

Multiplying by Φ_X and integrating over electronic coordinates leads to

$$E_Y\langle \Phi_X|\Phi_Y\rangle = \langle \Phi_X|\hat{H}_{\rm e} + \hat{V}_{\rm eN}|\Phi_Y\rangle. \tag{19}$$

We can take the gradient ∇_j of this expression to obtain

$$\begin{aligned}(\nabla_j E_Y)\langle \Phi_X|\Phi_Y\rangle + E_Y\langle \nabla_j\Phi_X|\Phi_Y\rangle + E_Y\langle \Phi_X|\nabla_j\Phi_Y\rangle \\ = \langle \nabla_j\Phi_X|\hat{H}_{\rm e} + \hat{V}_{\rm eN}|\Phi_Y\rangle + \langle \Phi_X|\nabla_j\hat{V}_{\rm eN}|\Phi_Y\rangle + \langle \Phi_X|\hat{H}_{\rm e} + \hat{V}_{\rm eN}|\nabla_j\Phi_Y\rangle \\ = E_Y\langle \nabla_j\Phi_X|\Phi_Y\rangle + \langle \Phi_X|(\nabla_j\hat{V}_{\rm eN})|\Phi_Y\rangle + E_X\langle \Phi_X|\nabla_j\Phi_Y\rangle.\end{aligned} \tag{20}$$

This reduces to

$$(\nabla_j E_Y)\langle \Phi_X|\Phi_Y\rangle + (E_Y - E_X)\langle \Phi_X|\nabla_j\Phi_Y\rangle = \langle \Phi_X|(\nabla_j\hat{V}_{\rm eN})|\Phi_Y\rangle. \tag{21}$$

When $Y \neq X$ we obtain

$$\langle \Phi_X|\nabla_j\Phi_Y\rangle = -\frac{\langle \Phi_X|(\nabla_j\hat{V}_{\rm eN})|\Phi_Y\rangle}{E_X - E_Y}. \tag{22}$$

If $Y = X$ we may write

$$\nabla_j E_X = \langle \Phi_X|(\nabla_j\hat{V}_{\rm eN})|\Phi_X\rangle. \tag{23}$$

In addition we have an orthogonality relation

$$\nabla_j \langle \Phi_X | \Phi_X \rangle = \langle \nabla_j \Phi_X | \Phi_X \rangle + \langle \Phi_X | \nabla_j \Phi_X \rangle = 0. \tag{24}$$

3.5. Connection between momentum and position matrix elements

According to Ehrenfest's theorem the evolution equations for the expectation values of position and momentum satisfy Newton's laws; in particular, we may write

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle \mathbf{R}_j \rangle = \frac{\langle \hat{\mathbf{P}} \rangle}{M_j}. \tag{25}$$

For this to be true for the isolated system (with no external force) the associated matrix elements must satisfy

$$-i \left(\frac{E_\mathrm{f} - E_\mathrm{i}}{\hbar} \right) \langle f | \mathbf{R}_j | i \rangle = \frac{\langle f | \hat{\mathbf{P}} | i \rangle}{M_j}. \tag{26}$$

The first-order nonadiabatic Hamiltonian can be written as

$$\sum_j \frac{1}{M_j} \langle \Phi_X | \hat{\mathbf{P}}_j \Phi_Y \rangle \cdot \hat{\mathbf{P}}_j = -i\hbar \sum_j \langle \Phi_X | \nabla_j \Phi_Y \rangle \cdot \frac{\hat{\mathbf{P}}_j}{M_j}. \tag{27}$$

3.6. Generalized Ziman relation

We can use this to write

$$\begin{aligned}
&\left\langle \Psi_f(\{\mathbf{R}\}) \left| -i\hbar \sum_j \langle \Phi_X | \nabla_j \Phi_Y \rangle \cdot \frac{\hat{\mathbf{P}}_j}{M_j} \right| \Psi_i(\{\mathbf{R}\}) \right\rangle \\
&\quad = \sum_l \left\langle \Psi_f(\{\mathbf{R}\}) \right| - i\hbar \sum_j \langle \Phi_X | \nabla_j \Phi_Y \rangle \left| \Psi_l(\{\mathbf{R}\}) \right\rangle \cdot \left\langle \Psi_l(\{\mathbf{R}\}) \left| \frac{\hat{\mathbf{P}}_j}{M_j} \right| \Psi_i(\{\mathbf{R}\}) \right\rangle \\
&\quad = \sum_l \left\langle \Psi_f(\{\mathbf{R}\}) \left| i\hbar \sum_j \frac{\langle \Phi_X | (\nabla_j \hat{V}_\mathrm{eN}) | \Phi_Y \rangle}{E_X - E_Y} \right| \Psi_l(\{\mathbf{R}\}) \right\rangle \\
&\qquad \times \left\langle \Psi_l(\{\mathbf{R}\}) \left| -i \left(\frac{E_l - E_i}{\hbar} \right) \mathbf{R}_j \right| \Psi_i(\{\mathbf{R}\}) \right\rangle.
\end{aligned} \tag{28}$$

It seems useful to recast this as

$$\left\langle \Psi_f(\{\mathbf{R}\}) \left| -i\hbar \sum_j \langle \Phi_X | \nabla_j \Phi_Y \rangle \cdot \frac{\hat{\mathbf{P}}_j}{M_j} \right| \Psi_i(\{\mathbf{R}\}) \right\rangle$$
$$= \sum_l \left\langle \Psi_f(\{\mathbf{R}\}) \left| \frac{E_l - E_i}{E_X(\{\mathbf{R}\}) - E_Y(\{\mathbf{R}\})} \sum_j \langle \Phi_X | (\nabla_j \hat{V}_{\mathrm{eN}}) | \Phi_Y \rangle \right| \Psi_l(\{\mathbf{R}\}) \right\rangle$$
$$\times \left\langle \Psi_l(\{\mathbf{R}\}) \left| \mathbf{R}_j \right| \Psi_i(\{\mathbf{R}\}) \right\rangle. \tag{29}$$

In a general Born–Oppenheimer setting we would expect both operators in the first matrix element to have the potential to produce a transition, while the $\mathbf{R}_j$ operator will predominantly exchange a single phonon (but can also mediate higher-order phonon exchange).

In the Bloch picture we take the nuclear positions to be the periodic equilibrium positions, so $E_X - E_Y$ will be constant; also we work with phonon modes instead of more general vibrational states, so we can expect single-phonon exchange from the $\mathbf{R}_j$ operator. When the phonon energy is not matched to the transition energy we would expect differences between the Born–Oppenheimer transition matrix element and the Bloch picture transition matrix element.

3.7. Screening effects

We would expect that when a nucleus moves, the tightly bound electrons will follow. Consequently, interactions between a nucleus and distant electrons should be screened by the tightly bound electrons. Discussion of this issue has appeared previously in the literature; see for example Refs. [32,33]. This effect should be in the formulas; however, as yet it does not seem very obvious how this screening comes about within the formalism.

To proceed, we focus our attention on a particular example in order to clarify how this works. Because the formalism focuses on the electronic wavefunction, we have the freedom to work with a classical description of the nuclear motion that we can visualise, in order to help understand the quantum mechanics of the electronic wavefunction. We consider two snapshots in time; including t_0 and t_1; where the difference between the two times is presumed to be small.

We begin by writing the time independent Schrödinger equation associated with the initial state wavefunction at $t = t_1$ as

$$E_1 \Phi_1 = \hat{H}_1 \Phi_1. \tag{30}$$

The final state wavefunction at $t = t_0$ satisfies

$$E_X \Phi_X = \hat{H}_0 \Phi_X. \tag{31}$$

Overlap matrix elements then satisfy

$$E_1 \langle \Phi_X | \Phi_1 \rangle = \langle \Phi_X | \hat{H}_1 | \Phi_1 \rangle, \tag{32}$$

$$E_X \langle \Phi_1 | \Phi_X \rangle = \langle \Phi_1 | \hat{H}_0 | \Phi_X \rangle. \tag{33}$$

We can subtract one with the complex conjugate of the other to obtain

$$(E_1 - E_X)\langle\Phi_X|\Phi_1\rangle = \langle\Phi_X|\hat{H}_1|\Phi_1\rangle - \langle\Phi_1^*|\hat{H}_0|\Phi_X^*\rangle. \tag{34}$$

Next, we would like to relate the initial state wavefunction Φ_1 to basis states defined at t_0. Since the difference between the two times is presumed to be small (so that the nuclei have not moved very far), we assume that it is possible to expand according to

$$\Phi_1 = \Phi_0 + \sum_j \left(\mathbf{R}_j^{(1)} - \mathbf{R}_j^{(0)}\right) \cdot \nabla_j \Phi_0 + \cdots \tag{35}$$

Since Φ_0 and Φ_X are now defined at the same time (with identical nuclear positions) they are orthogonal

$$\langle\Phi_X|\Phi_0\rangle = 0 \tag{36}$$

and we end up with

$$(E_1 - E_X)\sum_j \left(\mathbf{R}_j^{(1)} - \mathbf{R}_j^{(0)}\right) \cdot \langle\Phi_X|\nabla_j\Phi_0\rangle + \cdots = \langle\Phi_X|\hat{H}_1|\Phi_1\rangle - \langle\Phi_1^*|\hat{H}_0|\Phi_X^*\rangle. \tag{37}$$

It may be useful to expand the Hamiltonians to obtain

$$\begin{aligned}
&(E_1 - E_X)\sum_j \left(\mathbf{R}_j^{(1)} - \mathbf{R}_j^{(0)}\right) \cdot \langle\Phi_X|\nabla_j\Phi_0\rangle + \cdots \\
&\quad = \left\langle \Phi_X \left| \sum_\alpha \frac{|\hat{\mathbf{p}}_\alpha|^2}{2m} + \sum_{\alpha<\beta} \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_\beta - \mathbf{r}_\alpha|} - \sum_{j,\alpha} \frac{Z_j e^2}{4\pi\epsilon_0|\mathbf{R}_j^{(1)} - \mathbf{r}_\alpha|} \right| \Phi_1 \right\rangle \\
&\qquad - \left\langle \Phi_1^* \left| \sum_\alpha \frac{|\hat{\mathbf{p}}_\alpha|^2}{2m} + \sum_{\alpha<\beta} \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_\beta - \mathbf{r}_\alpha|} - \sum_{j,\alpha} \frac{Z_j e^2}{4\pi\epsilon_0|\mathbf{R}_j^{(0)} - \mathbf{r}_\alpha|} \right| \Phi_X^* \right\rangle.
\end{aligned} \tag{38}$$

We see that the transition matrix elements written in this form involves contributions from nuclear Coulomb, electronic Coulomb, and electronic potential energy terms in the Hamiltonian.

It is the case that a mathematical cancellation occurs for the contributions to the transition matrix element; for example

$$\begin{aligned}
&(E_1 - E_X)\sum_j \left(\mathbf{R}_j^{(1)} - \mathbf{R}_j^{(0)}\right) \cdot \langle\Phi_X|\nabla_j\Phi_0\rangle + \cdots \\
&\quad = \langle\Phi_X|\hat{H}_1 - \hat{H}_0|\Phi_0\rangle \\
&\quad = \left\langle \Phi_X \left| -\sum_{j,\alpha} \frac{Z_j e^2}{4\pi\epsilon_0|\mathbf{R}_j^{(1)} - \mathbf{r}_\alpha|} \right| \Phi_1 \right\rangle - \left\langle \Phi_X \left| -\sum_{j,\alpha} \frac{Z_j e^2}{4\pi\epsilon_0|\mathbf{R}_j^{(0)} - \mathbf{r}_\alpha|} \right| \Phi_1 \right\rangle.
\end{aligned} \tag{39}$$

We see that the relation including screening evaluates to one that involves the bare nuclear charge, and that this connects with the result above in Eq. (22). However, given this situation it seems that the better way to think about the transition matrix element might be to make use of the Hamiltonians including electronic contributions for each term individually as in Eq. (38), so that the subtraction will involve matrix elements referenced to effective (screened) nuclear charges instead of bare nuclear charges.

3.8. Effective charge parameterization

We are interested in the computation of an electronic matrix element of the form

$$\hat{\mathcal{M}}_{X,0} = \sum_j \frac{\hbar}{M_j} \langle \Phi_X | \nabla_j \Phi_0 \rangle \cdot \hat{\mathbf{P}}_j . \tag{40}$$

Probably the place to start is by making a connection with the classical version of the problem, where for small $t_1 - t_0$ we have

$$\mathbf{R}_j^{(1)} - \mathbf{R}_j^{(0)} = \frac{\mathbf{P}_j^{(0)}}{M_j}(t_1 - t_0) + \cdots \tag{41}$$

Consequently, we might write

$$\begin{aligned}
&\frac{(E_1 - E_X)(t_1 - t_0)\mathcal{M}_{X,0}}{\hbar} \\
&\quad = \sum_j (\mathbf{R}_j^{(1)} - \mathbf{R}_j^{(0)}) \cdot \langle \Phi_0 | \nabla_j \Phi_X \rangle \\
&\qquad \rightarrow \left\langle \Phi_X \left| \sum_\alpha \frac{|\hat{\mathbf{p}}_\alpha|^2}{2m} + \sum_{\alpha<\beta} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_\beta - \mathbf{r}_\alpha|} - \sum_{j,\alpha} \frac{Z_j e^2}{4\pi\epsilon_0 |\mathbf{R}_j^{(1)} - \mathbf{r}_\alpha|} \right| \Phi_1 \right\rangle \\
&\qquad - \left\langle \Phi_1^* \left| \sum_\alpha \frac{|\hat{\mathbf{p}}_\alpha|^2}{2m} + \sum_{\alpha<\beta} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_\beta - \mathbf{r}_\alpha|} - \sum_{j,\alpha} \frac{Z_j e^2}{4\pi\epsilon_0 |\mathbf{R}_j^{(0)} - \mathbf{r}_\alpha|} \right| \Phi_X^* \right\rangle .
\end{aligned} \tag{42}$$

In essence, this gives a practical way to evaluate the classical part of the matrix element in a modern computation, such as a density functional calculation.

In the event that the electronic kinetic energy is ineffective in mediating a transition, we parameterize this as

$$\frac{(E_0 - E_X)(t_1 - t_0)\mathcal{M}_{X,0}}{\hbar} \rightarrow \sum_j (\mathbf{R}_j^{(1)} - \mathbf{R}_j^{(0)}) \cdot \left\langle \Phi_X \left| \left(-\nabla_j \sum_\alpha \frac{Z_j^* e^2}{4\pi\epsilon_0 |\mathbf{R}_j - \mathbf{r}_\alpha|} \right)_{\mathbf{R}_j^{(0)}} \right| \Phi_0 \right\rangle \tag{43}$$

since E_1 is very close to E_0. The matrix element with this parameterization becomes

$$\hat{\mathcal{M}}_{X,0} \rightarrow \frac{1}{E_0 - E_X} \sum_j \frac{\hbar}{M_j} \left\langle \Phi_X \left| \left(-\nabla_j \sum_\alpha \frac{Z_j^* e^2}{4\pi\epsilon_0 |\mathbf{R}_j - \mathbf{r}_\alpha|} \right)_{\mathbf{R}_j^{(0)}} \right| \Phi_0 \right\rangle \cdot \hat{\mathbf{P}}_j . \tag{44}$$

3.9. A sector reduction in the Born–Oppenheimer approximation

We can now return to the sector Hamiltonian and interactions with other sectors in the framework of the Born–Oppenheimer approximation. The diagonal electronic matrix element of the Hamiltonian is

$$\hat{H}_{n,n} = \langle\Phi_0|\hat{H}|\Phi_0\rangle = \sum_j \frac{\langle\Phi_0|\,|\hat{\mathbf{P}}_j|^2|\Phi_0\rangle}{2M_j} + \sum_{j<k} \frac{Z_j Z_k e^2}{4\pi\epsilon_0|\mathbf{R}_k - \mathbf{R}_j|} + E_0(\{\mathbf{R}\}), \tag{45}$$

where we have included the non-adiabatic contribution. This sector Hamiltonian with no further modification could be used to define general vibrational states (as are used in molecular problems). Later on, we will develop a second-order correction to this that gives the leading order correction due to phonon exchange

Since the non-adiabatic part of the Born–Oppenheimer Hamiltonian mediates phonon exchange in this formalism, we can write generally for $n' \neq n$

$$\begin{aligned}\hat{H}_{n,n'} &= \Big|n\Big\rangle \left\{ \sum_{Y\neq X} |\Phi_X\rangle\Big\langle n\Big|\langle\Phi_X|\hat{H}|\Phi_Y\rangle\Big|n'\Big\rangle\langle\Phi_Y| \right\} \Big\langle n'\Big| \\ &= \Big|n\Big\rangle \left\{ \sum_{Y\neq X} |\Phi_X\rangle\Big\langle n\Big| \sum_j \frac{\langle\Phi_X|\,|\hat{\mathbf{P}}|^2|\Phi_Y\rangle}{2M_j}\Big|n'\Big\rangle\langle\Phi_Y| \right\} \Big\langle n'\Big|. \end{aligned} \tag{46}$$

In the event that a phonon mode basis is defined consistent with this diagonal sector Hamiltonian, then the second-order sector-changing interaction for indirect coupling between $|n\rangle$ and $|n+2\rangle$ can be written as

$$\begin{aligned}&\Big\langle\Phi_0\Big|\hat{H}_{n,n+1}\Big[E - \hat{H}_{n+1,n+1}\Big]^{-1}\hat{H}_{n+1,n+2}\Big|\Phi_0\Big\rangle \\ &\quad\rightarrow \Big|n\Big\rangle \sum_{X\neq 0}\Big\langle n\Big|\sum_j \frac{\langle\Phi_0|\,|\hat{\mathbf{P}}_j|^2|\Phi_X\rangle}{2M_j}\Big|n+1\Big\rangle\Big[E - \hat{H}_{n+1,n+1}\Big]^{-1} \\ &\qquad \Big\langle n+1\Big|\sum_j \frac{\langle\Phi_X|\,|\hat{\mathbf{P}}_j|^2|\Phi_0\rangle}{2M_j}\Big|n+2\Big\rangle\Big\langle n+2\Big|. \end{aligned} \tag{47}$$

A similar expression can be developed for the other second-order interaction Hamiltonian.

It will become clear later on that the diagonal sector Hamiltonian here is dynamic. If we would like to make use of the static part of the Hamiltonian to define a reference, then the dynamic part of what is in the diagonal sector Hamiltonian above would contribute to the off-diagonal interaction.

3.10. Discussion

We see that phonon exchange arises from the non-adiabatic part of the Hamiltonian in the Born–Oppenheimer approximation, as has been noted in previous work. The development in this section revisits some of the ideas put forth by Ziman [29], who was interested in the connection between phonon exchange in the Bloch picture and in the Born–Oppenheimer picture.

In the Born–Oppenheimer picture the phonon exchange operator is a bit more complicated. In the reduction above we identified terms that could be identified as first-order and second-order in the reduction of the non-adiabatic

Hamiltonian. The strongest effect is due to single-phonon exchange, as expected and as known in the literature. Two-phonon exchange is clearly present, and since there are nonlinearities present in the interaction operator as a function of nuclear coordinates, we would expect higher-order phonon exchange processes as well (but of course these we expect to constitute smaller effects).

At this point we have sufficient development of the Born–Oppenheimer picture that we are able to make a more complete connection with the Brillouin–Wigner formalism. If we adopt the diagonal sector Hamiltonian (without any higher-order corrections) then we have a definition of the vibrational states, which allows us to construct the projection operator machinery required by the Brillouin–Wigner formalism. The model that results is very powerful, but has probably not seen much use (since it is a bit complicated).

4. Second-order Interactions

At this point we encounter a subtle technical issue in connection with the second-order interactions (recall here Eq. (14)). As a practical matter this technical issue involves only a minor difference in the answers we end up with later on (and as such may be more important as a philosophical issue). It concerns a differentiation between the static and dynamic parts of the second-order interaction, and is motivated by how we intend to use the model later on.

At issue is the origin of the phonon fluctuations under consideration here, which are to be used in the phonon–nuclear model. For example, in general we have some freedom in the definition of the phonon mode structure mathematically, and we know that our answers for the electron–phonon part of the problem will be the same independent of what phonon mode basis we use as long as we include all terms to all orders in the calculation. The same is true for the more complicated coupled phonon–nuclear–electron problem that motivates our analysis here. However, because this latter problem is so complicated, we are not intending to include terms to all orders (fluctuations will be described only at second order), which means that our model will definitely depend on our definition of the phonon modes.

The issue then is which definition is likely to give us the best results later on (and this is where the argument is likely to seem more philosophical than mathematical). We know that there is a static screening effect in which the conduction electrons screen the Coulomb interactions between the metal ions. Now, if this were all there was to the problem, then probably we would expect no fluctuation effect. The idea is that static screening acts the same as a (static) modification of the ion–ion interaction. Which means that we could include the effect completely just by adjusting the phonon modes and frequencies when we analyze the phonon–nuclear problem.

The intuition then is that when we consider electron–phonon interactions, the parts of the interaction that lead to simple static corrections to the ion-ion potential we know cannot produce the fluctuations we are interested in for the phonon–nuclear problem. On the other hand, the interactions that could only be accounted for by an additional dynamical degree of freedom in the problem will produce the fluctuations that we are interested in. Consequently, our attention is focused on sorting out the static and dynamic parts of the second-order interaction. Most importantly, we need to make sure that the phonon mode definitions include all of the static part of the second-order interaction (and none of the dynamic part).

The program in what follows then is to identify the part of the second-order interaction which constitutes the static part, and then to isolate it from the dynamic part of the interaction. Once this is done, we can use the dynamic part of the interaction to model the phonon fluctuations of interest.

4.1. Static part of the second-order interaction, resonant sector

To proceed, we need to isolate the static part of the interaction. The issues are simplest in the case of the resonant sector, so we begin our discussion focusing on this case. We consider one of the second-order interaction terms, and write (assuming that the n_0 sector is the one on resonance)

$$\left\langle \Phi_0 \left| \hat{H}_{n_0,n_0+1} \left[E - \hat{H}_{n_0+1,n_0+1} \right]^{-1} \hat{H}_{n_0+1,n_0} \right| \Phi_0 \right\rangle$$
$$\rightarrow \left| n_0 \right\rangle \sum_{X \neq 0} \left\langle n_0 \left| \sum_j \frac{\langle \Phi_0 | \, |\hat{\mathbf{P}}_j|^2 | \Phi_X \rangle}{2M_j} \right| n_0 + 1 \right\rangle \frac{1}{-\hbar\omega_0 + F_0 - F_X}$$
$$\left\langle n_0 + 1 \left| \sum_k \frac{\langle \Phi_X | \, |\hat{\mathbf{P}}_k|^2 | \Phi_0 \rangle}{2M_j} \right| n_0 \right\rangle \left\langle n_0 \right|, \tag{48}$$

where in the denominator $\hbar\omega_0$ is the phonon energy associated with phonon exchange of the highly excited mode. The difference between the (vibration-averaged) electronic state energies is $F_X - F_0$; for example, in the Born–Oppenheimer approximation the eigenvalues for the electronic Hamiltonian $E_0(\{\mathbf{R}\})$ and $E_X(\{\mathbf{R}\})$ depend on the nuclear positions, and here we need these to be averaged in the $n_0 + 1$ sector.

The static part of this interaction for this term can be extracted by taking

$$\left(\frac{1}{-\hbar\omega_0 + F_0 - F_X} \right)_{\text{static}} = \frac{1}{F_0 - F_X}. \tag{49}$$

The elimination of the phonon frequency in the second-order terms generally in the resonant sector allows us to extract the static part of this second-order interaction.

4.2. Static part of the interaction in other sectors

In the off-resonant sectors, things are a bit more complicated, and we probably need to think about it some. The basic issue is that the second-order interactions in general come with off-resonant denominators of the form

$$\frac{1}{E - \hat{H}_{n',n'}}. \tag{50}$$

As we consider sectors that are further and further off of resonance, the corresponding diagonal sector energy will be increasingly different from E. The simplest approach is to retain the resonant sector definition for the off-resonant sectors. The associated physical statement is that the screening in the off-resonant sectors is assumed at lowest order to be the same as in the resonant sector. Such a scheme would be most consistent with the basic Born–Oppenheimer picture, and should be effective if the system is not far off of resonance (although it is not obvious at this point, in a subsequent paper we will find that it is difficult to push a highly excited phonon mode sufficiently off of resonance to cause a significant reduction in screening).

Nonetheless, there is some freedom in the choice of the diagonal sector Hamiltonian off of resonance, which could be exploited to simplify the overall calculation. The issue is that if we decide to fix the phonon mode definitions and operators based on the resonant sector, then as we go further off of resonance there will be an increasing difference between the on-resonance phonon mode definitions and operators and their off-resonant counterparts. Much later on (in a following paper) we will find it to be advantageous to use these off-resonant phonon mode definitions. Consequently, it makes sense to examine briefly here how it works for a diagonal sector Hamiltonian off of resonance. One of the terms contributing to the second-order phonon exchange interaction in this case is

$$\left\langle \Phi_0 \left| \hat{H}_{n,n+1} \left[E - \hat{H}_{n+1,n+1} \right]^{-1} \hat{H}_{n+1,n} \right| \Phi_0 \right\rangle$$
$$= \left| n \right\rangle \sum_{X \neq 0} \left\langle n \left| \sum_j \frac{\langle \Phi_0 | \, |\hat{\mathbf{P}}_j|^2 | \Phi_X \rangle}{2M_j} \right| n+1 \right\rangle \frac{1}{-(n-n_0+1)\hbar\omega_0 + F_0 - F_X}$$
$$\left\langle n+1 \left| \sum_j \frac{\langle \Phi_X | \, |\hat{\mathbf{P}}_j|^2 | \Phi_0 \rangle}{2M_j} \right| n \right\rangle \left\langle n \right|. \tag{51}$$

The generalization of the static approximation in this case involves

$$\frac{1}{-(n-n_0+1)\hbar\omega_0 + F_0 - F_X} \;\rightarrow\; \frac{1}{-(n-n_0)\hbar\omega_0 + F_0 - F_X}. \tag{52}$$

In this kind of a picture the mode frequency changes off of resonance, so strictly speaking the off resonant energy will no longer be $(n-n_0)\hbar\omega_0$. To account for this, we will write

$$(n-n_0)\hbar\omega_0 \;\rightarrow\; \hat{E}_{\rm off}. \tag{53}$$

In the resonant sector, $\hat{E}_{\rm off}$ is zero; if we use the resonant sector static interaction off of resonance, then we would take $\hat{E}_{\rm off}$ to be zero; if there is negligible frequency shift, then $\hat{E}_{\rm off}$ will be replaced by $(n-n_0)\hbar\omega_0$; and finally, if the frequency shifts are important off of resonance then we can account for it by using a more accurate estimate $[n\hbar\omega(\hat{E}_{\rm off}) - n_0\hbar\omega_0]$.

4.3. Specification of the vibrational states

Now we come back to the problem of the definition of the vibrational states. We focus first on the second-order contribution. When we use the static approximation, or its off-resonant generalization above, we end up with equivalent weights from the case where a phonon is created, and from the case when a phonon is destroyed. Because of this we are able to simplify things by making use of the identity

$$\sum_{n'} \left| n \right\rangle \left\langle n \left| \hat{A} \right| n' \right\rangle \left\langle n' \left| \hat{B} \right| n \right\rangle \left\langle n \right| = \left| n \right\rangle \left\langle n \left| \hat{A}\hat{B} \right| n \right\rangle \left\langle n \right| \tag{54}$$

and write the diagonal sector Hamiltonian as

$$\hat{H}_n^{\rm diagonal} = \sum_j \frac{\langle \Phi_0 | \, |\hat{\mathbf{P}}_j|^2 | \Phi_0 \rangle}{2M_j} + \sum_{j<k} \frac{Z_j Z_k e^2}{4\pi\epsilon_0 |\mathbf{R}_k - \mathbf{R}_j|} + E_0(\{\mathbf{R}\})$$
$$+ \sum_{X \neq 0} \left(\sum_j \frac{\langle \Phi_0 | \, |\hat{\mathbf{P}}_j|^2 | \Phi_X \rangle}{2M_j} \right) \frac{1}{-\hat{E}_{\rm off} + F_0 - F_X} \left(\sum_k \frac{\langle \Phi_X | \, |\hat{\mathbf{P}}_k|^2 | \Phi_0 \rangle}{2M_k} \right). \tag{55}$$

This is an interesting result (good for both on resonance and off-resonance), and also a useful one. If we define the vibrational states in any sector from the eigenfunctions of this Hamiltonian, then by definition no transitions between vibrational states occur (which is why no projection operators are needed).

4.4. Off-diagonal sector Hamiltonians

If we follow the general line of argument from above, then in a model where we use phonon modes defined in the resonant sector we would write

$$\begin{aligned}
&\left\langle \Phi_0 \middle| \hat{H}_{n,n\pm1} \left[E - \hat{H}_{n\pm1,n\pm1} \right]^{-1} \hat{H}_{n\pm1,n\pm2} \middle| \Phi_0 \right\rangle \\
&\quad \rightarrow \left| n \right\rangle \sum_{X\neq 0} \left\langle n \middle| \sum_j \frac{\langle \Phi_0 | \, |\hat{\mathbf{P}}_j|^2 | \Phi_X \rangle}{2M_j} \middle| n \pm 1 \right\rangle \\
&\qquad \left[\frac{1}{-\hat{E}_{off} \mp \hbar\hat{\omega}_0 + F_0 - F_X} - \frac{1}{F_0 - F_X} \right] \\
&\qquad \left\langle n \pm 1 \middle| \sum_k \frac{\langle \Phi_X | \, |\hat{\mathbf{P}}_k|^2 | \Phi_0 \rangle}{2M_k} \middle| n \pm 2 \right\rangle \left\langle n \pm 2 \right|
\end{aligned} \tag{56}$$

as the contribution arising from two-phonon exchange.

However, we can develop a more general result. Suppose that choose part of the Hamiltonian of Equation (55) in the resonant sector for the construction of the reference problem against which to define phonon fluctuations (call this $\hat{H}_0$), then in general we can develop relevant expressions for both diagonal and sector-changing interactions through

$$\begin{aligned}
\hat{H} =& \hat{H}_0 + \sum_n \left\{ \left| n \right\rangle \left\langle n \middle| \hat{H}(E) - \hat{H}_0 \middle| n \right\rangle \left\langle n \right| + \left| n \right\rangle \left\langle n \middle| \hat{H}(E) - \hat{H}_0 \middle| n+2 \right\rangle \left\langle n+2 \right| \right. \\
&\left. + \left| n \right\rangle \left\langle n \middle| \hat{H}(E) - \hat{H}_0 \middle| n-2 \right\rangle \left\langle n-2 \right| \right\},
\end{aligned} \tag{57}$$

where $\hat{H}(E)$ stands in the for the Hamiltonian of Eq. (55) taken at the appropriate off-resonant energy. What is interesting about this approach is that the kinetic energy term

$$\sum_j \frac{\langle \Phi_0 | \, |\hat{\mathbf{P}}_j|^2 | \Phi_0 \rangle}{2M_j}$$

in the Born–Oppenheimer approximation can be defined to contain a static part and a dynamic part. The more general definition will pick up sector-changing transitions beyond those due to second-order phonon exchange.

4.5. Discussion

At this point we have achieved a convergence of the Born–Oppenheimer line of development, and the Brillouin–Wigner line of development. We are now in a position to develop useful specifications of the vibrational modes as we like systematically in both resonant and off-resonant sectors. One of our goals in this work was to develop expressions that we could use to compute phonon fluctuations to add to our phonon–nuclear model. We now have Eqs. (56) and (57) for the associated off-diagonal sector Hamiltonians in the Born–Oppenheimer approximation. This was one of our goals in this work.

5. Fixed Basis Model for Phonon Modes

We have succeeded now in making the connection between the Born–Oppenheimer picture and the Brillouin–Wigner formalism, and in constructing formulas for the specification of the vibrational modes and fluctuations. However, because the model is so general it is inconvenient to evaluate them (without having a set of wavefunctions from a density functional calculation). What is needed is a model something like the Bloch picture, but which is referenced to the Born–Oppenheimer approximation.

The motivates our interest first in a fixed basis model, and then in the following section a fixed basis crystal model. In the fixed basis model of this section, the idea is to use perturbation theory to develop an approximate version of the Born–Oppenheimer formulation that assumes slow variations around the fixed-point reference. In this sense the fixed-point model is an approximation to the Born–Oppenheimer picture; however, it may be better to think of it as a fixed-point picture in the same sense as the Born–Oppenheimer picture or Bloch picture. We can develop it directly from the Born–Oppenheimer picture, but because it is referenced to a fixed-point wavefunction, it is strictly no longer the Born–Oppenheimer picture. An important issue for us is that phonon exchange in this fixed-point model is consistent with Born–Oppenheimer phonon exchange (which is different from Bloch picture phonon exchange).

5.1. First-order interaction with a fixed basis

The first order of business then is to develop suitable expansions for the Born–Oppenheimer wavefunction in terms of fixed basis states, which are made up of the Born–Oppenheimer states with nuclei fixed at their equilibrium positions

$$\Phi(\{\mathbf{r}\};\{\mathbf{R}\}) = \Phi(\{\mathbf{r}\};\{\mathbf{R}^{(0)}\}) + \sum_j (\mathbf{R}_j - \mathbf{R}_j^{(0)}) \cdot \left[\nabla_j \Phi(\{\mathbf{r}\};\{\mathbf{R}\})\right]_{\{\mathbf{R}^{(0)}\}} + \cdots \tag{58}$$

The electronic transition matrix element in the Born–Oppenheimer picture can be written in terms of fixed basis wavefunctions as

$$\begin{aligned}
&\langle \Phi_X(\{\mathbf{r}\};\{\mathbf{R}\})|\ |\hat{\mathbf{P}}_j|^2 |\Phi_Y(\{\mathbf{r}\};\{\mathbf{R}\})\rangle \\
&\quad = \left\langle \Phi_X(\{\mathbf{r}\};\{\mathbf{R}^{(0)}\}) + \sum_k (\mathbf{R}_k - \mathbf{R}_k^{(0)}) \cdot \left[\nabla_k \Phi_X(\{\mathbf{r}\};\{\mathbf{R}\})\right]_{\{\mathbf{R}^{(0)}\}} + \cdots \right| |\hat{\mathbf{P}}_j|^2 \\
&\qquad \left| \Phi_Y(\{\mathbf{r}\};\{\mathbf{R}^{(0)}\}) + \sum_k (\mathbf{R}_k - \mathbf{R}_k^{(0)}) \cdot \left[\nabla_k \Phi_Y(\{\mathbf{r}\};\{\mathbf{R}\})\right]_{\{\mathbf{R}^{(0)}\}} + \cdots \right\rangle.
\end{aligned} \tag{59}$$

Since we are interested in matrix elements where $Y \neq X$, the lowest-order contribution vanishes

$$\begin{aligned}
&\langle \Phi_X(\{\mathbf{r}\};\{\mathbf{R}^{(0)}\})|\ |\hat{\mathbf{P}}_j|^2 |\Phi_Y(\{\mathbf{r}\};\{\mathbf{R}^{(0)}\})\rangle \\
&\qquad = |\hat{\mathbf{P}}_j|^2 \langle \Phi_X(\{\mathbf{r}\};\{\mathbf{R}^{(0)}\})|\Phi_Y(\{\mathbf{r}\};\{\mathbf{R}^{(0)}\})\rangle \\
&\qquad = 0.
\end{aligned} \tag{60}$$

For the first-order contributions we may write

$$\sum_k (\mathbf{R}_k - \mathbf{R}_k^{(0)})|\hat{\mathbf{P}}_j|^2 \cdot \langle \nabla_k \Phi_X | \Phi_Y \rangle_0 + \sum_k |\hat{\mathbf{P}}_j|^2 (\mathbf{R}_k - \mathbf{R}_k^{(0)}) \cdot \langle \nabla_k \Phi_X | \Phi_Y \rangle_0$$
$$= \sum_k (\mathbf{R}_k - \mathbf{R}_k^{(0)})|\hat{\mathbf{P}}_j|^2 \cdot \left(\langle \nabla_k \Phi_X | \Phi_Y \rangle_0 + \langle \Phi_X | \nabla_k \Phi_Y \rangle_0 \right) - 2i\hbar \langle \Phi_X | \nabla_j \Phi_Y \rangle_0 \cdot \hat{\mathbf{P}}_j, \tag{61}$$

where the notation $\langle \cdots | \cdots \rangle_0$ here means that the wavefunction and the gradient of the wavefunction involve a fixed basis (and hence no dependence on $\{\mathbf{R}\}$). Since the Born–Oppenheimer wavefunctions satisfy

$$\nabla_j \langle \Phi_X | \Phi_Y \rangle = \langle \nabla_j \Phi_X | \Phi_Y \rangle + \langle \Phi_X | \nabla_j \Phi_Y \rangle = 0, \tag{62}$$

we end up with

$$\langle \Phi_X(\{\mathbf{r}\};\{\mathbf{R}\})| \, |\hat{\mathbf{P}}_j|^2 | \Phi_Y(\{\mathbf{r}\};\{\mathbf{R}\})\rangle = -2i\hbar \langle \Phi_X | \nabla_j \Phi_Y \rangle_0 \cdot \hat{\mathbf{P}}_j + \cdots \tag{63}$$

We can generate higher-order interactions in this way systematically; however, for what follows we will be satisfied working with the first-order interaction.

5.2. Diagonal second-order interaction

We can make use of this result for single-phonon exchange to evaluate the lowest-order contribution to the diagonal part of the second-order interaction

$$\sum_{X \neq 0} \left(\sum_j \frac{\langle \Phi_0 | \, |\hat{\mathbf{P}}_j|^2 | \Phi_X \rangle}{2M_j} \right) \frac{1}{-\hat{E}_{\rm off} + F_0 - F_X} \left(\sum_k \frac{\langle \Phi_X | \, |\hat{\mathbf{P}}_k|^2 | \Phi_0 \rangle}{2M_k} \right)$$
$$\rightarrow \quad -\sum_j \sum_k \hat{\mathbf{P}}_j \cdot \left\{ \sum_{X \neq 0} \frac{\hbar^2}{M_j M_k} \frac{\langle \Phi_0 | \nabla_j \Phi_X \rangle_0 \langle \Phi_X | \nabla_k \Phi_0 \rangle_0}{-\hat{E}_{\rm off} + F_0 - F_X} \right\} \cdot \hat{\mathbf{P}}_k. \tag{64}$$

5.3. Non-adiabatic contribution

The part of the non-adiabatic interaction that does not involve electronic excitation can be written as

$$\sum_j \frac{\langle \Phi_0 | \, |\hat{\mathbf{P}}_j|^2 \, | \Phi_0 \rangle - |\hat{\mathbf{P}}_j|^2}{2M_j}$$
$$= \sum_j \left(-\frac{i\hbar}{M_j} \right) \langle \Phi_0 | \nabla_j \Phi_0 \rangle_0 \cdot \hat{\mathbf{P}}_j$$
$$+ \sum_{j,k} \left(-\frac{i\hbar}{2M_j} \right) \left\{ (\mathbf{R}_j - \mathbf{R}_j^{(0)}) \cdot \langle \nabla_j \Phi_0 | \nabla_k \Phi_0 \rangle_0 \cdot \hat{\mathbf{P}}_k + \hat{\mathbf{P}}_j \cdot \langle \nabla_j \Phi_0 | \nabla_k \Phi_0 \rangle_0 \cdot (\mathbf{R}_k - \mathbf{R}_k^{(0)}) \right\}$$
$$+ \sum_j \frac{\hbar^2}{2M_j} \left(\langle \nabla_j \Phi_0 | \nabla_j \Phi_0 \rangle_0 - \langle \Phi_0 | \nabla_j^2 \Phi_0 \rangle \right). \tag{65}$$

The first term on the right-hand side describes a residual single-phonon interaction, which might be connected with current-induced phonon generation. The second term on the right-hand side will later on result in a first-order dynamical correction to the screening. Were we to adopt a strict static Hamiltonian in the resonant sector for the definition of the phonon modes, this term would likely not be included, but instead by thought of as a kind of two-phonon exchange term similar to the second-order phonon exchange interaction we have considered explicitly. The interpretation of the last term on the right-hand side is less clear; however, we might expect second-order coupling if a strong electrical current is present that may be significant if the current is strong.

5.4. Electronic energy

We found previously that the diagonal sector Hamiltonian including the second-order interaction in the static approximation could be used to define the vibrational states. With a fixed electronic basis we no longer have a convenient specification of the dependence of the electronic energy on the nuclear positions, which motivates us here to consider expanding it out to second order around the equilibrium positions. We may write

$$\begin{aligned} E_0(\{\mathbf{R}\}) &= \langle \Phi_0(\{\mathbf{r}\};\{\mathbf{R}\})|\hat{H}_{\rm e}+\hat{V}_{\rm eN}|\Phi_0(\{\mathbf{r}\};\{\mathbf{R}\})\rangle \\ &= E_0(\{\mathbf{R}^{(0)}\}) + \sum_j (\mathbf{R}_j-\mathbf{R}_j^{(0)})\cdot(\nabla_j E_0)_0 + \frac{1}{2}\sum_{j,k}(\mathbf{R}_j-\mathbf{R}_j^{(0)})\cdot(\nabla_j\nabla_k E_0)_0\cdot(\mathbf{R}_k-\mathbf{R}_k^{(0)})+\cdots \end{aligned} \tag{66}$$

From the discussion above we know that

$$\nabla_j E_0 = \langle \Phi_0|\nabla_j \hat{V}_{\rm eN}|\Phi_0\rangle. \tag{67}$$

We can use a similar approach for $\nabla_j\nabla_k E_0$; we begin with

$$E\Phi = (\hat{H}_{\rm e}+\hat{V}_{\rm eN})\Phi$$

and differentiate twice to obtain

$$\begin{aligned} &(\nabla_j\nabla_k E)\Phi + (\nabla_j E)(\nabla_k\Phi) + (\nabla_k E)(\nabla_j\Phi) + E\nabla_j\nabla_k\Phi \\ &\quad = (\nabla_j\nabla_k\hat{V}_{\rm eN})\Phi + (\nabla_j\hat{V}_{\rm eN})(\nabla_k\Phi) + (\nabla_k\hat{V}_{\rm eN})(\nabla_j\Phi) + (\hat{H}_{\rm e}+\hat{V}_{\rm eN})\nabla_j\nabla_k\Phi. \end{aligned} \tag{68}$$

We use this to compute

$$\begin{aligned} &\nabla_j\nabla_k E + (\nabla_j E)\langle\Phi|\nabla_k\Phi\rangle + (\nabla_k E)\langle\Phi|\nabla_j\Phi\rangle + E\langle\Phi|\nabla_j\nabla_k\Phi\rangle \\ &\quad = \langle\Phi|(\nabla_j\nabla_k\hat{V}_{\rm eN})|\Phi\rangle + \langle\Phi|(\nabla_j\hat{V}_{\rm eN})|\nabla_k\Phi\rangle + \langle\Phi|\nabla_k\hat{V}_{\rm eN}|\nabla_j\Phi\rangle + \langle\Phi|\hat{H}_{\rm e}+\hat{V}_{\rm eN}|\nabla_j\nabla_k\Phi\rangle. \end{aligned} \tag{69}$$

We can simplify this to obtain

$$\begin{aligned} \nabla_j\nabla_k E = {}& \langle\Phi|(\nabla_j\nabla_k\hat{V}_{\rm eN})|\Phi\rangle + \langle\Phi|(\nabla_j\hat{V}_{\rm eN})|\nabla_k\Phi\rangle + \langle\Phi|\nabla_k\hat{V}_{\rm eN}|\nabla_j\Phi\rangle \\ &- (\nabla_j E)\langle\Phi|\nabla_k\Phi\rangle - (\nabla_k E)\langle\Phi|\nabla_j\Phi\rangle. \end{aligned} \tag{70}$$

Since $\nabla_j\nabla_k E$ is real, we can write

$$\nabla_j \nabla_k E = \langle \Phi | (\nabla_j \nabla_k \hat{V}_{\rm eN}) | \Phi \rangle + \langle \nabla_k \Phi | (\nabla_j \hat{V}_{\rm eN}) | \Phi \rangle + \langle \nabla_j \Phi | \nabla_k \hat{V}_{\rm eN} | \Phi \rangle - (\nabla_j E) \langle \nabla_k \Phi | \Phi \rangle - (\nabla_k E) \langle \nabla_j \Phi | \Phi \rangle. \quad (71)$$

These can be combined to produce

$$\nabla_j \nabla_k E = \langle \Phi | (\nabla_j \nabla_k \hat{V}_{\rm eN}) | \Phi \rangle + \frac{1}{2} \langle \Phi | (\nabla_j \hat{V}_{\rm eN}) | \nabla_k \Phi \rangle + \frac{1}{2} \langle \Phi | \nabla_k \hat{V}_{\rm eN} | \nabla_j \Phi \rangle + \frac{1}{2} \langle \nabla_k \Phi | (\nabla_j \hat{V}_{\rm eN}) | \Phi \rangle + \frac{1}{2} \langle \nabla_j \Phi | \nabla_k \hat{V}_{\rm eN} | \Phi \rangle. \quad (72)$$

We can make use of

$$\nabla_j \Phi = \left[E(\mathbf{R}) - \hat{H}_{\rm e} - \hat{V}_{\rm eN} \right]^{-1} \Big(\nabla_j [\hat{V}_{\rm eN} - E(\mathbf{R})] \Big) \Phi,$$

which leads to

$$\nabla_j \nabla_k E = \langle \Phi | (\nabla_j \nabla_k \hat{V}_{\rm eN}) | \Phi \rangle + \frac{1}{2} \left\langle \Phi \left| (\nabla_j \hat{V}_{\rm eN}) \left[E(\mathbf{R}) - \hat{H}_{\rm e} - \hat{V}_{\rm eN} \right]^{-1} (\nabla_k [\hat{V}_{\rm eN} - E(\mathbf{R})]) \right| \Phi \right\rangle + \frac{1}{2} \left\langle \Phi \left| (\nabla_k \hat{V}_{\rm eN}) \left[E(\mathbf{R}) - \hat{H}_{\rm e} - \hat{V}_{\rm eN} \right]^{-1} (\nabla_j [\hat{V}_{\rm eN} - E(\mathbf{R})]) \right| \Phi \right\rangle + \frac{1}{2} \left\langle \Phi \left| (\nabla_k [\hat{V}_{\rm eN} - E(\mathbf{R})]) \left[E(\mathbf{R}) - \hat{H}_{\rm e} - \hat{V}_{\rm eN} \right]^{-1} (\nabla_j \hat{V}_{\rm eN}) \right| \Phi \right\rangle + \frac{1}{2} \left\langle \Phi \left| (\nabla_j [\hat{V}_{\rm eN} - E(\mathbf{R})]) \left[E(\mathbf{R}) - \hat{H}_{\rm e} - \hat{V}_{\rm eN} \right]^{-1} (\nabla_k \hat{V}_{\rm eN}) \right| \Phi \right\rangle. \quad (73)$$

Finally, we can expand in terms of electronic basis states to obtain

$$(\nabla_j \nabla_k E_0)_0 = \langle \Phi | (\nabla_j \nabla_k \hat{V}_{\rm eN}) | \Phi \rangle_0 + \sum_{X \neq 0} \frac{\langle \Phi_0 | (\nabla_j \hat{V}_{\rm eN}) | \Phi_X \rangle_0 \langle \Phi_X | (\nabla_k \hat{V}_{\rm eN}) | \Phi_0 \rangle_0}{E_0 - E_X} + \sum_{X \neq 0} \frac{\langle \Phi_0 | (\nabla_k \hat{V}_{\rm eN}) | \Phi_X \rangle_0 \langle \Phi_X | (\nabla_j \hat{V}_{\rm eN}) | \Phi_0 \rangle_0}{E_0 - E_X}. \quad (74)$$

5.5. Coulomb interaction between nuclei and equilibrium

The Coulomb interaction between the nuclei can be expanded as well; we write

$$V_{NN}(\{\mathbf{R}\}) = \sum_{j'<k'} \frac{Z_{j'} Z_{k'} e^2}{4\pi\epsilon_0 |\mathbf{R}_{k'} - \mathbf{R}_{j'}|}$$
$$= V_{NN}(\{\mathbf{R}^{(0)}\}) + \sum_j (\mathbf{R}_j - \mathbf{R}_j^{(0)}) \cdot (\nabla_j V_{NN})_0$$
$$+ \frac{1}{2} \sum_j \sum_k (\mathbf{R}_j - \mathbf{R}_j^{(0)}) \cdot (\nabla_j \nabla_k V_{NN})_0 \cdot (\mathbf{R}_k - \mathbf{R}_k^{(0)}) + \cdots \quad (75)$$

Since the second-order contribution to the total energy in this model involves both nuclear position and momentum variables, the equilibrium positions are determined only from forces associated with the electronic energy and nuclear Coulomb interaction. We may write

$$(\nabla_j E_0)_0 + (\nabla_j V_{NN})_0 = 0. \quad (76)$$

5.6. Harmonic approximation for the diagonal sector Hamiltonian

We can expand the diagonal sector Hamiltonian (in the absence of current) to second-order to obtain

$$\hat{H}_n^{\text{diagonal}} \rightarrow \sum_j \frac{|\hat{\mathbf{P}}_j|^2}{2M_j} + V_{NN}(\{\mathbf{R}^{(0)}\}) + E_0(\{\mathbf{R}^{(0)}\}) + \sum_j \frac{\hbar^2}{2M_j} \left(\langle \nabla_j \Phi_0 | \nabla_j \Phi_0 \rangle_0 - \langle \Phi_0 | \nabla_j^2 \Phi_0 \rangle \right)$$
$$+ \frac{1}{2} \sum_j \sum_k (\mathbf{R}_j - \mathbf{R}_j^{(0)}) \cdot (\nabla_j \nabla_k V_{NN})_0 \cdot (\mathbf{R}_k - \mathbf{R}_k^{(0)})$$
$$+ \frac{1}{2} \sum_j \sum_k (\mathbf{R}_j - \mathbf{R}_j^{(0)}) \cdot (\nabla_j \nabla_k E_0)_0 \cdot (\mathbf{R}_k - \mathbf{R}_k^{(0)})$$
$$+ \sum_{j,k} \left(-\frac{i\hbar}{2M_j} \right) \left\{ (\mathbf{R}_j - \mathbf{R}_j^{(0)}) \cdot \langle \nabla_j \Phi_0 | \nabla_k \Phi_0 \rangle_0 \cdot \hat{\mathbf{P}}_k + \hat{\mathbf{P}}_j \cdot \langle \nabla_j \Phi_0 | \nabla_k \Phi_0 \rangle_0 \cdot (\mathbf{R}_k - \mathbf{R}_k^{(0)}) \right\}$$
$$- \sum_j \sum_k \hat{\mathbf{P}}_j \cdot \left\{ \sum_{X \neq 0} \frac{\hbar^2}{M_j M_k} \frac{\langle \Phi_0 | \nabla_j \Phi_X \rangle_0 \langle \Phi_X | \nabla_k \Phi_0 \rangle_0}{-\hat{E}_{off} + F_0 - F_X} \right\} \cdot \hat{\mathbf{P}}_k. \quad (77)$$

We can simplify this by defining the classical energy at equilibrium according to

$$H_0 = V_{NN}(\{\mathbf{R}^{(0)}\}) + E_0(\{\mathbf{R}^{(0)}\}) + \sum_j \frac{\hbar^2}{2M_j} \left(\langle \nabla_j \Phi_0 | \nabla_j \Phi_0 \rangle_0 - \langle \Phi_0 | \nabla_j^2 \Phi_0 \rangle \right). \quad (78)$$

We can define force constants through

$$\mathbf{K}_{jk} = (\nabla_j \nabla_k V_{NN})_0 + (\nabla_j \nabla_k E_0)_0. \quad (79)$$

Further simplification can be obtained by defining a matrix associated with the inverse mass according to

$$\frac{1}{2}\mathbf{L}_{jk} = \frac{1}{2M_j}\mathbf{I}\delta_{jk} - \sum_{X\neq 0}\frac{\hbar^2}{M_j M_k}\frac{\langle\Phi_0|\nabla_j\Phi_X\rangle_0\langle\Phi_X|\nabla_k\Phi_0\rangle_0}{-\hat{E}_{\rm off}+F_0-F_X}. \tag{80}$$

The Hamiltonian in the harmonic approximation becomes

$$\begin{aligned}\hat{H}_n^{\rm diagonal} \;\rightarrow\; & H_0 + \frac{1}{2}\sum_{j,k}\hat{\mathbf{P}}_j\cdot\mathbf{L}_{jk}\cdot\hat{\mathbf{P}}_k + \frac{1}{2}\sum_{j,k}(\mathbf{R}_j-\mathbf{R}_j^{(0)})\cdot\mathbf{K}_{jk}\cdot(\mathbf{R}_k-\mathbf{R}_k^{(0)}) \\ & + \frac{1}{2}\sum_{j,k}\left[(\mathbf{R}_j-\mathbf{R}_j^{(0)})\cdot\mathbf{J}_{jk}\cdot\hat{\mathbf{P}}_k + \hat{\mathbf{P}}_j\cdot\mathbf{J}_{kj}\cdot(\mathbf{R}_k-\mathbf{R}_k^{(0)})\right],\end{aligned} \tag{81}$$

where

$$\mathbf{J}_{jk} = \left(-\frac{i\hbar}{M_j}\right)\langle\nabla_j\Phi_0|\nabla_k\Phi_0\rangle_0. \tag{82}$$

5.7. Off-diagonal interaction

We can write for the phonon exchange contribution to the off-diagonal interaction in a similar picture

$$\begin{aligned}&\left\langle\Phi_0\left|\hat{H}_{n,n\pm1}\left[E-\hat{H}_{n\pm1,n\pm1}\right]^{-1}\hat{H}_{n\pm1,n\pm2}\right|\Phi_0\right\rangle \\ &\quad\rightarrow\; -\sum_j\sum_k\left|n\right\rangle\left\langle n\left|\hat{\mathbf{P}}_j\right|n\pm1\right\rangle\cdot\sum_{X\neq0}\frac{\hbar^2}{M_jM_k}\langle\Phi_0|\nabla_j\Phi_X\rangle_0\langle\Phi_X|\nabla_k\Phi_0\rangle_0 \\ &\qquad\times\left[\frac{1}{-\hat{E}_{\rm off}\mp\hbar\hat{\omega}_0+F_0-F_X}-\frac{1}{F_0-F_X}\right]\left\langle n\pm1\left|\hat{\mathbf{P}}_k\right|n\pm2\right\rangle\left\langle n+2\right|.\end{aligned} \tag{83}$$

Since phonon modes can be defined for this problem, we can express the vibrational states now as

$$\left|n\right\rangle \;\rightarrow\; |n\rangle\overline{\Psi}, \tag{84}$$

where $|n\rangle$ is a number state of the highly excited phonon mode, and where $\overline{\Psi}$ is made up of all the other modes. Since we are focused only on phonon exchange with the highly excited mode we may write

$$\left\langle n\left|\hat{\mathbf{P}}_j\right|n\pm1\right\rangle \;\rightarrow\; \langle n|\hat{\mathbf{P}}_j|n\pm1\rangle. \tag{85}$$

For the phonon exchange contribution to the off-diagonal sector Hamiltonian we have

$$\left\langle \Phi_0 \left| \hat{H}_{n,n\pm1} \left[E - \hat{H}_{n\pm1,n\pm1} \right]^{-1} \hat{H}_{n\pm1,n\pm2} \right| \Phi_0 \right\rangle$$
$$\rightarrow \; - \sum_j \sum_k |n\rangle\langle n|\hat{\mathbf{P}}_j|n\pm1\rangle \cdot \sum_{X\neq 0} \frac{\hbar^2}{M_j M_k} \langle\Phi_0|\nabla_j \Phi_X\rangle_0 \langle\Phi_X|\nabla_k \Phi_0\rangle_0$$
$$\times \left[\frac{1}{-\hat{E}_{\rm off} \mp \hbar\hat{\omega}_0 + F_0 - F_X} - \frac{1}{-F_0 - F_X} \right] \langle n\pm1|\hat{\mathbf{P}}_k|n\pm2\rangle\langle n+2|. \quad (86)$$

In addition, if we work with a strict static phonon basis, then one of the terms that we encountered in the reduction of the non-adiabatic interaction will contribute to the off-diagonal interaction. In this case, the associated interaction will take the form

$$|n\rangle\langle n| \sum_{j,k} \left(-\frac{i\hbar}{2M_j} \right) \Big\{ (\mathbf{R}_j - \mathbf{R}_j^{(0)}) \cdot \langle\nabla_j \Phi_0|\nabla_k \Phi_0\rangle_0 \cdot \hat{\mathbf{P}}_k$$
$$+ \hat{\mathbf{P}}_j \cdot \langle\nabla_j \Phi_0|\nabla_k \Phi_0\rangle_0 \cdot (\mathbf{R}_k - \mathbf{R}_k^{(0)}) \Big\} |n\pm2\rangle\langle n\pm2|. \quad (87)$$

This sector-changing interaction will then be the lowest-order interaction in this kind of model.

5.8. Discussion

As mentioned above the fixed-point model developed here constitutes a picture in its own right on the same basic footing as the Born–Oppenheimer picture and Bloch picture. It is much simpler than the Born–Oppenheimer picture, and nearly as powerful. We have not seen much in the way of application of this model in the literature; in times past it was occasionally mentioned in discussions about the connection between the Born–Oppenheimer approximation and Bloch picture. This seems unfortunate as the fixed-point model looks like it could be very useful.

In any case, we have succeeded in making a connection now between the fixed-point model and the Brillouin–Wigner formalism. This gives us basic formulas for determining the phonon modes (including the static part of the second-order interaction), and for evaluating the off-diagonal sector Hamiltonian which determine the phonon fluctuations at second order. In the fixed-point picture based on a strict static resonant sector definition of the phonon modes, the lowest-order contribution to the phonon fluctuations arises from the non-adiabatic interaction; second-order phonon exchange contributes at the next order.

6. Longitudinal Dielectric Constant from Phonon Dispersion

In the previous section we developed relations for the fixed-point picture from the Born–Oppenheimer picture. In the special case that the fixed-point model is evaluated for a periodic lattice, we end up with an interesting picture in which phonon exchange works the same as in the Born–Oppenheimer approximation. We can make use of this model now to describe phonon fluctuations in our phonon–nuclear model.

However, the amount of development that has led up to this point is considerable. It would be nice if we were able to use the formalism to compute some interesting result that has been obtained previously, in order to gain confidence generally in the results obtained so far. To this end we consider the development of the phonon dispersion relation for a metal crystal. This problem seems of interest because it has received so much attention previously in the literature in the context of the Bloch picture.

The issue that we will focus on here in particular is the establishment of a connection with the longitudinal dielectric constant. For example, the problem of phonon dispersion in metals involves many different issues. We will oversimplify things in our treatment here in order to focus on the longitudinal dielectric constant. When done, we will find that our second-order formalism leads to a dielectric model consistent with the field theory version of the result good to ω^2. It makes clear how phonon exchange in a Born–Oppenheimer based model contributes to the dielectric constant; and finally it provides an important check on the consistency of the fixed-point model against known results in the literature.

6.1. Secular equation in general

Usually the phonon modes are determined from an eigenvalue equation that comes from Newton's laws. In this case we may write

$$\frac{\mathrm{d}}{\mathrm{d}t}(\mathbf{R}_j - \mathbf{R}_j^{(0)}) = \sum_k \mathbf{L}_{jk}\mathbf{P}_k + \sum_k \mathbf{J}_{kj} \cdot (\mathbf{R}_k - \mathbf{R}_k^{(0)}),$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{P}_j = -\sum_k \mathbf{K}_{jk} \cdot (\mathbf{R}_k - \mathbf{R}_k^{(0)}) - \sum_k \mathbf{J}_{jk} \cdot \mathbf{P}_k. \tag{88}$$

The phonon frequencies can then be determined in general from

$$-i\omega \begin{pmatrix} \mathbf{R}_j - \mathbf{R}_j^{(0)} \\ \mathbf{P}_j \end{pmatrix} = \sum_k \begin{pmatrix} \mathbf{J}_{kj} & \mathbf{L}_{jk} \\ -\mathbf{K}_{jk} & -\mathbf{J}_{jk} \end{pmatrix} \begin{pmatrix} \mathbf{R}_k - \mathbf{R}_k^{(0)} \\ \mathbf{P}_k \end{pmatrix}, \tag{89}$$

which requires solving for all of the atomic displacements simultaneously. This result is appropriate for a general fixed-point picture model; we have as yet not taken advantage of periodicity in the metal crystal.

6.2. Secular matrix for a monatomic crystal

Much of the relevant literature is concerned with the case of a monatomic metal crystal, where the basic formulas are simplest. It is possible within the framework of the approach that we have taken to develop results for the secular equation. We begin by asserting that the classical position and momentum vectors can be obtained from the real part of the complex versions given by

$$\mathbf{R}_j(t) = \mathbf{R}_j^{(0)} + \mathbf{u}_\mathbf{q} \mathrm{e}^{-i\omega t} \mathrm{e}^{i\mathbf{q}\cdot\mathbf{R}_j^{(0)}}, \tag{90}$$

$$\mathbf{P}_j(t) = \mathbf{v}_\mathbf{q} \mathrm{e}^{-i\omega t} \mathrm{e}^{i\mathbf{q}\cdot\mathbf{R}_j^{(0)}}. \tag{91}$$

The associated mode eigenvalue equation is then

$$-i\omega \begin{pmatrix} \mathbf{u}_\mathbf{q} \\ \mathbf{v}_\mathbf{q} \end{pmatrix} = \begin{pmatrix} \mathbf{J}^{\mathrm{T}}(\mathbf{q}) & \mathbf{L}(\mathbf{q}) \\ -\mathbf{K}(\mathbf{q}) & -\mathbf{J}(\mathbf{q}) \end{pmatrix} \begin{pmatrix} \mathbf{u}_\mathbf{q} \\ \mathbf{v}_\mathbf{q} \end{pmatrix}, \tag{92}$$

where

$$\mathbf{J}(\mathbf{q}) = \sum_k \mathbf{J}_{jk} \mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}_k^{(0)} - \mathbf{R}_j^{(0)})}, \tag{93}$$

$$\mathbf{K}(\mathbf{q}) = \sum_k \mathbf{K}_{jk} \mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}_k^{(0)} - \mathbf{R}_j^{(0)})}, \tag{94}$$

$$\mathbf{L}(\mathbf{q}) = \sum_k \mathbf{L}_{jk} \mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}_k^{(0)} - \mathbf{R}_j^{(0)})}. \tag{95}$$

Note that these secular equations are more complicated than what is usually used in Bloch picture models. Our definition for the transformed force constant matrix is the same as the Bloch picture version (we have the freedom to take the reference site $\mathbf{R}_j^{(0)}$ as the origin), but we require in addition $\mathbf{J}(\mathbf{q})$ and $\mathbf{L}(\mathbf{q})$ matrices which do not show up in the normal Bloch picture model.

6.3. Transformed force matrix

We can split the $\mathbf{K}(\mathbf{q})$ matrix into two parts; one due to interactions between the nuclei; and one due to the electronic energy

$$\mathbf{K}(\mathbf{q}) = \mathbf{K}^{(\mathrm{N})}(\mathbf{q}) + \mathbf{K}^{(\mathrm{e})}(\mathbf{q}). \tag{96}$$

The force constant associated with ion–ion interactions is

$$\mathbf{K}_{jk}^{(\mathrm{N})} = (1 - \delta_{j,k}) \left(\nabla_j \nabla_k \frac{(Ze)^2}{4\pi\epsilon_0 |\mathbf{R}_k - \mathbf{R}_j|} \right)_{\mathbf{R}_j^{(0)}, \mathbf{R}_k^{(0)}}, \tag{97}$$

so we may write

$$\mathbf{K}^{(\mathrm{N})}(\mathbf{q}) = \sum_k (1 - \delta_{j,k}) \left(\nabla_j \nabla_k \frac{(Ze)^2}{4\pi\epsilon_0 |\mathbf{R}_k - \mathbf{R}_j|} \right)_{\mathbf{R}_j^{(0)}, \mathbf{R}_k^{(0)}} \mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}_k^{(0)} - \mathbf{R}_j^{(0)})}. \tag{98}$$

The force constant associated with the electronic energy is

$$\mathbf{K}_{j,k}^{(\mathrm{e})} = \sum_{X \neq 0} \frac{\langle \Phi_0 | (\nabla_j \hat{V}_{\mathrm{eN}}) | \Phi_X \rangle_0 \langle \Phi_X | (\nabla_k \hat{V}_{\mathrm{eN}}) | \Phi_0 \rangle_0}{E_0 - E_X} + \frac{\langle \Phi_0 | (\nabla_k \hat{V}_{\mathrm{eN}}) | \Phi_X \rangle_0 \langle \Phi_X | (\nabla_j \hat{V}_{\mathrm{eN}}) | \Phi_0 \rangle_0}{E_0 - E_X}, \tag{99}$$

which leads to

$$\mathbf{K}^{(\mathrm{e})}(\mathbf{q}) = \sum_k \sum_{X \neq 0} \left(\frac{\langle \Phi_0 | (\nabla_j \hat{V}_{\mathrm{eN}}) | \Phi_X \rangle_0 \langle \Phi_X | (\nabla_k \hat{V}_{\mathrm{eN}}) | \Phi_0 \rangle_0}{E_0 - E_X} + \frac{\langle \Phi_0 | (\nabla_k \hat{V}_{\mathrm{eN}}) | \Phi_X \rangle_0 \langle \Phi_X | (\nabla_j \hat{V}_{\mathrm{eN}}) | \Phi_0 \rangle_0}{E_0 - E_X} \right) \mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}_k^{(0)} - \mathbf{R}_j^{(0)})}. \tag{100}$$

6.4. Transformed inverse mass matrix

We can similarly decompose the inverse mass matrix $\mathbf{L}(\mathbf{q})$ into two pieces; one associated with the physical inverse mass; and one associated with the non-adiabatic second-order interaction

$$\mathbf{L}(\mathbf{q}) = \mathbf{L}^{(\mathrm{M})}(\mathbf{q}) + \mathbf{L}^{(\mathrm{eN})}(\mathbf{q}). \tag{101}$$

For the physical inverse mass contribution, we may write

$$\mathbf{L}^{(\mathrm{M})}(\mathbf{q}) = \frac{\mathbf{I}}{M}. \tag{102}$$

For the second-order contribution due to electron–phonon interactions, in the resonant sector we have

$$\mathbf{L}^{(\mathrm{eN})}(\mathbf{q}) = -\sum_k \sum_{X\neq 0} \frac{2\hbar^2}{M^2} \frac{\langle\Phi_0|\nabla_j\Phi_X\rangle_0\langle\Phi_X|\nabla_k\Phi_0\rangle_0}{E_0 - E_X} \mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}_k^{(0)}-\mathbf{R}_j^{(0)})}. \tag{103}$$

We recall that

$$\langle\Phi_X|\nabla_j\Phi_Y\rangle = -\frac{\langle\Phi_X|(\nabla_j\hat{V}_{\mathrm{eN}})|\Phi_Y\rangle}{E_X - E_Y},$$

so that we may write the second-order contribution to the transformed inverse mass matrix as

$$\mathbf{L}^{(\mathrm{eN})}(\mathbf{q}) = \sum_k \sum_{X\neq 0} \frac{2\hbar^2}{M^2} \frac{\langle\Phi_0|(\nabla_j\hat{V}_{\mathrm{eN}})|\Phi_X\rangle_0\langle\Phi_X|(\nabla_k\hat{V}_{\mathrm{eN}})|\Phi_0\rangle_0}{(E_0 - E_X)^3} \mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}_k^{(0)}-\mathbf{R}_j^{(0)})}. \tag{104}$$

6.5. Transformation of the **J** matrix

We may write

$$\begin{aligned}\mathbf{J}(\mathbf{q}) &= \sum_k \left(-\frac{i\hbar}{M}\right) \langle\nabla_j\Phi_0|\nabla_k\Phi_0\rangle_0 \, \mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}_k^{(0)}-\mathbf{R}_j^{(0)})} \\ &= \sum_k \sum_{X\neq 0} \left(-\frac{i\hbar}{M}\right) \frac{\langle\Phi_0|(\nabla_j\hat{V}_{\mathrm{eN}})|\Phi_X\rangle_0\langle\Phi_X|(\nabla_k\hat{V}_{\mathrm{eN}})|\Phi_0\rangle_0}{(E_0 - E_X)^2} \, \mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}_k^{(0)}-\mathbf{R}_j^{(0)})}.\end{aligned} \tag{105}$$

Now we have a complete set of definitions for the transformed matrices of the fixed-point model which can be used for detailed calculations (we will ultimately require further results for the electronic matrix elements in order to evaluate numerically).

6.6. Simplified ion model

Almost all of the literature on electron–phonon coupling makes the assumption that the core electrons follow the nucleus, and focuses on the resulting interactions between ions and conduction electrons. We can implement this model within the formalism above through the replacements

$$\hat{V}_{\rm eN} \;\rightarrow\; \hat{V}_{\rm ei} = \sum_{j,k} U(|\mathbf{r}_j - \mathbf{R}_k|), \tag{106}$$

$$\frac{Z_j Z_k e^2}{4\pi\epsilon_0 |\mathbf{R}_k - \mathbf{R}_j|} \;\rightarrow\; V_{j,k}(|\mathbf{R}_k - \mathbf{R}_j|), \tag{107}$$

where

$$\lim_{|\mathbf{R}_k - \mathbf{R}_j| \rightarrow \infty} V_{j,k}(|\mathbf{R}_k - \mathbf{R}_j|) = \frac{Z_j^* Z_k^* e^2}{4\pi\epsilon_0 |\mathbf{R}_k - \mathbf{R}_j|}. \tag{108}$$

However, in what follows we will pursue an even simpler version of the model in which

$$\hat{V}_{\rm ei} \;\rightarrow\; -\sum_{j,k} \frac{Z_k^* e^2}{4\pi\epsilon_0 |\mathbf{R}_k - \mathbf{r}_j|} \tag{109}$$

and

$$V_{j,k}(|\mathbf{R}_k - \mathbf{R}_j|) \;\rightarrow\; \frac{Z_j^* Z_k^* e^2}{4\pi\epsilon_0 |\mathbf{R}_k - \mathbf{R}_j|}. \tag{110}$$

This will reduce the complexity of the calculations to follow. It is of course well known that the electron–ion potential is softer than a Coulomb potential, and there is no difficulty with replacing this Coulomb model with a better pseudopotential model anywhere in the calculations that follow.

6.7. Reduction of the transformed force constant matrix

In order to identify the longitudinal dielectric constant, it will be easiest to simply evaluate the different transformed matrices. To this end, we can make use of the discrete Fourier transform of the normalized Coulomb potential to write

$$\frac{1}{|\mathbf{R} - \mathbf{r}|} = \frac{1}{V} \sum_{\mathbf{K}} \frac{4\pi}{|\mathbf{K}|^2} {\rm e}^{i\mathbf{K}\cdot(\mathbf{R}-\mathbf{r})}. \tag{111}$$

The electron–ion interaction can then be written as

$$\hat{V}_{\rm ei} = -\sum_{j,k} \frac{Z_k^* e^2}{\epsilon_0 V} \sum_{\mathbf{K}} \frac{1}{|\mathbf{K}|^2} {\rm e}^{i\mathbf{K}\cdot(\mathbf{R}_k - \mathbf{r}_j)} \tag{112}$$

and the gradient becomes

$$\nabla_k \hat{V}_{\rm ei} = -i \sum_j \frac{Z_k^* e^2}{\epsilon_0 V} \sum_{\mathbf{K}} \frac{\mathbf{K}}{|\mathbf{K}|^2} e^{i\mathbf{K}\cdot(\mathbf{R}_k - \mathbf{r}_j)}. \tag{113}$$

We can use this to reduce the transformed force constant matrix

$$\begin{aligned}
\mathbf{K}^{(\rm e)}(\mathbf{q}) \;\rightarrow\; & -\sum_k \sum_{X\neq 0} \sum_{\mathbf{K}} \sum_{\mathbf{K}'} \left(\frac{Z^* e^2}{\epsilon_0 V}\right)^2 \frac{\mathbf{K}\mathbf{K}'}{|\mathbf{K}|^2|\mathbf{K}'|^2} \frac{1}{E_0 - E_X} {\rm e}^{i\mathbf{K}\cdot\mathbf{R}_j} {\rm e}^{i\mathbf{K}'\cdot\mathbf{R}_k} \\
& \left\langle \Phi_0 \left| \sum_l {\rm e}^{-i\mathbf{K}\cdot\mathbf{r}_l} \right| \Phi_X \right\rangle \left\langle \Phi_X \left| \sum_{l'} {\rm e}^{-i\mathbf{K}'\cdot\mathbf{r}_{l'}} \right| \Phi_0 \right\rangle {\rm e}^{i\mathbf{q}\cdot(\mathbf{R}_k^{(0)} - \mathbf{R}_j^{(0)})} \\
& -\sum_k \sum_{X\neq 0} \sum_{\mathbf{K}} \sum_{\mathbf{K}'} \left(\frac{Z^* e^2}{\epsilon_0 V}\right)^2 \frac{\mathbf{K}\mathbf{K}'}{|\mathbf{K}|^2|\mathbf{K}'|^2} \frac{1}{E_0 - E_X} {\rm e}^{i\mathbf{K}\cdot\mathbf{R}_k} {\rm e}^{i\mathbf{K}'\cdot\mathbf{R}_j} \\
& \left\langle \Phi_0 \left| \sum_l {\rm e}^{-i\mathbf{K}\cdot\mathbf{r}_l} \right| \Phi_X \right\rangle \left\langle \Phi_X \left| \sum_{l'} {\rm e}^{-i\mathbf{K}'\cdot\mathbf{r}_{l'}} \right| \Phi_0 \right\rangle {\rm e}^{i\mathbf{q}\cdot(\mathbf{R}_k^{(0)} - \mathbf{R}_j^{(0)})}.
\end{aligned} \tag{114}$$

We can take advantage of the random phase approximation; to proceed we split this into coherent and incoherent pieces

$$\mathbf{K}^{(\rm e)}(\mathbf{q}) = \mathbf{K}^{(\rm e)}_{\rm coh}(\mathbf{q}) + \mathbf{K}^{(\rm e)}_{\rm inc}(\mathbf{q}), \tag{115}$$

where the coherent part is

$$\begin{aligned}
\mathbf{K}^{(\rm e)}_{\rm coh}(\mathbf{q}) = & \sum_k \sum_{X\neq 0} \sum_{\mathbf{K}} \left(\frac{Z^* e^2}{\epsilon_0 V}\right)^2 \frac{\mathbf{K}\mathbf{K}}{|\mathbf{K}|^4} \frac{1}{E_0 - E_X} \\
& \left[{\rm e}^{i(\mathbf{q}-\mathbf{K})\cdot(\mathbf{R}_k^{(0)} - \mathbf{R}_j^{(0)})} + {\rm e}^{i(\mathbf{q}+\mathbf{K})\cdot(\mathbf{R}_k^{(0)} - \mathbf{R}_j^{(0)})} \right] \\
& \left\langle \Phi_0 \left| \sum_l {\rm e}^{-i\mathbf{K}\cdot\mathbf{r}_l} \right| \Phi_X \right\rangle \left\langle \Phi_X \left| \sum_{l'} {\rm e}^{i\mathbf{K}\cdot\mathbf{r}_{l'}} \right| \Phi_0 \right\rangle.
\end{aligned} \tag{116}$$

Note that

$$\begin{aligned}
& \left\langle \Phi_0 \left| \sum_l {\rm e}^{-i\mathbf{K}\cdot\mathbf{r}_l} \right| \Phi_X \right\rangle \left\langle \Phi_X \left| \sum_{l'} {\rm e}^{i\mathbf{K}\cdot\mathbf{r}_{l'}} \right| \Phi_0 \right\rangle \\
& \quad = \left\langle \Phi_0 \left| \sum_l {\rm e}^{i\mathbf{K}\cdot\mathbf{r}_l} \right| \Phi_X \right\rangle \left\langle \Phi_X \left| \sum_{l'} {\rm e}^{-i\mathbf{K}\cdot\mathbf{r}_{l'}} \right| \Phi_0 \right\rangle,
\end{aligned} \tag{117}$$

so we may write

$$\mathbf{K}^{(\mathrm{e})}_{\mathrm{coh}}(\mathbf{q}) = \sum_k \sum_{X\neq 0} \sum_{\mathbf{K}} 2\left(\frac{Z^* e^2}{\epsilon_0 V}\right)^2 \frac{\mathbf{K}\mathbf{K}}{|\mathbf{K}|^4} \frac{1}{E_0 - E_X} \mathrm{e}^{i(\mathbf{q}-\mathbf{K})\cdot(\mathbf{R}^{(0)}_k - \mathbf{R}^{(0)}_j)} \left\langle \Phi_0 \left| \sum_l \mathrm{e}^{-i\mathbf{K}\cdot\mathbf{r}_l} \right| \Phi_X \right\rangle \left\langle \Phi_X \left| \sum_{l'} \mathrm{e}^{i\mathbf{K}\cdot\mathbf{r}_{l'}} \right| \Phi_0 \right\rangle. \tag{118}$$

6.8. Reduction of the transformed inverse mass matrix

A similar computation can be done for the electron–ion part of the transformed inverse mass matrix; we may write

$$\begin{aligned}\mathbf{L}^{(\mathrm{ei})}(\mathbf{q}) &= \sum_k \sum_{X\neq 0} \frac{2\hbar^2}{M^2} \frac{\langle\Phi_0|(\nabla_j \hat{V}_{\mathrm{ei}})|\Phi_X\rangle_0 \langle\Phi_X|(\nabla_k \hat{V}_{\mathrm{ei}})|\Phi_0\rangle_0}{(E_0 - E_X)^3} \mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}^{(0)}_k - \mathbf{R}^{(0)}_j)} \\ &\rightarrow -\sum_k \sum_{X\neq 0} \sum_{\mathbf{K}} \sum_{\mathbf{K}'} \frac{2\hbar^2}{M^2} \left(\frac{Z^* e^2}{\epsilon_0 V}\right)^2 \frac{\mathbf{K}\mathbf{K}'}{|\mathbf{K}|^2|\mathbf{K}'|^2} \frac{1}{(E_0 - E_X)^3} \mathrm{e}^{i\mathbf{K}\cdot\mathbf{R}^{(0)}_j} \mathrm{e}^{i\mathbf{K}'\cdot\mathbf{R}^{(0)}_k} \\ &\quad \left\langle \Phi_0 \left| \sum_l \mathrm{e}^{-i\mathbf{K}\cdot\mathbf{r}_l} \right| \Phi_X \right\rangle \left\langle \Phi_X \left| \sum_{l'} \mathrm{e}^{-i\mathbf{K}'\cdot\mathbf{r}_{l'}} \right| \Phi_0 \right\rangle \mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}^{(0)}_k - \mathbf{R}^{(0)}_j)}. \end{aligned} \tag{119}$$

We can divide this into coherent and incoherent parts

$$\mathbf{L}^{(\mathrm{ei})}(\mathbf{q}) = \mathbf{L}^{(\mathrm{ei})}_{\mathrm{coh}}(\mathbf{q}) + \mathbf{L}^{(\mathrm{ei})}_{\mathrm{inc}}(\mathbf{q}). \tag{120}$$

The coherent part involves terms where $\mathbf{K} + \mathbf{K}' = 0$

$$\mathbf{L}^{(\mathrm{ei})}_{\mathrm{coh}}(\mathbf{q}) = \sum_k \sum_{X\neq 0} \sum_{\mathbf{K}} \frac{2\hbar^2}{M^2} \left(\frac{Z^* e^2}{\epsilon_0 V}\right)^2 \frac{\mathbf{K}\mathbf{K}}{|\mathbf{K}|^4} \frac{1}{(E_0 - E_X)^3} \mathrm{e}^{i(\mathbf{q}-\mathbf{K})\cdot(\mathbf{R}^{(0)}_k - \mathbf{R}^{(0)}_j)} \left\langle \Phi_0 \left| \sum_l \mathrm{e}^{-i\mathbf{K}\cdot\mathbf{r}_l} \right| \Phi_X \right\rangle \left\langle \Phi_X \left| \sum_{l'} \mathrm{e}^{i\mathbf{K}\cdot\mathbf{r}_{l'}} \right| \Phi_0 \right\rangle. \tag{121}$$

We assume the coherent part dominates, and that the residual incoherent part can be neglected, consistent with the random phase approximation.

6.9. Reduction of the transformed **J** matrix

Due to the similarity between these different transformed matrices, we can write directly

$$\mathbf{J}(\mathbf{q}) = \mathbf{J}_{\mathrm{coh}}(\mathbf{q}) + \mathbf{J}_{\mathrm{inc}}(\mathbf{q}), \tag{122}$$

where

$$\mathbf{J}_{\rm coh}(\mathbf{q}) = -\sum_k \sum_{X\neq 0} \sum_{\mathbf{K}} \frac{i\hbar}{M} \left(\frac{Z^* e^2}{\epsilon_0 V}\right)^2 \frac{\mathbf{K}\mathbf{K}}{|\mathbf{K}|^4} \frac{1}{(E_0 - E_X)^2} e^{i(\mathbf{q}-\mathbf{K})\cdot(\mathbf{R}_k^{(0)} - \mathbf{R}_j^{(0)})} \left\langle \Phi_0 \left| \sum_l e^{-i\mathbf{K}\cdot\mathbf{r}_l} \right| \Phi_X \right\rangle \left\langle \Phi_X \left| \sum_{l'} e^{i\mathbf{K}\cdot\mathbf{r}_{l'}} \right| \Phi_0 \right\rangle. \tag{123}$$

6.10. Transformed ion-ion part of the force matrix

The transformed ion–ion part of the force matrix in this model is

$$\begin{aligned}\mathbf{K}^{(\rm i)}(\mathbf{q}) &= \sum_k (1-\delta_{j,k}) \left(\nabla_j \nabla_k \frac{(Z^* e)^2}{4\pi\epsilon_0 |\mathbf{R}_k - \mathbf{R}_j|}\right)_{\mathbf{R}_j^{(0)}, \mathbf{R}_k^{(0)}} e^{i\mathbf{q}\cdot(\mathbf{R}_k^{(0)} - \mathbf{R}_j^{(0)})} \\ &= \sum_k \sum_{\mathbf{K}} (1-\delta_{j,k}) \frac{(Z^* e)^2}{\epsilon_0 V} \frac{\mathbf{K}\mathbf{K}}{|\mathbf{K}|^2} e^{i(\mathbf{q}-\mathbf{K})\cdot(\mathbf{R}_k^{(0)} - \mathbf{R}_j^{(0)})}.\end{aligned} \tag{124}$$

6.11. Connection with literature longitudinal dielectric constant

It seems useful to make a connection with the literature, which focuses on the longitudinal dielectric constant. Perhaps the most straightforward way to do this is to make use of

$$\mathbf{P}_j \;\rightarrow\; -i\omega M_j (\mathbf{R}_j - \mathbf{R}_j^{(0)}) \tag{125}$$

and write the model in terms of a frequency-dependent force model

$$\begin{aligned}&\frac{1}{2}\sum_{j,k} \hat{\mathbf{P}}_j \cdot \mathbf{L}_{jk} \cdot \hat{\mathbf{P}}_k + \frac{1}{2}\sum_{j,k} (\mathbf{R}_j - \mathbf{R}_j^{(0)}) \cdot \mathbf{K}_{jk} \cdot (\mathbf{R}_k - \mathbf{R}_k^{(0)}) \\ &\quad + \frac{1}{2}\sum_{j,k} \left[(\mathbf{R}_j - \mathbf{R}_j^{(0)}) \cdot \mathbf{J}_{jk} \cdot \hat{\mathbf{P}}_k + \hat{\mathbf{P}}_j \cdot \mathbf{J}_{kj} \cdot (\mathbf{R}_k - \mathbf{R}_k^{(0)}) \right] \\ &\qquad \rightarrow\; \frac{1}{2}\sum_j \frac{|\hat{\mathbf{P}}_j|^2}{2M} + \frac{1}{2}\sum_{j,k} (\mathbf{R}_j - \mathbf{R}_j^{(0)}) \cdot \left[\mathbf{K}_{jk} - iM\omega[\mathbf{J}_{jk} + \mathbf{J}_{jk}^{\rm T}] - M^2\omega^2 \mathbf{L}_{jk}^{(\rm ei)} \right] \cdot (\mathbf{R}_k - \mathbf{R}_k^{(0)}).\end{aligned} \tag{126}$$

The idea here is to view the various **J** and **L** matrices as providing dynamical corrections to the force constant matrix. From such a perspective it would make sense to define a dynamical version of the transformed force matrix from the coherent parts of the $\mathbf{J}(\mathbf{q})$, $\mathbf{K}(\mathbf{q})$ and $\mathbf{L}(\mathbf{q})$ transformed matrices according to

$$\mathbf{K}^{(\rm eff)}(\mathbf{q},\omega) \;\rightarrow\; \sum_k \sum_{\mathbf{K}} \left\{ \frac{1-\delta_{j,k}}{\epsilon_0} + \left[\frac{1}{\epsilon(\mathbf{K},\omega)} - \frac{1}{\epsilon_0} \right] \right\} \frac{(Z^* e)^2}{\epsilon_0 V} \frac{\mathbf{K}\mathbf{K}}{|\mathbf{K}|^2} e^{i(\mathbf{q}-\mathbf{K})\cdot(\mathbf{R}_k^{(0)} - \mathbf{R}_j^{(0)})}, \tag{127}$$

where

$$\frac{1}{\epsilon(\mathbf{K},\omega)} = \frac{1}{\epsilon_0} + \sum_{X\neq 0} \frac{2e^2}{\epsilon_0^2 V|\mathbf{K}|^2} \left[\frac{1}{E_0 - E_X} - \frac{\hbar\omega}{(E_0 - E_X)^2} - \frac{(\hbar\omega)^2}{(E_0 - E_X)^3} \right] \left\langle \Phi_0 \left| \sum_l \mathrm{e}^{-i\mathbf{K}\cdot\mathbf{r}_l} \right| \Phi_X \right\rangle \left\langle \Phi_X \left| \sum_{l'} \mathrm{e}^{i\mathbf{K}\cdot\mathbf{r}_{l'}} \right| \Phi_0 \right\rangle . \tag{128}$$

This suggests that the model which we are working with involves dynamical terms which match up to second order a more sophisticated model based on

$$\frac{1}{\epsilon(\mathbf{K},\omega)} = \frac{1}{\epsilon_0} + \sum_{X\neq 0} \frac{2e^2}{\epsilon_0^2 V|\mathbf{K}|^2} \frac{1}{\hbar\omega + E_0 - E_X} \left\langle \Phi_0 \left| \sum_l \mathrm{e}^{-i\mathbf{K}\cdot\mathbf{r}_l} \right| \Phi_X \right\rangle \left\langle \Phi_X \left| \sum_{l'} \mathrm{e}^{i\mathbf{K}\cdot\mathbf{r}_{l'}} \right| \Phi_0 \right\rangle . \tag{129}$$

The static limit of this dielectric constant is consistent with Nozieres and Pines [34]. The explicit frequency dependence of this model is similar to that appearing in the model of Ehrenreich and Cohen [35]. We might expect that if we were to include higher-order dynamical terms that more terms in the associated geometric series would be generated, resulting ultimately in this full dynamical longitudinal dielectric model.

6.12. Discussion

We have succeeded in this section of implementing a fixed-point picture model for the phonon dispersion relation of a monatomic metal crystal, and we have evaluated it in the special case of a simple Coulomb interaction for the electron-ion interaction in order to extract the associated longitudinal dielectric model. We find that the resulting dielectric model matches the literature result from field theory up to and including second-order (ω^2), which helps to verify the model, and also to clarify how things work. For example, we can see that it is the second-order phonon-exchange interaction in the fixed-point model that produces the ω^2 term. The discussions in [36,37] may be relevant here. We note that there was other earlier work in which the dispersion relation and the longitudinal dielectric constant have been studied within the Born–Oppenheimer approximation [38].

7. Summary and Conclusions

In earlier work we have developed a model that describes coherent energy exchange under conditions of fractionation between nuclei and a highly excited phonon mode. To compare with experiment, we begin with the basic theory described in [18], we make use of the interpretation (based on coherent energy exchange between acoustic vibrations and excitation of the lowest nuclear level in ^{201}Hg) described in [17], and a specific model consistent with this interpretation. What we found was a substantial disagreement between the resulting model and experimental observations.

The resulting disagreement could be due to a problem with the underlying theory, issues with our proposed interpretation, or errors in the model and/or model parameters. We were motivated in this work by a concern that the problem might be in the basic theory; in particular we had neglected phonon fluctuations due to coupling with conduction electrons. Our interest in modeling the effect ultimately resulted in this study. The problem that we encountered is that electron–phonon interactions in metals is usually formulated in the Bloch picture, but there are differences between how phonon exchange works in the Bloch picture and in the Born–Oppenheimer picture. We are interested in models that involve off-resonant interactions, and the equivalence of the two pictures has been argued for on-resonance; consequently, we are interested in phonon exchange in a Born–Oppenheimer picture to describe phonon fluctuations.

It seemed ultimately to be simplest just to start from scratch, and follow the development of the Born–Oppenheimer approximation in a Brillouin–Wigner formulation that is well matched to other models we have been constructing. The Brillouin–Wigner formalism is suited to taking into account the strong first-order interaction, and otherwise separating the phonon and electron degrees of freedom. In the end we have a model that describes the second-order coupling of equivalent "dressed" phonons (in the Brillouin–Wigner sense) which gives rise to the fluctuations of interest in the phonon–nuclear model.

However, in the process we have covered a lot of developmental ground, so there is reason to be concerned as to whether the fixed-point model we are working with is free of errors. In order to test this, we decided to develop relations that describe the phonon dispersion relation for a monatomic metal crystal, which is probably the best known relevant problem from Bloch picture models in the literature. The longitudinal dielectric constant consistent with this model results in the same static model as is obtained from the Bloch picture, and gives results up to second order that are in agreement with literature results from field theory. This provides confidence in the preceding development.

We have made use of simple Coulomb potentials for the electron-ion interaction, which is appropriate for long wavelength vibrations. For computations involving shorter wavelength phonons we would need to make use of better electron-ion potentials. This is discussed extensively in the literature, and the modification of the formulas for this case is straightforward. The reduction of the many-electron matrix elements into simpler models is also straightforward, and will have to be addressed in using these results for detailed calculations.

A reviewer noted that this paper seems to lack a major punchline. In response it seems useful to spell out the major punchlines for this paper, and for what we found subsequently when we made use of it. The first is that there does not exist in the literature a systematic treatment of Born–Oppenheimer and related approximations adapted for the case of a metal, which in our view is suitable for the development of a fluctuation model; the biggest contribution of this paper then is to provide a useful foundation in a relevant language. Another significant result is the clarification of how the longitudinal dielectric constant of a metal comes about in the lowest orders of perturbation theory in a Born–Oppenheimer approximation. Although it is mentioned in a few works that such a result was known previously, we have not found a clear discussion of it. Another important result which we found when we used the model described here to develop a fluctuation model is that the results from the Born–Oppenheimer picture are very different from what we get with a Bloch picture model. In the literature the two pictures are largely viewed as equivalent in connection with describing phonon exchange in metals; while perhaps true for screening and for lowest-order phonon exchange, this is certainly not the case for phonon fluctuations. And finally, we will discuss in a following publication that a fluctuation model based on the Born–Oppenheimer picture is inappropriate above a certain size scale, so that a fluctuation model based on the Bloch picture must be used. On the other hand, fluctuations for a nano-scale metal sample should be treated using a Born–Oppenheimer model.

References

[1] M. Fleischmann, S. Pons and M. Hawkins, *J. Electroanal. Chem.* **201** (1989) 301; errata **263** (1990) 187.
[2] M. Fleischmann, S. Pons, M.W. Anderson, L.J. Li and M. Hawkins, *J. Electroanal. Chem.* **287** (1990) 293.
[3] E. Storms, *Science of Low Energy Nuclear Reaction: A Comprehensive Compilation of Evidence and Explanations about Cold Fusion*, World Scientific, New Jersey (2004).
[4] P.L. Hagelstein, M.C.H. McKubre, D.J. Nagel, T.A. Chubb and R.J. Hekman, *Proc. ICCF11* (2004) 23.
[5] P.L. Hagelstein, Constraints on energetic particles in the Fleischmann– Pons experiment, *Naturwissenschaften* **97** (2010) 345.
[6] P.L. Hagelstein, A unified model for anomalies in metal deuterides, *Proc. ICCF9* (2002) 121.
[7] P.L. Hagelstein and I.U. Chaudhary, Level splitting in association with the multiphoton Bloch—Siegert shift, *J. Phys. B: At. Mol. Phys.* **41** (2008) 035601.
[8] P.L. Hagelstein and I.U. Chaudhary, Models relevant to excess heat production in Fleischmann–Pons experiments, *Low-energy Nuclear Reactions Sourcebook, ACS Symposium Series* **998** (2008) 249.

[9] P.L. Hagelstein and I.U. Chaudhary, Energy exchange in the lossy spin–boson model, *J. Cond. Mat. Nucl. Sci.* **5** (2011) 52.
[10] P.L. Hagelstein and I.U. Chaudhary, Dynamics in the case of coupled degenerate states, *J. Cond. Mat. Nucl. Sci.* **5** (2011) 72.
[11] P.L. Hagelstein and I.U. Chaudhary, Second-order formulation and scaling in the lossy spin–boson model, *J. Cond. Mat. Nucl. Sci.* **5** (2011) 87.
[12] P.L. Hagelstein and I.U. Chaudhary, Local approximation for the lossy spin—boson model, *J. Cond. Mat. Nucl. Sci.* **5** (2011) 102.
[13] P.L. Hagelstein and I.U. Chaudhary, Coherent energy exchange in the strong coupling limit of the lossy spin–boson model, *J. Cond. Mat. Nucl. Sci.* **5** (2011) 116.
[14] P.L. Hagelstein and I.U. Chaudhary, Generalization of the lossy spin-–boson model to donor and receiver systems, *J. Cond. Mat. Nucl. Sci.* **5** (2011) 140.
[15] P.L. Hagelstein and I.U. Chaudhary, Errata and comments on a recent set of papers in Journal of Condensed Matter in Nuclear Science, *J. Cond. Mat. Nucl. Sci.* **7** (2012) 1.
[16] P.L. Hagelstein and I.U. Chaudhary, Including nuclear degrees of freedom in a lattice hamiltonian, *J. Cond. Mat. Nucl. Sci.* **7** (2011) 35.
[17] P.L. Hagelstein and I.U. Chaudhary, A model for collimated emission in the Karabut experiment, *Proc. ICCF17*, in press.
[18] P.L. Hagelstein and I.U. Chaudhary, Phonon–nuclear coupling for anomalies in condensed matter nuclear science, *J. Cond. Mat. Nucl. Sci.* , submitted.
[19] P.L. Hagelstein, Bird's Eye View of Phonon Models for Excess Heat in the Fleischmann–Pons Experiment, *J. Cond. Mat. Nucl. Sci.* **6** (2011) 169.
[20] P.L. Hagelstein and I.U. Chaudhary, Models for excess heat in PdD and NiH, *Proc. ICCF17*, in press.
[21] A.B. Karabut, Research into powerful solid X-ray laser (wave length is 0.8–1.2 nm) with excitation of high current glow discharge ions, *Proc. 11th Int. Conf. on Emerging Nuclear Energy Systems*, 29 September–4 October 2002, Albuquerque, New Mexico, USA, pp. 374–381.
[22] A.B. Karabut, Experimental research into characteristics of X-ray emission from solid-state cathode medium of high-current glow discharge, *Proc. 10th Int. Conf. on Cold Fusion*, August 24–29, 2003, Cambridge, MA, USA.
[23] A.B. Karabut, Research into characteristics of x-ray emission laser beams from solid-state cathode medium of high current glow discharge, *Proc. 11th Int. Conf. on Cold Fusion*, 31 October-–5 November, 2004, France, pp. 253–257.
[24] A.B. Karabut, Study of energetic and temporal characteristics of x-ray emission from solid state cathode medium of high current glow discharge, *Proc. 12th Int. Conf. on Cold Fusion*, December 2-–7, 2006, Japan, pp. 344-–350.
[25] A.B. Karabut and E.A. Karabut, Research into energy spectra of X-ray emission from solid cathode medium during the high current glow discharge operation and after the glow discharge current switch off, *Proc. 14th Int. Conf. on Cold Fusion*, August 10-–15, 2008, USA.
[26] A.B. Karabut, E.A. Karabut and P.L. Hagelstein, Spectral and temporal characteristics of X-ray emission from metal electrodes in a high-current glow discharge, *J. Cond. Mat. Nucl. Sci.* **6** (2012) 217.
[27] L.J. Sham and J.M. Ziman, The electron–phonon interaction, *Solid State Phys.* **15** (1963) 221.
[28] S.K. Joshi and A.K. Rajagopa, Lattice dynamics of metals, *Solid State Phys.* **22** (1969) 159.
[29] J.M. Ziman, The electron–phonon interaction, according to the adiabatic approximation, *Math. Proc. Cambridge Philos. Soc.* **51** (1955) 707.
[30] J. C. Taylor, The electron–phonon interaction, according to the adiabatic approximation, *Math. Proc. Cambridge Philos. Soc.* **52** (1956) 693.
[31] H. Feshbach, A unified theory of nuclear reactions, II *Ann. Phys.* **19** (1962) 287.
[32] R.A. Deegan, electron–phonon interaction in the tight-binding approximation: Validity of the Bloch formulation, *Phys. Rev. B 5* (1972) 1183.
[33] J. Ashkenazi, M. Dacorogna and M. Peter, On the equivalence of the Frolich and Bloch approaches to the electron–phonon coupling, *Sol. State Comm.* **29** (1979) 181.
[34] P. Nozieres and D. Pines, A dielectric formulation of the many body problem: Application to the free electron gas, *Il Nuovo Cimento* **9** (1958) 470.
[35] H. Ehrenreich and M.L. Cohen, Self-consistent field approach to the many-electron problem, *Phys. Rev.* **115** (1959) 786.
[36] E.G. Brovman and Yu. Kagan, The phonon spectrum of metals, *Sov. Phys. JETP* **25** (1967) 364.

[37] B.T. Geilikman, The adiabatic approximation and Fröhlich model in the theory of metals, *J. Low. Temp. Phys.* **4** (1971) 189 .
[38] R. M. Pick, M.H. Cohen and R. M. Martin, Microscopic theory of force constants in the adiabatic approximation, *Phys. Rev. B* **1** (1970) 910.