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Interaction between electronic and nuclear motion in linear chains

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Summary. The geometrical structure of linear chains is discussed with reference to procedures for treating both electronic and nuclear motion and illustrated with reference to recent density functional calculations.

Key words: Electronic motion – Nuclear motion – Linear chains

1. Introduction

In the now nearly classical text on solid state theory by Peierls [1] there is one Section [5.3] which has been quoted more than anything else in that book. The topic discussed there is the question which geometric structure in a one-dimensional lattice has the lowest energy, a metallic one with uniform distances, or a dimerized or in general a "polymerized" geometry with insulating properties. Peierls primarily discusses the modification of the band structure which can be expected to occur in a linear chain with uniform internuclear distances if the chain is dimerized, i.e. if alternating internuclear distances are introduced. Sheer symmetry reasons will give rise to a gap in middle of the band, corresponding in k space to the line delimiting the border between the first and second Brillouin zone of the dimerized structure. The one electron energies of the states with highest wave numbers in the first Brillouin zone will thereby be lowered. If the total energy of the system were equal to the sum of the occupied one electron energies that would lead to a lower total energy for a system with an originally half-filled band. The degree of filling of the band plays an important part in this connection. Thus if all other factors are unchanged, the dimerized conformation would have a lower energy.

Peierls himself is much more careful than many of those who quote him: "*It is therefore likely that a one-dimensional model could never have metallic properties. However, a complete discussion of this question would have to allow for the fact that, as was stressed in Section 1.2, the adiabatic approximation is not valid in the case of a metal, so that the energies calculated with the nuclei at rest cannot be used in physical arguments without great care.*"

The situation just described is referred to as the Peierls theorem or more commonly the Peierls transition. The latter term is particularly misleading, since no mention has been made of an actual physical or chemical phenomenon. If in a theoretical model one makes an assumption about the geometrical structure of a system, and if a calculation shows that another structure has a lower energy, this may be an indication that the actual geometrical structure is of the second type, provided the calculation is reasonably realistic. Nothing can be claimed about an actual transition in an experimental situation, though. In his description of the similar Jahn–Teller effect Ballhausen [2] has characterized the semantic aspect of this situation very appropriately: *This statement does not mean that the molecule is formed possessing a degenerate state, immediately discovers this, and then proceeds to distort*". To use the term "transition" is therefore quite misleading [3].

The term "Peierls theorem" is more motivated. In order to invoke a theorem one must be very careful, though, to check that the conditions under which it is valid, are satisfied. In this paper we illustrate several aspects of "Peierls theorem" with reference to a set of recently carried out band calculations combined with geometry optimization for certain linear chains of the first row atoms [4, 5].

A little more explicitly Peierls' arguments are as follows in a case where a dimerized situation is compared to a geometry with uniform distances. First-order perturbation theory is used to calculate the non-diagonal matrix element associated with "dimerizing" displacements of the nuclei, with respect to the two Bloch functions with wave numbers $+k$ and $-k$ which have the same energy in the uniform case. The displacements and therefore the perturbation have the periodicity of the dimerized lattice, which implies that this matrix element is different from zero. Consequently, such a perturbation opens up gaps in the bands at the "new" zone boundaries.

What has just been summarized can certainly be termed a theorem. Whether this will lead to a lowering of the total energy is however a more complicated question. To begin with the total electronic energy is not necessarily the sum of the occupied one-electron energies – whether it is or not depends on the particular approximation chosen. Secondly, the total energy also involves the nuclei, and even if we stay at the Born–Oppenheimer approximation the change in "elastic" energy due to the nuclear displacements must also be taken into account. As a result some linear chains are metallic and others are insulating.

With the present paper we make an attempt to relate "Peierls' theorem" to various ways of describing the interaction between electronic and nuclear motion, both as treated traditionally and in a radically different, recently developed time-dependent approach. It is quite clear that this coupling – termed vibronic for molecules and electron–phonon for solids – is the central issue for "Peierls' theorem". In Section 2 we review a general approach to this problem in terms of mean field densities and fluctuations for both nuclei and electrons. That formulation is useful for setting a common stage for phonons and electrons and their interactions. In Section 3 we describe the time-dependent approach Electron Nuclear Dynamics [END], which offers a general framework and very promising practical procedures for actual calculations of the interaction between electronic and nuclear motion at many different levels of approximation. Against this background we review in Section 4 some of the density functional calculations for linear and zig-zag chains with special reference to their geometric structure and its relation to their band structure. In the final section we summarize our points of view.

2. Mean fields and fluctuations

The "Peierls theorem" touches a central aspect of the quantum theory of matter, the interaction between electronic and nuclear motion. So far most quantum chemical calculations are aimed at getting approximate solutions of the time-independent Schrödinger equation within the Born–Oppenheimer approximation. In other words for a frozen nuclear configuration variation or perturbation calculations yield an approximate total wave function and/or corresponding total energy. In principle a set of such calculations for different nuclear conformations lead to a potential energy surface, and one or several minima on that surface determine the possible more or less stable nuclear conformation(s). When a potential energy surface is available it is also possible to use either classical or quantum mechanics to study small vibrations around the equilibrium positions of the nuclei.

This well-known picture lacks an essential ingredient, namely the immediate interaction between electronic and nuclear motion. In principle we should be looking for approximate solutions of the Schrödinger equation for *all* the particles in the system, nuclei and electrons. Just as in the traditional solutions the interactions between electrons and between moving electrons and fixed nuclei are more or less accounted for, in the more general case we should account for the interactions between *moving* nuclei and moving electrons. The static aspect of the picture based on the potential energy surface concept shows up in the fact that the force acting on a nucleus – the negative of the gradient of the potential energy – is a function of the *nuclear coordinates only.* For that reason there is no feedback either from the electronic or the nuclear motions.

The term “total energy” usually refers to the expectation value of the total electronic Hamiltonian including the nuclear repulsion, but *not* the nuclear kinetic energy. A set of such total energies for different nuclear geometries form a potential energy surface [PES]. In traditional time-independent theory PES constitutes the central concept for combining electronic and vibrational structure. Whether a PES has been calculated explicitly from the electronic structure (a very rare situation), or its existence is just taken for granted and it is characterized by some parameters to be determined semi-empirically, the nuclei are described as “moving” on that surface. In other words PES constitutes the potential for the nuclear motion, classically or quantum mechanically. A reasonably realistic description of a “Peierls transition” should involve an attempt to solve the equation for this nuclear motion.

The term “vibrational structure” normally refers only to small vibrations around nuclear equilibrium positions. In such a case a harmonic approximation of PES near a minimum yields a description in terms of independent harmonic oscillators or equivalently of non-interacting phonons. If terms of order higher than two are included in the expansion of the potential, anharmonic effects can be taken into account, which in a quantum mechanical treatment is expressed by the term phonon–phonon interaction.

Electron–electron and electron–phonon interactions must also be included. In the next section we will briefly describe a time-dependent method which permits all these interactions to be taken into account in a very explicit way, at various levels of approximation. In order to appreciate how that is done it is instructive to first consider a more traditional approach in a way inspired by Allen et al. [6].

We study a monatomic crystal with nuclei of charge Z. The nuclear mass is denoted by M and the electronic mass by m. We use atomic units but write out m, which is then equal to 1, in order to emphasize the distinction between electronic and nuclear kinetic energy. We thus *do not* work with any Born–Oppenheimer approximation. The total Hamiltonian is written as

$$\boldsymbol{H}_{\mathrm{Tot}} = \frac{1}{2M}\sum_{l}^{\mathrm{BK}} P_l^2 + \frac{1}{2m}\sum_{i}^{\mathrm{BK}} p_i^2 + \frac{1}{2}\int \mathrm{d}v\,\mathrm{d}v'\,\rho_{\mathrm{tot}}(\mathbf{r})v(\mathbf{r}-\mathbf{r}')\rho_{\mathrm{tot}}(\mathbf{r}'), \tag{1}$$

where

$$v(\mathbf{r}-\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|} \tag{2}$$

denotes the Coulomb interaction. The total density operator

$$\rho_{\mathrm{tot}}(\mathbf{r}) = Z\sum_{l}^{\mathrm{BK}} \delta(\mathbf{r}-\mathbf{R}_l) - \sum_{i}^{\mathrm{BK}} \delta(\mathbf{r}-\mathbf{r}_i), \tag{3}$$

is the sum of a lattice density operator

$$\rho_{\mathrm{L}}(\mathbf{r}) = Z\sum_{l}^{\mathrm{BK}} \delta(\mathbf{r}-\mathbf{R}_l) \tag{4}$$

and an electronic density operator

$$\rho_{\mathrm{el}}(\mathbf{r}) = -\sum_{l}^{\mathrm{BK}} \delta(\mathbf{r}-\mathbf{r}_i). \tag{5}$$

The vector $\mathbf{R}_l = \mathbf{l} + \mathbf{u}_l$, denoting the nuclear positions, is written as a sum of the equilibrium position $\mathbf{l}$ and a displacement vector $\mathbf{u}_l$. Combining Eqs. (1) and (3) we retrieve the usual expression for the potential energy operator,

$$\frac{1}{2}\sum_{l\neq l'}^{\mathrm{BK}} \frac{Z^2}{|\mathbf{R}_l-\mathbf{R}_{l'}|} - \sum_{l,i}\frac{Z}{|\mathbf{R}_l-\mathbf{r}_i|} + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}. \tag{6}$$

Using the form (1) for the Hamiltonian we can introduce mean-field theory concepts for both nuclei and electrons and build up hierarchies of solutions.

With small vibrations the mean positions of the nuclei are the equilibrium positions, $\langle \mathbf{R}_l\rangle = \mathbf{l}$, so that the mean lattice density operator is

$$\rho_{\mathrm{ML}}(\mathbf{r}) = \langle\rho_{\mathrm{L}}(\mathbf{r})\rangle = Z\sum_{l}^{\mathrm{BK}} \delta(\mathbf{r}-\mathbf{l}). \tag{7}$$

The fluctuation operator

$$\rho_{\mathrm{FL}}(\mathbf{r}) = \rho_{\mathrm{L}}(\mathbf{r}) - \rho_{\mathrm{ML}}(\mathbf{r}), \tag{8}$$

then represents the departure from the mean-field density of the lattice.

Similarly, we introduce a mean-field density for the electrons: $\langle\rho_{\mathrm{el}}(\mathbf{r})\rangle$. If this expression is interpreted as the quantum mechanical expectation value of the electronic density operator with respect to an exact or approximate wave function, it can be written in terms of the corresponding reduced first order density matrix $\gamma(x|x') = \gamma(\mathbf{r},\zeta|\mathbf{r}',\zeta')$:

$$\begin{aligned}\langle\rho_{\mathrm{el}}(\mathbf{r})\rangle &= -\int \mathrm{d}x_1\,\delta(\mathbf{r}-\mathbf{r}_1)\gamma(x_1|x_1')\\ &= -\int \mathrm{d}v_1\,\delta(\mathbf{r}-\mathbf{r}_1)N(\mathbf{r}_1,\mathbf{r}_1)\\ &= -N(\mathbf{r},\mathbf{r}) = -\rho(\mathbf{r}).\end{aligned} \tag{9}$$

Here N denotes the number density matrix

$$N(\boldsymbol{r}, \boldsymbol{r}') = \int \mathrm{d}\zeta\, \gamma(\boldsymbol{r}, \zeta | \boldsymbol{r}', \zeta) \tag{10}$$

and its diagonal element $\rho(\boldsymbol{r}) = N(\boldsymbol{r}, \boldsymbol{r})$ is the density in the chosen state. As in the lattice case there is an electronic density fluctuation operator,

$$\rho_{\mathrm{Fel}}(\boldsymbol{r}) = \rho_{\mathrm{el}}(\boldsymbol{r}) - \rho(\boldsymbol{r}). \tag{11}$$

Using Eqs. (8) and (11) we write the potential energy part of the Hamiltonian (1) as

$$\begin{aligned} \frac{1}{2}\int \mathrm{d}v\, \mathrm{d}v'\, v(\boldsymbol{r} - \boldsymbol{r}')\{ & 2\rho_{\mathrm{el}}(\boldsymbol{r})[\rho_{\mathrm{ML}}(\boldsymbol{r}') - \rho(\boldsymbol{r}')] + 2\rho_{\mathrm{FL}}(\boldsymbol{r})[\rho_{\mathrm{ML}}(\boldsymbol{r}') - \rho(\boldsymbol{r}')] \\ & + \rho_{\mathrm{ML}}(\boldsymbol{r})\rho_{\mathrm{ML}}(\boldsymbol{r}') - \rho(\boldsymbol{r})\rho(\boldsymbol{r}') + \rho_{\mathrm{FL}}(\boldsymbol{r})\rho_{\mathrm{FL}}(\boldsymbol{r}') \\ & + 2\rho_{\mathrm{FL}}(\boldsymbol{r})\rho_{\mathrm{Fel}}(\boldsymbol{r}') + \rho_{\mathrm{Fel}}(\boldsymbol{r})\rho_{\mathrm{Fel}}(\boldsymbol{r}')\}. \end{aligned} \tag{12}$$

The Hamiltonian can then be written as a sum of four parts which will allow for a certain reinterpretation of its contents

$$\boldsymbol{H}_{\mathrm{Tot}} = \boldsymbol{H}_{\mathrm{el}} + \boldsymbol{H}_{\mathrm{ph}} + \boldsymbol{H}_{\mathrm{int}} + \boldsymbol{H}_{\mathrm{extra}} \tag{13}$$

with

$$\boldsymbol{H}_{\mathrm{el}} = \frac{1}{2m}\sum_{i}^{\mathrm{BK}} p_i^2 + \int \mathrm{d}v\, \mathrm{d}v'\, \rho_{\mathrm{el}}(\boldsymbol{r})v(\boldsymbol{r} - \boldsymbol{r}')[\rho_{\mathrm{ML}}(\boldsymbol{r}') - \rho(\boldsymbol{r}')], \tag{14a}$$

$$\boldsymbol{H}_{\mathrm{ph}} = \frac{1}{2M}\sum_{l}^{\mathrm{BK}} P_l^2 + \int \mathrm{d}v\, \mathrm{d}v'\, \rho_{\mathrm{FL}}(\boldsymbol{r})v(\boldsymbol{r} - \boldsymbol{r}')[\rho_{\mathrm{ML}}(\boldsymbol{r}') - \rho(\boldsymbol{r}')], \tag{14b}$$

$$\boldsymbol{H}_{\mathrm{int}} = \frac{1}{2}\int \mathrm{d}v\, \mathrm{d}v'\, \rho_{\mathrm{F}}(\boldsymbol{r})v(\boldsymbol{r} - \boldsymbol{r}')\rho_{\mathrm{F}}(\boldsymbol{r}'), \tag{14c}$$

$$\boldsymbol{H}_{\mathrm{extra}} = \frac{1}{2}\int \mathrm{d}v\, \mathrm{d}v'\, v(\boldsymbol{r} - \boldsymbol{r}')\{\rho_{\mathrm{ML}}(\boldsymbol{r})\rho_{\mathrm{ML}}(\boldsymbol{r}') - \rho(\boldsymbol{r})\rho(\boldsymbol{r}')\}. \tag{14d}$$

Here we have introduced the notation

$$\rho_{\mathrm{F}}(\boldsymbol{r}) = \rho_{\mathrm{FL}}(\boldsymbol{r}) + \rho_{\mathrm{Fel}}(\boldsymbol{r}) \tag{15}$$

for the total fluctuation operator $\rho_{\mathrm{tot}}(\boldsymbol{r}) - \langle\rho_{\mathrm{tot}}(\boldsymbol{r})\rangle$.

The electron operator $\boldsymbol{H}_{\mathrm{el}}$ describes the interaction between the electrons and the mean field of all other particles, but no explicit interparticle interactions. The "phonon operator", $\boldsymbol{H}_{\mathrm{ph}}$, describes the interactions between the lattice fluctuations and the mean field of all other particles. All explicit interactions are contained in $\boldsymbol{H}_{\mathrm{int}}$. The remaining term, Eq. (14d) is actually a constant, but an essential one, since it forms part of the Madelung energy:

$$\boldsymbol{H}_{\mathrm{extra}} = \frac{1}{2}\sum_{l,l'}^{\mathrm{BK}} \frac{Z^2}{|\boldsymbol{l} - \boldsymbol{l}'|} - \frac{1}{2}\int \mathrm{d}v\, \mathrm{d}v'\, \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}. \tag{16}$$

Both the electron and the phonon Hamiltonians are sums of one-particle Hamiltonians,

$$\boldsymbol{H}_{\mathrm{el}} = \sum_i \boldsymbol{h}_{\mathrm{el},i}, \tag{17a}$$

$$\boldsymbol{h}_{\mathrm{el},i} = \frac{p_i^2}{2m} - \sum_{l,l'}^{\mathrm{BK}} \frac{Z}{|\boldsymbol{r}_i - \boldsymbol{l}|} + \int \mathrm{d}v' \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}, \tag{17b}$$

$$\boldsymbol{H}_{\mathrm{ph}} = \sum_l \boldsymbol{h}_{\mathrm{ph},l}, \tag{18a}$$

$$\boldsymbol{h}_{\mathrm{ph},l} = \frac{P_l^2}{2M} + Z \int \mathrm{d}v\, \rho_{\mathrm{M}}(\boldsymbol{r}) \left\{ \frac{1}{|\boldsymbol{R}_l - \boldsymbol{r}|} - \frac{1}{|\boldsymbol{l} - \boldsymbol{r}|} \right\} \tag{18b}$$

Here $\rho_{\mathrm{M}}(\boldsymbol{r}) = \langle \rho_{\mathrm{tot}}(\boldsymbol{r}) \rangle$ is the total mean density operator.

The potential in the one electron Hamiltonian (17b) apparently describes the electrostatic interaction between a certain electron and the nuclei at their mean positions as well as its interaction with the mean-electron density. In other words (17b) is a Hartree Hamiltonian.

The "phonon operator", Eq. (18b), describes the interaction between the mean density of all the particles and the *difference* between the potential due to a displaced nucleus and one at its equilibrium position. It is important to notice that in the present formulation a particular nucleus interacts *only with the mean density*, not explicitly with the other nuclei. A Taylor expansion of the potential in Eq. (18b) in terms of the small displacements gives

$$\frac{1}{|\boldsymbol{R}_l - \boldsymbol{r}|} = \frac{1}{|\boldsymbol{l} - \boldsymbol{r}|} - \frac{\boldsymbol{u}_l \cdot (\boldsymbol{l} - \boldsymbol{r})}{|\boldsymbol{l} - \boldsymbol{r}|^3} + \frac{3[\boldsymbol{u}_l \cdot (\boldsymbol{l} - \boldsymbol{r})]^2 - |\boldsymbol{u}_l|^2 |\boldsymbol{l} - \boldsymbol{r}|^2}{2|\boldsymbol{l} - \boldsymbol{r}|^5} + \cdots, \tag{19}$$

which yields a harmonic approximation of the Hamiltonian (18b),

$$\boldsymbol{h}_{\mathrm{ph},l} = \frac{P_l^2}{2M} + \frac{1}{2} \sum_{\alpha,\beta}^{x,y,z} K_{\alpha\beta}^{(l)} u_{l\alpha} u_{l\beta}. \tag{20}$$

This expression can now be treated classically or quantum mechanically. In either case it describes a set of independent harmonic oscillators with frequencies independent of the wave vector. The lack of dispersion is due to the fact that no interaction between displacements on neighboring nuclei has been taken into account, even though the force constants $K_{\alpha\beta}^{(l)}$ represent interaction between different nuclei in their equilibrium positions. This is sometimes characterized by the term "Einstein oscillators". A more realistic description of phonons can be obtained by a different partitioning of the primary Hamiltonian (1).

The traditional way of treating electrons and phonons as two separate "worlds" and then taking their interaction into account as a perturbation is obtained if the approach sketched here is followed up. Solutions of the electronic problem at whatever level of approximation chosen yield (among other things) a mean electron density which can be used to construct a potential for the nuclear motion. The forces on the nuclei then only depend on the positions of the other nuclei and there is no immediate mutual interaction between nuclei and electrons.

3. Electron nuclear dynamics

A radically different way of approaching this fundamental problem is offered by the recently developed Electron Nuclear Dynamics [END] method [7–15]. In END approximate solutions of the *time-dependent* Schrödinger equation for all particles in the system are obtained by means of the Time-Dependent Variation Principle [TDVP] [16–18]. Applied to the type of problem discussed in the present paper this means that the mutual interaction between electronic and nuclear motion is built into the treatment from the very beginning. The forces on the nuclei then depend on time-dependent electronic *and* nuclear parameters.

Within the general END framework a number of options are available. The nuclei can be treated classically or quantum mechanically. For the electrons one first chooses a particular level of approximation for the total wave function. That function then depends on a number of time-dependent complex parameters, which we denote here by the compound notation z. If we work with classical nuclei, the nuclear positions, $\boldsymbol{R}$, and their momenta, $\boldsymbol{P}$, serve as nuclear time-dependent parameters.

In such a situation TDVP leads to the following set of coupled first-order differential equations for the four sets of parameters,

$$\mathrm{i}\boldsymbol{C}\frac{\partial z}{\partial t} = \frac{\partial E}{\partial z^*}, \qquad -\mathrm{i}\boldsymbol{C}^*\frac{\partial z^*}{\partial t} = \frac{\partial E}{\partial z}, \tag{21a}$$

$$\frac{\partial \boldsymbol{R}}{\partial t} = \frac{\partial E}{\partial \boldsymbol{P}}, \qquad -\frac{\partial \boldsymbol{P}}{\partial t} = \frac{\partial E}{\partial \boldsymbol{R}}. \tag{21b}$$

Here E is the total energy including the nuclear kinetic energy. If the total wave function is a single determinant, written as $|z\rangle$ to emphasize its crucial dependence on the complex parameters z, the matrix $\boldsymbol{C}$ is related to the normalization of that determinant as follows:

$$S(z^*, z) = \langle z|z\rangle, \tag{22a}$$

$$C_{\alpha\beta} = \frac{\partial^2 \ln S}{\partial z_\alpha^* \partial z_\beta}. \tag{22b}$$

The total energy E depends on the nuclear positions $\boldsymbol{R}_l$ both via the Hamiltonian and through the total wave function. Like E its gradient with respect to the nuclear positions also depends on the electronic parameters z. That guarantees immediate response to the nuclear motion from the electronic system through Eqs. (21b). Similarly, in the first two sets of equations, (21a), the derivatives of E with respect to the electronic parameters depend both on electronic and nuclear parameters. That in turn guarantees immediate response to changes in the electronic parameters.

The coupled equations of motion, Eq. (21), imply

$$\frac{\partial E}{\partial t} = 0. \tag{23}$$

In other words, use of the solutions of the equations of motion guarantees a total energy which is constant in time.

In the special case when there are no electronic parameters, or in other words the electrons are "frozen" in a reference state, the equations of motion reduce to

$$\frac{\partial \boldsymbol{R}}{\partial t}=\frac{\partial E}{\partial \boldsymbol{P}}, \qquad -\frac{\partial \boldsymbol{P}}{\partial t}=\frac{\partial E}{\partial \boldsymbol{R}}. \tag{24}$$

The total energy now only depends on the nuclear parameters. If we also freeze the nuclei, we have

$$\boldsymbol{P}=\frac{\partial \boldsymbol{P}}{\partial t}=0, \tag{25a}$$

$$\frac{\partial \boldsymbol{R}}{\partial t}=0, \qquad \frac{\partial E}{\partial \boldsymbol{R}}=0. \tag{25b}$$

Thus the only points on the potential energy surface $E(\boldsymbol{R})$ that are compatible with the equations of motion, are the extremum points. From this point of view the concept of a potential energy surface is debatable even in the special situation where it is normally used.

Assuming that Eqs. (25) yield a set of equilibrium positions $\boldsymbol{R}_{\mathrm{e}}$, we thus have

$$\left(\frac{\partial E}{\partial \boldsymbol{R}}\right)_{\mathrm{e}}=0. \tag{26}$$

In the neighborhood of these equilibrium positions we expand the energy in the displacements $\boldsymbol{R}_l-\boldsymbol{R}_{l\mathrm{e}}=u_l$,

$$E(\boldsymbol{R})=E(\boldsymbol{R}_{\mathrm{e}})-\frac{1}{2}\sum_{l\alpha,l'\beta}\left(\frac{\partial^2 E}{\partial R_{l\alpha}\partial R_{l'\beta}}\right)_{\mathrm{e}} u_{l\alpha}u_{l'\beta}+\cdots \tag{27}$$

Having located the equilibrium positions we can use the equations of motion Eq. (24) for moving nuclei to study small vibrations around these positions,

$$\frac{\partial R_{l\alpha}}{\partial t}=\frac{\partial u_{l\alpha}}{\partial t}=\frac{P_{l\alpha}}{M}, \qquad -\frac{\partial P_{l\alpha}}{\partial t}=\sum_{l'\beta}\left(\frac{\partial^2 E}{\partial R_{l\alpha}\partial R_{l'\beta}}\right)_{\mathrm{e}} u_{l'\beta}. \tag{28}$$

If finally the electronic reference wave function is replaced by a more general function depending on a set of electronic parameters z, we can use the full set of coupled equations of motion, Eq. (21), to investigate the immediate mutual coupling of electronic and vibrational structure. In practice this means explicit functions $\boldsymbol{R}_j(t)$ and $\boldsymbol{P}_j(t)$ for the nuclear positions and momenta, as well as electronic parameters $z_\alpha^*(t)$ and $z_\alpha(t)$, which can be for example the molecular orbital coefficients of a chosen set of basis functions. Thus one can follow explicitly in time how the dynamical molecular orbitals vary with the nuclear geometry and momenta.

The END procedure has been applied – so far primarily for illustrative purposes – to a monatomic linear chain [19] and a zig-zag chain of nitrogen atoms [20]. In both cases a PPP type Hamiltonian [21] was used. The results demonstrate how an END analysis can be carried out for such systems, and show explicitly how the coupling between electronic and nuclear motion is brought in. This is only the beginning of a very promising development.

4. Uniform and dimerized geometries in linear chains of some first row atoms

In this section we review a set of calculations of energy bands and geometric structures for systems, which demonstrate certain aspects of "Peierls' theorem".

This type of calculations constitute a kind of "zeroth-order" approximation to the more advanced developments sketched in the previous sections.

In a strictly linear chain of atoms the nuclear equilibrium positions are restricted to one direction which we denote as the z-axis,

$$\boldsymbol{R}_l = R_l \boldsymbol{e}_z. \tag{29}$$

A chain with uniform internuclear distances a has $R_l = la$ and the equilibrium value of a is given by

$$\frac{\partial E}{\partial R_l} = 0 \quad \text{for all } l, \tag{30}$$

i.e.

$$\frac{\partial E}{\partial a} = l\frac{\partial E}{\partial R_l} = 0, \tag{31}$$

which holds for $a = a_e$.

A dimerized chain has two kinds of internuclear distances,

$$R_{2j-1} = (2j-1)a; \qquad R_{2j} = 2ja + u. \tag{32}$$

The equilibrium values of a and u are given by

$$\frac{\partial E}{\partial R_{2j-1}} = \frac{\partial E}{\partial R_{2j}} = 0 \quad \text{for all } j. \tag{33}$$

These equations imply

$$\frac{\partial E}{\partial a} = (2j-1)\frac{\partial E}{\partial R_{2j-1}} + 2j\frac{\partial E}{\partial R_{2j}} = 0, \tag{34a}$$

$$\frac{\partial E}{\partial u} = \frac{\partial E}{\partial R_{2j}} = 0 \tag{34b}$$

with solutions $a = a_e$ and $u = u_e$.

Thus a "Peierls transition" occurs if $u_e \neq 0$. A "real" Peierls transition would involve two different physical situations and thus two different energies.

The framework introduced here can serve to describe a set of calculations carried out recently for both strictly linear and zig-zag chains of some of the atoms in the first row of the periodic system [4, 5]. Using the particular version of the LMTO method developed for helical polymers [22, 23] we have carried out band calculations for a number of linear chains with uniform and alternating internuclear distances, of hydrogen, lithium, boron, carbon and nitrogen atoms. These calculations are based on density functional theory and total energies were calculated according to the procedures developed within that theory. Based on these computations a numerical and graphical search for solutions of Eqs. (31) and (34) was carried out.

In the hydrogen chain with uniform distances a broad band is half-filled with the Fermi energy about 7 eV above the bottom of the band. Dimerization opens up a gap at the Fermi energy and the total energy is lowered. In this particular case the lowest energy actually occurs for a "molecularized" state, when the chain has dissociated into non-interacting hydrogen molecules.

The lithium chain behaves according to Peierls' description. For uniform distances a 2 eV wide valence band of σ-type is half-filled. Dimerization leads to band gap of about 0.4 eV and a total energy lowering of about 0.02 eV per diatomic unit. The two internuclear distances, 4.75 and 5.30 Bohr bracket the distance 5.05 Bohr in the diatomic lithium molecule.

In a uniform boron chain the 5.17 eV wide σ-band is completely filled. A doubly degenerate π-band is partially filled to one fourth of its capacity. Upon dimerization the total energy increases. A gap opens up between the two halves of the σ-band, but nothing happens to that part of the π-band which is occupied. This explains why it does not pay for this chain to dimerize. The energy gain in the lower half of the σ-band is lost in the upper half, since both are occupied. The bond length in the chain, 2.90 Bohr, can be compared to the 3.01 Bohr in the diatomic boron molecule.

In a uniform carbon chain the valence σ-band of width around 6.5 eV is again completely filled. The π-band is now half-filled with a Fermi energy about 4.2 eV above the bottom of the band. In this case it pays for the chain to dimerize, since the gap which opens up in the π-band occurs at the Fermi level. Dimerization leads to a lowering of the total energy of about 0.25 eV per diatomic unit, accompanied by a π-band gap of 0.79 eV and a slightly larger gap in the σ-band.

In the uniform nitrogen chain the completely filled σ-band has a width of around 7 eV. The π-band is now filled to 3/4 of its capacity with a Fermi level 8.71 eV above the bottom of the π-band. For that reason the gaps which open up upon dimerization do not occur at the Fermi level. As a result the strictly linear nitrogen chain has its lowest energy with uniform internuclear distances of 2.34 Bohr, i.e. slightly less than the nitrogen double bond distance.

This situation for the nitrogen chain is modified if another degree of freedom is introduced, so that a zig-zag chain is obtained [5]. The π-band is then no longer degenerate. Instead, in a chain with uniform distances we have two completely filled σ-bands and one half-filled non-degenerate π-band. Dimerization opens up gaps in all three bands, $\sim$1.6 eV in the lowest σ-band, $\sim$0.4 eV in the second σ-band, and $\sim$1.2 eV in the π-band at the Fermi level. The optimized bond lengths were found to be 2.50 and 2.67 Bohr, to be compared with 2.37 Bohr for a nitrogen double bond and 2.74 Bohr for a nitrogen single bond.

5. Conclusion

The numerical results reported in the previous section have been obtained with LMTO calculations, i.e. from a particular way of solving the Kohn–Sham density functional equations. This particular procedure has been shown to yield quite reliable results for a large number of polymers [24]. The results for the linear chains corroborate that statement, since they are entirely in line with chemical intuition.

These calculations have been included in the present paper as illustrations of several aspects of what might be called "Peierls' theorem". This theorem should not be misunderstood to simply claim that systems with one-dimensional lattices cannot be metallic. The character of the bands and the degree of filling play an essential part. Thus a careful investigation of a traditional kind can yield very valuable information about the geometric structure as related to the band structure. Still this cannot be the last word since the detailed mutual interaction between electronic and nuclear motion is neglected. A thorough understanding of the problems associated with "Peierls transitions" requires a more detailed treatment of both electrons and nuclei and of their interaction. The method of Electron

Nuclear Dynamics, which has been sketched in section III of the paper, offers a number of possibilities to achieve that goal.

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