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1991 J. Phys.: Condens. Matter 3 5515

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Calculations of phonon frequencies and dielectric constants of alkali hydrides via the density functional method

D Kh Blat†, N E Zein‡ and V I Zinenko†

† E I Kirensky Institute of Physics, Krasnoyarsk, USSR

‡ I V Kurchatov Institute of Atomic Energy, Moscow 123182, USSR

Received 23 April 1990, in final form 28 March 1991

Abstract. A convenient method for calculating phonon frequencies at $q = 0$ and macroscopic dielectric constants in cubic insulators is developed in the framework of the density functional method; it is applicable to the case of both local and non-local pseudopotentials. The equilibrium unit-cell volume, bulk modulus, equation of state, optical vibration frequencies and static dielectric constants are calculated for LiH and NaH.

1. Introduction

In the present paper we consider some aspects of the 'first-principle' calculations of the long-wavelength optical phonons in alkali hydrides. Though the connection between the dynamical matrix $D_{\alpha\beta}^{ss'}$ and the static dielectric matrix $\chi(q + g, q + g')$ in insulators was recognized more than twenty years ago (Adler 1962, Sham 1969, Pick *et al* 1970), the first microscopic calculations for $\chi(q + g, q + g')$ and $D_{\alpha\beta}^{ss'}(q)$ were made only recently in the framework of the density functional (DF) method. In insulators and semiconductors, due to noticeable inhomogeneity of the electron density along various directions in the unit cell, it seems most natural and promising to combine the DF method with the pseudopotential (PP) approach in k -space (Ihm *et al* 1979). Nevertheless, even in this approach, calculations can be made in several ways and the papers dealing with dielectric screening and phonon frequencies may be conventionally divided in two groups, according to the method used. The first approach employs the so-called direct or frozen-phonon method, based on a supercell energy and force constant calculations (see, e.g. Chadi and Martin 1976, Wendel and Martin 1978, Martin and Kunc 1981, Yin and Cohen 1982, Resta and Kunc 1986 and references therein). In the second case, dielectric susceptibility, $\chi(q + g, q + g')$, is calculated directly (Van Camp *et al* 1979, Baroni and Resta 1986, Hybertsen and Louie 1987). Both approaches were used to calculate the frequencies of lattice vibrations, including the $q \rightarrow 0$ case, as well as the static dielectric constants in Si, Ge, LiCl and a number of other insulators and semiconductors. Each has its own merits and shortcomings. In particular, the direct method calculations are restricted to the case of q at points of reasonably high symmetry

and requires high accuracy, which is especially inconvenient in the case of $q \rightarrow 0$ vibrations. On the other hand, the full dielectric matrix calculations are pretty cumbersome and, what is more, in the case of the non-local pseudopotential, $D_{\alpha\beta}^{ss'}(q)$ is expressed in terms of an analogue of $\chi(q + g, q + g')$, rather than via the matrix χ itself (Brovman and Kagan 1974), which requires additional efforts to be made.

Earlier it was noticed (Zein 1984) that to calculate $D_{\alpha\beta}^{ss'}(q)$ in the DF approach, only the $X_{q, vk}^{as}$ vectors, being the solution of a certain system of linear equation, are needed. Generally, these $X_{q, vk}^{as}$ are the derivatives of eigenfunctions of the occupied states with respect to displacements u^{as} of the s -type ions. In essence, these vectors are a convolution of the matrix $\hat{\chi}$ and potential \hat{V}_c with the eigenvector $\varphi_{vk}(g)$. The right-hand side of the system represents a generalized force which can be self-consistently calculated using the known $X_{q, vk}^{as}$ and φ_{vk} . The dynamical matrix, $D_{\alpha\beta}^{ss'}(q)$, is calculated after finding the system solution by iterations. To some extent this approach synthesizes the direct and dielectric matrix approaches, since, in fact, it analytically repeats the steps usually taken numerically in the frozen-phonon method. Note that all calculations can also be made at any q and for non-local pseudopotentials without calculating the whole $\hat{\chi}$ matrix. In the present paper such an approach is applied to finding optical vibration frequencies for cubic insulators in the limit $q \rightarrow 0$, which are known to be non-analytical in q (Born and Huan 1958). Explicit, well defined expressions for the transverse (ω_{TO}) and longitudinal (ω_{LO}) optical frequencies, macroscopic dielectric constant ϵ_∞ and effective charge \bar{Z} are derived analogously to the corresponding expressions for these values via the $\chi(q + g, q + g')$ matrix (Pick et al 1970).

This general scheme was checked for the case of Si. We reproduced the results obtained by the direct method (Yin and Cohen 1982) and by the dielectric matrix method (Baroni and Resta 1986). Afterwards it was applied to the infrared vibration-frequency calculations in the alkali hydrides LiH and NaH, which are insulators with a wide gap $E_g \sim 6$ –10 eV. Thus they can be considered as a limiting case for the validity of the local approximation for the DF. On the other hand, there exist both the set of local PP of the Heine-Animalu type, which were thoroughly fitted in pure metals (Bratkovsky et al 1982), and the set of non-local *ab initio* PP (Bachelet et al 1982) that permits one to make mutual verification of results. The hydrogen PP coincides with its potential $-1/r$ and, thus, the theory does not contain any new free parameters. To check the quality of the pseudopotentials used, some volume characteristics of hydrides were calculated: unit-cell equilibrium volumes, energies and bulk moduli. Previously they were usually calculated by the APW (Hama and Kawakami 1988), KKR (Kulikov 1978) or Hartree-Fock (Dovesi et al 1984) methods. The calculated data are in good agreement with the experiment and with the results obtained by other methods. After this checking was completed, the infrared vibration characteristics were obtained by using the same PP. For LiH, the values obtained point out that either the core of the Li ion is pretty soft and the concept of the PP is not valid for our purposes or, more probably, that it is necessary to go beyond the LDA in this case. Authors are not aware of experimental data on NaH crystals (see also Dyck and Jex 1981), but the difference of the results obtained with the two independent sets of the PP makes the experimental data rather interesting.

The paper is organized as follows. In section 2 the relevant formulae for calculating E and $D_{\alpha\beta}^{ss'}(q)$ are summarized for completeness. We investigate the limit of $q \rightarrow 0$ and derive explicit, well converging expressions for ω_{LO} , ω_{TO} , ϵ_∞ and \bar{Z} . Various aspects of the calculational procedure and the results obtained are discussed in section 3. In the appendix the acoustic sum rule for \bar{Z} , defined by our procedure, is proved.

2. The dynamical matrix within density functional method

As noted in the introduction, at present the local version of the density functional method is the only real basis for calculating the static properties in solids. The accuracy of the method was repeatedly checked in calculating structural properties and phonon frequencies of various solids. The total energy of the crystal having unit-cell volume Ω and s ions in the cell with the basis vectors ρ_s in the local density approximation can be written in the k -representation (Ihm *et al* 1979) as follows:

$$\frac{E}{N} = E_{ii} + \frac{1}{N} \sum_k \epsilon_{vk} \Theta_{vk} + \frac{bZ}{\Omega} - \frac{1}{2} \sum_{g \neq 0} \frac{4\pi n^2(g)}{\Omega g^2} + \int_{\Omega} d^3r (\epsilon_{xc}(r) - \mu_{xc}(r))\rho(r) + \mu_{xc}(g=0)Z \tag{1}$$

where $\Theta_{vk} = 1$ or 0 , depending on whether $\epsilon_{vk} < \epsilon_F$ or $\epsilon_{vk} > \epsilon_F$. $\epsilon_{xc}(\rho)$ is the density of homogeneous electron-gas exchange-correlation energy, $\mu_{xc}(\rho) = d(\epsilon_{xc}(\rho))/d\rho$, while E_{ii} is the interaction energy of point ions with charges Z_s on the background of a homogeneous negative charge. The eigenvectors $\varphi_{vk}(g)$ correspond to the eigenvalues ϵ_{vk} of the Schrödinger equation

$$(\hat{H} - \epsilon_{vk})\varphi_{vk} = 0$$

$$H_k(g, g') = (k + g)^2/2\delta_{gg'} + U(k + g, k + g') \tag{2}$$

with the total potential $U(k + g, k + g') = V_e(k + g, k + g') + V_i(g - g') - \delta(g - g')b/\Omega$, where $V_e(k, p')$ is a non-local pseudopotential representing electron-ion interaction:

$$V_e(k + g, k + g') = \sum_s [U_{NL}^s(k + g, k + g') + U_L^s(g - g')] \exp(-i(g - g')\rho_s)$$

$b/\Omega = \lim_{q \rightarrow 0} [V_e(q, q) + 4\pi Z/\Omega q^2]$ from (Brovman and Kagan 1974), and

$$V_i(q \neq 0) = \frac{4\pi n(g)}{\Omega g^2} + \mu_{xc}(g) \quad V_i(0) = 0 \quad \mu_{xc}(g) = \frac{1}{\Omega} \int d^3r e^{-ig'r} \mu_{xc}(\rho(r)).$$

Pressure can be found by differentiating (1) with respect to the volume, Ω , and by the subsequent use of the Hellman-Feynman theorem (Yin 1983):

$$-p\Omega = \Omega \frac{\partial E}{\partial \Omega} = -\frac{1}{3}E_{ii} + \frac{1}{N} \sum_k \left\langle \varphi_{vk} \frac{\partial \hat{H}_e}{\partial \Omega} \varphi_{vk} \right\rangle - \frac{bZ}{\Omega} + \int_{\Omega} d^3r (\epsilon_{xc}(r) - \mu_{xc}(r))\rho(r) - \frac{1}{6} \sum_{g \neq 0} \frac{4\pi n^2(g)}{\Omega g^2} \tag{3}$$

where

$$\hat{H}_e(k + g, k + g') = \frac{1}{2}(k + g)^2\delta_{gg'} + V_e(k + g, k + g') - b/\Omega\delta_{gg'}$$

and $\langle X_\alpha \hat{A} X_\beta \rangle$ denotes $\sum_{gg'} X_\alpha(g)A(g, g')X_\beta(g')$.

Expressions for the dynamical matrix $D_{\alpha\beta}^{ss'}(q)$ calculations may be found directly from (1), if we imagine that s and s' ions are displaced from their equilibrium positions

by the vector $u_R^{ss} = u^{as} \exp(iqR)$ and find the total energy variation by perturbation theory up to $u^{as}u^{\beta s'}$ terms, closely following the procedure, carried out numerically in performing the frozen-phonon calculations (Zein 1984). To simplify the notation, we shall further consider only the crystals with cubic symmetry. Then

$$D_{\alpha\beta}^{ss'}(q) = \bar{D}_{\alpha\beta}^{ss'}(q) - \delta_{ss'} \sum_{s't'} \bar{D}_{\alpha\beta}^{ss'}(0) \quad (4)$$

$$\bar{D}_{\alpha\beta}^{ss'}(q) = 2 \sum_k \langle X_{q,\nu k}^{as} W_{c,qk}^{\beta s'} \varphi_{\nu k} \rangle$$

where the $X_{q,\nu k}^{as}$ vector satisfies the system

$$(\hat{H}_{k+q} - \varepsilon_{\nu k}) X_{q,\nu k}^{as} = W_{q,k}^{as} \varphi_{\nu k}; \quad W_{q,k}^{as}(g, g') = W_{cq,k}^{as}(g, g') + W_i^{as}(g - g')$$

$$W_{cq,k}^{as}(g, g') = (q + g - g')^\alpha V_c^s(q + k + g, k + g') e^{-i(g-g')\rho},$$

$$W_i^{as}(g) = -\frac{4\pi R_q^{as}(g)}{\Omega(q+g)^2} + i \left[\frac{1}{\Omega} \int_{\Omega} d^3r e^{-igr} \frac{d\mu_{xr}(\rho(r))}{d\rho(r)} R_q^{as}(r) \right] = W_i[R^{as}] \quad (5)$$

$$R_q^{as}(g) = 2 \sum_{k\nu g'} X_{q,\nu k}^{as}(g + g') \varphi_{\nu k}(g') \Theta_{\nu k}$$

which can be solved by iteration.

$D_{\alpha\beta}^{ss'}(q)$ is the ion-lattice dynamical matrix, with the charges Z_i . The equivalence of $D_{\alpha\beta}^{ss'}(q)$ defined by (4) and (5) to the conventional expressions for $D_{\alpha\beta}^{ss'}$ can be checked directly, too. For the non-local pseudopotential case, one should use the generalization (Brovman and Kagan 1974) of the conventional expressions (Sham 1969, Pick *et al* 1970) for the dynamical matrix:

$$D_{\alpha\beta}^{ss'}(q) = \sum_{k,\nu\nu'} \langle \varphi_{\nu'k+q} W_{cq,k}^{as} \varphi_{\nu k} \rangle \left(\frac{\Theta_{\nu k} - \Theta_{\nu'k+q}}{\varepsilon_{\nu'k+q} - \varepsilon_{\nu k}} \right) \langle \varphi_{\nu'k+q} W_{q,k}^{\beta s'} \varphi_{\nu k} \rangle \quad (6)$$

which, in the case of the local pseudopotential, are transformed into the conventional one.

Now let us expand $X_{q,\nu k}^{as}$ into a complete set of eigenfunctions $\varphi_{\nu'k+q}(g)$ with the wavevector $q + k$ and find the expansion coefficients from (5). For $X_{q,\nu k}^{as}$ we obtain

$$\Theta_{\nu k} X_{q,\nu k}^{as} = \sum_{\nu'} \frac{\Theta_{\nu k}}{\varepsilon_{\nu'k+q} - \varepsilon_{\nu k}} \varphi_{\nu'k+q} \langle \varphi_{\nu'k+q} W_{q,k}^{as} \varphi_{\nu k} \rangle$$

and $D_{\alpha\beta}^{ss'}(q)$ from (4) goes over into (6).

It is worth noting at this stage that, in principle, our approach is completely equivalent to the frozen-phonon method and the same numerical results for $D_{\alpha\beta}^{ss'}(q)$ could be obtained by using both the methods, provided the one and the same approximation for the DF is taken. However, it seems to us that the $D_{\alpha\beta}^{ss'}(q)$ calculations with (4) and (5) are more convenient, especially in the limit of $q \rightarrow 0$, when non-analytical terms can be yielded separately. Let us consider this case more thoroughly. It is clear, in particular, from the form (6) of $D_{\alpha\beta}^{ss'}(q)$ that in insulators the electron intraband transitions are not contained in $D_{\alpha\beta}^{ss'}(q)$. Thus in the limit of $q \rightarrow 0$, due to the orthogonality of $\varphi_{\nu k}$ with various ν , it is convenient to select blocks with $g = 0$ and $g \neq 0$ in $\chi(q + g, q + g')$, which depend on q differently (Pick *et al* 1970). After this blocking it is seen that the RHS of (5)

includes both the terms $W_r^{\alpha s}$ that are regular in q , (at $q \rightarrow 0$), and irregular terms $W_l^{\alpha s}$ proportional to $q^\alpha q^\beta / q^2$. In the cubic crystals

$$W_{\alpha q, k}^{\alpha s}(0) \rightarrow -4\pi Z_s q^\alpha / \Omega q^2 \quad W_{q, k}^{\alpha s}(0) \rightarrow -4\pi \bar{Z}_s q^\alpha / \Omega q^2 \quad W_{\alpha q, k}^{\alpha s}(g \neq 0) \rightarrow W_{\alpha r}^{\alpha s}$$

$$W_{q, k}^{\alpha s}(g \neq 0) \rightarrow W_r^{\alpha s} + (4\pi \bar{Z}_s / \Omega \epsilon_\infty) n^\alpha n^\gamma W_l^\gamma(g \neq 0) \quad n^\alpha = q^\alpha / q$$

and the solution, $X_{q, \nu k}^{\alpha s}$, of the system (5) also naturally breaks up into regular and longitudinal terms:

$$X_{q, \nu k}^{\alpha s} = X_{r, \nu k}^{\alpha s} + (4\pi / \Omega \epsilon_\infty) \bar{Z}_s n^\alpha n^\gamma X_l^\gamma + Y_{\nu k}^{\alpha s, \gamma} q^\gamma \tag{7}$$

where $X_{r, \nu k}^{\alpha s}$, $X_l^{\alpha s}$ are, respectively, the regular and longitudinal contributions with ϵ_∞ and \bar{Z}_s demanding further self-consistent determination. In (7) the $\sim q^\gamma$ terms are kept, since in calculating $W_{q, \nu k}^{\alpha s}(0) \sim -(4\pi/q^2)(X_{q, \nu k}^{\alpha s} \varphi_{\nu k})$, it is these terms that make it proportional to q^α/q^2 . The $Y_{\nu k}^{\alpha s, \gamma}$ coefficient is found from (5)

$$Y_{\nu k}^{\alpha s, \gamma}(g) = \sum_{\nu' \neq \nu} \frac{\partial \varphi_{\nu' k}}{\partial k_\gamma} \frac{1}{\epsilon_{\nu' k} - \epsilon_{\nu k}} P_{\nu' \nu, k}^{\alpha s}$$

$$P_{\nu' \nu, k}^{\alpha s} = \langle \varphi_{\nu' k} W_{r k}^{\alpha s} \varphi_{\nu k} \rangle + (4\pi \bar{Z}_s / \Omega \epsilon_\infty) n^\alpha n^\beta \left(\langle \varphi_{\nu' k} W_{l k}^{\beta s} \varphi_{\nu k} \rangle - \left\langle \frac{\partial \varphi_{\nu' k}}{\partial k_\beta} \varphi_{\nu k} \right\rangle \right). \tag{8}$$

By equating coefficients for the regular and longitudinal terms, we obtain

$$(\hat{H}_k - \epsilon_{\nu k}) X_r^{\alpha s} = W_{r k}^{\alpha s} \varphi_{\nu k} \quad (\hat{H}_k - \epsilon_{\nu k}) X_l^\gamma = W_{l k}^{\gamma s} \varphi_{\nu k} + \partial \varphi_{\nu k} / \partial k_\gamma \tag{9}$$

as well as self-consistent expressions for $W_{q, \nu k}^{\alpha s}(g)$ and $W_{l, k}^\alpha(g)$. They are determined for $g \neq 0$ and vanish for $g = 0$.

$$W_{r, k}^{\alpha s}(g, g') = W_{\alpha r, k}^{\alpha s}(k + g, k + g') + W_r^{\alpha s}(R_r^{\alpha s}) \quad W_{l, k}^\alpha(g, g') = W_l^{\alpha s}(R_l^{\alpha s})$$

$$R_r^{\alpha s}(g) = 2 \sum_{k \nu g'} X_{r, \nu k}^{\alpha s}(g + g') \varphi_{\nu k}(g') \Theta_{\nu k} \quad R_l^\alpha(g) = 2 \sum_{k \nu g'} X_{l, \nu k}^\alpha(g + g') \varphi_{\nu k}(g') \Theta_{\nu k}. \tag{10}$$

As defined, the $W_{l, k}^{\alpha s}(g, g')$ quantities are antisymmetric in g and g' . In the appendix it is shown that $W_{r, k}^{\alpha s}$ also conserves this property. Therefore, the RHS of system (9) is orthogonal to $\varphi_{\nu k}$ and this system always has a solution. Though the system determinant equals zero, the condition $\sum_g X_{r(i)}^{\alpha s}(g) \varphi_{\nu k}(g) = 0$ fixes the solution.

The \bar{Z}_s and ϵ_∞ values are found from the condition of the self-consistency at $g = 0$. Since the $X_{r, \nu k}^{\alpha s}$ vector is orthogonal to $\varphi_{\nu k}$, the contribution to them arises only from the $\sim Y_{\nu k}^{\alpha s, \gamma}$ terms in (8):

$$-\bar{Z}_s \frac{4\pi q^\alpha}{\Omega \epsilon_\infty q^2} = -Z_s \frac{4\pi q^\alpha}{\Omega q^2} + \left(\frac{4\pi q^\gamma}{\Omega q^2} \right)^2 \sum_{k, \nu' \neq \nu} \frac{\langle (\partial \varphi_{\nu' k} / \partial k_\gamma) \varphi_{\nu k} \rangle \Theta_{\nu k}}{\epsilon_{\nu' k} - \epsilon_{\nu k}} P_{\nu' \nu, k}^{\alpha s}. \tag{11}$$

To determine \bar{Z}_s and ϵ_∞ separately, keep in mind that

$$\langle (\partial \varphi_{\nu' k} / \partial k_\gamma) \varphi_{\nu k} \rangle = -\langle \varphi_{\nu' k} (\partial \varphi_{\nu k} / \partial k_\gamma) \rangle$$

and that, after summing over k with $P_{\nu' \nu, k}^{\alpha s}$ from (8), there arise terms in the cubic crystals that are proportional to $\delta_{\alpha\gamma}$ and $\delta_{\beta\gamma}$. Then it is clear that the RHS of (11) contains vectors

$X_{r,k}^{\alpha s}$ and $X_{l,k}^{\alpha}$ written in the form of an expansion in $\varphi_{\nu k}$ from the solution of the system (9). Thus, in essence, (11) is

$$-\tilde{Z}_s = -Z_s + 2 \sum_k \left\langle \frac{\partial \varphi_{\nu k}}{\partial k_\alpha} X_{rk}^{\alpha s} \right\rangle \Theta_{\nu k} + \frac{4\pi\tilde{Z}}{\Omega\varepsilon_\infty} 2 \sum_k \left\langle \frac{\partial \varphi_{\nu k}}{\partial k_\alpha} X_{lk}^{\alpha} \right\rangle \Theta_{\nu k}.$$

By separating s -dependent and s -independent terms in this equation (in non-cubic crystals, terms proportional to $n^\alpha n^\beta$), we obtain:

$$\tilde{Z}_s = Z_s - \frac{2}{3} \sum_{k,\alpha} \left\langle \frac{\partial \varphi_{\nu k}}{\partial k_\alpha} X_{r,\nu k}^{\alpha s} \right\rangle \Theta_{\nu k} \quad \varepsilon_\infty = 1 + \frac{4\pi}{\Omega} \frac{2}{3} \sum_{k,\alpha} \left\langle \frac{\partial \varphi_{\nu k}}{\partial k_\alpha} X_{lk}^{\alpha} \right\rangle \Theta_{\nu k}. \quad (12)$$

The \tilde{Z}_s , thus defined automatically satisfy the acoustic sum rule $\sum_s \tilde{Z}_s = 0$, as shown in the appendix.

An analogous decomposition into regular and irregular terms should be carried out in (4), by using the identity

$$2\langle X_l^\beta W_{cr}^{\alpha s} \varphi_{\nu k} \varphi_{\nu k} \rangle = 2\langle (\partial \varphi_{\nu k} / \partial k_\beta) X_{r,\nu k}^\alpha \rangle = (Z_s - \tilde{Z}_s) \delta_{\alpha\beta}$$

which follows from (9). Then in $D_{\alpha\beta}^{ss'}(q)$, terms corresponding to longitudinal vibration frequencies arise

$$D_{\alpha\beta}^{ss'}(q) \Rightarrow D_{\alpha\beta,r}^{ss'}(0) + (4\pi\tilde{Z}_s\tilde{Z}_{s'}/\Omega\varepsilon_\infty)n^\alpha n^\beta \quad (13)$$

$$D_{\alpha\beta,r}^{ss'}(0) = D_{\alpha\beta,ril}^{ss'}(0) - 2 \sum_{k,\nu} \langle X_{r,\nu k}^{\alpha s} W_{r,k}^{\beta s'} \varphi_{\nu k} \rangle.$$

For crystals with two atoms in the unit cell it follows immediately that $D_{\alpha\beta}^{ss'} = D_{\alpha\beta}^{ss'} \delta_{\alpha\beta}$ and

$$\omega_{\Gamma 0}^2 = -D^{12}/\mu \quad \omega_{\Gamma 0}^2 = \omega_{\Gamma 0}^2 + 4\pi\tilde{Z}_s^2/\Omega\varepsilon_\infty\mu \quad (14)$$

where μ is: $\mu^{-1} = M_1^{-1} + M_2^{-1}$. The system of equations (9), (10), (11) and (12) completely determines the lattice dynamics in the limit of $q \rightarrow 0$. Its solution is achieved via 3–4 iterations with an accuracy of 10^{-3} .

3. Details of the calculation and discussion

The calculations have been carried out by using the local Heine–Animalu type pseudopotentials, their parameters taken from the paper by Bratkovsky *et al* (1982), as well as the non-local *ab initio* pseudopotentials from the work of Bachelet *et al* (1982). As compared with the work of Bachelet *et al* (1982), the only difference in construction of the non-local pseudopotentials concerned its decomposition into local and non-local parts. The local part was chosen as

$$U_L(p) = -(4\pi Z/\Omega p^2) \exp(-p^2 \gamma^2) \cos(pr_0) \quad (15)$$

and the non-local part was selected so that their sum for the s , p , d components coincided with that of Bachelet *et al* (1982). Such redistribution of the PP between its local and non-local parts permits the number of plane waves N_g , in the basis set to be slightly diminished. Besides, some non-local PP's for Li were constructed from atom configurations differing from those in Bachelet *et al* (1982). Usually, the calculations for the local PP case were made using 59 plane waves and those for the non-local case using 137 waves. The Fourier

Table 1. MeH hydrides and pure Me volume properties, calculated at $\Omega = \Omega_{\text{exp}}$, $\gamma = 0.5$ for all the non-local PP, $cc = 2.0$ for PP from set 3 and 4. $\Omega_{\text{Li}} = 161.5$ au, $\Omega_{\text{Na}} = 254.49$ au, $\Omega_{\text{LiH}} = 112.99$ au, $\Omega_{\text{NaH}} = 197.22$ au, $\Omega_{\text{Si}} = 270.011$ au.

NN	Element and its PP parameters	Me		MeH		
		E (au)	p (kbar)	E (au)	p (kbar)	B (kbar)
1	Li ^a	-0.253	0.1	-0.835	-14.0	495.6
2	Li ^b	-0.264	5.2	-0.849	17.1	243.6
3	Li ($s^{0.5}p^{0.25}$)	-0.271	10.3	-0.836	-20.0	
4	Li ($s^{0.1}p^{0.1}$)	-0.273	11.4	-0.845	-13.6	
	Li (expt.)		0		0	341.0
5	Na ^a	-0.224	0.1	-0.763	32.4	184.1
6	Na ^b	-0.213	6.3	-0.804	44.7	206.2
	Na (expt.)		0		0	197.2
7	Si ^b	-9.30	27.8	—	—	—

^a Bratkovsky *et al* 1982.

^b Bachelet *et al* 1982.

transformed image of $U_{\text{NL}}(k + g, k + g')$ was calculated numerically by integration over 21 points in the r -space. The $\partial \hat{H}_e / \partial k^\alpha$ derivatives necessary for $\partial \varphi_{\nu k} / \partial k^\alpha$ determination were found analytically, while $\partial \varphi_{\nu k} / \partial k^\alpha$ themselves were obtained from the solution of the system

$$(\hat{H}_k - \varepsilon_{\nu k}) \partial \varphi_{\nu k} / \partial k^\alpha = -(\partial \hat{H} / \partial k^\alpha - \partial \varepsilon_{\nu k} / \partial k^\alpha) \varphi_{\nu k} \quad (16)$$

with the additional condition $\langle \partial \varphi_{\nu k} / \partial k^\alpha | \varphi_{\nu k} \rangle = 0$. Usually the \hat{H} matrix was transformed into Jacobi form and only two lower eigenvalues and their eigenvectors were found. Integration in the k -space was made over 102 points in the $1/48$ irreducible part of the Brillouin zone with the quadratic interpolation of the functions between them. We used the approximation of Perdew and Zunger (1981) for $\varepsilon_{xc}(\rho)$, which was based on the Monte Carlo results (Ceperley 1978). To find $\partial V_i(g) / \partial u^{\text{as}}$ with the previously obtained $V_i(g)$, 2–3 iterations are required.

The technique was verified for the case of Si with non-local PP from the work of Bachelet *et al* (1982). The results are summarized in tables 1 and 2 and closely reproduce the values of ω_{TO} and ε_∞ in Si, obtained previously with similar PP by Yin and Cohen (1982) and Baroni and Resta (1986). The $\bar{Z}_s = 0$ in this case due to the symmetry of the diamond-type lattice.

Under normal conditions, alkali hydrides are insulators having NaCl-type structure. There occurs a first-order transition in NaH, KH and CsH to the CsCl-type structure under a certain pressure, which is probably accompanied by metallization (Hochheimer *et al* 1985, Duclos *et al* 1987). In table 1 we summarized the energy, pressure and bulk modulus values for LiH and NaH. The calculations were made with the local Heine–Animalu-type PP with the parameters taken from the work of Bratkovsky *et al* (1982) and with non-local PP from that of Bachelet *et al* (1982). For LiH, the PP was also constructed from the $s^{0.1}p^{0.1}$ atom configuration, this being closer to the Li ion state in the LiH crystal. This set of the PP's was chosen to check the influence of the PP form on the results obtained. In all cases, the application of the PP used yielded zero pressure for the experimental volume in pure metals with a rather high accuracy. Both the energy

Table 2. Phonon frequencies and dielectric constants for LiH, NaH and Si. PP parameters are those from corresponding set in table 1, and ω is in THz.

NN	ω_{TO}	ω_{LO}	ϵ_∞	\bar{Z}
1 LiH	18.1	28.3	4.81	1.03
2 LiH	10.0	24.2	5.64	1.09
3 LiH	12.7	24.4	5.88	1.05
4 LiH	12.5	24.5	5.93	1.06
expt. LiH	18.4	33.5	3.61	1.11
5 NaH	8.52	12.3	3.54	0.94
6 NaH	5.15	10.6	3.71	0.99
7 Si	15.0	15.0	12.2	0
expt. Si	15.5	15.5	11.4	0

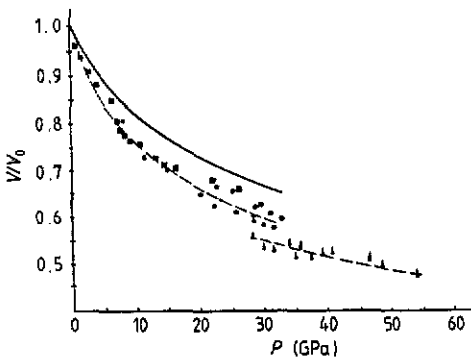


Figure 1. The NaH equation of state. Calculations (full curve) were carried out for the B1 phase. Experimental data (broken curve—to guide the eye) are from the paper of Duclos *et al* (1987).

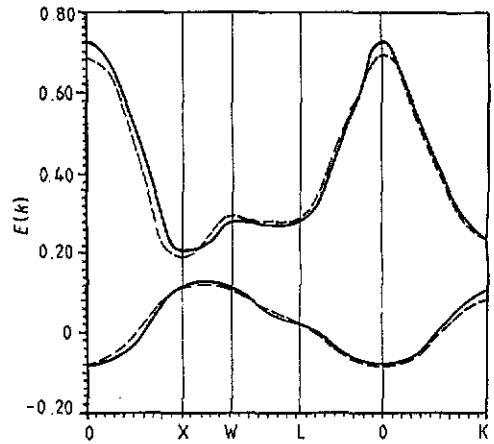


Figure 2. The ϵ dependence on k for symmetry directions in the BZ of LiH. Full curve: calculations with the PP from the paper of Bachelet *et al* (1982); broken curve: APW calculations of Hama and Kawakami (1988). The bottoms of low-lying bands are matched.

and pressure were calculated according to (1) and (3). The sensitivity of results to the change of N_g is negligible in the case of N_g greater than 137 for the non-local PP and 59 for the local case. In the recent paper by Duclos *et al* (1987) the equation of state was investigated for NaH in the interval of 0–600 kbar. The transition to the B2 phase of CsCl type occurs at $p \sim 300$ kbar. Our data for the equation of state, calculated with (1) and (3), are shown in figure 1 and appear to be in good agreement with experiment. We also find the transition from the B1 phase to the B2 insulator phase at approximately 300 kbar, but, since the possibility of the electron system metallization should be taken into account, this value should be determined more accurately. For the same reason we omitted data concerning the B2 phase.

In figure 2 the $\epsilon_{\nu k}$ dependence on k for LiH is shown for the PP, with parameters taken from the work of Bachelet *et al* (1982). It is well known that these dependences obtained by the DF method are hardly worth comparing with the experiment, especially in insulators. Therefore we compared them with the analogous curves, calculated using

the APW method (Hama and Kawakami 1988) with the same DF as in our work. The curves are in good agreement, if the uncertainty in the choice of the zero point is ruled out by matching the bottoms of the bands at $k = 0$. Using these PP, we calculated ω_{TO} , ω_{LO} , \bar{Z} and ϵ_{∞} , following (9), (10), (12) and (14). The results are presented in table 2. For the LiH case, the transverse frequency calculated with the local PP is in good agreement with the experiment (Verble *et al* 1968), but the use of various PP results in appreciable deviations of the values. The difference in the data obtained with the local and non-local PP should in principle be awaited, as the parameters of the local PP are fitted to reproduce the properties of pure metals and the 'transferability' (Bachelet *et al* 1982) under changing one class of crystals (metals) to another (insulators) may be lost by them. However, the difference between the non-local theory and the experiment points out that either the local approximation fails for the DF in insulators with such a wide gap, or the concept of the DF itself is violated. The second item is valid only for non-local potentials, when the introduction of the functional, depending only on ρ , has only variational meaning. We believe that corresponding experiments on NaH are desirable.

4. Conclusion

In this paper we present the algorithm for calculating the optical vibration frequencies at $q = 0$ and macroscopic dielectric constants in dielectrics. It can be used both with the local and non-local PP's. As an example, we have calculated the properties of some alkali hydrides. No extra PP parameters were used as compared with pure metals: all of them were previously fitted to reproduce pure metals properties (Bratkovsky *et al* 1982) or were obtained from the atom calculations (Bachelet *et al* 1982). Both the NaH and LiH equilibrium data are well reproduced in our calculations but the values obtained with different forms of the PP's differ significantly; this can be attributed to a failure of the PP method or/and the local approximation. Unfortunately, due to the lack of the experimental data for NaH one cannot judge whether our approach with the local PP is successful in this case. Therefore, the corresponding additional experiments are highly desirable. The authors believe that the approach presented permits the investigation of the influence of the electron subsystem on phonon frequencies in dielectrics in a rather simple manner.

Appendix

Below it will be shown that \bar{Z}_s , defined by (12), satisfy the acoustic sum rule $\sum_s \bar{Z}_s = 0$ (Pick *et al* 1970). Let us introduce the value $X_r^\alpha = \sum_s X_r^{\alpha s}$. Then

$$(\hat{H}_k - \epsilon_{\nu k})X_r^\alpha = \sum_s W_r^{\alpha s} \varphi_{\nu k}. \quad (\text{A1})$$

It follows from (5), that $\sum W_{1,\nu k}^{\alpha s} = (g - g')^\alpha V_c(k + g, k + g')$. Suppose that

$$W_k^{\alpha s} = \sum_s W_k^{\alpha s} = (g - g')^\alpha V(k + g, k + g'). \quad (\text{A2})$$

The solution of the system (A1) with these $W_{\nu k}^{\alpha s}$ is

$$X_r^\alpha = -(k + g)^\alpha \varphi_{\nu k}(g) + \lambda_{\nu k}^\alpha \varphi_{\nu k}(g) \quad (\text{A3})$$

where $\lambda_{\nu k}^{\alpha}$ can be found from the condition of the orthogonalization of X_r^{α} to $\varphi_{\nu k}$. $R^{\alpha}(g) = \sum_s R_0^{\alpha s}(g)$ can be found with these X_r^{α} , as it follows from rewriting (5):

$$R_q^{\alpha s}(g) = \sum_{kg'} [X_{q,k}^{\alpha s}(g+g')\varphi_{\nu k}(g') - X_{q,k}^{\alpha s}(-g+g')\varphi_{\nu k}(g')]\Theta_{\nu k} \quad (\text{A4})$$

and

$$R^{\alpha}(g) = -g^{\alpha} \sum_{kg'} \varphi_{\nu k}(g+g')\varphi_{\nu k}(g')\Theta_{\nu k} = -g^{\alpha} \rho(g). \quad (\text{A5})$$

Finding $W_{i,\nu k}^{\alpha s}$ with this $R^{\alpha}(g)$ we see that (A2) is true and the self-consistent solution of (A1) is $X_r^{\alpha}(g)$, defined by (A3). Besides, this X_r^{α} can be used to calculate the sum

$$\sum_s \bar{Z}_s = \sum_s Z_s + 2 \sum_k \left\langle \frac{\partial \varphi_{\nu k}}{\partial k_{\alpha}} (k+g)^{\alpha} \varphi_{\nu k} \right\rangle \Theta_{\nu k} = \sum_s Z_s - \sum_k \langle \varphi_{\nu k} \varphi_{\nu k} \rangle \Theta_{\nu k}$$

which is zero, as the sum $\sum_k \langle \varphi_{\nu k} \varphi_{\nu k} \rangle \Theta_{\nu k}$ equals $Z = \sum_s Z_s$ —the total charge of the elementary cell—due to the normalizing condition.

Despite this, $R_{0,k}^{\alpha s}(-g) = -R_{0,k}^{\alpha s}(g)$ from (A4) and this results in the orthogonality of the RHS of (9) and $\varphi_{\nu k}$.

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