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THE GENERALIZED PSEUDOATOM FORMALISM IN LATTICE DYNAMICS

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The change I in potential due to a phonon is expressed in terms of the susceptibility and the effective charge vector. It is analytic in metals or where χ^{eff} is zero, and hence can be uniquely split into parts which rigidly follow the ions and parts which deform as the ions move. This 'generalised pseudoatom' is neutral. The dynamical matrix is expressed in terms of I both in the reciprocal lattice representation and other representations.

We show first that the charge density of a finite system is a sum of uniquely-defined pseudoatoms, each consisting of a part moving rigidly with an ion and a part which deforms /1/. Suppose the ion at $\underline{R}_j^0$ moves to $\underline{R}_j^0 + \delta \underline{R}_j$. The change in charge density to first-order is $\underline{f}_j(\underline{r}) \cdot \delta \underline{R}_j$. Now $\underline{f}_j(\underline{r})$ can be written

$$\underline{f}_j(\underline{r}) = -\nabla \rho_j(\underline{r} - \underline{R}_j^0) + \nabla \times \underline{B}_j(\underline{r} - \underline{R}_j^0) \quad (1).$$

Thus to first order in $\delta \underline{R}_j$, the total charge density of the system is

$$n_0(\underline{r}) + \sum_j (\rho_j(\underline{r} - \underline{R}_j) + \delta \underline{R}_j \cdot \nabla \times \underline{B}_j(\underline{r} - \underline{R}_j^0)) \quad (2).$$

Translational invariance /1/ makes $n_0(\underline{r})$ zero. The term $\rho_j(\underline{r} - \underline{R}_j)$ is the part which moves rigidly with the ion and the other term is the deformation.

In crystals the ions move collectively as phonons. For (2) to be valid, the charge density must be analytic in $\underline{q}$, the wave-vector of the phonon. Let the equilibrium position vector of the κ ion in the unit cell at $\underline{\ell}$ be $\underline{R}^0(\underline{\ell}, \kappa) \equiv \underline{\ell} + \underline{R}^0(\kappa)$. This is displaced $\delta \underline{R}(\kappa) \exp[i\underline{q} \cdot \underline{R}^0(\underline{\ell}, \kappa)]$ by the phonon. The change in the electronic charge density is written

$$\frac{1}{\tau} \sum_{\kappa} \sum_{\underline{g}} \delta \underline{R}(\kappa) \cdot \underline{f}_e(\underline{q} + \underline{g}, \kappa) \exp[i(\underline{q} + \underline{g}) \cdot \underline{r}] \exp[i\underline{g} \cdot \underline{R}(\kappa)] \quad (3)$$

where $\underline{g}$ are reciprocal lattice vectors and τ is the cell volume. The change in the total charge density is written $\underline{f}(\underline{q} + \underline{g}, \kappa)$. We write the potential of the nucleus and the core electrons as $W(\underline{r} - \underline{R}(\underline{\ell}, \kappa); \kappa)$. Then

$$\underline{f}_e(\underline{q} + \underline{g}, \kappa) = i \sum_{\underline{g}'} \chi(\underline{q} + \underline{g}, \underline{q} + \underline{g}') (\underline{q} + \underline{g}') W(\underline{q} + \underline{g}', \kappa) \exp[i(\underline{g} - \underline{g}') \cdot \underline{R}(\kappa)] \quad (4)$$

The electron-phonon operator can be expressed in terms of $\underline{f}$ and W .

$$\underline{I}(\underline{q} + \underline{g}, \kappa) = i(\underline{q} + \underline{g}) W(\underline{q} + \underline{g}, \kappa) + \nu(\underline{q} + \underline{g}) \underline{f}_e(\underline{q} + \underline{g}, \kappa) \quad (5)$$

where ν is the Coulomb interaction. Then

$$\underline{I}(\underline{q} + \underline{g}, \kappa) = i \sum_{\underline{g}'} \epsilon^{-1}(\underline{q} + \underline{g}, \underline{q} + \underline{g}') (\underline{q} + \underline{g}') W(\underline{q} + \underline{g}', \kappa) \exp[i(\underline{g} - \underline{g}') \cdot \underline{R}(\kappa)] \quad (6)$$

where ϵ is the dielectric function matrix. Inverting /2/

$$(q + g)W(q + g, \kappa) = i \sum \epsilon(q + g, q + g') I(q + g, \kappa) \exp[i(g - g') \cdot R(\kappa)] \quad (7)$$

I is the change in potential felt by a classical point charge. I' is the change felt by a valence electron: it includes exchange and correlation.

To investigate the analyticity of I , we write $I(q + g, \kappa)$ in terms of the 'susceptibility' χ^Λ and the effective charge vector $\tilde{Z}(q, \kappa) / 3$:

$$\chi^\Lambda = \chi + \chi \left(\frac{\Lambda}{v} - v \right) \chi^\Lambda \quad (8)$$

$$\tilde{Z}(q + g, \kappa) = -i \left((q + g)W(q + g, \kappa) / v(q + g) + \sum_{g' \neq 0} \hat{\chi}(q + g, q + g') \right. \\ \left. (q + g)W(q + g', \kappa) \exp[i(g - g') \cdot R(\kappa)] \right) \quad (9)$$

$$\text{In insulators and metals } \lim_{q \rightarrow 0} \tilde{Z}(q, \kappa) = i \tilde{Z}^{\text{eff}}(\kappa) \cdot q \quad (10)$$

where $\tilde{Z}^{\text{eff}}(\kappa)$ is the effective charge tensor. Hence

$$I(q, \kappa) = -\epsilon^{-1}(q, q) v(q) \tilde{Z}(q, \kappa) \quad (11)$$

and

$$I(q + g, \kappa) = -v(q + g) \left(\tilde{Z}(q + g, \kappa) + \hat{\chi}(q + g, q) \epsilon^{-1}(q, q) v(q) \tilde{Z}(q, \kappa) \right) \quad (12)$$

There can only be non-analytic behaviour in the limit $q \rightarrow 0$. In insulators the second term in (12) is non-analytic if $\tilde{Z}^{\text{eff}}(\kappa)$ is non-zero so $I(q + g, \kappa)$ is analytic if and only if $\tilde{Z}^{\text{eff}}(\kappa)$ is zero. In a metal $v(q) \epsilon^{-1}(g, q) \rightarrow -1/\chi(q, q)$, both $\chi^\Lambda(q, q)$ and $\chi^\Lambda(q + g, q)$ tend to a finite limit and $I(q + g, \kappa)$ is always analytic. Thus in metals, and in those insulators where $\tilde{Z}^{\text{eff}}(\kappa)$ is zero I is analytic and so are I' and f . Each such vector field can be uniquely decomposed into vectors parallel and perpendicular to $q + g$, i.e.

$$f(q + g, \kappa) = i(- (q + g) \rho(q + g, \kappa) + (q + g) \times B(q + g, \kappa)) \quad (13)$$

$$I'(q + g, \kappa) = i(-q + g) u(q + g, \kappa) + (q + g) \times \omega(q + g, \kappa) \quad (14)$$

In real space, this decomposition gives (2) for f and a similar result for I' . In insulators where $\tilde{Z}^{\text{eff}}(\kappa)$ is non-zero f is not analytic and the charge density cannot completely be described in terms of pseudoatoms /2/.

One advantage of the formalism is that the pseudoatom is neutral

$$\lim_{q \rightarrow 0} \rho(q, \kappa) = i \cdot q \cdot \tilde{Z}^{\text{eff}}(\kappa) \cdot q \epsilon^{-1}(q, q) v(q) / 4\pi e^2 = 0 \quad (15)$$

Another is that it gives the potential which an electron sees when a phonon is present. The rigid part of this potential is

$$u(q + g, \kappa) = (q + g) \cdot I'(q + g, \kappa) / |q + g|^2 \quad (16)$$

The main part of the effective interaction between the ions is /3,2/

$$V(q + g, \kappa; q + g', \kappa') = W(q + g, \kappa) \epsilon^{-1}(q + g, q + g') W(q + g', \kappa') / v(q + g) \quad (17)$$

Using (17) and the inversion procedure (7), the dynamical matrix becomes

$$\frac{(M(\kappa) M(\kappa'))^{-1/2}}{\sqrt{g, g'}} \sum_{\tilde{q}, \tilde{q}'} \tilde{I}(\tilde{q} + g, \kappa) \otimes \tilde{I}^*(\tilde{q} + g', \kappa') \epsilon^*(\tilde{q} + g, \tilde{q} + g') \exp[i(\tilde{q} + g') \cdot \tilde{R}(\kappa)] \\ - i(\tilde{q} + g) \cdot \tilde{R}(\kappa') \tilde{I} / v(\tilde{q} + g) \quad (18)$$

This expression is in the reciprocal-lattice representation. It can be

generalised to other representations by considering ϵ as a matrix and $\underline{I}$ as a 'vector'. Then the dynamical matrix in a general representation is

$$\frac{(M(\underline{k})M(\underline{k}'))^{-1/2}}{\uparrow} \sum_{\mu_1, \mu_2} (\underline{I}(\underline{q}, \underline{k}))_{\mu_1} \otimes (\underline{I}^*(\underline{q}, \underline{k}')/\nu(\underline{q}))_{\mu_2} (\underline{\epsilon}^*(\underline{q}))_{\mu_1 \mu_2} \exp[i\underline{q} \cdot (\underline{R}(\underline{k}) - \underline{R}(\underline{k}'))] \quad (19)$$

This expression (19) avoids the inversion procedure needed to derive χ from χ^0 .

Using the R.P.A. expression for $\underline{\epsilon}$, the dynamical matrix becomes $\underline{C}' + \underline{D}'$ where

$$\underline{C}' = \frac{(M(\underline{k})M(\underline{k}'))^{-1/2}}{\uparrow} \sum_{\mu} (\underline{I}(\underline{q}, \underline{k}))_{\mu} \otimes (\underline{I}^*(\underline{q}, \underline{k}')/\nu(\underline{q}))_{\mu} + \text{exchange, etc., terms} \quad (20)$$

$$\underline{D}' = \frac{(M(\underline{k})M(\underline{k}'))^{-1/2}}{\uparrow} \sum_{\mu_1, \mu_2} (\underline{I}(\underline{q}, \underline{k}))_{\mu_1} \otimes (\underline{I}^*(\underline{q}, \underline{k}'))_{\mu_2} (\chi^0(\underline{q}))_{\mu_1 \mu_2} \quad (21)$$

Sinha /4/ has obtained a similar formula to this with χ in place of χ^0 ;

however, his definition of $\underline{I}$ is different from ours.

Equations (20 and (21) are useful when we can use the pseudoatom concept. Then we replace $\underline{I}$ by $\underline{I}'$ and incorporate all the exchange, etc., effects into $\underline{C}'$. $\underline{I}'$ can then be written in the pseudoatom form (17), i.e.

$$(\underline{I}'(\underline{q}, \underline{k}))_{\mu} = (\nabla u(\underline{q}))_{\mu} - (\nabla \times \underline{\omega}(\underline{q}))_{\mu} \quad (22)$$

The neutrality of the pseudoatom means that the cancellation between the large Coulombic attractive and repulsive terms has already been accomplished. If there is a suitable approximation for the potential u , and $\underline{\omega}$ can be neglected, it is practical to calculate $\underline{I}'(\underline{q}, \underline{k})$ in certain representations, e.g. (l, m) orbitals or the tight-binding representation /4/.

When $\underline{z}(\underline{q}, \underline{k})$ is pure imaginary in a cubic material, the only direction for $\underline{z}(\underline{q}, \underline{k})$ is along $\underline{q}$, so that $\underline{I}'(\underline{q}, \underline{k})$ has no deformation part. When there is inversion symmetry, $\chi(\underline{q}, \underline{q} + \underline{g})$ is real, so that $\underline{z}(\underline{q}, \underline{k})$ is pure imaginary provided $\underline{g} \cdot \underline{R}(\underline{k})$ is an integer times π . This occurs in cubic crystals with one ion per unit cell or with the NaCl structure, but not with the diamond structure or the Al5 structure. Thus $\underline{I}'(\underline{q}, \underline{k})$ has no deformation in the alkali metals, nor in Nb, Mo, MoC and TaC, but may have significant deformation in Ge and Si and the Al5 metals. It would be of interest to measure the change in electron-phonon coupling and in T_C in Nb, Pb and Mo caused by strains which alter the symmetry and thus allow deformation.

The second term of (12) is in the $\underline{q}$ -direction, so that if $\underline{q}$ is perpendicular to $\underline{g}$ it contributes a deformation part to $\underline{I}(\underline{q} + \underline{g}, \underline{k})$. If $\underline{I}(\underline{q} + \underline{g}, \underline{k})$ is calculated from a band-structure calculation, this term is neglected, but in metals it contributes to the elastic constants.

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