

## Dynamical effective charges in semiconductors: a pseudopotential approach†

P Vogl‡

Institut für theoretische Physik, Universität Graz, A-8600 Graz, Austria

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**Abstract.** A method for an *ab-initio* calculation of transverse dynamical effective charges  $Z^*$  in partially covalent semiconductors within the framework of pseudopotential theory is presented. It is based on previously established expressions for  $Z^*$  in terms of the inverse microscopic dielectric function of the crystal but circumvents the direct inversion of the latter. In contrast to earlier calculations the results are definitely boundary insensitive. Moreover, the acoustic sum rule expressing charge neutrality is inherently guaranteed. Within the local empirical pseudopotential method a simple analytical model calculation, which is compared with the bond orbital model, as well as a full numerical computation is performed. For III-V compounds the resulting  $Z^*$  underestimate the experimental effective charges by  $\sim 30\%$  while good agreement for II-VI materials is obtained. Reasons for these findings are discussed and the effects of several refinements are estimated.

### 1. Introduction

Transverse dynamical effective charges  $Z^*$  are fundamental quantities in the lattice dynamics of semiconductors, determining the long-range part of the force constants in the long-wavelength limit, the Froehlich electron-optical-phonon coupling, parts of the piezoelectric coefficients, etc.) (see e.g. Maradudin 1974). A number of empirical and semi-empirical models have been developed for  $Z^*$  (Wemple 1973, Lawaetz 1971, Hübner 1975, Harrison 1973, Harrison and Ciraci 1974) among which Harrison's bond-orbital model (BOM), a simplified tight binding model, appears to be the most elaborated. A first-principle calculation of  $Z^*$  has been attempted only by Bennett and Maradudin (1972), henceforth cited as BM. However, as pointed out by Martin (1974), their calculation was based on an incorrect expression for  $Z^*$  (see § 2.1), yielding boundary-sensitive results which violate charge neutrality. Sham (1969, 1974), Pick *et al* (1970), and Bilz *et al* (1974) could express  $Z^*$  in terms of the off-diagonal elements (in  $(\mathbf{G}, \mathbf{G}')$ -space where  $\mathbf{G}, \mathbf{G}'$  are reciprocal lattice vectors) of the Fourier transform of the inverse microscopic dielectric function  $\epsilon^{-1}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}')$  of the perfect crystal. Although a number of inversion procedures for  $\epsilon$  have been developed (Van Vechten and Martin 1972, Bertoni *et al* 1974, Hanke 1973, Bilz *et al* 1974, Hanke and Sham 1975, Louie *et al* 1975) none of them seems particularly suited for a calculation of  $Z^*$ . Charge neutrality imposes a constraint on the sum of all off-diagonal elements of  $\epsilon^{-1}$  (Sham 1969, 1974, Pick *et al* 1970) which is difficult to control and to guarantee within these procedures.

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‡ Present address: University of Illinois, Physics Department, Urbana, Illinois 61801, USA.

In this paper we present a method for a first-principle pseudopotential calculation for  $Z^*$  which guarantees definitely boundary-insensitive results as well as charge neutrality at each step of the calculation. The method is based on the microscopic expression for  $Z^*$  in terms of  $\epsilon^{-1}$  of Sham (1969), Pick *et al* (1970), and Vogl (1976), but circumvents the direct inversion of  $\epsilon$ . This is achieved by constructing the self-consistent potential induced by a long-wavelength lattice displacement within the framework of the pseudopotential theory (§4). For the present the latter potential is calculated using the local empirical pseudopotential method. A detailed numerical (§6) as well as a qualitative analysis based on a Heine-Jones type band structure (§5) is performed for several III-V and II-VI semiconductors. The latter yields an analytical model for  $Z^*$  which closely resembles the expressions obtained within the BOM in spite of the diametrically opposed approaches. The numerical computations underestimate the experimental  $Z^*$  by 20–30% for the III-V's. The discrepancies are shown to be appreciably diminished by taking into account orthogonality hole corrections and exchange effects (§6).

## 2. Basic definitions

We consider a perfect insulator or intrinsic semiconductor as made up of ions including core electrons which move rigidly with the nuclei and a corresponding number of interacting valence electrons. The ions are treated as point charges  $Z_\alpha$  with equilibrium positions  $\mathbf{x}_{l\alpha}$ ,  $l$  denoting the lattice cell and  $\alpha$  the ions in the cell. The valence electron-ion potential will be described by a pseudopotential. For convenience we put the protonic charge  $e = 1$ .

Consider displacements  $\mathbf{u}_{l\alpha}$  of the ions at  $\mathbf{x}_{l\alpha}$  of the form

$$\mathbf{u}_{l\alpha} = A_q \mathbf{e}(\mathbf{q} | \alpha) \exp(i\mathbf{q} \cdot \mathbf{x}_{l\alpha}) + \text{h.c.}, \quad (2.1)$$

where  $\mathbf{e}(\mathbf{q} | \alpha)$  denotes a unit vector characterising the mode (optic or acoustic) of wave-vector  $\mathbf{q}$  ( $\Omega_0^{-1/3} \gg q \gg \Omega^{-1/3}$  where  $\Omega$  is the crystal volume and  $\Omega_0$  the volume of the unit cell) and the amplitude  $A_q$ . Impose the electrical boundary condition  $\mathbf{E}(\mathbf{q}) = 0$ , i.e. keep the macroscopic electric field in the crystal  $\bar{\mathbf{E}}(\mathbf{q}) = \mathbf{E}(\mathbf{q})$  constant. Then, in the long-wavelength limit, the macroscopic polarisation†  $\tilde{\mathbf{P}}(\mathbf{q}) = \mathbf{P}(\mathbf{q})|_{\bar{\mathbf{E}}=0}$  induced by (2.1) can be expressed by

$$\lim_{q \rightarrow 0} \mathbf{q} \cdot \tilde{\mathbf{P}}(\mathbf{q}) = \frac{1}{\Omega_0} \sum_{\alpha} \hat{q}_\lambda Z_{\lambda\mu}^*(\alpha) e_\mu(\alpha) A_q, \quad (2.2)$$

which defines the Born or transverse effective charge tensor  $Z_{\lambda\mu}^*(\alpha)$  for ions of type  $\alpha$  (e.g. Maradudin 1974). In equation (2.2),  $\hat{q} = \mathbf{q}/|\mathbf{q}|$  and  $e(\alpha) = e(0|\alpha)$ . Using Poisson's equation one can see that  $\mathbf{Z}^*(\alpha)$  is a dipole moment per unit displacement,

$$Z_{\lambda\mu}^*(\alpha) = - \int d^3r r_\lambda \tilde{f}_\mu(\mathbf{r}, \alpha), \quad (2.3)$$

where  $-\tilde{f}_\mu(\mathbf{r}, \alpha)$  is the first-order change in the charge density at distance  $\mathbf{r}$  from an ion at  $\mathbf{x}_\alpha$  due to unit displacement of this ion in the  $\mu$ -direction and keeping  $\bar{\mathbf{E}} = 0$  (Martin 1972, Vogl 1976). Charge neutrality together with the translational invariance condition

† The tilde will be used to indicate the boundary condition  $\mathbf{E}(\mathbf{q}) = 0$  throughout the paper.

$$\frac{\partial \rho^{(0)}(\mathbf{r})}{\partial r_\mu} = \sum_{\lambda\alpha} \tilde{f}_\mu(\mathbf{r} - \mathbf{x}_{\lambda\alpha}, \alpha) \quad (2.4)$$

yield the so-called acoustic sum rule (Sham 1969, 1974, Pick *et al* 1970)

$$\sum_\alpha Z_{\lambda\mu}^*(\alpha) = - \int d^3r r_\lambda \frac{\partial \rho^{(0)}(\mathbf{r})}{\partial r_\mu} = 0. \quad (2.5)$$

Throughout the paper we shall consider cubic, binary compounds where  $Z_{\lambda\mu}^*(\alpha) = Z^*(\alpha) \delta_{\lambda\mu} = \pm Z^* \delta_{\lambda\mu}$ . Experimentally  $Z^*$  may be obtained from the difference between the squares of the longitudinal and transverse optical frequencies in the long-wavelength limit (Lucovsky *et al* 1971, Sham 1969),

$$\omega_L^2 = \omega_T^2 + \frac{4\pi Z^{*2}}{\epsilon_\infty \mu \Omega_0}, \quad (2.6)$$

$\mu$  being the reduced mass of the two ions in a unit cell and  $\epsilon_\infty$  the macroscopic dielectric function. It should be noted that equation (2.6) holds exactly within the harmonic and adiabatic lattice dynamics (Sham 1969, 1974).

### 2.1. The approach of BM

From (2.2) and (2.3) one sees that  $Z^*$  is proportional to the mean polarisation  $\bar{\mathbf{P}}$  induced by a small rigid displacement of one sublattice relative to the other. Denoting the correspondingly induced periodic charge density per unit displacement by  $\delta\rho(\mathbf{r})$ , one can write

$$\bar{\mathbf{P}} = \frac{1}{\Omega_0} \int_{\Omega_0} d^3r r \delta\rho(\mathbf{r}) + \frac{1}{\Omega_0} \int_{S_0} ds r \hat{\mathbf{n}} \cdot \mathbf{P}(\mathbf{r}), \quad (2.7)$$

where  $\hat{\mathbf{n}}$  is a unit vector normal to the surface  $S_0$  of  $\Omega_0$ . As pointed out by Martin (1974), BM incorrectly neglected the surface integral on the RHS of (2.7) yielding  $Z^*(\alpha)$ 's which would depend on the choice of  $\Omega_0$  and even violate equation (2.5). The error of BM can be seen more strikingly by Fourier analysing the totally induced (periodic) polarisation  $\mathbf{P}(\mathbf{r}) = \bar{\mathbf{P}} + \mathbf{P}^{(1)}(\mathbf{r})$ ,  $\mathbf{P}^{(1)}(\mathbf{r})$  arising from Fourier coefficients with nonzero reciprocal lattice vectors. Using Poisson's equation and Green's theorem, (2.7) reads

$$\bar{\mathbf{P}} = \frac{1}{\Omega_0} \int_{\Omega_0} d^3r r (-\nabla \cdot \mathbf{P}^{(1)}(\mathbf{r})) + \bar{\mathbf{P}} + \frac{1}{\Omega_0} \int_{S_0} ds r \hat{\mathbf{n}} \cdot \mathbf{P}^{(1)}(\mathbf{r}), \quad (2.8)$$

which shows that the first term on the RHS of (2.8), which was solely considered by BM, is in fact *independent* of  $\bar{\mathbf{P}}$  (K Baumann 1977, private communication).

### 3. Dielectric formalism

A proper starting point for a calculation of  $Z^*$  is to express (2.3) in terms of the microscopic dielectric function  $\epsilon(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}')$  ( $\mathbf{G}, \mathbf{G}'$  are reciprocal lattice vectors) employing the method of long waves which avoids the accumulation of charge at the surface of the crystal. In order to specify our notation as well as the model to be constructed later on we briefly rederive  $Z^*$  as a functional of  $\epsilon$  or  $\epsilon^{-1}$  using a formalism developed by the author (Vogl 1976).

The static density response function  $\chi(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}')$  measures the first-order change in the electron density  $\delta n$  when the crystal is perturbed by a small electric potential, whose Fourier transform we denote by  $\delta V_b(\mathbf{q} + \mathbf{G})$ . In matrix notation, one has (Sham 1974, Pines and Nozières 1966)

$$\delta \mathbf{n} = \chi \delta \mathbf{V}_b = \chi^p \delta \phi, \quad (3.1)$$

$$\delta \phi = \epsilon^{-1} \delta \mathbf{V}_b = \delta \mathbf{V}_b + \mathbf{v} \delta \mathbf{n}, \quad (3.2)$$

$$\epsilon^{-1} = 1 + \mathbf{v} \chi, \quad \epsilon = 1 - \mathbf{v} \chi^p, \quad (3.3)$$

where  $\delta \phi$  is the self-consistent electric potential set up by  $\delta \mathbf{V}_b$  and  $\chi^p$  is known as the proper or irreducible polarisation. The Coulomb interaction  $\mathbf{v}$  is replaced by

$$\begin{aligned} v(\mathbf{q} + \mathbf{G}) &= 4\pi e^2 / |\mathbf{q} + \mathbf{G}|^2 & \mathbf{q} \neq 0 \\ &= 0 & \mathbf{q} = 0, \end{aligned} \quad (3.4)$$

which conveniently expresses the electrical neutrality of the system. By means of a polarisation  $\hat{\chi}$  defined by

$$\chi(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') = \hat{\chi}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') + \hat{\chi}(\mathbf{q} + \mathbf{G}, \mathbf{q}) v(\mathbf{q}) \chi(\mathbf{q}, \mathbf{q} + \mathbf{G}'), \quad (3.5)$$

the long-range part  $v(\mathbf{q})$  of the Coulomb interaction can be extracted from  $\chi$ . Therefore  $\hat{\chi}$  behaves regularly for  $\mathbf{q} \rightarrow 0$ ; in addition, Ward identities yield  $\hat{\chi}(0, \mathbf{G}) = 0$  (Sham 1969, 1974).

In the spirit of the adiabatic principle we consider the frozen-in lattice wave (2.1) corresponding to a bare potential with Fourier components  $\delta V_b(\mathbf{G} \pm \mathbf{q})$  where

$$\delta V_b(\mathbf{q} + \mathbf{G}) = i \sum_{\alpha} v(\mathbf{q} + \mathbf{G}, \alpha) \exp(-i\mathbf{G} \cdot \mathbf{x}_{\alpha}) (\mathbf{q} + \mathbf{G}) \cdot \mathbf{e}(\mathbf{q} | \alpha) A_{\alpha}. \quad (3.6)$$

In (3.6),  $v(\mathbf{q} + \mathbf{G}, \alpha) / \Omega_{\text{per atom}}$  is the unscreened atomic form factor for ions of type  $\alpha$ . From the self-consistent, total potential  $\delta \phi(\mathbf{q} + \mathbf{G})$  induced by the lattice wave we now extract all parts proportional to the macroscopic electric field  $\mathbf{E}(\mathbf{q}) = i\mathbf{q} \delta \phi(\mathbf{q})$  being induced via Umklapp processes:

$$\delta \phi(\mathbf{q} + \mathbf{G}) = \sum_{\mathbf{G}'} \tilde{\epsilon}^{-1}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') \delta V_b(\mathbf{q} + \mathbf{G}') + \frac{\epsilon^{-1}(\mathbf{q} + \mathbf{G}, \mathbf{q})}{\epsilon^{-1}(\mathbf{q}, \mathbf{q})} \delta \phi(\mathbf{q}), \quad (3.7)$$

$$\tilde{\epsilon}^{-1}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') = (1 - \delta_{\mathbf{G}\mathbf{0}}) [\delta_{\mathbf{G}\mathbf{G}'} + v(\mathbf{q} + \mathbf{G}) \hat{\chi}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') (1 - \delta_{\mathbf{G}'\mathbf{0}})]. \quad (3.8)$$

If we keep  $\mathbf{E}(\mathbf{q}) = 0$ , the second term on the RHS of (3.7) obviously vanishes while the first term, which we denote by  $\delta \tilde{\phi}(\mathbf{q} + \mathbf{G})$ , remains unchanged. A detailed proof of this plausible assertion has been given (Vogl 1976). Consequently  $\tilde{\epsilon}^{-1}$  can be interpreted as the inverse dielectric function at fixed macroscopic electric field. By equations (3.1)–(3.8) one can easily establish a further relation,

$$\hat{\chi}(\mathbf{q}, \mathbf{q} + \mathbf{G}) = \sum_{\mathbf{G}'} \chi^p(\mathbf{q}, \mathbf{q} + \mathbf{G}') \tilde{\epsilon}^{-1}(\mathbf{q} + \mathbf{G}', \mathbf{q} + \mathbf{G}). \quad (3.9)$$

In analogy to equations (3.7) and (3.8), one finds the density response function  $\tilde{\chi}$  for  $\bar{\mathbf{E}} = 0$ , defined by  $\delta \mathbf{n}|_{\bar{\mathbf{E}}=0} = \tilde{\chi} \delta \mathbf{V}_b$ , to be

$$\tilde{\chi}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') = \hat{\chi}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') (1 - \delta_{\mathbf{G}'\mathbf{0}}). \quad (3.10)$$

With these results one arrives at the desired expressions

$$\mathbf{q} \cdot \tilde{\mathbf{P}}(\mathbf{q}) = \frac{1}{\Omega_0} \sum_{\alpha} Z_{\lambda}(\mathbf{q}|\alpha) e_{\lambda}(\mathbf{q}|\alpha) A_{\mathbf{q}}, \quad (3.11)$$

$$\begin{aligned} Z_{\lambda}(\mathbf{q}|\alpha) &= Z_{\alpha} q_{\lambda} - \sum_{\mathbf{G}} \tilde{\chi}(\mathbf{q}, \mathbf{q} + \mathbf{G}) v(\mathbf{q} + \mathbf{G}, \alpha) (q_{\lambda} + G_{\lambda}) \exp(-i\mathbf{G} \cdot \mathbf{x}_{\alpha}) \\ &= Z_{\lambda\mu}^{*}(\alpha) q_{\mu} + O(q^2). \end{aligned} \quad (3.12)$$

Equation (3.12) has been previously obtained by Sham (1969), Pick *et al* (1970). The short-range nature of  $\tilde{\chi}$  (or its analyticity as a function of  $\mathbf{q}$ ) guarantees that  $Z^{*}$  as given by (3.12) is a well-defined, boundary insensitive quantity.

#### 4. Pseudopotential approach

In the form of (3.12),  $Z^{*}(\alpha)$  appears to be intractable. If  $\epsilon$ , obtained by a pseudopotential calculation, is inverted numerically (Van Vechten and Martin 1972, Louie *et al* 1975; by (3.3), (3.5) this also yields  $\tilde{\chi}$ ) it is difficult to keep the crucial charge neutrality condition equation (2.5), which represents a constraint on the off-diagonal response, under control. Neither do the inversion procedures based on a tight binding approach (Hanke 1973, Bilz *et al* 1974, Hanke and Sham 1975, Turner and Inkson 1976) automatically maintain (2.5).

A proper starting point is obtained, however, by rewriting (3.12) with the aid of (3.9), (3.10) as

$$Z_{\lambda}(\mathbf{q}|\alpha) = Z_{\alpha} q_{\lambda} - \frac{1}{i} \sum_{\mathbf{G} \neq 0} \chi^p(\mathbf{q}, \mathbf{q} + \mathbf{G}) \delta\tilde{\phi}_{\lambda}(\mathbf{q} + \mathbf{G}, \alpha), \quad (4.1)$$

$$\delta\tilde{\phi}_{\lambda}(\mathbf{q} + \mathbf{G}, \alpha) = i \sum_{\mathbf{G}' \neq 0} \tilde{\epsilon}^{-1}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') v(\mathbf{q} + \mathbf{G}', \alpha) (q_{\lambda} + G'_{\lambda}) \exp(-i\mathbf{G}' \cdot \mathbf{x}_{\alpha}) \quad (4.2)$$

with  $\delta\tilde{\phi}_{\lambda}$  being the total induced potential for unit displacement of the  $\alpha$  sublattice in the  $\lambda$ -direction in a lattice wave of wavevector  $\mathbf{q}$  and keeping  $\bar{\mathbf{E}} = 0$ . Although (4.1) is still exact, it offers the following 'minimal' model: In order to obtain an electronic contribution to  $Z^{*}$ , it is seen from (4.1) that  $\chi^p$  must necessarily be non-diagonal, whereas charge neutrality allows for a diagonal approximation for  $\tilde{\epsilon}^{-1}$ , as will be shown below. Instead of constructing a diagonal  $\tilde{\epsilon}^{-1}$  (Martin 1969, see also Bertoni 1974) one may use empirically determined  $\delta\tilde{\phi}$ 's in equation (4.1) which is done in the present work. In any case, one circumvents the inversion of  $\epsilon$  (cf. (3.3)).

In the Hartree approximation, which will be adopted for  $\chi^p$ ,  $\chi^p$  is given by the usual Lindhard type polarisability in terms of the single-particle Bloch states  $|n\mathbf{k}\rangle$  and energies  $E_{n\mathbf{k}}$  (see e.g. Sham 1974). These will be calculated using the local, empirical pseudopotential method (Cohen and Heine 1970) and neglecting spin-orbit effects (for a detailed discussion of all approximations, see § 6). Then the one-electron Hamiltonian is

$$H_{\mathbf{k}}(\mathbf{G}, \mathbf{G}') = \frac{\hbar^2(\mathbf{k} + \mathbf{G})^2}{2m} \delta_{\mathbf{G}\mathbf{G}'} + V(\mathbf{G} - \mathbf{G}'), \quad (4.3)$$

$$V(\mathbf{G}) = \frac{1}{\Omega_0} \sum_{\alpha} \exp(-i\mathbf{G} \cdot \mathbf{x}_{\alpha}) \phi_{\alpha}^{(0)}(\mathbf{G}), \quad (4.4)$$

where  $\mathbf{V}$  denotes the self-consistent perfect lattice potential and  $\phi_\alpha^{(0)}(\mathbf{G})/\Omega_{\text{per atom}}$  the atomic form factors for  $\alpha$ -ions. In addition, we use a rigid-ion approximation for  $\delta\tilde{\phi}_\lambda$ ,

$$\delta\tilde{\phi}_\lambda(\mathbf{q} + \mathbf{G}, \alpha) = i\phi_\alpha^{(0)}(\mathbf{q} + \mathbf{G})(q_\lambda + G_\lambda) \exp(-i\mathbf{G} \cdot \mathbf{x}_\alpha). \quad (4.5)$$

The RHS of (4.5) seems to correspond to a rigid-ion approximation for the total potential  $\delta\phi_\lambda$ . Since, however, the long-range part of the phonon-induced electron-ion potential (corresponding to the second term on the RHS of (3.7)) has a non-vanishing curl (Ginter and Mycielski 1971, Pindor 1973), an irrotational approximation for  $\delta\phi_\lambda$  is actually a rigid-ion approximation for  $\delta\tilde{\phi}_\lambda$ , which is the quantity required in equation (4.1).

At the moment we also neglect orthogonalisation hole corrections, taking ion core charges  $Z_\alpha = +n$  for elements in the  $n$ th column of the periodic table. From the long-wavelength limit of (4.1), we finally obtain

$$Z^*(\alpha) = Z_\alpha + \frac{4}{\Omega} \sum_{\mathbf{G} \neq 0} \sum_{n'n\mathbf{k}} \frac{\theta_{n\mathbf{k}}(1 - \theta_{n'\mathbf{k}})}{(E_{n\mathbf{k}} - E_{n'\mathbf{k}})^2} \left\langle n\mathbf{k} \left| \frac{\hbar}{m} p_x \right| n'\mathbf{k} \right\rangle \times \langle n'\mathbf{k} | \exp(i\mathbf{G} \cdot \mathbf{r}) | n\mathbf{k} \rangle \phi_\alpha^{(0)}(\mathbf{G}) G_x \exp(-i\mathbf{G} \cdot \mathbf{x}_\alpha), \quad (4.6)$$

where  $\theta_{n\mathbf{k}} = 1$  if  $n$  is one of the four valence bands, and  $\theta_{n\mathbf{k}} = 0$  otherwise. It remains to show that  $Z^*(\alpha)$ , as given by (4.6), fulfills the acoustic sum rule (2.5). This follows from the relation ( $\mathbf{p} = -i\hbar\nabla$ )

$$n \neq n': \left\langle n'\mathbf{k} \left| \frac{\partial V(\mathbf{r})}{\partial r_\lambda} \right| n\mathbf{k} \right\rangle = -\frac{i}{\hbar} (E_{n'\mathbf{k}} - E_{n\mathbf{k}}) \langle n'\mathbf{k} | p_\lambda | n\mathbf{k} \rangle, \quad (4.7)$$

and the  $f$ -sum-rule

$$\frac{4\Omega_0}{m\Omega} \sum_{n'n\mathbf{k}} \frac{\theta_{n\mathbf{k}}(1 - \theta_{n'\mathbf{k}})}{E_{n'\mathbf{k}} - E_{n\mathbf{k}}} |\langle n\mathbf{k} | p_x | n'\mathbf{k} \rangle|^2 = \sum_\alpha Z_\alpha = 8, \quad (4.8)$$

which is a consequence of the orthonormality and completeness of the Bloch states and Kramer's symmetry (see eg Adler 1962). Note that the *same*  $\phi^{(0)}$  has to be used in (4.5) as for the Bloch states in  $\chi^p$  in order to fulfill (2.5).

## 5. An analytical model

Physical insight into expression (4.6) can be obtained by using a Heine-Jones type model (Heine and Jones 1969) for the Bloch states required in  $\chi^p$ , keeping only  $V(111)$  and  $V(220)$ . Such a calculation of  $\chi^p$  has been carried out by Tyuterev (1975). In  $1/8$  of the Jones zone, corresponding to a reciprocal lattice vector in the set  $\{220\}$ , a  $4 \times 4$  Hamiltonian is diagonalised, coupling the states, e.g.  $\mathbf{k}$ ,  $\mathbf{k} + (220)$ ,  $\mathbf{k} + (111)$ ,  $\mathbf{k} + (11\bar{1})$ . The resulting band structure coincides with that obtained by Heine and Jones (1969). If this model is used for a calculation of equation (4.6), the resulting expression for  $Z^*$  is simple enough to be found by mere inspection, if we neglect the small  $V(220)$  compared to  $V(111)$ :

$$Z^*(\alpha) = Z_\alpha - 8 \frac{w_\alpha^2}{w_1^2 + w_2^2}, \quad (5.1)$$

where  $w_\alpha = \phi_\alpha^{(0)}(111)/\Omega_{\text{per atom}}$  for the ions of type  $\alpha = 1, 2$ ; (5.1) obviously satisfies (2.5) and correctly yields  $Z^* = 0$  for  $Z_1 = Z_2$  and  $w_1 = w_2$ . We note that the denominator in

(5.1) arises from the band gap  $\propto |V(111)|^2$  in this model. If we introduce the symmetric and antisymmetric form factors  $w_{S,A} = (w_1 \pm w_2)/2$  and designate the cation sublattice (group II, III) by  $\alpha = 1$  and the anions (group VI, V) by  $\alpha = 2$ ,  $Z^*$  for the cations takes the form

$$Z^* = -\Delta Z - \frac{8w_S w_A}{w_S^2 + w_A^2}, \quad (5.2)$$

where  $\Delta Z = (Z_2 - Z_1)/2$ . Using the form factors tabulated by Cohen and Heine (1970) we list the resulting  $Z^*$  in table 1. Note that  $Z^* = Z^*(1) > 0$  because of  $w_S < 0$ ,  $w_1 > w_2$ . Although equation (5.2) underestimates the experimental values it correctly

**Table 1.** Transverse dynamical effective charges and macroscopic dielectric constants. The second, third and fourth column were obtained from equations (5.2), (4.6), (6.2), respectively.

Crystal	$Z^*$			$\epsilon_\infty$			
	Bond orbital model†	Analytical model	Theory	Theory + orthogonality hole	Experiment‡	Theory	Experiment§
GaP	2.29	2.36	2.11	2.25	2.04	8.7	9.1
GaAs	2.20	1.23	1.74	1.87	2.16	11.3	10.9
GaSb	1.90	1.03	1.81	1.89	2.15	11.1	14.4
InP	2.55	1.23	1.81	2.01	2.55	9.5	9.6
InAs	2.34	1.57	1.61	1.78	2.53	11.8	12.3
InSb	2.25	1.20	2.09	2.21	2.42	11.5	15.7
ZnS	2.01	1.98	2.07	—	2.15	4.7	5.2
ZnSe	1.99	1.88	1.99	2.11	2.03	5.1	5.9
ZnTe	1.99	1.50	2.03	—	2.00	5.5	7.3
CdTe	2.07	1.84	2.05	2.19	2.35	5.4	7.2

† Harrison and Ciraci (1974)

‡ Lucovsky *et al* (1971)

§ Van Vechten (1969)

reproduces a number of trends. To show this, we first compare (5.2) with  $Z^*$  obtained by the BOM. The BOM contains a polar energy  $V_3$  and a covalent energy  $V_2$  as fundamental parameters. The occupation numbers of the two orbitals forming a bond are  $1 \pm \alpha_p$ , where  $\alpha_p = V_3/(V_2^2 + V_3^2)^{1/2}$ . For  $Z^*$ , the BOM yields

$$Z^* = -\Delta Z + 4\alpha_p + 4\alpha_p(1 - \alpha_p^2)c, \quad (5.3)$$

where  $c$  is an adjustable parameter of the order of 1. Harrison and Ciraci (1974) proposed  $c = 0.9$ . For highly polar materials, the dynamic contribution to  $Z^*$  in equation (5.3) becomes small compared to the static effective ionic charge  $-\Delta Z + 4\alpha_p$ . Recently Harrison (1976) developed a model which correlates the parameters of the BOM with the pseudopotential parameters. Within this model,  $w_S$  and  $w_A$  are identified with  $\sqrt{2V_2}$  and  $\sqrt{2V_3}$ , respectively. Following this prescription and Taylor-expanding a square root  $(1 - \alpha_p^2)^{1/2}$  ( $\alpha_p^2 \leq 0.6$  in all materials) one finds expression (5.2) to pass into the form of (5.3) with  $c = 1$ . In spite of this appealing theoretical agreement the numerical values of  $Z^*$  obtained by the BOM (5.3) and by (5.2) differ appreciably (table 1). This arises from  $w_A$  (taken from Cohen and Heine (1970)) being systematically smaller than  $\sqrt{2V_3}$  (obtained by Harrison and Ciraci (1974) within the BOM) for III-V's.

Certain differences between (5.2) and (5.3) are exhibited by defining a polarity  $p$  by

$$w_A = p|w_s|, \quad (5.4)$$

( $0 \leq p \leq 1$  if  $w_1 \leq 0$  and  $w_2 \leq 0$  which is the case in nearly all materials). Then equation (5.2) can be written in the form

$$Z^* = -\Delta Z + 4p + 4p \frac{1 - p^2}{1 + p^2}. \quad (5.5)$$

This shows that in the present model  $Z^*$  increases monotonically with  $p$  and cannot exceed the chemical valence  $-\Delta Z + 4$  for  $p \rightarrow 1$ , in contrast to expression (5.3). Moreover, because of the denominator  $1 + p^2$ , the relative dynamical contribution to  $Z^*$  is smaller in (5.5) than in (5.3) and probably underestimates it. Although the form factors which we used in (5.2) or (5.5) need not agree exactly with the empirical values of Cohen and Heine (1970) (due to the severe truncation of  $\mathbf{V}$ ) a systematic increase of  $w_A$  or the polarity  $p$ , which is required to achieve better agreement with the experiment, merely brings  $Z^*$  nearer to the static effective charge diminishing the relative dynamical contribution.

Altogether, with regard to the fact that (5.2) or (5.5) contains no free parameters, the model satisfactorily reproduces the weak dependence of the experimental  $Z^*$  on polarity and resembles remarkably the BOM although it underestimates somewhat the dynamical charge-transfer contribution to  $Z^*$ .

## 6. Numerical results, discussion, refinements

The numerical computations were based on equation (4.6). The band structure was calculated within the local empirical pseudopotential method. The form factors which we took from Cohen and Heine (1970) are based on Cohen and Bergstresser (1966). A slightly different set based on Walter and Cohen (1969) altered  $Z^*$  for GaAs and GaP only by a few per cent.  $V(\mathbf{G})$  was truncated at  $|\mathbf{G}|^2 = 11$  although  $\phi^{(0)}(\mathbf{G})$  enters equation (4.6) not only through the band structure which would justify this procedure. We therefore included form factors up to  $|\mathbf{G}|^2 = 19$  for GaAs which yielded negligible changes of  $Z^*$ . This is to be expected since  $Z^*$  is influenced more sensitively by the bandstructure than by  $\phi^{(0)}(\mathbf{G})$  itself. To achieve convergence, 59 and 89 plane waves were taken into account for the III-V's and II-VI's, respectively. The  $\mathbf{k}$ -summation in equation (4.6) was carried out using the special  $\mathbf{k}$ -scheme developed by Monkhorst and Pack (1976). For only 10 special  $\mathbf{k}$  points in the irreducible wedge (1/48) of the BZ the  $f$ -sum rule equation (4.8) was fulfilled with a tolerance of 0.6% for the III-V's and 0.9% for the II-VI's investigated. As a further check we calculated  $\epsilon_\infty$  in the Hartree approximation (table 1). We note that the results for  $\epsilon_\infty$  differ for some materials appreciably from the values found by BM who included only 27 plane waves.

The resulting transverse effective charges are presented in table 1. The values are typically 20–30% too small for the III-V's but agree well with the experimental  $Z_{\text{exp}}^*$  for II-VI compounds. The latter agreement is probably caused by the nearly complete charge transfer in II-VI's yielding  $Z^*$  practically equal to the chemical valence. Only the results for III-V materials can therefore be considered as a critical test for the method.

We first note the exceptional result for GaP where  $Z^* > Z_{\text{exp}}^*$ . This arises from an unplausibly small  $\phi_{\text{Ga}}^{(0)}(\sqrt{3})$  yielding  $w_A = 0.12$  Ryd for GaP ( $w_A = 0.07$  for GaAs,

$w_A = 0.06$  for GaSb) which doubtless overestimates the polarity and consequently  $Z^*$  (cf (5.5)). Let us discuss the main approximations separately:

### 6.1. Locality, neglect of spin-orbit effects

The lowest-order correction to a local pseudopotential is to replace the electronic mass  $m$  in (4.3) by an effective mass (Cohen and Heine 1970, Chelikowsky *et al* 1973). A 10% variation of  $m$  in GaAs was found to induce a 0.5% variation of  $Z^*$  which indicates a physical as well as numerical stability of the results. Although locality is thought to be the most severe approximation in the present calculation since a local EPM is known to yield charge densities which differ appreciably from the experimental values (Chelikowsky and Cohen 1976), we conclude from the refinements to be discussed below that this approximation yields  $Z^*$  correctly within 10–15%. The spin-orbit coupling may influence  $Z^*$  for the heavier elements although the assumption that integral properties of the wavefunctions are weakly affected by it (BM) seems plausible.

### 6.2. Rigid-ion approximation

For long-wavelength optical displacements involved in the calculation of  $Z^*$ , a rigid-ion approximation is doubtless the most natural one; it has been used with success in pseudopotential calculations of, e.g., deformation potentials (even acoustic ones; Yee and Myers (1976), Cerdeira and Cardona (1972), Savaria and Brust (1969)) and pressure-induced gap variations (Tsay *et al* 1974). We note, on the other hand, that this approximation could be removed in an *ab-initio* calculation. Since only  $\dagger \delta\tilde{\phi}_\lambda(\mathbf{G}, \alpha) = \delta\phi_\lambda(\mathbf{G}, \alpha)$  enters  $Z^*$ , the feasible construction of the self-consistent pseudopotential for a lattice where one sublattice is displaced rigidly by a small distance would be necessary.

### 6.3. Orthogonalisation hole

The part of the energy dependence of the pseudopotential which can be incorporated in equation (4.3) by using an effective mass negligibly influences  $Z^*$  (see § 6.1). However, a 10% effect may be expected from orthogonality hole corrections to the pseudo-charge densities (Heine and Weaire 1970, Shaw and Harrison 1967). Since calculations of the amount of charge excluded from the core are not available for semiconductors we estimated it as follows: In metals the valence charge density, represented by a single OPW, is reduced approximately by a factor of two in the core region (Animalu and Heine 1965). This holds qualitatively for s waves (mean value of  $\cos^2 x$  versa 1) as well as for p waves ( $x^2 \cos^2 x$  versa  $x^2$ ). Although many OPW's are required to represent the valence charge density in semiconductors, the pseudo-charge density is known to have predominantly p character in III-V's and s character in II-VI's (Walter and Cohen 1971, Chelikowsky and Cohen 1976). Assuming therefore that half of the pseudo-charge is pushed out of the core, one should replace the ionic charges  $Z_\alpha$  by  $Z_\alpha(1 + \delta_\alpha)$  where

$$\delta_\alpha = \frac{1}{2} \frac{\langle e_{ps}^\alpha \rangle_{\text{core}}}{\Omega_0} \frac{4\pi}{3} R_{c,\alpha}^3 \quad (6.1)$$

$R_{c,\alpha}$  denoting the core radius (Winkler 1955) and  $\langle e_{ps}^\alpha \rangle_{\text{core}}$  the pseudo-charge inside the core of ions  $\alpha$ . The latter charge was estimated from Walter and Cohen (1971) and

$\dagger$  Note that  $\delta\tilde{\phi}_\lambda$ , in contrast to  $\delta\phi_\lambda$ , is continuous for  $q \rightarrow 0$ .

Chelikowsky and Cohen (1976). Corresponding to these enhancements of the ionic charges the electronic wavefunctions have to be renormalized. Writing the uncorrected effective charges  $Z^*(\alpha) \equiv Z_\alpha - E_\alpha$ , by equation (2.5) one obtains

$$Z_{\text{corr}}^*(\alpha) = Z_\alpha(1 + \delta_\alpha) - E_\alpha(1 + \gamma), \quad (6.2)$$

$$\gamma = \frac{1}{8}(Z_1\delta_1 + Z_2\delta_2). \quad (6.3)$$

The renormalisation parameter  $\gamma$  has been assumed to be the same for all valence bands.  $\delta_\alpha$  could also be obtained qualitatively by scaling the depletion hole charges  $\delta_\alpha^M$  which have been calculated by Shaw and Harrison (1967) for metals, with the ratio of the core pseudo-charge density in the metal (which we assume to be equal to the average pseudo-charge density) and in the semiconductor. This prescription gives

$$\delta_\alpha = \frac{\langle e_{\text{ps}}^2 \rangle_{\text{core}} / \Omega_0}{8 / \Omega_0} \delta_\alpha^M. \quad (6.4)$$

The  $\delta_\alpha$ 's obtained from (6.1) and (6.4) are given in table 2 and agree reasonably for III-V's. For II-VI compounds the smaller values obtained by (6.4) seem to be more plausible due to the nearly complete charge transfer ( $\langle e_{\text{ps}}^{\text{cation}} \rangle_{\text{core}} \rightarrow 0$  from which follows  $Z_{\text{corr}}^*(\alpha) \rightarrow Z^*(\alpha)$ ) and the uncertainty in  $R_c$  for Cd and Zn.

**Table 2.** Orthogonalisation holes for zincblende semiconductors.  $\delta_{\text{cation}} \equiv \delta_1$  and  $\delta_{\text{anion}} \equiv \delta_2$  are obtained from equation (6.1).  $\delta_{\text{cation}}^s$  is obtained from equation (6.4).

Crystal	$\delta_{\text{cation}}$	$\delta_{\text{anion}}$	$\delta_{\text{cation}}^s$
Si	0.02	0.02	—
Ge	0.04	0.04	—
GaP	0.06	0.04	0.07
GaAs	0.08	0.09	0.07
GaSb	0.06	0.09	0.07
InP	0.09	0.04	0.12
InAs	0.10	0.09	0.12
InSb	0.07	0.12	0.12
ZnSe	0.04	0.07	0.02
CdTe	0.07	0.08	0.02

The resulting  $Z_{\text{corr}}^*$ , listed in table 1, are 10% larger than  $Z^*$  thereby diminishing the discrepancies between theory and experiment.

#### 6.4. Hartree approximation

The exchange effects can be approximated by replacing  $\chi^p \equiv \chi_{\text{H}}^p$  by

$$\chi_{\text{ex}}^p = \chi_{\text{H}}^p(1 + \mathbf{fv}\chi_{\text{H}}^p)^{-1} \quad (6.5)$$

where  $f(\mathbf{q} + \mathbf{G})$  accounts for the exchange processes and tends to 1/2 for large momentum transfer (Hubbard 1957, Sham 1974). In the long-wavelength limit, treating  $1 + \mathbf{fv}\chi_{\text{H}}^p$  as a diagonal matrix, and using  $\chi_{\text{H}}^p$  from Walter and Cohen (1970) we obtain, for GaAs,  $\chi_{\text{ex}}^p = \chi_{\text{H}}^p \times 1.09$  for reciprocal lattice vectors  $\mathbf{G} \in \{111\}$ . Although a self-consistent Hartree-Fock calculation would be necessary to guarantee equation (2.5) this estimate

indicates that exchange corrections further increase the dynamical contribution to  $Z^*$  by  $\sim 10\%$ .

In conclusion, a more elaborate but feasible calculation of  $Z(q|\alpha)$  by the methods developed in this paper, seems to be a promising starting point for an *ab-initio* lattice dynamics in covalent semiconductors.

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