Semiconductor effective charges and dielectric constants in the tight-binding approach

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The calculation of the effective charges and dielectric constants of common III-V and II-VI semiconductors is revised. The expectation value of the position operator on the sp^3s* tight-binding basis set is expressed in terms of a semiconductor-class-related constant, which is found to be related to the covalency of the compounds. Within this approach, the computed dielectric properties are in very good agreement with experiment. [S0163-1829(97)52744-5]

The macroscopic electric polarization of an insulating crystal was defined until recently as the dipole of the electronic charge density in one unit cell. However, as has been shown in Ref. 1, such a quantity is ill defined unless the periodic charge density can be decomposed in terms of neutral, localized contributions. The key ingredient in the development of the modern theory of polarization[2] has been to relate these neutral charge distributions with the contributions arising from the Wannier functions describing the ground state of the insulating crystal. The electronic contribution to the macroscopic polarization is indeed related to the dipole of the Wannier functions. In its usual first-principles implementation, this dipole can be expressed in a more convenient way in terms of a geometrical phase associated to the periodic parts of the occupied Bloch wave functions. In this way, derivatives of the macroscopic polarization, such as Born effective charges and piezoelectricity, can be computed by finite differences. This new approach has provided a more efficient and elegant way to compute, for instance, piezoelectric constants[2] than traditional linear response theory.[3] The calculation of macroscopic polarization-related properties in terms of the Wannier functions has so far only been performed for the Born effective charges of GaAs.[4] This is due to the computationally expensive determination of Wannier functions within the usual *ab initio* approaches.[4] Hence, from a computational point of view, an accurate description of the dielectric properties of simple cubic semiconductors, using simplified model Hamiltonians, presents a strong interest.

The empirical tight-binding model (ETB) (Ref. 5) is a very computationally convenient technique for investigating dielectric properties. Using bonding and antibonding orbitals as a basis set, Harrison[5] has shown that many of the dielectric properties of solids can be described within the ETB model, thereby introducing very few parameters in the model Hamiltonian. These parameters are generally fitted to some selected band properties that are extracted from experiment or *ab initio* calculations. However, it has been argued by some authors[6] that ETB models have to include in their fit-

ting procedure of the Hamiltonian matrix elements quantities that are sensitive to the electronic wave functions, such as the effective charges. In order to demonstrate this statement they have used an sp^3 basis set, as modified by Harrison, to include the Louie peripheral states.[10] Essentially, this procedure consists in including the effects of an excited s state as a perturbation to the other interactions in view of correcting some conduction band features of common semiconductors while retaining the analytical character of the model. With this basis set they have found that the calculated effective charges have an enormous error (more than 10%) with respect to the experimental ones.

At variance with Ref. 6, we will demonstrate in this paper that there is no need to fit the ETB Hamiltonian matrix elements to the effective charges, since they can be simply related to some selected energies in the Brillouin Zone (BZ). In particular, a considerable improvement in the accuracy of the computed effective charges can be obtained within the sp^3s* basis set,[7] since it describes to a better extent than the Harrison basis the conduction bands *and* the principal deformation potentials. Moreover, we will introduce a *semiconductor-class-related* constant which, when fitted to a prototypical compound of each class (e.g., GaAs for III-V and ZnTe for II-VI materials), considerably improves the theoretical agreement with experiment. This constant will be related to the covalency of the compounds and used to calculate their dielectric constants.

For a diatomic crystal, the Born effective charge $Z^\star_{\alpha\beta}$ measures the linear macroscopic polarization **P** induced by a relative displacement **u** of the two sublattices

$$eZ^\star_{\alpha\beta}=\Omega \left.\frac{\partial P_\alpha}{\partial u^\beta}\right|_{\mathbf{u}=0}, \tag{1}$$

where Ω is the unit-cell volume and α,β refer to the different components along the Cartesian axes. Since in the case of cubic crystals $Z^\star_{\alpha\beta}$ is diagonal, this quantity can be obtained by the difference in macroscopic polarization between two

states of the crystal under the hypothesis that the solid remains an insulator. Assuming a relative displacement $\mathbf{u}$ along the z direction, the difference $P_e(\mathbf{u}) - P_e(\mathbf{u}=\mathbf{0})$ in electronic polarization can be evaluated in terms of the phases $\varphi^{(\mathbf{u})}(\mathbf{k},\mathbf{k}')$, which are defined as the phases of the determinant of the generalized overlap matrices $S_{nm}^{(\mathbf{u})}(\mathbf{k},\mathbf{k}') = \langle \chi_n^{(\mathbf{u})}(\mathbf{k}) | \chi_m^{(\mathbf{u})}(\mathbf{k}') \rangle$, where n,m are indexes of the occupied bands and $|\chi_n^{(\mathbf{u})}(\mathbf{k})\rangle$ are the periodic parts of the Bloch wave functions obtained by diagonalization of the corresponding Hamiltonian. The electronic part of the polarization $P_e(\mathbf{u})$ indeed takes the following form:

$$P_e(\mathbf{u}) = -\frac{e}{(2\pi)^3} \int_A d\mathbf{k}_\perp \, \phi^{(\mathbf{u})}(\mathbf{k}_\perp), \qquad (2)$$

with

$$\phi^{(\mathbf{u})}(\mathbf{k}_\perp) = \int_0^{|\mathbf{G}|} dk_\| \frac{\partial}{\partial k_\|'} \varphi^{(\mathbf{u})}(\mathbf{k},\mathbf{k}') \Bigg|_{\mathbf{k}'=\mathbf{k}}, \qquad (3)$$

where A is the base of a prism that has the same volume as the BZ and $\mathbf{G} = 2\pi/a\,\hat{\mathbf{z}}$. The one-dimensional integral connects a $\mathbf{k}_\perp$ point in the basal plane with the corresponding $\mathbf{k}_\perp + \mathbf{G}$ on the opposite surface of the prism. In practice, the Bloch wave functions are computed on a uniform mesh and satisfy the periodic gauge condition, i.e., $|\chi_n^{(\mathbf{u})}(\mathbf{k}+\mathbf{G})\rangle = e^{-i\mathbf{G}\cdot\mathbf{r}} |\chi_n^{(\mathbf{u})}(\mathbf{k})\rangle$. If we discretize the one-dimensional integral with J points, and use a finite difference formula to evaluate the derivative, the expression (3) for the Berry phase $\phi^{(\mathbf{u})}(\mathbf{k}_\perp)$ can be approximated as

$$\phi^{(\mathbf{u})}(\mathbf{k}_\perp) = \text{Im} \log \prod_{j=1}^{J-1} \det S_{nm}^{(\mathbf{u})}(\mathbf{k}_j, \mathbf{k}_{j+1})$$

$$\equiv \sum_{j=1}^{J-1} \varphi^{(\mathbf{u})}(\mathbf{k}_j, \mathbf{k}_{j+1}), \qquad (4)$$

where $\mathbf{k}_j = \mathbf{k}_\perp + (j - 1/J - 1)\,\mathbf{G}$, $j = 1, \ldots, J-1$.

In the empirical tight-binding scheme, the Hamiltonian is represented in terms of an orthogonal basis set of atomiclike orbitals, characterized by site and symmetry indexes. Restricting the matrix elements of the Hamiltonian to first neighbors ensures that the model is simple enough, while retaining a good reproduction of the valence-band and the lower conduction-band dispersions (even of indirect-gap materials). Following the work of Chadi,[8] the spin-orbit interaction only affects the on-site matrix elements of the Hamiltonian. The strain has been included in the modification of both the bond angles and the transfer matrix elements.[9] This constitutes the most widely used formulation of the ETB model and has given many reliable results on different quantities.

Since the displacement of a sublattice corresponds to the creation of a frozen optical phonon in the crystal, the ETB parameters have to describe not only the valence bands but also the conduction bands to a good extent. In order to reproduce at best the deformation potentials of the compounds, we choose from the literature the parameters of Ref. 9 for the III-V compounds, and those of Refs. 12 and 13 for the II-VI

TABLE I. Effective charges calculated in the ETB approach for different III-V and II-VI compounds compared to the experimental values (Ref. 16). DA refers to the calculation within the diagonal approximation of the position operator while BV labels those obtained by Bennetto and Vanderbilt (Ref. 6) with the same approximation but with a different basis set. $\lambda_c = C_i \alpha_c$, where α_c is the covalency of the bond defined by Harrison (Ref. 5) and C_i is the class-dependent constant fitted to bring into agreement the $Z^\star$ values of GaAs and ZnTe with experiment (indicated by a star). DA $-\lambda_c$ refers to the value of $Z^\star$ obtained with the inclusion of the λ_c constant in the diagonal ansatz.

		DA	BV	λ_c	C_i	α_c	DA$-\lambda_c$	Expt.
	GaAs	2.08	1.73	0.96	1.091	0.88	2.16	2.16*
	GaSb	1.85	1.41	0.97	1.091	0.89	1.94	2.15
	GaP	2.04	1.88	0.94	1.091	0.86	2.23	2.04
III-V	AlSb	1.78	1.48	0.97	1.091	0.89	1.88	1.93
	InAs	2.22	2.11	0.91	1.091	0.83	2.52	2.53
	InSb	2.13	1.86	0.93	1.091	0.85	2.35	2.42
	InP	2.20	2.26	0.88	1.091	0.81	2.59	2.55
	ZnTe	1.96	2.05	0.99	1.478	0.67	2.00	2.00*
II-VI	ZnSe	2.07	1.86	0.98	1.478	0.66	2.13	2.03
	ZnS	1.93	1.89	0.98	1.478	0.66	2.01	2.15
	CdTe	2.21	1.92	0.92	1.478	0.62	2.47	2.35

compounds, which have been explicitly fitted to the hydrostatic a and uniaxial b deformation potentials.

We are now faced with a fundamental problem in the determination of the effective charges within the ETB approach: the evaluation of the matrix elements of $S_{nm}^{(\mathbf{u})}(\mathbf{k},\mathbf{k}')$ requires the knowledge of the representation of the position operator on the ETB basis. Indeed, the diagonalization of the ETB Hamiltonian provides the necessary Bloch functions from which the corresponding periodic parts are obtained by multiplying by the correct phase factor. The first natural *ansatz* is to assume that the position operator is diagonal in the basis set with expectation values equal to the positions of the atoms [we will call this the diagonal approximation (DA)]. This *ansatz* would correspond to the rather unphysical assumption of locating all the charge of the cation and anion hybrids at the center of the atoms.[6] In other words, any displacement of the hybrid charge along the bonds is neglected.

For each compound, we consider its ideal zinc-blende structure at the experimental lattice constant a_0 and a distorted one obtained by displacing a sublattice along $\hat{\mathbf{z}}$ with $\mathbf{u} = u\hat{\mathbf{z}}, u = 0.0001a_0/4$. The calculation of the effective charges $Z^\star$ has been performed using a 16×16 discretization of the basal plane and $J=160$ points for the one-dimensional integration. The values of the Born effective charges $Z^\star$ calculated within the DA approximation are reported in Table I. For comparison, we report also the values obtained by the authors of Ref. 6. For convenience, we have chosen the origin of the Cartesian coordinates at the center of the anion-cation bond. Since the ETB basis set is centered on cation and anion sites, different convergence rates for the $Z^\star$ calculated by displacing one of the two sublattices have been obtained (for $J=160$ the acoustic sum rule is valid within a few percent[11]). The reported values of the effective charges correspond, therefore, to the average value of the $Z^\star$ obtained in

the two cases with the same sampling of the BZ. This first improvement with respect to the Harrison basis is immediately evident.

In order to improve the results obtained with the diagonal approximation *ansatz*, we could try to include some off-diagonal terms, i.e., some on-site matrix elements between s and p orbitals obtained by, e.g., *ab initio* calculations. However, a worsening of the results has been proven to follow.[6] Instead, we choose to remain in the ETB framework and proceed in a different way: we keep the diagonal approximation but assume that the hybrid charge is somewhat displaced along the bonds, as the physics of the problem suggests. The expectation value of the position operator is then multiplied by a constant λ_c that measures the displacement of the hybrid charge from the atomic positions (which would include all kinds of off-diagonal interactions among orbitals[14]). It is worth noticing that a similar constant has been introduced, within the bond-orbital model, by Harrison[5] in order to improve the agreement of the theoretical predictions with respect to the experimental results for a large variety of physical properties. However, to our knowledge, no simple relation of this other constant to general features of the compounds has been stated. Since the hybrid basis can be expressed in terms of the sp^3s^* basis set, it is easy to show that both constants are related proportionally with a factor of $\sqrt{3}$.[15]

For the sake of simplicity, we choose the same constant for each atomiclike orbital centered on the anion and cation sites. Moreover, since the response of each type of material to a sublattice displacement must have an equivalent character within each class, depending on the atomic charges of the elements *and* on the covalent character of each compound, we do assume that λ_c depends on the covalency α_c of the compounds defined by Harrison[5] by a class-dependent constant C_i according to

$$\lambda_c = C_i \alpha_c \quad i = \text{III} - \text{V}, \text{II} - \text{VI}, \cdots , \qquad (5)$$

where α_c has been defined as $\alpha_c = V_2 / \sqrt{V_2^2 + V_3^2}$.[5] The terms V_2 and V_3 correspond to the covalent and polar energies per bond, respectively. Thus, α_c is a measure of the deviation of the covalent character of the bond. The constant C_i has been fitted, for each class of semiconductors, to bring into agreement the Z^* values of GaAs and ZnTe with experiment. We point out that we could have used the ionicity α_i,[5] or the covalency corrected by the inclusion of the peripheral s^* state,[10] in the definition of λ_c, but this would only change the value of C_i for each class and neither the physics nor the trends of the results. The values of Z^*, with including the λ_c constant in the diagonal *ansatz* of the position operator, are reported in Table I. The agreement with the experimental values is considerably increased. In general, the errors are less than 5%. The only deviation to these results is the Z^* values of GaSb, GaP, and ZnS (whose errors are less than 10%). This discrepancy can be attributed to a less accurate description of the conduction bands and/or the deformation potentials. Moreover, we must report that, since the experimental deformation potentials are affected by a considerable error [in some cases more than 20% (Ref. 9)], the scaling parameters of the transfer matrix elements are thus affected, to some extent, by the same error. We note that the effective
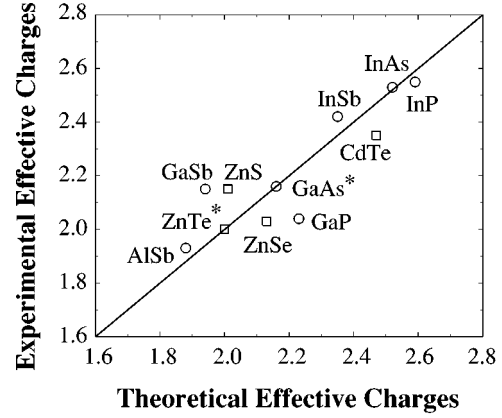

FIG. 1. Effective charges calculated in the ETB approach with the diagonal approximation of the position operator and the λ_c parameters discussed in the text, compared to the experimental values of Ref. 16. The stars refer to the compounds whose Z^* has been fitted to experiment. The circles, squares correspond to III-V and II-VI compounds, respectively.

charge of GaP fits exactly with experiment even with $\lambda_c = 1$. This result is probably fortuitous since, as discussed above, the DA approximation does not correspond to the real physics of the problem.

Finally, the overall agreement of our results for Z^* with respect to the experimental values is more evident in Fig. 1. A better agreement (evidently with different C_i for each class) would have been possible with the inclusion of the variation of the on-site elements due to the lowering of the symmetry by crystal-field effects.[9]

In order to have more confidence in the *ansatz* we introduced, we now calculate the dielectric susceptibility of the compounds considered using the values of the λ_c constants determined above. According to the approximate perturbative scheme of Ref. 5, the linear dielectric susceptibility χ can be recast for a uniform static electric field applied in the z direction to a covalent periodic solid as (in Ry atomic units)

$$\chi = \frac{4}{\Omega} \sum_{\mathbf{k}} \sum_{n,n'} \left[\theta(n\mathbf{k}) - \theta(n'\mathbf{k}) \right] \frac{|\langle n\mathbf{k}|z|n'\mathbf{k}\rangle|^2}{(\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}})}, \qquad (6)$$
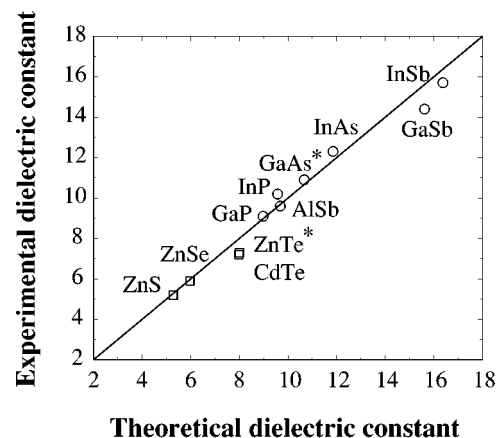

FIG. 2. Dielectric constants ϵ_∞ calculated in the ETB approach with the diagonal approximation of the position operator and the λ_c parameters discussed in the text, compared to the experimental values.[5]

where Ω is the volume of the unit cell, $|n\mathbf{k}\rangle$ and $\epsilon_{n\mathbf{k}}$ are the eigenstates and eigenvalues of the crystal Hamiltonian, and $\theta(n\mathbf{k})$ is the electronic occupation number. In order to evaluate Eq. (6), we develop the $|n\mathbf{k}\rangle$ basis functions in the ETB basis and use the λ_c constants introduced above. The high-frequency dielectric constant ϵ_∞ can then be calculated according to the relation $\epsilon_\infty = 1 + 4\pi\chi$. We used more than 3000 $\mathbf{k}$ points in the irreducible wedge of the BZ to attain a convergence of less than 1% together with the λ_c constants of Table I to calculate ϵ_∞.[17] In Fig. 2, we compare the theoretical results with the experimental values. In this case, the agreement is generally better than for the $Z^\star$, since the electronic dielectric susceptibility does not require a fit to the deformation potentials. Since the principal contribution to χ originates from the transitions to the nearly parallel bands at energies corresponding to the L_6^c and $L_{4,5}^c$ conduction states,[5] the good agreement we found is an indirect test of the quality of the sp^3s^* basis set in describing the essential conduction band features.

In conclusion, our results indicate that (i) the fitting procedure of the ETB parameters must preserve the conduction—as well as valence—bands essential features (and this is a requirement every ETB model must satisfy), (ii) the deformation potentials must be well reproduced by the scaling parameters of the transfer matrix elements of the ETB Hamiltonian (possibly by the variation of the on-site elements), and finally, (iii) for the quantities that are sensitive to the electronic wave functions, such as the piezoelectric constants, the expectation values of the operators on the wave functions can be fitted in such a way that some class-dependent constants allow a determination of the general trends of these quantities. The C_i constants we introduced above are an example of this procedure, and can be reasonably used in the calculation of the linear and nonlinear optical properties of semiconducting materials.

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[14] Strictly speaking, the constant we introduce here takes into account the polarization effects coming from the interactions among s and p orbitals of each atomic species. Two different constants in the off-diagonal matrix elements of $\mathbf{r}$ (for anion and cation s and p orbitals) could be equivalently introduced, and possibly fitted as described in the text. This would, however, introduce further parameters in the fitting procedure with a corresponding loss of simplicity.

[15] This can be shown by remembering that the hybrids h_1 and h_2, centered on the cation and anion sites and oriented in the $[111]$ and $[1\bar{1}\bar{1}]$ directions, respectively, an be written in the sp^3s^* basis set as

$$|h_1\rangle = \frac{1}{\sqrt{5}}[|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle + |s^*\rangle],$$

$$|h_2\rangle = \frac{1}{\sqrt{5}}[|s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle + |s^*\rangle].$$

Moreover, the expectation value of the component of z of $\mathbf{r}$ on bonding and antibonding states is proportional to $\langle h_1|z|h_1\rangle - \langle h_2|z|h_2\rangle$[5] and the constant λ_c multiples $a/4[1,1,1]$.

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