

## Role of tight-binding parameters and scaling laws on effective charges in semiconductors

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(Received 10 August 1999)

We compute the transverse effective charges for several compound semiconductors by using the empirical tight-binding model and the Berry-phase approach. We compare different parametrizations showing that a suitable tuning of the scaling laws for the radial part of the hopping parameters provides a fairly good prediction of the effective charges even with the minimal  $sp^3$  basis set. In contrast new and refined parametrizations that reproduce very well the dispersion of the conduction band at equilibrium by including  $d$  and/or  $s^*$  polarization orbitals may underestimate the effective charges. We suggest that the root of such a discrepancy may rest with the difficulty of determining the scaling laws for polarization orbital.

### I. INTRODUCTION

Very recently, Bennetto and Vanderbilt have shown how to compute the transverse effective charge of compound semiconductors in the framework of the tight binding (TB) approach and the Berry-phase scheme.<sup>1</sup> They also pointed out that the  $sp^3$  Harrison parametrization seriously underestimates the transverse charge in most of the cases.<sup>2</sup> Besides the use of a semiempirical Hamiltonian, the main further approximation of this framework comes from the representation of the position operator assumed to be diagonal in the tight-binding basis set. However, including on-site matrix elements between  $s$  and  $p$  orbitals does not seem to improve the results, nor does using a nonorthogonal basis set, as proposed by van Schilfgaarde and Harrison.<sup>3</sup>

Subsequently, Di Ventura and Fernandez<sup>4</sup> have made a similar calculation with the more refined  $sp^3s^*$  parametrization by Priester, Allan, and Lannoo.<sup>5</sup> They claim that an improvement is obtained by expanding the basis set to the excited  $s^*$  orbital and by expressing the expectation value of the position operator in terms of a constant that measures the displacement of the charge from the atomic positions.

However, still within the diagonal representation of the position operator, different results can be obtained depending on the parameter set and, in particular, on the scaling laws for the radial part in the hopping coefficient.

Actually, the dispersion relations of the electronic states strongly depend on the tight-binding parametrization (both diagonal and off diagonal). The inclusion of more distant neighbors or the expansion of the orbital basis set is known to improve the comparison of the conduction bands to the *ab initio* and the experimental data. This issue would be particularly helpful in calculating the dielectric and optical properties of the semiconductors at fixed atomic positions.

On the other hand, the scaling laws for the radial part of the off diagonal terms determine how the bands (and the eigenvectors) change with atomic displacements. The Harrison prescription used in Ref. 1, for instance, was derived by comparison to the trend with compression in the free-electron system,<sup>6</sup> but recently more accurate predictions were obtained by considering the *ab initio* deformation potentials.<sup>5</sup>

The effective charge depends both on the tight-binding

parameters and the scaling rules, since it can be obtained from the change in valence-band eigenvectors induced by one sublattice displacement. In this work we compute the effective charges for several II-VI, III-V, and IV-IV zincblende semiconductors showing that the values of the effective charges are very sensitive to the scaling laws of some two-center integrals.

It turns out that a better reproduction of the conduction bands at equilibrium, as obtained, for instance, by expanding the basis set, does not guarantee *per se* improved effective charges. On the other hand, an accurate tailoring of the scaling laws does sensibly improve the results for most semiconductors even within a minimal  $sp^3$  basis set.

### II. CALCULATION METHOD

The transverse charge  $(e_T^*)_{\alpha\gamma}$  of an atom in a crystal is a tensor that represents the variation of the total polarization  $\mathbf{P}^{TOT}$  in the  $\alpha$  direction with the displacement  $\mathbf{d}$  of the sublattice at which the atom belongs in the  $\gamma$  direction:

$$(e_T^*)_{\alpha\gamma} = \Omega \left. \frac{\partial \mathbf{P}_\alpha^{TOT}}{\partial \mathbf{d}_\gamma} \right|_{\mathbf{d}=\mathbf{0}}, \quad (1)$$

where  $\Omega$  is the unit-cell volume and  $\alpha$  and  $\gamma$  are Cartesian indices. Expression (1) can be more easily evaluated by the finite-difference method. The change in polarization due to an atom displacement  $\mathbf{d}$  is the sum of the ionic and the electronic contributions:

$$\Delta \mathbf{P}^{TOT} = \frac{Z\mathbf{d}}{\Omega} + [\mathbf{P}(\mathbf{d}) - \mathbf{P}(\mathbf{0})], \quad (2)$$

where  $Z$  is the core charge of the atom.

According to the theory of King-Smith and Vanderbilt<sup>7</sup> the electronic contribution to the polarization takes the form

$$\mathbf{P} = \frac{ie}{(2\pi)^3} \sum_n \int_{BZ} d\mathbf{k} \langle u_{n\mathbf{k}} | \nabla_{\mathbf{k}} | u_{n\mathbf{k}} \rangle, \quad (3)$$

where  $n$  runs over occupied bands and  $u_{n\mathbf{k}}$  is the periodic part of the Bloch wave functions. For sake of simplicity we

now restrict ourselves to the case of the diatomic cubic crystal. The extension to a more general case is straightforward along the lines of Ref. 7.

By considering one sublattice displacement along  $z$  and a discretization of the prismatic Brillouin zone (BZ) such as  $\mathbf{k}_\perp \equiv (k_{x_i}, k_{y_i})$  and  $k_j \equiv k_{z_j}$  with  $0 \leq j \leq J-1$ , it has been shown<sup>7</sup> that Eq. (3) becomes

$$P_z = -\frac{2e(\Delta k)^2}{(2\pi)^3} \sum_{\mathbf{k}_\perp} \Phi(k_\perp), \quad (4)$$

where  $(\Delta k)^2 \equiv (k_{x_{i+1}} - k_{x_i})(k_{y_{i+1}} - k_{y_i})$  is a small area in the  $xy$  plane, and

$$\Phi(k_\perp) \equiv \text{Im} \ln \prod_{j=0}^{J-1} \det \langle u_{m, \mathbf{k}_\perp, k_j} | u_{n, \mathbf{k}_\perp, k_{j+1}} \rangle. \quad (5)$$

Here

$$u_{n, \mathbf{k}_\perp, k_j} \equiv u_{n, \mathbf{k}_\perp, k_0} e^{-i\mathbf{G}_\parallel \cdot \mathbf{r}} \quad (6)$$

satisfies the periodic boundary condition with  $\mathbf{G}_\parallel = (2\pi/a)\hat{\mathbf{z}}$ , where  $a$  is the lattice parameter.

In the orthogonal tight-binding approach the periodic part of the electronic wave function is written as

$$u_{n, \mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{k} \cdot \mathbf{r}} \sum_{i\alpha} C_{i\alpha}^n(\mathbf{k}) \psi_{i\alpha, \mathbf{k}}(\mathbf{r}) \quad (7)$$

and the basis set  $\{\psi_{i\alpha, \mathbf{k}}\}$  is generated by a combination of orthogonal, localized orbitals  $\varphi_{i\alpha}(\mathbf{r} - \mathbf{R} - \mathbf{x}_i) \equiv |i\alpha\mathbf{R}\rangle$ :

$$\psi_{i\alpha, \mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot (\mathbf{R} + \mathbf{x}_i)} \varphi_{i\alpha}(\mathbf{r} - \mathbf{R} - \mathbf{x}_i). \quad (8)$$

$\mathbf{R}$  runs over the  $N$  Bravais vectors,  $\mathbf{x}_i$  are the atomic positions inside the unit cell, and  $\alpha$  is the orbital symmetry. The coefficients  $C_{i\alpha}^n(\mathbf{k})$  are the solutions of the eigenvalue equation

$$\sum_{l\beta} [H_{i\alpha, l\beta}(\mathbf{k}) - E_n(\mathbf{k}) \delta_{i\alpha, l\beta}] C_{l\beta}^n(\mathbf{k}) = 0, \quad (9)$$

where  $E_n(\mathbf{k})$  are the electronic band energies, and the Hamiltonian matrix elements  $H_{i\alpha, l\beta}(\mathbf{k})$  are

$$H_{i\alpha, l\beta}(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{x}_i + \mathbf{x}_l)} \langle i\alpha\mathbf{0} | H(\mathbf{R} - \mathbf{x}_i + \mathbf{x}_l) | l\beta\mathbf{R} \rangle. \quad (10)$$

From Eqs. (7) and (8) with  $\mathbf{k}_j \equiv (\mathbf{k}_\perp, k_j)$ , the matrix element in Eq. (5) becomes

$$\begin{aligned} \langle u_{m, \mathbf{k}_{j-1}} | u_{n, \mathbf{k}_j} \rangle &= \frac{1}{N} \sum_{l\beta\mathbf{R}'} C_{l\beta}^{m*}(\mathbf{k}_{j-1}) \sum_{i\alpha\mathbf{R}} C_{i\alpha}^n(\mathbf{k}_j) \\ &\times \langle l\beta\mathbf{R}' | e^{i\mathbf{k}_j \cdot (\mathbf{R} + \mathbf{x}_i - \mathbf{r}) - i\mathbf{k}_{j-1} \cdot (\mathbf{R}' + \mathbf{x}_l - \mathbf{r})} | i\alpha\mathbf{R} \rangle. \end{aligned} \quad (11)$$

As proposed in Ref. 1 we assume the position operator to be diagonal on the atomic basis set, i.e.,

TABLE I. Scaling law parameters  $n_{ll'm}$  of the hopping terms as proposed by Harrison (Harr.) (Ref. 2), Priestler, Allan, and Lannoo (PAL) (Ref. 5), and present work (PW).

$n_{ll'm}$	Harr.	PAL	PW
$ss\sigma$	2.0	3.76	3.5
$sp\sigma$	2.0	2.0	3.0
$pp\sigma$	2.0	1.98	2.0
$pp\pi$	2.0	2.16	2.5
$s^*p$	-	2.0	(2.0)

$$\begin{aligned} \langle \varphi_{i\alpha}(\mathbf{r} - \mathbf{R} - \mathbf{x}_i) | e^{i\mathbf{k} \cdot \mathbf{r}} | \varphi_{l\beta}(\mathbf{r} - \mathbf{R}' - \mathbf{x}_l) \rangle \\ = e^{i\mathbf{k} \cdot (\mathbf{R} + \mathbf{x}_i)} \delta_{i\alpha l\beta} \delta_{\mathbf{R}' \mathbf{R}}, \end{aligned} \quad (12)$$

which implies

$$\langle u_{m, \mathbf{k}_j} | u_{n, \mathbf{k}_{j+1}} \rangle = \sum_{i\alpha} C_{i\alpha}^{m*}(\mathbf{k}_{j-1}) C_{i\alpha}^n(\mathbf{k}_j) \quad (13)$$

for  $0 \leq j < J-1$  and

$$\langle u_{m, \mathbf{k}_{j-1}} | u_{n, \mathbf{k}_j} \rangle = \sum_{i\alpha} C_{i\alpha}^{m*}(\mathbf{k}_{j-1}) C_{i\alpha}^n(\mathbf{k}_0) e^{-i\mathbf{G}_\parallel \cdot \mathbf{x}_i} \quad (14)$$

for  $j=J-1$ . The eigenvectors  $C$  involved in the previous equations are determined by the choice of the Hamiltonian matrix elements in Eq. (10). The diagonal elements represent the orbital energies of the isolated atom modified by orthogonalization process and by the crystal field. Off-diagonal elements do not vanish only if  $|\mathbf{R} - \mathbf{x}_i + \mathbf{x}_l|$  is smaller than the maximum interaction distance. Slater and Koster<sup>8</sup> have shown that  $\langle i\alpha\mathbf{0} | H | l\beta\mathbf{R} \rangle$  can be decomposed in terms of the direction cosines of  $\mathbf{R} - \mathbf{x}_i + \mathbf{x}_l$  by a small number of two-center integrals (hoppings)  $V_{ll'm}$ , where the indices  $ll'$  indicate the symmetry of the orbitals  $\alpha$  and  $\beta$  and  $m$  the angular momentum components along the common axes ( $\sigma$  or  $\pi$ ), respectively. According to Ref. 8 the diagonal elements and the two-center integrals at the equilibrium atomic positions can be fitted to the *ab initio* electronic bands.

In the empirical tight-binding scheme the hoppings  $V_{ll'm}$ , fitted on the equilibrium band structure, are then assumed to scale with the interatomic distance following a suitable decaying function. By comparing the band dispersion obtained from tight-binding and from free-electron theory, Froyeu and Harrison<sup>6</sup> proposed a simple power law for  $V_{ll'm}$ , such as

$$V_{ll'm}(r) = V_{ll'm}(r_0) \left( \frac{r_0}{r} \right)^{n_{ll'm}}, \quad (15)$$

where  $r_0$  are the equilibrium distances and the exponents  $n_{ll'm}$  are all equal to 2.

However, more refined fittings of the scaling laws can be exploited, where  $n_{ll'm}$  do depend on the orbital symmetry. Some recent parametrizations<sup>5,9</sup> are reported in Tables I and II. In the following we will show how the choice of  $n_{ll'm}$  and of  $V_{ll'm}(r_0)$  independently affect the values of the effective charges.

TABLE II. Scaling low parameters  $n_{ll'm}$  of the hopping terms, as proposed by Jancu *et al.* (Ref. 9) for some prototypical III-V compounds.

$n_{ll'm}$	InP	GaAs	AlSb	GaSb
$ss\sigma$	3.113	3.640	3.245	4.041
$sp\sigma$	3.582	3.582	3.702	3.644
$pp\sigma$	1.825	2.045	1.763	1.524
$pp\pi$	4.153	4.126	4.152	4.203
$sd\sigma$	1.993	1.954	1.721	1.799
$s^*p\sigma$	1.692	1.712	1.772	1.770
$pd\sigma$	1.772	1.827	1.797	1.753
$pd\pi$	1.732	1.651	1.557	1.642

### III. RESULTS

In our calculations we choose as unit cell the conventional cubic cell containing 8 atoms. The BZ integration is performed by Monkhorst and Pack mesh<sup>10</sup> of  $16 \times 16$  points in the  $\mathbf{k}_\perp$  plane and on a string of 48 points along  $k_z$ . We displaced the cations by  $10^{-3}$  Å in the  $z$  direction inducing a change in the  $P_z$  component only. Such a mesh reproduces the results of Bennetto and Vanderbilt<sup>1</sup> up to the second decimal digit either for cation or anion displacements. Convergence to the first digit is already found for a  $\mathbf{k}_\perp$  mesh of  $4 \times 4$  and 8 points along  $k_z$ . Since Bennetto and Vanderbilt<sup>1</sup> have shown that the  $sp^3$  “universal” Harrison parametrization<sup>2,6</sup> systematically underestimates the effective charges, we first compared effective charges for four prototypical III-V compounds (GaAs, AlSb, InP, and GaSb) as produced by the Harrison parametrization and by the two very recent and performing parametrizations proposed by Priester *et al.*<sup>5</sup> and Jancu *et al.*<sup>9</sup>

The parametrization by Priester *et al.* is grounded on a  $sp^3s^*$  basis set and it is nearly identical to that one proposed by Vogl *et al.*<sup>9</sup> but for the scaling laws. The extended basis was introduced to obtain a good reproduction of both the valence and the conduction bands at equilibrium in a first-neighbor approximation. The  $s^*$  orbital couples only to  $p$  states; this interaction shifts down the  $p$  antibonding states providing for a better reproduction of the indirect gap with respect to the simple  $sp^3$  basis set. The dependence of the radial part of the hoppings on the interatomic distance (i.e.,  $n_{ss\sigma}$ ,  $n_{pp\sigma}$ , and  $n_{pp\pi}$ ) have been fitted by Priester *et al.*<sup>5</sup> to reproduce a good variation of the band gap with hydrostatic pressure only, so that the performance of the parametrization for internal deformations in the unit cell is not included in the fitting. The orbital-dependent exponents  $n_{ll'm}$  are given in Table I.

A more accurate and complete fitting procedure of both parameters and exponents has been performed very recently by Jancu *et al.*<sup>9</sup> by including the  $d$  polarization orbitals, which provide a very good fitting of the two lowest conduction bands and by fitting also the uniaxial deformation potentials. In this work an extended  $sp^3d^5s^*$  basis set has been used and a careful fitting on the *ab initio* bands at equilibrium (both valence and conduction) is obtained by using as starting values of the hoppings the ones provided by a symmetry analysis of free electron and TB bands. The differences between the on-site energies agree with the free-atom

TABLE III. Effective transverse charge in atomic units calculated with Harrison,<sup>1,2</sup> Priester, Allan, Lannoo,<sup>5</sup> and Jancu *et al.*<sup>9</sup> models, compared to experimental values.

Compound	Expt.	Harr.	PAL	Jancu
GaAs	2.16	1.73	1.49	1.38
AlSb	1.93	1.48	1.17	1.99
InP	2.55	2.26	2.16	1.75
GaSb	2.15	1.41	1.10	1.43

values, except for the excited  $d$  levels, pushed at higher energies by the orthogonalization procedure. The scaling laws are determined by comparing to deformation potentials of several band positions at  $\Gamma$ ,  $X$ , and  $L$ , including the uniaxial deformation. Still the ansatz  $n_{ss^*\sigma} = n_{s^*s^*} = 0$  and  $n_{dd\sigma} = n_{dd\pi} = n_{dd\delta} = n_{s^*d\sigma} = 2$  has been taken in order to simplify the fitting procedure and because of the lack in reliable informations on high-energy bands. The other exponents are reported in Table II. The localized charge density around the nuclei provided by the mostly localized orbital set has been considered responsible for the steepest distance dependence of these integrals with respect to the other exponent.

Both Priester *et al.*<sup>5</sup> and Jancu *et al.*<sup>9</sup> parametrizations have been generated including the spin-orbit coupling. However, we found that this feature has little influence on the estimate of the effective charges. In fact the errors due to the neglect of the spin-orbit coupling turns out to be 1–2%. For sake of comparison to other TB parametrizations, we report in Table III the effective charges calculated with the TB parametrization of Priester *et al.* and Jancu *et al.* without spin-orbit coupling.

As shown in Table III the parametrization of Priester *et al.* predicts effective charges by far lower than the experimental values,<sup>12</sup> even lower than those given by the Harrison  $sp^3$  parametrization. Conversely, the parametrization of Jancu *et al.* provides a very good result for AlSb, but still sizably underestimates the effective charges of the other compounds. These results suggest that the expansion of the basis set, a very good reproduction of the valence and lowest conduction bands, and a satisfactory fitting to only few deformation potentials do not guarantee *per se* a reliable estimate of the effective charges. Obviously, a better result would have been obtained by including the effective charges themselves in the global fitting procedure, which is, however, a nonlinear process where the independent role of the different TB parameters (on site and hoppings) and the scaling laws is likely to be hidden. For this reason we tried to understand for a very limited set of paradigmatic semiconductors how much the separate effects of orbital expansion and scaling laws affect the value of the effective charges. We report in Table IV our results for GaAs, ZnSe, and SiC for different equilibrium parametrizations but the same Harrison scaling laws ( $n_{ll'm} = 2$ ). The parameters by Harrison,<sup>2</sup> Vogl *et al.*,<sup>11</sup> and Chadi and Cohen<sup>13</sup> have been used for GaAs and ZnSe and those of Harrison, Vogl *et al.*, and Robertson<sup>14</sup> for SiC.

All these parametrizations underestimate the experimental values; the simple  $sp^3$  parametrization by Chadi performs slightly better than the others. In particular, we notice that the  $e_T^*$  values obtained with the  $sp^3s^*$  basis set are always

TABLE IV. Effective transverse charge in atomic units calculated with different parametrizations, by Harrison scaling laws, and our scaling laws, compared to experimental values.

Compound	Parametrization	$e_T^*$	Harr.	PW
GaAs	Harrison ( $sp^3$ )		1.72	2.09
	Vogl <i>et al.</i> ( $sp^3s^*$ )	2.16	1.47	1.87
	Chadi ( $sp^3$ )		1.91	2.31
ZnSe	Harrison ( $sp^3$ )		1.79	2.10
	Vogl <i>et al.</i> ( $sp^3s^*$ )	2.03	0.87	1.27
	Chadi ( $sp^3$ )		1.93	2.47
SiC	Harrison ( $sp^3$ )		1.97	2.19
	Vogl <i>et al.</i> ( $sp^3s^*$ )	2.57	1.44	1.57
	Robertson ( $sp^3s^*$ )		1.57	1.73

worse than those calculated with the  $sp^3$  set. This fact confirms that the inclusion of  $s^*$  polarization orbitals generally lowers the value of  $e_T^*$ . One possible reason for such a behavior could be the contribution of polarization orbitals to the valence states, which might change sizably with sublattice displacements. In particular, it is likely that the very reasonable  $n_{ll'm}=2$  scaling law ansatz for the polarization orbitals is not suited to reproduce their actual effect on the valence states.

Getting back to a safer ground, i.e., the scaling laws for the  $sp^3$  basis set, the work of Jancu *et al.*<sup>9</sup> suggests that, in the case of orthogonal TB at first neighbors, the exponents can be much larger than the Harrison prediction. This is in agreement with the prediction of linearized muffin-tin orbital–atomic spherical approximation (LMTO-ASA) calculations in transition metals by Sluiter and Singh<sup>15</sup> and to the linear combination of atomic orbitals (LCAO) calculations for silicon by Grosso and Piermarocchi.<sup>16</sup> Since here we are just interested in understanding the trends with  $n_{ll'm}$ , we selected a set of qualitative (i.e., not fitted) scaling laws which takes into account the hierarchy among the  $n_{ll'm}$  provided by the *ab initio* calculations:  $n_{ss\sigma} > n_{sp\sigma} > n_{pp\pi} > n_{pp\sigma}$ . The exponents used in the present work (PW) are reported in Table I. The effective charges at GaAs, ZnSe, and SiC obtained with our choice (PW) of the scaling laws are reported in Table IV.

The new set of exponents systematically increases the effective charge for all the compounds and parametrizations reported in Table IV. This behavior makes the combination of our set of exponents (PW) with the  $sp^3$  Harrison parametrization the best performing choice. In fact the underestimation of the effective charges produced by the  $sp^3s^*$  parametrization is not remedied by the improved scaling laws (PW) for the  $sp^3$  basis only. In order to check if a proper tuning of the scaling laws is indeed the key ingredient for the calculation of reliable effective charges within the TB model, we compare (Table V and Fig. 1) the effective charges of several III-V and II-VI compounds as given by our set of exponents and the Harrison exponents, all within the Harrison  $sp^3$  choice of equilibrium TB parameters. Notice that a sizable improvement in the effective charges is obtained just by tuning the scaling laws for minimal and universal  $sp^3$  parametrization.

TABLE V. At given lattice spacing  $d$ , experimental transverse charges for zincblende semiconductors compared with values calculated by tight-binding model using Harrison's scaling laws (Harr.) and our choice (PW).

Compound	$d$ (Å)	Expt.	Harr.	PW
ZnSe	2.45	2.03	1.79	2.10
ZnS	2.34	2.15	1.83	2.12
ZnTe	2.64	2.00	1.73	2.07
CdTe	2.81	2.35	1.86	2.17
GaAs	2.45	2.16	1.72	2.09
GaSb	2.65	2.15	1.41	1.77
GaP	2.36	2.04	1.88	2.23
InSb	2.81	2.42	1.85	2.25
InP	2.54	2.55	2.26	2.63
SiC	1.88	2.57	1.97	2.19

#### IV. CONCLUSIONS

The importance of the scaling laws in predicting the charge transfer due to a lattice displacement, outlined in the previous section, can be also illustrated (see the Appendix) by a simple analytical calculation for a diatomic molecule with one  $s$  orbital for each atom. Assuming  $|\epsilon_1 - \epsilon_2| = 3$  eV as the difference in the on-site energies and taking  $t(r) = t_0(r_0/r)^n$  as hopping integral ( $r_0 = 2$  Å), the charge transfer due to a molecular stretching of  $10^{-3}$  Å is computed analytically as a function of  $t_0$  and  $n$ , and shown in Fig. 2. The charge transfer is clearly more sensitive to the change of the exponent  $n$  with respect to the change of the hopping parameter  $t_0$ . Concerning the choice of the basis set, one should consider that the inclusion of polarization orbitals ( $s^*$  and  $d$ ) affects the prediction of the effective charges in two ways: it modifies the hopping values for the  $sp^3$  orbitals at equilibrium,  $V_{llm}(r_0)$ , and it introduces additional scaling laws. According to our findings the former effect should be small, while the second could be larger. In particular, if the scaling laws of polarization orbitals have rather small exponents, such as those chosen by Priester *et al.* ( $n=2$ ), the effective charge turns out to be sizably underestimated. This

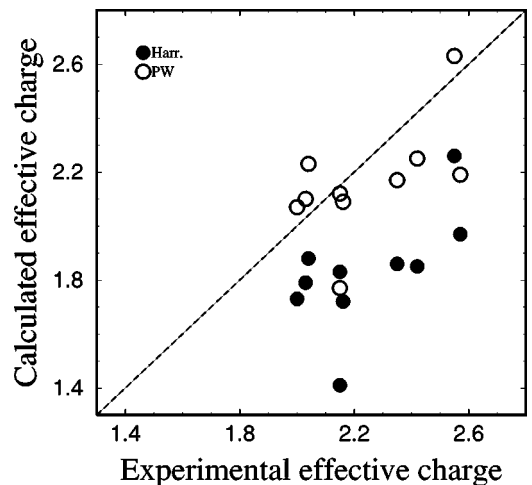


FIG. 1. Calculated effective charge with Harrison (Harr.) and our scaling laws (PW) vs experimental values.

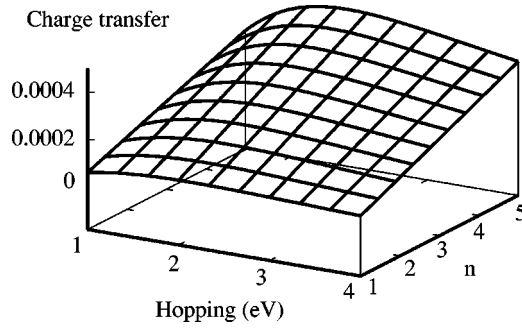


FIG. 2. Charge transfer (atomic units) in a stretched diatomic molecule as a function of the equilibrium hopping integral  $t_0$  and the exponent of the scaling law  $n$ .

drawback seems to be counterbalanced by a large value of the exponent for  $V_{sp\sigma}$ , as it happens to occur in some cases of the Jancu *et al.* parametrization. In the case of minimal  $sp^3$  basis set with large  $n_{sp\sigma}$  value, such as in the parametrization suggested in the present work, a satisfactory estimation of the effective charge is obtained. One should also consider that the diagonal approximation in Eq. (12) could perform differently for different basis sets. Unfortunately, in the TB model we have no access to the Wannier-like orbitals needed to systematically improve over the latter approximation. However, the attempt made by Bennetto and Vanderbilt to go beyond the diagonal approximation by also including matrix elements between  $s$  and  $p$  atomiclike orbitals shows that at least the first-order correction to Eq. (12) does not change the effective charges significantly. Therefore, although based on an additional ansatz [Eq. (12)], we think that a viable procedure to improve the TB parametrization might come from the simultaneous fitting of band structure at equilibrium (both valence and conduction), hydrostatic deformation potential, and effective charges. This procedure

might be simpler than the fitting of all the nonhydrostatic deformation potentials.

#### ACKNOWLEDGMENTS

We thank Marcella Iannuzzi (University of Milano-Bicocca) for technical support.

#### APPENDIX

The secular equation for a diatomic molecule is

$$\begin{pmatrix} \epsilon_1 & t \\ t & \epsilon_2 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \lambda \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}, \quad (\text{A1})$$

where  $\epsilon_i$  are the on-site energies,  $t$  is the hopping integral,  $c_i$  are the eigenvector coefficients, and  $\lambda$  is the energy eigenvalue. Solving for  $c_2$  we find

$$\|c_2\|^2 = \frac{4t^2(r)}{8t^2(r) + 2\Delta^2[1 - \sqrt{1 + 4t^2(r)/\Delta^2}]}, \quad (\text{A2})$$

where  $\Delta = |\epsilon_1 - \epsilon_2|$ . The charge transfer in atomic units,  $\Delta Q_2$ , due to a bond elongation  $\delta$  is therefore

$$\Delta Q_2 = \|c_2(r_0 + \delta)\|^2 - \|c_2(r_0)\|^2. \quad (\text{A3})$$

By considering a Taylor expansion of  $t(r)$  at the first order in the elongation  $\delta$ ,

$$t(r_0 + \delta) = t_0 \left( 1 - n \frac{\delta}{r_0} \right), \quad (\text{A4})$$

we obtain a simple expression for  $\Delta Q_2$  as a function of the exponent  $n$  of the scaling law and the hopping integral at equilibrium  $t_0$ ; the latter is shown in Fig. 2.

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