

## Optical matrix elements in tight-binding calculations

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Calculations of the optical properties of solids require knowledge of momentum matrix elements. Within the tight-binding method, these are not readily available since wave functions are expanded in an unknown basis. A popular solution to this problem is based on taking the  $\mathbf{k}$ -space gradient of the tight-binding Hamiltonian. This technique was previously claimed to be exact, but is in fact only approximate since intra-atomic contributions are omitted. We highlight the reason for this misconception. By comparison to exact results from a simple model it is demonstrated, however, that the  $\mathbf{k}$ -gradient term provides a good approximation to the interatomic contribution. Subsequently, we demonstrate that adding a  $\mathbf{k}$ -independent intra-atomic term to the momentum matrix leads to excellent agreement with exact results for momentum matrix elements and dielectric spectra.

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### I. INTRODUCTION

Tight-binding calculations of the electronic properties of solids have become increasingly popular ever since the work of Slater and Koster.<sup>1</sup> The method was originally developed as a simplified method for the description of localized  $d$ -band electronic states. It is, however, quite general provided an adequate basis set is adopted and it has been shown that even highly delocalized  $s$ - $p$  states are accurately described in the non-orthogonal version of the tight-binding scheme.<sup>2</sup> Hence, the method combines versatility and simplicity. In addition, under the assumption of transferability of the Slater-Koster parameters, the method is readily applied to systems with broken translational invariance such as low-dimensional structures and clusters.<sup>3</sup> Among the quantities, which are successfully calculated by the tight-binding approach, are elastic constants, phonon spectra, vacancy formation energy and surface energy<sup>2,4</sup> as well as cluster formation energies and magnetic moments.<sup>5</sup>

The application of tight-binding methods to optical properties of bulk materials dates back several decades. Among the earliest examples, dielectric spectra of semiconductors were calculated by Dresselhaus and Dresselhaus<sup>6</sup> and photoemission spectra of metals were calculated by Smith using a scheme combining tight-binding  $d$  orbitals and plane-wave  $s$ - $p$  orbitals.<sup>7</sup> The calculation of optical properties is considerably more complicated since momentum matrix elements (MMEs) between initial and final states in the entire first Brillouin zone are needed in addition to the band structure. In Refs. 6 and 7 this complication was circumvented by the ‘‘substitution’’  $\mathbf{p} \rightarrow (m_0/\hbar)\nabla_{\mathbf{k}}H$  ( $m_0$  being the free-electron mass) which relates the momentum operator to the Hamilton operator. Hence, once the matrix elements of  $H$  are determined from a fit to the experimental band structure or a first principles calculation, the MMEs are readily available. In Ref. 6 this substitution was introduced as an approximation whereas its usage in Ref. 7 was regarded as exact. Later work has added to this confusion. Xu<sup>8</sup> and Chang and Aspnes<sup>9</sup> derived expressions for MMEs between Bloch states in terms of MMEs between atomic states localized on the same atom (intra-atomic) or states localized on neighboring

atoms (interatomic). By exploiting symmetry arguments the number of independent parameters was greatly reduced. From a fit to an empirical pseudopotential calculation, Chang and Aspnes obtained intra-atomic MMEs for GaAs, which exceeded interatomic ones.<sup>9</sup> Quite surprisingly, a work by Lew Yan Voon and Ram-Mohan,<sup>10</sup> which was later extended by Graf and Vogl,<sup>11</sup> then claimed to provide solid proof for the substitution  $\mathbf{p} \rightarrow (m_0/\hbar)\nabla_{\mathbf{k}}H$  in tight-binding calculations. Apart from computational convenience, the consequence of such a proof would be that intra-atomic MMEs must be exactly zero, as argued by Cruz and co-workers.<sup>12</sup>

In the present paper, we aim to resolve this confusion by (i) highlighting the source of the erroneous conclusions of Refs. 10 and 11, and by (ii) providing a direct comparison of the approximate tight-binding results with exact results from a model for which an analytical solution exists. The simple one-dimensional Kronig-Penney model is applied for this purpose. As a starting point, we briefly repeat the derivation of the tight-binding MMEs following the line in Ref. 12. To this end we consider a general tight-binding eigenstate,

$$|n, \mathbf{k}\rangle = \sum_{\alpha} c_{n\alpha}(\mathbf{k}) |\alpha, \mathbf{k}\rangle; \quad |\alpha, \mathbf{k}\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} |\alpha, \mathbf{R}\rangle, \quad (1)$$

where  $\mathbf{R}$  is the lattice vector,  $N$  is the number of lattice sites, and  $|\alpha, \mathbf{R}\rangle$  is an atomic orbital centered at position  $\mathbf{R}$  and characterized by the label  $\alpha$ . This label specifies the symmetry of the orbital ( $s$ ,  $p$ , etc.) and, in the case of several atoms per unit cell, accounts for the relative position within the unit cell. For simplicity, this case will not be explicitly considered here, but all results may readily be generalized to cover this case as well. The basic assumption of Ref. 12 is that the overlap between atomic orbitals on different sites is negligibly small. In this situation, it follows that  $\langle \beta, \mathbf{R}' | \mathbf{r} | \alpha, \mathbf{R} \rangle = \{ \mathbf{R} \delta_{\alpha\beta} + \mathbf{d}_{\beta\alpha} \} \delta_{\mathbf{R}\mathbf{R}'}$ , where  $\mathbf{d}_{\beta\alpha} = \langle \beta, \mathbf{0} | \mathbf{r} | \alpha, \mathbf{0} \rangle$  is the intra-atomic contribution. These two terms, in turn, produce two contributions to the MME via the commutator relation  $\mathbf{p} = im_0/\hbar [H, \mathbf{r}]$ , i.e.,

$$\begin{aligned}
\langle n, \mathbf{k} | \mathbf{p} | m, \mathbf{k} \rangle &= \frac{im_0}{\hbar N} \sum_{\alpha, \beta} c_{n\beta}^*(\mathbf{k}) c_{m\alpha}(\mathbf{k}) \sum_{\mathbf{R}, \mathbf{R}'} e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} \\
&\times (\mathbf{R} - \mathbf{R}') (\beta, \mathbf{R}' | H | \alpha, \mathbf{R}) \\
&+ \frac{im_0}{\hbar N} \sum_{\alpha, \beta} c_{n\beta}^*(\mathbf{k}) c_{m\alpha}(\mathbf{k}) \\
&\times \sum_{\mathbf{R}, \mathbf{R}'} e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} \sum_{\gamma} \{ (\beta, \mathbf{R}' | H | \gamma, \mathbf{R}) \mathbf{d}_{\gamma\alpha} \\
&- \mathbf{d}_{\beta\gamma} (\gamma, \mathbf{R}' | H | \alpha, \mathbf{R}) \}. \quad (2)
\end{aligned}$$

By substituting  $e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} (\mathbf{R} - \mathbf{R}') = -i \nabla_{\mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')}$  and utilizing the fact that  $H |n, \mathbf{k}\rangle = E_{n, \mathbf{k}} |n, \mathbf{k}\rangle$  the relation above reduces to

$$\begin{aligned}
\langle n, \mathbf{k} | \mathbf{p} | m, \mathbf{k} \rangle &= \frac{m_0}{\hbar} \sum_{\alpha, \beta} c_{n\beta}^*(\mathbf{k}) c_{m\alpha}(\mathbf{k}) \nabla_{\mathbf{k}} \langle \beta, \mathbf{k} | H | \alpha, \mathbf{k} \rangle \\
&+ \frac{im_0}{\hbar} \{ E_{n, \mathbf{k}} - E_{m, \mathbf{k}} \} \sum_{\alpha, \beta} c_{n\beta}^*(\mathbf{k}) c_{m\alpha}(\mathbf{k}) \mathbf{d}_{\beta\alpha}. \quad (3)
\end{aligned}$$

It is the latter, intra-atomic term, which is claimed to be exactly zero in Refs. 10 and 11. It is quite clear from the above derivation that this is not the case, however. Also, if this claim were correct it would imply that all MMEs in a periodic system of well-separated atoms should vanish. This is because the gradient  $\nabla_{\mathbf{k}} \langle \beta, \mathbf{k} | H | \alpha, \mathbf{k} \rangle$  vanishes in a system of well-separated atoms due to the lacking overlap between orbitals or, equivalently, due to the perfectly flat bands obtained in this case. This clearly demonstrates that the ‘‘proofs’’ of Refs. 10 and 11 are false and it also highlights the source of the error: only interatomic transitions are treated in  $\mathbf{k}$  space in the tight-binding formalism. Hence, only these contributions to the MME are retained using the substitution  $\mathbf{p} \rightarrow (m_0/\hbar) \nabla_{\mathbf{k}} H$ . The erroneous conclusions of Refs. 10 and 11 can be traced to the implied ‘‘operator identity’’  $\mathbf{r} = -i \nabla_{\mathbf{k}}$ . While this relation clearly holds for matrix elements between basis states of the form  $|n, \mathbf{k}\rangle = e^{i\mathbf{k} \cdot \mathbf{r}} |n\rangle$ , with  $|n\rangle$  independent of  $\mathbf{k}$ , it is in fact incorrect for tight-binding basis states of the form given in Eq. (1). This is readily seen from the matrix element of the difference

$$\langle \beta, \mathbf{k} | (\mathbf{r} + i \nabla_{\mathbf{k}}) | \alpha, \mathbf{k} \rangle = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} (\beta, \mathbf{0} | (\mathbf{r} - \mathbf{R}) | \alpha, \mathbf{R}), \quad (4)$$

which does not vanish. In fact, if the separation between atoms is much greater than the spatial width of the atomic orbitals so that we may neglect all inter-atomic contributions in Eq. (4) it follows that

$$\langle \beta, \mathbf{k} | (\mathbf{r} + i \nabla_{\mathbf{k}}) | \alpha, \mathbf{k} \rangle \approx (\beta, \mathbf{0} | \mathbf{r} | \alpha, \mathbf{0}) = \mathbf{d}_{\beta\alpha}. \quad (5)$$

Hence, the missing term is precisely the intra-atomic contribution in this case. In a connected paper, Boykin<sup>13</sup> has re-derived the erroneous results of Refs. 10 and 11 by expanding of the phase-factor of the electromagnetic field  $e^{i\mathbf{q} \cdot \mathbf{r}}$  in the tight-binding basis. In Eq. (15) of this paper, however, the author incorrectly uses an argument concerning  $\mathbf{k}$ -vector

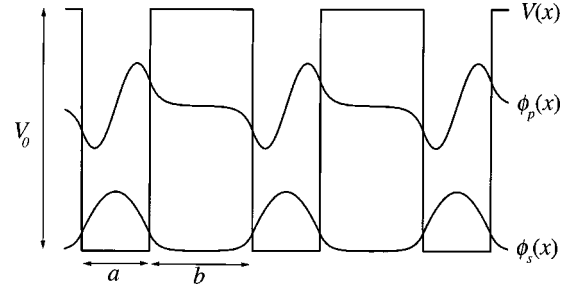


FIG. 1. The one-dimensional Kronig-Penney potential and the two lowest Bloch states.

conservation to exclude intra-atomic coupling by the field, which explains the agreement with Refs. 10 and 11.

## II. KRONIG-PENNEY MODEL AND TIGHT-BINDING APPROXIMATION

We now turn to a comparison between approximate and exact results for which we consider the one-dimensional Kronig-Penney model,<sup>14</sup> which provides quasi-analytical results for the band structure as well as MMEs. Subsequently, a two-state tight-binding description is fit to the Kronig-Penney model allowing approximate tight-binding MMEs to be derived. By comparison to the exact result, the accuracy of the  $\mathbf{p} \rightarrow (m_0/\hbar) \nabla_{\mathbf{k}} H$  substitution may then be assessed. The Kronig-Penney model is the simplest electronic model incorporating a periodic potential. It is comprised of a series of potential wells of width  $a$  separated by barriers of width  $b$  and height  $V_0$ , c.f. Fig. 1. A virtue of this simple model is that the coupling between neighboring wells can be adjusted to resemble both strong-coupling ( $b \ll a$ ) and weak-coupling ( $b \sim a$ ) situations. The band structure relating an eigenvalue  $E$  to a wave number  $k$  is obtained from the dispersion relation<sup>14</sup>

$$\cos(kL) = \cosh(k_0 b) \cos(k_1 a) + \frac{k_0^2 - k_1^2}{2k_0 k_1} \sinh(k_0 b) \sin(k_1 a), \quad (6)$$

where  $L = a + b$ ,  $\hbar k_0 = \sqrt{2m_0(V_0 - E)}$ , and  $\hbar k_1 = \sqrt{2m_0 E}$ . Throughout, we only consider the lowest and first excited band and in order to adhere to usual notation these are denoted the ‘‘s’’ and ‘‘p’’ bands, respectively. An example of these band states is shown in Fig. 1.

We now introduce the tight-binding approximation to the Kronig-Penney model. To fit the two bands we use a two-state basis formed by the ‘‘atomic’’  $s$  and  $p$  states, i.e., the two lowest eigenstates of an isolated potential well. If we restrict ourselves to interactions between nearest neighbors the two-state Hamiltonian is given by

$$\begin{aligned}
\vec{H} &= \begin{pmatrix} E_S + 2E_{SS} \cos(kL) & 2iE_{SP} \sin(kL) \\ -2iE_{SP} \sin(kL) & E_P + 2E_{PP} \cos(kL) \end{pmatrix} \\
&\equiv \begin{pmatrix} H_{SS} & iH_{SP} \\ -iH_{SP} & H_{PP} \end{pmatrix}. \quad (7)
\end{aligned}$$

Hence, neglecting the complications arising from nonorthogonal basis states, the tight-binding approximation is uniquely determined by the five parameters  $E_S$ ,  $E_P$ ,  $E_{SS}$ ,  $E_{PP}$ , and  $E_{SP}$ . By requiring an exact match to the Kronig-

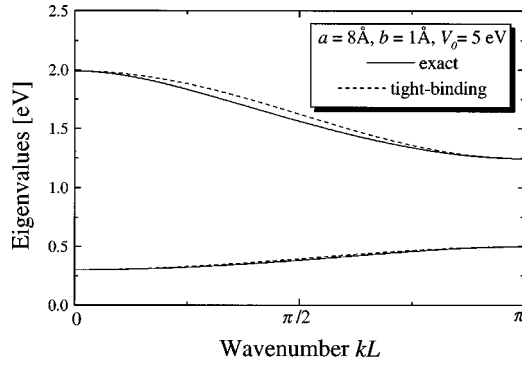


FIG. 2. The exact band structure obtained from the solution to the Kronig-Penney model (solid lines) in comparison to the fitted tight-binding approximation (dashed lines).

Penney eigenvalues at  $kL=0$  and  $kL=\pi$ , all parameters but the last are determined. Since only a single parameter is left we cannot require an exact match to both eigenvalues at, e.g.,  $kL=\pi/2$ . However, we have found that the following expression for  $E_{SP}$  approximately minimizes the total error:

$$E_{SP} = \frac{1}{4} [E_{\pi/2}^2 - E_{\pi/2}(E_S + E_P) + E_S E_P]^{1/2}, \quad (8)$$

where  $E_{\pi/2}$  is the lowest Kronig-Penney eigenvalue at  $kL = \pi/2$ . This expression corresponds to half the value needed to match  $E_{\pi/2}$  exactly. As an example of the agreement between the exact calculation and the tight-binding approximation we have plotted the two band structures in Fig. 2. The parameters used in the figure ( $a = 8 \text{ \AA}$  and  $b = 1 \text{ \AA}$ ) represent a strong-coupling case and the fit is seen to be quite satisfactory. The fit can be improved by the inclusion of overlap parameters but these are neglected here.

In order to distinguish between the different contributions to the MME we introduce the notation  $p_k = (m_0/\hbar) \partial H / \partial k$ . The matrix elements of this operator are readily obtained from the eigenvectors of the tight-binding approximation Hamiltonian Eq. (7),

$$\begin{aligned} \langle 1,k | p_k | 2,k \rangle &= \frac{-i}{(H_{SS} - E_{1,k})^2 + H_{SP}^2} \begin{pmatrix} iH_{SP} \\ H_{SS} - E_{1,k} \end{pmatrix} \\ &\times \begin{pmatrix} \frac{m_0}{\hbar} H'_{SS} & i \frac{m_0}{\hbar} H'_{SP} \\ -i \frac{m_0}{\hbar} H'_{SP} & \frac{m_0}{\hbar} H'_{PP} \end{pmatrix} \begin{pmatrix} H_{PP} - E_{2,k} \\ iH_{SP} \end{pmatrix}, \end{aligned} \quad (9)$$

where  $E_{1,k}$  and  $E_{2,k}$  are the eigenvalues and the prime designates  $\partial/\partial k$ . The eigenvectors have been chosen so as to make the result real-valued. Obviously, the MME in Eq. (9) approaches zero as the separation between potential wells is increased since  $H'_{SS}$ ,  $H'_{PP}$ , and  $H'_{SP}$  vanishes if there is no overlap between adjacent ‘‘atomic’’ orbitals.

### III. COMPARISON AND RESULTS

From the solution of the Kronig-Penney model the exact MME is available. Hence, a direct comparison between exact

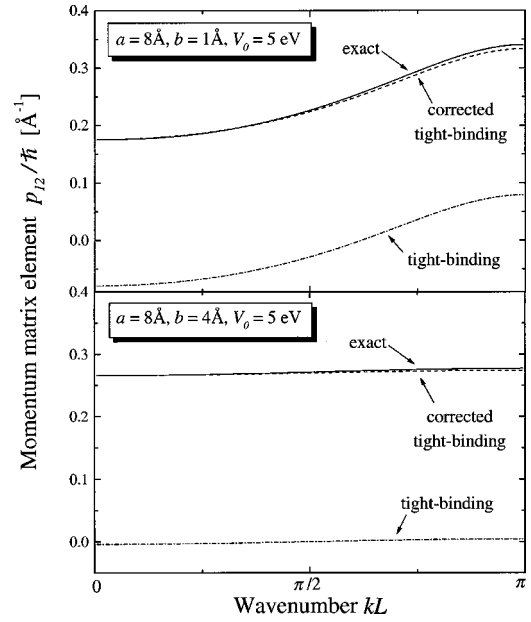


FIG. 3. Comparison between exact, tight-binding, and corrected tight-binding momentum dispersion curves. Notice the constant vertical displacement of the tight-binding curves.

and approximate results is possible. In Fig. 3 the results are shown for a strong-coupling ( $a = 8 \text{ \AA}$  and  $b = 1 \text{ \AA}$ ) case and weak-coupling ( $a = 8 \text{ \AA}$  and  $b = 4 \text{ \AA}$ ) case. The MME obtained from Eq. (9) is shown as the curve labeled ‘‘tight binding.’’ Clearly, there is a significant discrepancy with the exact result. It may be noticed that the shapes of the tight-binding curves are similar to the exact results but displaced vertically. The discrepancy is especially pronounced in the weak-coupling case. In this situation, the tight-binding MME is close to zero as expected from the above arguments. Conversely, the exact result is essentially equal to the MME obtained for an ‘‘intra-atomic’’ transition between  $s$  and  $p$  states belonging to the same potential well. Hence, the vertical displacement simply represents the omitted intra-atomic term. It is noted that the displacements in the weak- and strong-coupling cases are approximately equal in agreement with this explanation.

A much better approximation to the exact MME may be obtained by explicitly adding an intra-atomic contribution to the momentum operator. In fact, Eq. (3) shows that the intra-atomic correction has an explicit  $k$  dependence due to the presence of the factor  $E_{n,k} - E_{m,k}$ . For simplicity, however, we neglect this dependence and simply add a  $k$ -independent term to the momentum matrix. With this modification the matrix element reads

$$\begin{aligned} p_{12}(k) &= \frac{-i}{(H_{SS} - E_{1,k})^2 + H_{SP}^2} \begin{pmatrix} iH_{SP} \\ H_{SS} - E_{1,k} \end{pmatrix} \\ &\times \begin{pmatrix} \frac{m_0}{\hbar} H'_{SS} & i \frac{m_0}{\hbar} H'_{SP} - iP_{SP} \\ -i \frac{m_0}{\hbar} H'_{SP} + iP_{SP} & \frac{m_0}{\hbar} H'_{PP} \end{pmatrix} \begin{pmatrix} H_{PP} - E_{2,k} \\ iH_{SP} \end{pmatrix} \\ &= \langle 1,k | p_k | 2,k \rangle + \frac{H_{SP}^2 - (H_{SS} - E_{1,k})^2}{H_{SP}^2 + (H_{SS} - E_{1,k})^2} P_{SP}. \end{aligned} \quad (10)$$

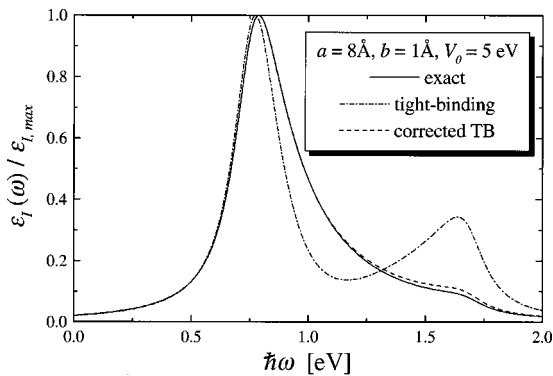


FIG. 4. Normalized spectra of the imaginary part of the dielectric constant for the three different models. The example illustrates the case of strong coupling between neighboring potential wells.

We adjust  $P_{SP}$  by fitting to the exact MME at  $kL=0$ . The curves obtained in this way are shown as the dashed ones labeled “corrected tight-binding” in Fig. 3. The agreement with the exact results is improved dramatically. In fact, overall errors are now generally less than a few percent. The error is slightly larger if extreme strong-coupling cases are considered and, conversely, the error is essentially zero in the weak-coupling regime. Hence, by adding an intra-atomic contribution, a reliable tight-binding scheme for calculations of optical properties is obtained. It should be noted that this modification amounts to introducing a single  $k$ -independent number. Hence, the added complication of the corrected model is not a serious one.

As a demonstration of the implications for actual calculations of optical properties we turn to the dielectric response. We assume that the Kronig-Penney model describes a semiconductor electronic system with the lower and upper bands filled and empty, respectively. As the model is one-dimensional the results apply immediately to simplistic calculations for, e.g., quantum wires with a periodic potential along the direction of the wire. We expect the trends to be generally valid, however. For simplicity, we limit our study to the imaginary part of the dielectric constant given by

$$\epsilon_I(\omega) = C \int_{-\pi/L}^{\pi/L} \frac{|p_{12}(k)|^2}{\{(E_{21}(k) - \hbar\omega)^2 + (\hbar\gamma)^2\} E_{21}^2(k)} dk, \quad (11)$$

where  $E_{21}(k) = E_{2,k} - E_{1,k}$ ,  $\hbar\gamma = 0.1 \text{ eV}$  is the linewidth and

$C$  is a material dependent constant. In Fig. 4 a comparison between exact, tight-binding and corrected tight-binding spectra is shown. As expected, the agreement between the exact and corrected tight-binding curves is excellent. The characteristic broadened square-root singularity around the band-gap energy is seen in all three curves. When normalized by the maximum value, the dielectric spectra all agree in this spectral range since the peak position is solely determined by the band gap. At higher photon energies, however, the uncorrected tight-binding curve deviates significantly from the exact result. This is a consequence of the incorrect momentum dispersion curve. At this point we wish to stress that the uncorrected tight-binding calculation may, in fact, be a reasonable approximation for real solids provided interatomic coupling is sufficiently strong that interatomic transitions are the dominating ones. As an example, the present authors have found the uncorrected tight-binding method to be in reasonable agreement with a pseudopotential calculation for Si. This agrees with Ref. 12, in which the intra-atomic term was found to contribute only 25% to the absorption in porous Si. Generally, the intra-atomic contribution is expected to be less important for transitions between ( $s, p$ ) bands than for transitions involving  $d$  bands due to the localized nature of the atomic  $d$  orbitals.

#### IV. CONCLUSION

In this paper, the question of how momentum matrix elements (MMEs) are obtained in tight-binding calculations is addressed. It is stressed that the substitution  $\mathbf{p} \rightarrow (m_0/\hbar)\nabla_{\mathbf{k}}H$  for the momentum operator is generally invalid since it completely neglects intra-atomic transitions. In order to judge the error, we have compared exact MMEs obtained from a one-dimensional Kronig-Penney model to matrix elements of  $(m_0/\hbar)\nabla_{\mathbf{k}}H$  calculated within the tight-binding approximation. In this manner, it is demonstrated that a significant error is introduced by omitting the intra-atomic contribution. The discrepancy increases with the separation between neighboring potential wells since this leads to an increasingly dominating intra-atomic contribution. We find, however, that by adding a  $k$ -independent intra-atomic term to the momentum matrix, agreement with the exact results is restored. This correction should generally improve tight-binding calculations of the optical properties of real solids.

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