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Relation between the interband dipole and momentum matrix elements in semiconductors

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It is shown that a frequently used relation between the interband momentum and dipole matrix elements (shortened to the "*p*-*r* relation") in semiconductors acquires an additional correction term if applied to finite-volume crystals treated with periodic boundary conditions. The correction term, which is a generalization of the one obtained by Yafet [Phys. Rev. **106**, 679 (1957)] for infinite crystals, does not vanish in the limit of infinite volume. We illustrate this with numerical examples for bulk GaAs and GaAs superlattices. The persistence of the correction term is traced to the subtle nature of the dipole matrix element with spatially extended wave functions. In contrast, a straightforward application of the findings by Blount [Solid State Phys. **13**, 305 (1962)] and Haug [*Theoretical Solid State Physics* (Pergamon, Oxford, 1972)] yields the usual *p*-*r* relation in the distribution sense, without any corrections, when Bloch wave functions normalized to delta functions in crystal momentum space are used. Our findings therefore show that, for the interband dipole matrix element, using Bloch wave functions under periodic boundary conditions is not the proper way to approach the infinite-volume limit. From our numerical evaluations, we find that the correction term is large in the case of interband transitions in bulk GaAs, and that it can be chosen to be small in the case of intersubband transitions in superlattices, which are important in the context of terahertz (THz) radiation. We also show that one can interpret the infinite-volume *p*-*r* relation in terms of a limiting procedure using progressively broadened wave packet states that approach delta-normalized Bloch wave functions. Finally, we discuss the *p*-*r* relation for nanostructures in the envelope function approximation and show that the cell-envelope factorization of the nanostructure dipole matrix element into a cell-matrix element and an envelope overlap integral involves the cell gradient-*k* rather than the cell dipole matrix element.

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I. INTRODUCTION

Dipole-allowed optical transitions can be characterized in terms of their dipole matrix elements or in terms of their momentum matrix elements. The use of the dipole matrix element has some practical advantages: (i) It facilitates the comparison with models of classical dipole oscillators and (ii) it provides immediate information on the approximate spatial extension of the oscillator (after dividing the dipole matrix element by the electron charge). Using the dipole matrix element is unproblematic in atomic and molecular optical transitions, where the wavelength of the light far exceeds the spatial extension of the atom and the electric field is effectively space independent. In that (atomic) case, the electron-light coupling Hamiltonian can be chosen in the form of the dipole approximation $-\mathbf{d}\cdot\mathbf{E}$ (where $\mathbf{d}=-e\mathbf{r}$ is the dipole operator, $-e$ the electron charge, and $\mathbf{E}$ the electric field amplitude), which has been found to be the proper physical choice of the coupling in the sense that the unperturbed atomic Hamiltonian represents a form-invariant physical quantity (see Ref. 1, Chap. 5.A.2, and references therein to the original literature). Of course, in general the light-matter coupling is based on the minimal coupling Hamiltonian that involves the $\mathbf{A}\cdot\hat{\mathbf{p}}$ term (where $\hat{\mathbf{p}}=-i\hbar\vec{\nabla}$ is the momentum operator and $\mathbf{A}$ the vector potential). In atoms, the matrix elements of $\mathbf{d}$ (or, equivalently, $\mathbf{r}$) and $\hat{\mathbf{p}}$ are related by the well-known relation

$$\hat{\mathbf{p}}=\frac{im}{\hbar}[H_0,\mathbf{r}]_-, \tag{1}$$

where the unperturbed Hamiltonian includes the static Coulomb interaction $V(\mathbf{r})$ between the electron and the atomic core, $H_0=\frac{\hat{\mathbf{p}}^2}{2m}+V(\mathbf{r})$. The matrix elements between, say, states $|1\rangle$ and $|2\rangle$, which are spatially restricted to the size of the atom, are then given by

$$\langle 2|\hat{\mathbf{p}}|1\rangle=\frac{im}{\hbar}(\epsilon_2-\epsilon_1)\langle 2|\mathbf{r}|1\rangle. \tag{2}$$

Since the time derivative of the position operator is given by $\dot{\mathbf{r}}=\frac{i}{\hbar}[H_0,\mathbf{r}]_-$ (or, equivalently, $\hat{\mathbf{p}}=m\dot{\mathbf{r}}$), Eq. (2) is sometimes seen as quantum mechanical analog to the classical relation between momentum and velocity, $\mathbf{p}=m\dot{\mathbf{r}}$ [with the time derivative approximately replaced by $i\omega\simeq i(\epsilon_2-\epsilon_1)/\hbar$]. Throughout this paper, we will refer to the relation given in Eq. (2), and all its generalizations, as *p*-*r* relations.

We recall, for later reference, that, while the operator relation Eq. (1) holds at each point in $\mathbf{r}$ space, deriving the *p*-*r* relation [Eq. (2)] includes the step that invokes $\langle 2|H_0=\langle 2|\epsilon_2$, which is valid because H_0 is Hermitian. In more algebraic detail, integrations by parts are carried out in the matrix element $\langle 2|H_0\mathbf{r}|1\rangle$, and the surface terms are shown to vanish.

The dipole approximation, in particular, the transition Hamiltonian $e\mathbf{r}\cdot\mathbf{E}$, is also routinely applied in calculations of interband transitions in solid state systems such as semiconductors (including bulk semiconductors, quantum wells, quantum wires, quantum dots), even though the spatial extents of the electron energy eigenstates of crystalline solids are not small compared to the typical wavelength of the radiation field. A common justification for using the dipole approximation here is that, for interband transitions, the proper length scale to compare with the wavelength is the size of the unit cell. Nevertheless, it is also known that evaluating the dipole matrix elements of Bloch wave functions, and thus deriving *p-r* relations analogous to Eq. (2), are conceptually nontrivial. We will point out below that, despite having been discussed in the literature for decades, some issues surrounding the *p-r* relations in semiconductors are still not satisfactorily resolved. The purpose of this paper is to clarify these issues.

We will use both Bloch wave functions defined over the infinite space domain and those defined in a box with periodic boundary conditions. It will facilitate our discussions to fix our notations for these wave functions here. An infinite-volume Bloch wave function is denoted by $\varphi^{(\infty)}_{\nu\mathbf{k}}(\mathbf{r})=\frac{1}{(2\pi)^{3/2}}e^{i\mathbf{k}\cdot\mathbf{r}}u_{\nu\mathbf{k}}(\mathbf{r})$, where $u_{\nu\mathbf{k}}(\mathbf{r})$ is the lattice-periodic part, ν is the band index, and the superscript "∞" indicates that the wave function is defined over an infinite volume. These Bloch waves are normalized to delta functions in $\mathbf{k}$ space. A popular way of avoiding distributions is the use of periodic boundary conditions (PBCs) which allows one to work with a finite volume υ, yet keeping the benefits of Bloch's theorem. These Bloch waves are denoted by $\varphi^{(\mathrm{vol})}_{\nu\mathbf{k}}(\mathbf{r})=\frac{1}{\sqrt{\upsilon}}e^{i\mathbf{k}\cdot\mathbf{r}}u_{\nu\mathbf{k}}(\mathbf{r})$. They are normalized to the volume, and the wave vectors are discrete. Throughout this paper, we use the following definitions for expectation values of an operator $\hat{O}$,

$$\langle u_{c\mathbf{k}'}|\hat{O}|u_{\mathrm{v}\mathbf{k}}\rangle_{\mathrm{cell}}=\frac{1}{\upsilon_c}\int_{\mathrm{cell}}d^3r\,u^*_{c\mathbf{k}'}(\mathbf{r})\hat{O}u_{\mathrm{v}\mathbf{k}}(\mathbf{r}),\tag{3}$$

$$\langle c\mathbf{k}'|\hat{O}|\mathrm{v}\mathbf{k}\rangle_{\mathrm{vol}}=\int_{\upsilon}d^3r\,\varphi^{(\mathrm{vol})*}_{c\mathbf{k}'}(\mathbf{r})\hat{O}\varphi^{(\mathrm{vol})}_{\mathrm{v}\mathbf{k}}(\mathbf{r}),\tag{4}$$

$$\langle c\mathbf{k}'|\hat{O}|\mathrm{v}\mathbf{k}\rangle_{\infty}=\int_{\substack{\mathrm{all}\\\mathrm{space}}}d^3r\,\varphi^{(\infty)*}_{c\mathbf{k}'}(\mathbf{r})\hat{O}\varphi^{(\infty)}_{\mathrm{v}\mathbf{k}}(\mathbf{r}),\tag{5}$$

and

$$\omega_{c\mathbf{k}',\mathrm{v}\mathbf{k}}=(\varepsilon_{c\mathbf{k}'}-\varepsilon_{\mathrm{v}\mathbf{k}})/\hbar.\tag{6}$$

Here, the subscript c denotes the conduction band, the subscript v the valence band, and υ_c is the cell volume.

We start by briefly recounting some previous discussions of the *p-r* relation in crystalline solids. Discussing the atomic version of the *p-r* relations, Haug noted on p. 370 of his book *Theoretical Solid State Physics*[2] that "the assumption [underlying the *p-r* relation] is that the eigenfunctions from which the matrix elements are formed decrease sharply enough, which is guaranteed in the exponential decrease of the atomic functions." Martin points out that electric polarization in crystals "cannot solely be derived in terms of the charge density in a unit cell"[3] and derives an additional surface term (he, however, did not consider the interband matrix elements or a *p-r* relation). Burt considers quantum wells[4] and notices that the dipole matrix element taken with a unit-cell integral depends on the choice of the unit cell, and hence cannot have any direct physical significance. Using $k\cdot p$ theory, he derives a *p-r* relation that involves the momentum matrix element reduced to the unit cell, but the matrix element of the dipole is still taken over the whole quantum well. Resta (see Ref. 5 and references therein) notes that, while $\varphi^{(\mathrm{vol})}_{\nu\mathbf{k}}(\mathbf{r})$ is υ periodic (meaning it obeys PBCs), the same is not true for the function $\mathbf{r}\varphi^{(\mathrm{vol})}_{\nu\mathbf{k}}(\mathbf{r})$. Combescot and Betbeder-Matibet[6] note that "the change from $\mathbf{A}\cdot\mathbf{p}$ to $\mathbf{E}\cdot\mathbf{d}$ relies on an integration by parts which is only valid for wave functions canceling at infinity, as in the case of atomic systems, but not for solids with lattice periodicity."

For Bloch wave functions in the infinite lattice, *p-r* relations involving matrix elements of the lattice-periodic parts $u_{\nu\mathbf{k}}(\mathbf{r})$ have been worked out in detail. Adams[7] derived a relation between the momentum matrix element (more precisely, the velocity matrix element in the presence of spin-orbit coupling) and that of $i\vec{\nabla}_{\mathbf{k}}$,

$$\langle u_{c\mathbf{k}}|\hat{\mathbf{p}}|u_{\mathrm{v}\mathbf{k}}\rangle_{\mathrm{cell}}=im\omega_{c\mathbf{k},\mathrm{v}\mathbf{k}}\langle u_{c\mathbf{k}}|i\vec{\nabla}_{\mathbf{k}}|u_{\mathrm{v}\mathbf{k}}\rangle_{\mathrm{cell}},\tag{7}$$

and Yafet[8] derives a *p-r* relation for matrix elements that are diagonal in $\mathbf{k}$,

$$\langle u_{c\mathbf{k}}|\hat{\mathbf{p}}|u_{\mathrm{v}\mathbf{k}}\rangle_{\mathrm{cell}}=im\omega_{c\mathbf{k},\mathrm{v}\mathbf{k}}\langle u_{c\mathbf{k}}|\mathbf{r}|u_{\mathrm{v}\mathbf{k}}\rangle_{\mathrm{cell}}+\mathbf{B}_{c\mathrm{v}}(\mathbf{k}),\tag{8}$$

where the additional correction term $\mathbf{B}_{c\mathrm{v}}(\mathbf{k})$ is given as a surface integral over the unit cell [see Eq. (14) in Ref. 8 and Eq. (2.15) in Ref. 9]. Blount[10] showed that the dipole matrix element evaluated over the whole volume is a $\mathbf{k}$-space distribution (delta function) multiplied by the matrix element of $i\vec{\nabla}_{\mathbf{k}}$ taken over the unit cell. He derived a Bloch space (i.e., $|\nu,\mathbf{k}\rangle_\infty$) representation of the $\mathbf{r}$ operator (using our notation),

$$\mathbf{r}=\sum_{\nu\nu'}\int_{BZ}d^3kd^3k'|\nu'\mathbf{k}'\rangle\langle\nu'\mathbf{k}'|\mathbf{r}|\nu\mathbf{k}\rangle\langle\nu,\mathbf{k}|,\tag{9}$$

where all states are understood to carry the subscript ∞. The matrix elements are

$$\begin{aligned}\langle\nu'\mathbf{k}'|\mathbf{r}|\nu\mathbf{k}\rangle_\infty=&-i\vec{\nabla}_{\mathbf{k}}\langle\nu'\mathbf{k}'|\nu\mathbf{k}\rangle_\infty\\&+\delta(\mathbf{k}-\mathbf{k}')\langle u_{\nu'\mathbf{k}'}|i\vec{\nabla}_{\mathbf{k}}|u_{\nu\mathbf{k}}\rangle_{\mathrm{cell}}.\end{aligned}\tag{10}$$

Blount discussed conditions under which the delta function in the first term, $\langle\nu'\mathbf{k}'|\nu\mathbf{k}\rangle_\infty=\delta(\mathbf{k}-\mathbf{k}')\delta_{\nu,\nu'}$, can be integrated by parts (over $\mathbf{k}$) without surface (in $\mathbf{k}$-space) terms, i.e., resulting in $\delta(\mathbf{k}-\mathbf{k}')i\vec{\nabla}_{\mathbf{k}}\delta_{\nu,\nu'}$ (in which case the the intraband term is indeed diagonal in both the band indices and the wave vector). For a general wave function (e.g., Refs. 10 and 11) $|\psi\rangle=\sum_\nu\int d^3kc_{\nu\mathbf{k}}|\nu\mathbf{k}\rangle$ the $\mathbf{r}$ operator acting on the coefficients $c_{\nu\mathbf{k}}$ is given by $\mathbf{r}=\delta_{\nu,\nu'}i\vec{\nabla}_{\mathbf{k}}+\langle u_{\nu'\mathbf{k}'}|i\vec{\nabla}_{\mathbf{k}}|u_{\nu\mathbf{k}}\rangle_{\mathrm{cell}}$, which is the standard form widely used not only in optics but also transport theory including in the theory of the anomalous Hall effect and related topics (see, for example, Ref. 12 and, for a recent review of the anomalous Hall effect, Ref. 13, and references therein). As mentioned in Ref. 13, it is sometimes worth remembering that the Bloch state representation (9) does not alter the basic properties of the position operator. If, therefore, the *p-r* relation for infinite systems can be derived using the Bloch space representation, it must also hold for the configuration space representation, in which the $\mathbf{r}$ operator is nothing but the factor $\mathbf{r}$ multiplying the wave function. More generally, it also means that for any crystal (with either

TABLE I. Synopsis of the matrix elements and relations between momentum and dipole matrix elements for crystals with infinite volume, nonvanishing boundary conditions (IV/NVBC), and finite volume, periodic boundary conditions (FV/PBC).

IV/NVBC	FV/PBC
$\langle c\mathbf{k}'\|\mathbf{r}\|v\mathbf{k}\rangle_\infty = \delta(\mathbf{k}-\mathbf{k}')\langle u_{c\mathbf{k}'}\|i\vec{\nabla}_{\mathbf{k}}\|u_{v\mathbf{k}}\rangle_{\text{cell}}$[a]	$\langle c\mathbf{k}\|\mathbf{r}\|v\mathbf{k}\rangle_{\text{vol}} \neq \langle u_{c\mathbf{k}}\|i\vec{\nabla}_{\mathbf{k}}\|u_{v\mathbf{k}}\rangle_{\text{cell}}$[b]
$\langle u_{c\mathbf{k}}\|\hat{\mathbf{p}}\|u_{v\mathbf{k}}\rangle_{\text{cell}} = im\omega_{c\mathbf{k},v\mathbf{k}}\langle u_{c\mathbf{k}}\|i\vec{\nabla}_{\mathbf{k}}\|u_{v\mathbf{k}}\rangle_{\text{cell}}$[c]	$\langle c\mathbf{k}\|\hat{\mathbf{p}}\|v\mathbf{k}\rangle_{\text{vol}} = im\omega_{c\mathbf{k},v\mathbf{k}}\langle u_{c\mathbf{k}}\|i\vec{\nabla}_{\mathbf{k}}\|u_{v\mathbf{k}}\rangle_{\text{cell}}$[d]
$\langle u_{c\mathbf{k}}\|\hat{\mathbf{p}}\|u_{v\mathbf{k}}\rangle_{\text{cell}} = im\omega_{c\mathbf{k},v\mathbf{k}}\langle u_{c\mathbf{k}}\|\mathbf{r}\|u_{v\mathbf{k}}\rangle_{\text{cell}} + \mathbf{B}_{cv}(\mathbf{k})$[e]	
$\langle c\mathbf{k}'\|\hat{\mathbf{p}}\|v\mathbf{k}\rangle_\infty = im\omega_{c\mathbf{k}',v\mathbf{k}}\langle c\mathbf{k}'\|\mathbf{r}\|v\mathbf{k}\rangle_\infty$[f]	$\langle c\mathbf{k}'\|\hat{\mathbf{p}}\|v\mathbf{k}\rangle_{\text{vol}} = im\omega_{c\mathbf{k}',v\mathbf{k}}\langle c\mathbf{k}'\|\mathbf{r}\|v\mathbf{k}\rangle_{\text{vol}} + \mathbf{C}_{c\mathbf{k}',v\mathbf{k}}$[g]

[a] Reference 10.

[b] Incorrectly proven with the equal sign in Ref. 2, Eq. (42.76).

[c] Reference 7; Eq. (42.71) in Ref. 2.

[d] Equation (42.71) in Ref. 2.

[e] References 8 and 9.

[f] Follows from [a] and [c]; see this paper, Sec. IV.

[g] This paper, Sec. II.

infinite or finite volume) potential fundamental issues with the **r** operator are present in any representation. The analysis given in the following deals specifically with finite volume and either periodic or zero boundary conditions. Here, the matrix elements of the position operator taken with Bloch wave functions depend on the choice of the unit cell (and in that sense are not well defined), and this problem cannot be solved by going from a configuration space representation to a Bloch space representation.

For the case of periodic boundary conditions (PBCs), an extended discussion of the various matrix elements and derivation of a p-r relation has been given by Haug.[2] He relates the momentum matrix element to the matrix element of $i\vec{\nabla}_{\mathbf{k}}$. The analysis in Ref. 2 then continues with a derivation of a relation formally analogous to Eq. (10), and from there a p-r relation [formally identical to Eq. (2)], for the case of PBCs. However, that relation is incorrect, as we discuss in Sec. II. In his proof, Haug shows that the term corresponding to the first term in Eq. (10) is diagonal in the band indices and hence vanishes in the p-r relation for interband transitions. While in infinite systems the first term is indeed diagonal in the band indices (at least under the conditions spelled out by Blount),[10] this is not true in PBC systems. In the latter, the **r**-matrix element depends on the choice of the unit cell, while the second term in Eq. (10) does not. Hence, there must be a nonvanishing contribution from the first term, even for interband transitions. The subtle mistake in the proof given in Ref. 2 can be traced back to an incorrect application of the $i\vec{\nabla}_{\mathbf{k}}$ operator on Bloch functions expressed in terms of Wannier functions.

The correct p-r relation in the case of PBCs contains a surface term (in configuration space) that compensates for the ambiguity related to the dipole matrix element that depends on the choice of the unit cell. Of course, the momentum matrix element does not have such an ambiguity, and from that consideration alone it is clear that there must be an additional term to the p-r relation. One might expect that, by now, those relations are given in the literature and are commonly accepted. However, we are not aware of a derivation and discussion of the p-r relation in PBC systems, and we present the derivation and numerical examples below. An additional motivation for doing so is the fact that many modern review articles and textbooks on semiconductor physics present p-r relations that are either not completely clear and well defined or that are actually incorrect. From a practical point of view, however, such errors in the formulation of the light-matter interaction might have only limited consequences, because in practice the size of the dipole matrix element and related quantities, such as the oscillator strength, are usually not obtained from *ab initio* calculations, but from a comparison of theoretical results with experimental data (e.g., Ref. 6).

One can roughly group the publications that include p-r relations in three classes: those using infinite volume (IV) and nonvanishing boundary conditions (NVBCs), those using finite volume (FV) and PBCs, and those dealing with nanostructures, hence using FV and vanishing (i.e., zero) boundary conditions. Focusing for the moment on the first two classes, we present in Table I an overview of what we believe to be the current state of knowledge (including our own results presented in Secs. II and IV). The table highlights important differences between the two cases (IV/NVBC and FV/PBC) that, by and large, are not reflected in modern review articles and textbooks.

The main objective of this paper is to derive and discuss the generalization of Eq. (2) to the FV/PBC case (Sec. II). We will illustrate the results for two cases that are of practical interest: the conduction to valence band transitions at the Γ point in GaAs, and the lowest intersubband transitions in a GaAs superlattice. We calculate the matrix elements directly from the wave functions. In the literature, the calculation of the matrix elements, in particular, the momentum matrix elements (e.g., Ref. 14), is sometimes performed without knowledge of the exact Bloch wave functions—see, for example, the approach in Refs. 15 and 16 (also paragraph 36 in Ref. 17). We will show in Sec. III that in bulk GaAs the value of the upper bound for the dipole matrix element is about a factor of 16 smaller than the value obtained from the momentum matrix elements, which is really that of the operator $i\vec{\nabla}_{\mathbf{k}}$ [see entry (c) of Table I], with the former being 0.36 Å and the latter 5.81 Å. A detailed analysis of the matrix elements has been given by Lew Yan Voon and Ram-Mohan.[15] In that reference, a p-r relation has been derived from a generalized Feynman-Hellman theorem. Their discussion involves both gradient-k matrix elements and matrix elements of the position operator z in configuration space representation, the latter being calculated for semiconductor quantum wells and superlattices, however, no clear distinction between the two forms is presented. Furthermore, calculated values of the position operator are only listed for the case of quantum wells and superlattices, not for bulk matrix elements. Quite generally, in the literature of heterostructure superlattices it is not uncommon to encounter calculations of intersubband dipole matrix elements based on the ordinary position (z) operator, i.e., the position operator in configuration space representation (e.g., Ref. 18). Since, as pointed out above, the dipole matrix element computed with the ordinary position operator is not meaningful (in the sense that it depends on the choice of unit cell), one might ask why the calculations for superlattices seem to be appropriate while a calculation for bulk crystals gives an blatant inconsistency (for example, the factor of 16 mentioned above). We will see in Sec. III that, unlike bulk, in a one-dimensional system such as a superlattice, it is possible to choose a unit cell such that the correction term in the *p*-*r* relation becomes rather small. For example, the choice of the unit cell in Ref. 18 is such that the unit-cell boundaries are located in the potential barrier region. This rather intuitive and widely used choice of unit cell happens to give numerical results for the matrix elements of the ordinary position operator that are rather similar to those obtained with the gradient-*k* operator. In contrast, in bulk GaAs there does not exist such an optimal choice of the unit cell. Many researchers seem to suspect such a discrepancy in bulk systems, and some suggest defining the dipole matrix element via the atomic *p*-*r* relation (i.e., the one without additional correction term): $\mathbf{r}_{c,\mathrm{v}}(\mathbf{k})|_{\text{defined}} = \langle u_{c\mathbf{k}}|\hat{\mathbf{p}}|u_{\mathrm{v}\mathbf{k}}\rangle_{\text{cell}}/(im\omega_{c\mathbf{k},\mathrm{v}\mathbf{k}})$. Such a definition for interband transitions in bulk semiconductors has been suggested, for example, in Refs. 19–23 (also compare the discussion in Ref. 24 for the case of molecules and molecular solids). We note that $\mathbf{r}_{c,\mathrm{v}}(\mathbf{k})|_{\text{defined}}$ is merely a symbol here: The definition says nothing about whether it is related to a matrix element of the $\mathbf{r}$ operator. Indeed, $\mathbf{r}_{c,\mathrm{v}}(\mathbf{k})|_{\text{defined}}$ is the same as the matrix element of the $i\vec{\nabla}_{\mathbf{k}}$ operator, which in turn is different from that of the $\mathbf{r}$operator [see entries (b), (c), and (d) of Table I]. (We note that Glutsch[20] uses this definition only for interband transition, while explicitly using the gradient-*k* formulation in the context of superlattices.)

In Sec. IV, we will also discuss briefly the *p*-*r* relation for infinite crystals (IV/NVBC). Combining the treatment of Blount[10] and Haug,[2] we show that in this case the *p*-*r* relation can be formulated in terms of distributions. In order to gain more insight into that relation, we show how to interpret it as a result of a limiting process involving normalizable wave packets, involving only the ordinary position operator in configuration space representation.

As a by-product of our discussion of the generalization of Eq. (2), we present (in Sec. V) an alternative derivation and extension of earlier findings by Burt[4,25] regarding the dipole approximation in nanostructures (e.g., quantum dots) and other structures that are of finite extent in at least one dimension, such as quantum wells and wires. In such structures, it is useful to introduce envelope functions that obey the boundary conditions appropriate to the quantum confined structure. Probably the simplest example would be a semiconductor quantum well of width L and with infinite barriers for the valence and conduction bands. The lowest-subband envelope function is then simply (with z being the direction normal to the quantum well) $\xi(z) = \sqrt{2/L}\cos(\pi z/L)$. If one would use the light-matter interaction in the dipole approximation, $-\mathbf{d}\cdot\mathbf{E}$, a possible source of error in evaluating the $\mathbf{r}$-matrix element might be to approximate $u_{\nu\mathbf{k}}$ by $u_{\nu\mathbf{0}}$ (which we will call the *zone-center approximation* or zca for short) and then to conclude that the dipole matrix element of the structure is a product of the envelope function overlap integral and the unit-cell dipole matrix element. As Burt noticed already, that would be incorrect. Specifically, for a one-dimensional model such as the quantum well example, this would mean that one would take the conduction band and valence band wave functions to be $\Psi_c(z) = \xi(z)u_{c,0}(z)$ and $\Psi_{\mathrm{v}}(z) = \xi(z)u_{\mathrm{v},0}(z)$, respectively. Burt concluded that

$$\int_{-\infty}^{\infty} dz\Psi_c^*(z)\, z\Psi_{\mathrm{v}}(z) \neq \langle u_{c0}|z|u_{\mathrm{v}0}\rangle_{\text{cell}} \int_{-\infty}^{\infty} dz\xi_c^*(z)\xi_{\mathrm{v}}(z) \tag{11}$$

(note the “not equal” sign). In particular, Burt noted that the matrix element $\langle u_{c0}|z|u_{\mathrm{v}0}\rangle_{\text{cell}}$ depends on the choice of the unit cell, while the z-matrix element of the entire finite structure, i.e., the left-hand side of Eq. (11), cannot depend on that choice. In Sec. V we give a general proof for the factorization of the dipole matrix element in terms of envelope function overlap integrals and cell-matrix elements, provided one takes the $\mathbf{k}$ dependence of $u_{\nu\mathbf{k}}$ into account. For example, the simple case of a quantum well, which emerges as a one-dimensional limiting case from our proof, reads

$$\int_{-\infty}^{\infty} dz\Psi_{c\ell'}^*(z)\, z\Psi_{\mathrm{v}\ell}(z) \simeq \langle u_{ck}|i\nabla_k|u_{\mathrm{v}k}\rangle_{\text{cell}}|_{k=0} \times \int_{-\infty}^{\infty} dz\xi_{c\ell'}^*(z)\xi_{\mathrm{v}\ell}(z). \tag{12}$$

Here, ℓ is the subband index. The factorization of an interband matrix element given as a product of cell-matrix element times envelope overlap integral, an example of which is given in Eq. (12), is used frequently in the literature because it has a very intuitive interpretation. In the following we will call any such factorization *cell-envelope factorization*. The usefulness of the cell-envelope factorization is particularly obvious, for example, in the case of transitions between envelopes that are of different parity, as the vanishing of the corresponding envelope overlap integral immediately indicates a vanishing transition element. Another example where the cell-envelope factorization is beneficial is the case of the quantum confined Stark effect, where the electric field transforms the square well into a triangular well and the concomitant reduction of the wave function overlap yields a reduction in the exciton absorption strength. The cell-envelope factorization poses generally no problem for the momentum matrix element, and has been used, for example, in Ref. 26 and also in Ref. 27, where the cell-envelope factorization allowed for a straightforward neglect of the envelope contribution.

Using the cell-envelope factorization for both the momentum and dipole matrix element of the nanostructure, we derive in Sec. V a *p*-*r* relation that does not contain an additional correction term. Burt[4] derived a quantum well *p*-*r* relation without an additional correction term, but in contrast to our treatment, he did not outline a path towards a *p*-*r* relation that involves cleanly separated cell-matrix elements and envelope overlap functions. Burt did note that, within the zone-center approximation, $u_{v\mathbf{k}} \simeq u_{v\mathbf{0}}$, the dipole matrix elements of a quantum well is very small. We present an alternative proof, generalized to three-dimensional nanostructures, and show that, for example, for a quantum dot,

$$\int_{\text{qu.dot}} d^3r\,\Psi_c^*(\mathbf{r})\mathbf{r}\Psi_v(\mathbf{r}) = \mathbf{0} + \text{nondipole terms}, \tag{13}$$

where "nondipole terms" refers to quadrupole and higher terms in a multipole expansion (for a detailed discussion of the multipole expansion of the light-matter coupling in semiconductor optics, see, e.g., Refs. 28–30).

Since incorrect use of the envelope/dipole approximation can be found in the literature, we hope that, by revisiting and extending Burt's analysis, we might help to increase the acceptance of the correct use of the envelope approximation in conjunction with the use of dipole matrix elements.

II. FINITE VOLUME (FV), PERIODIC BOUNDARY CONDITIONS (PBCs)

In this section, we derive the *p*-*r* relation for the case of a finite crystal with periodic boundary conditions and examine the limiting behavior of this relation as the size of the crystal goes to infinity. The wave functions are v periodic, meaning that $\varphi_{v\mathbf{k}}^{(\text{vol})}(\mathbf{r} + N_i\mathbf{a}_i) = \varphi_{v\mathbf{k}}^{(\text{vol})}(\mathbf{r})$, where, for $i = 1,2,3$, N_i and $\mathbf{a}_i$ are the number of cells and primitive translation vectors, respectively. We first note that the commutator $\hat{\mathbf{p}} = \frac{im}{\hbar}[H_0,\mathbf{r}]_-$ holds at any point $\mathbf{r}$ (including the boundary points, where the spatial derivatives are well defined by virtue of the periodic boundary conditions), and we can integrate over the finite volume v to obtain the general *p*-*r* relation:

$$\int_v d^3r\,\varphi_{c\mathbf{k}'}^{(\text{vol})*}(\mathbf{r})\hat{\mathbf{p}}\varphi_{v\mathbf{k}}^{(\text{vol})}(\mathbf{r}) = i\frac{m}{\hbar}\int_v d^3r\,\varphi_{c\mathbf{k}'}^{(\text{vol})*}(\mathbf{r})[H_0\mathbf{r} - \mathbf{r}H_0]\varphi_{v\mathbf{k}}^{(\text{vol})}(\mathbf{r}). \tag{14}$$

Integrating by parts, or, equivalently, using Green's theorem (e.g., Ref. 31), yields a term in which H_0 operates on $\varphi_{c\mathbf{k}'}^{(\text{vol})*}(\mathbf{r})$ and a surface term. Replacing, in the usual way, $H_0\varphi_{v\mathbf{k}}^{(\text{vol})}(\mathbf{r})$ by $\varepsilon_{v\mathbf{k}}\varphi_{v\mathbf{k}}^{(\text{vol})}(\mathbf{r})$ and $H_0\varphi_{c\mathbf{k}'}^{(\text{vol})*}(\mathbf{r})$ by $\varepsilon_{c\mathbf{k}'}\varphi_{c\mathbf{k}'}^{(\text{vol})*}(\mathbf{r})$ we obtain readily

$$\int_v d^3r\,\varphi_{c\mathbf{k}'}^{(\text{vol})*}(\mathbf{r})\hat{\mathbf{p}}\varphi_{v\mathbf{k}}^{(\text{vol})}(\mathbf{r}) = i\frac{m}{\hbar}[\varepsilon_{c\mathbf{k}'} - \varepsilon_{v\mathbf{k}}]\int_v d^3r\,\varphi_{c\mathbf{k}'}^{(\text{vol})*}(\mathbf{r})\mathbf{r}\varphi_{v\mathbf{k}}^{(\text{vol})}(\mathbf{r}) + \mathbf{C}_{c\mathbf{k}',v\mathbf{k}}, \tag{15}$$

with the additional surface term

$$\mathbf{C}_{c\mathbf{k}',v\mathbf{k}} = +\frac{1}{2}\int_{s(v)} d\mathbf{S}\cdot[\varphi_{c\mathbf{k}'}^*(\mathbf{r})\hat{\mathbf{p}}\varphi_{v\mathbf{k}} + (\hat{\mathbf{p}}\varphi_{c\mathbf{k}'}(\mathbf{r}))^*\varphi_{v\mathbf{k}}(\mathbf{r})]\mathbf{r}. \tag{16}$$

Here, $s(v)$ is the crystal's surface, $d\mathbf{S}$ an outward pointing surface element, and the dot product is between the surface element and the gradient of the wave functions (here written as a momentum operator acting on the wave functions). It is this term that is generally neglected in *p*-*r* relations for FV/PBC systems. As mentioned above, a correction term involving a surface integral over the unit cell has been derived for infinite systems in Ref. 8, and is denoted by $\mathbf{B}_{cv}(\mathbf{k})$ in Table I. We note that, in general, $\mathbf{C}_{c\mathbf{k}',v\mathbf{k}}$ is not diagonal in $\mathbf{k}$ (see Sec. III C), and therefore the term in the square brackets in Eq. (16) is only periodic in the crystal (v periodic), but not in the unit cell (i.e., not v_c periodic). However, in the diagonal elements $\mathbf{C}_{c\mathbf{k},v\mathbf{k}}$ that term is lattice periodic (v_c periodic), and the diagonal elements are equal to the correction term $\mathbf{B}_{cv}(\mathbf{k})$.

In one-dimensional (1D) crystals of length $L = Na$, located between an arbitrary left boundary point $x = L_0$ and the right boundary point $x = L_0 + L$, the surface term is particularly simple, as it consists only of a difference of two terms, one at each side of the crystal, multiplied by its position. Using the L periodicity of the wave functions and their spatial derivatives, we have

$$C_{ck',vk} = -i\frac{\hbar}{2}L\left(\varphi_{ck'}^{(\text{vol})*}\frac{\partial\varphi_{vk}^{(\text{vol})}}{\partial x} - \varphi_{vk}^{(\text{vol})}\frac{\partial\varphi_{ck'}^{(\text{vol})*}}{\partial x}\right)\Bigg|_{x=L_0} \tag{17}$$

$$= -i\frac{\hbar}{2}e^{i(k-k')x}\left(u_{ck'}^*\frac{\partial u_{vk}}{\partial x} - u_{vk}\frac{\partial u_{ck'}^*}{\partial x} + i(k+k')u_{ck'}^*u_{vk}\right)\Bigg|_{x=L_0}. \tag{18}$$

We note that the surface term does not depend on the crystal's volume (L), which in turn implies that it does not vanish if L goes to infinity. Apparently, the case of an infinite crystal has to be treated conceptually differently and cannot be obtained from an infinite-volume limit of the finite system with periodic boundary conditions. Second, we note that the surface term depends on the arbitrary (left) boundary point of the crystal, L_0. The point can be chosen anywhere in an arbitrary unit cell, and thus defines the interval of the unit cell (the leftmost unit cell extending from L_0 to $L_0 + a$). Of course, the momentum matrix element [left-hand side of Eq. (15)] does not depend on the choice of the unit cell, and the L_0 dependence of the surface term cancels exactly that of the dipole matrix element, which is proportional to $\langle ck'|x|vk\rangle_{\text{vol}} = \int_{L_0}^{L_0+L} dx\,\varphi_{ck'}^{(\text{vol})*}(x)x\varphi_{vk}^{(\text{vol})}(x)$. We will come back to this point when we discuss numerical examples in Sec. III.

The presence of the nonvanishing surface term $C_{ck',vk}$ implies that H_0 does not act as a Hermitian operator in the matrix element $\int_v d^3r\,\varphi_{c\mathbf{k}'}^{(\text{vol})*}(\mathbf{r})H_0\mathbf{r}\varphi_{v\mathbf{k}}^{(\text{vol})}(\mathbf{r})$ in Eq. (14). We discuss this issue in more detail here. For a spatial differential operator of the form $\beta(i\vec{\nabla})^n$, with β a real constant and n a positive integer, its being Hermitian, relative to an inner product defined as an integral over a spatial domain, is equivalent to the vanishing of the surface terms arising from the integration by parts. A sufficient condition for this to happen is when the functions on which this operator acts are restricted to those that are either L periodic (and possess continuous derivatives up to order n) or zero at the boundaries. For the case under consideration, our Hilbert space does consist of (normalizable) L-periodic functions, $\varphi(x + L) = \varphi(x)$. However, the position operator x is not L periodic, and neither is the function $x\varphi(x)$ (cf. Ref. 5), i.e., the operator x maps $\varphi(x)$ to a state outside of our Hilbert space. Therefore, one must conclude that either x is not a legitimate operator in our Hilbert space, in which case Eq. (14) is meaningless, or our Hilbert space should be extended to include non-L-periodic functions, in which case H_0 may not be Hermitian in the matrix element $\langle ck'|H_0x|vk\rangle_{\text{vol}}$. As explained above, this problem is obtained for any size L of the crystal and persists at the limit $L \to \infty$.

We can gain yet another perspective on the problem by constructing an operator that preserves L periodicity and is equal to x inside the physical domain. In this case, denoting the L-periodic position operator by $\hat{x}$, we have

$$\langle ck'|[H_0,\hat{x}]_-|vk\rangle_{\text{vol}} = (\varepsilon_{ck'} - \varepsilon_{vk})\langle ck'|\hat{x}|vk\rangle_{\text{vol}}. \tag{19}$$

This equation can be proven by doing integration by parts and noting that all functions are L periodic, which eliminates the surface terms. It is straightforward to construct an L-periodic x operator. Denoting by $S_{a,b}(x) = \theta(b-x) + \theta(x-a) - 1$ the function that is unity in the interval $a \leqslant x \leqslant b$ and zero elsewhere [$\theta(x)$ being the Heavyside step function], we have

$$\hat{x} = \sum_{n=-\infty}^{\infty} (x - L_0 - nL) S_{L_0+nL,L_0+(n+1)L}(x). \tag{20}$$

The operator $\hat{x}$ has a sawtooth shape and therefore does not grow as x goes to infinity, but rather duplicates the x operator from the physical crystal volume ($n = 0$). It satisfies Eq. (19), but the commutator $im/\hbar[H_0,\hat{x}]_-$ is no longer equal to the momentum operator at all x. Straightforward differentiation yields

$$[H_0,\hat{x}]_- = -\frac{\hbar^2}{2m}\left(2\frac{\partial \hat{x}}{\partial x}\frac{\partial}{\partial x} + \frac{\partial^2 \hat{x}}{\partial x^2}\right). \tag{21}$$

Using

$$\frac{\partial \hat{x}}{\partial x} = 1 + \sum_{n=-\infty}^{\infty} (x - L_0 - nL)[\delta(x - L_0 - nL) - \delta(x - L_0 - (n+1)L)], \tag{22}$$

we obtain a generalization of Eq. (1),

$$\hat{p} = \frac{im}{\hbar}[H_0,\hat{x}]_- + \hat{C}, \tag{23}$$

where we defined the L-periodic operator

$$\hat{C} = i\hbar \sum_{n=-\infty}^{\infty} (x - L_0 - nL)[\delta(x - L_0 - nL) - \delta(x - L_0 - (n+1)L)]\frac{\partial}{\partial x} + i\frac{\hbar}{2}\frac{\partial^2 \hat{x}}{\partial x^2}, \tag{24}$$

with

$$\frac{\partial^2 \hat{x}}{\partial x^2} = \sum_{n=-\infty}^{\infty} \left\{[\delta(x - L_0 - nL) - \delta(x - L_0 - (n+1)L)] + (x - L_0 - nL)\left[\frac{\partial \delta(x - L_0 - nL)}{\partial x} - \frac{\partial \delta(x - L_0 - (n+1)L)}{\partial x}\right]\right\}. \tag{25}$$

It is now easy to evaluate matrix elements over the length L, say, again from $x = L_0 - \eta$ to $x = L_0 + L - \eta$ (with $\eta \downarrow 0$) with the point $x = L_0$ inside that interval, of the commutator p-r relation Eq. (23),

$$\langle ck'|\hat{p}|vk\rangle_{\text{vol}} = \frac{im}{\hbar}\langle ck'|[H_0,\hat{x}]_-|vk\rangle_{\text{vol}} + \langle ck'|\hat{C}|vk\rangle_{\text{vol}}. \tag{26}$$

The volume integration in the C term picks up the delta-function contributions at $x = L_0$ from $n = 0$ and $n = -1$ terms, and yields $C_{ck',vk} = \langle ck'|\hat{C}|vk\rangle_{\text{vol}}$, exactly as in Eq. (17). Using Eq. (19) and noting that, for our chosen volume, we can replace $\langle ck'|\hat{x}|vk\rangle_{\text{vol}}$ by $\langle ck'|x|vk\rangle_{\text{vol}}$, we finally obtain

$$\langle ck'|\hat{p}|vk\rangle_{\text{vol}} = \frac{im}{\hbar}(\varepsilon_{ck'} - \varepsilon_{vk})\langle ck'|x|vk\rangle_{\text{vol}} + C_{ck',vk}. \tag{27}$$

This shows that an L-periodic position operator, combined with "normal" manipulations of Hermitian operators, yields the same p-r relation as a "normal" position operator (defined as the factor x from $-\infty$ to ∞) combined with straightforward integration by parts of the volume matrix elements of the commutator $[H_0,x]_-$.

We conclude this section with a brief comment about the derivation of a p-r relation in the FV/PBC case, derived for $\mathbf{k}' = \mathbf{k}$ in Ref. 2. The p-r relation derived there [Eq. (42.78) in that reference] does not contain the additional surface term $\mathbf{C}_{c\mathbf{k},v\mathbf{k}}$. The proof in Ref. 2 proceeds in two steps. First, the following relation [Eq. (42.71) in Ref. 2],

$$\int_v d^3r \varphi^{(\text{vol})*}_{c\mathbf{k}}(\mathbf{r})\hat{\mathbf{p}}\varphi^{(\text{vol})}_{v\mathbf{k}}(\mathbf{r}) = i\frac{m}{\hbar}[\varepsilon_{c\mathbf{k}} - \varepsilon_{v\mathbf{k}}]\int_{\text{cell}} d^3r u^*_{c\mathbf{k}}(\mathbf{r}) i\vec{\nabla}_{\mathbf{k}} u_{v\mathbf{k}}(\mathbf{r}), \tag{28}$$

is shown (for clarity, we use our notation rather than that of Ref. 2). The proof of this relation utilizes integration by parts of Bloch wave functions that obey PBCs. In the second step, the dipole matrix element is written as [Eq. (42.76) in Ref. 2, again in our notations]

$$\langle c\mathbf{k}|\mathbf{r}|v\mathbf{k}\rangle_{\text{vol}} = \frac{1}{i}\int_v d^3r \varphi^{(\text{vol})*}_{c\mathbf{k}}(\mathbf{r})\vec{\nabla}_{\mathbf{k}}\varphi^{(\text{vol})}_{v\mathbf{k}}(\mathbf{r}) + \int_{\text{cell}} d^3r u^*_{c\mathbf{k}}(\mathbf{r}) i\vec{\nabla}_{\mathbf{k}} u_{v\mathbf{k}}(\mathbf{r}). \tag{29}$$

It is then claimed that the first term on the right-hand side is zero, for which a proof is presented. Equations (28) and (29) are then taken together to give the p-r relation without the correction term, in contradiction to our result above. We will show here that the proof for the vanishing of $\int_v d^3r \varphi^{(\text{vol})*}_{c\mathbf{k}}(\mathbf{r})\vec{\nabla}_{\mathbf{k}}\varphi^{(\text{vol})}_{v\mathbf{k}}(\mathbf{r})$ contains an essential error and is thus not valid. The "proof" in Ref. 2 is as follows. First, the Bloch functions are represented in terms of Wannier functions, then the gradient-k acts on the expansion coefficients but not on the Wannier functions, and then the orthogonality between the conduction and valence band Wannier functions is invoked. The subtle error in this argument is that it misses the fact that the gradient-k of Bloch wave functions under periodic boundary conditions cannot be evaluated with a Wannier expansion of Wannier functions which are themselves v periodic. Let us illustrate this, for clarity, in a 1D model. The Wannier expansion for band ν (=c or v) reads

$$\varphi^{(\text{vol})}_{\nu k}(x) = \frac{1}{\sqrt{N}}\sum_m \mathrm{w}_{\nu,m}(x)e^{ikR_m}. \tag{30}$$

Here, $\mathrm{w}_{\nu,m}(x) \equiv \mathrm{w}_\nu(x - R_m)$ is the Wannier function localized at lattice point $R_m = ma$, and the sum over m extends over the finite number N of units cells in the crystal. Being constructed as finite superpositions of L-periodic Bloch wave functions, the Wannier functions are also L periodic, i.e., $\mathrm{w}_{\nu,m}(x+L)=\mathrm{w}_{\nu,m}(x)$ on the real line (i.e., x from $-\infty$ to ∞). The wave vector k assumes the discrete values $k_\ell = \frac{2\pi}{L}\ell$ (ℓ integer) because of the PBCs. If we were to use Eq. (30) to evaluate the k derivative of $\varphi^{(\mathrm{vol})}_{\nu k}(x)$ at $k=k_\ell$, we would conclude that

$$\frac{\partial}{\partial k}\varphi^{(\mathrm{vol})}_{\nu k}(x)\bigg|_{k=k_\ell} \tag{31}$$

equals

$$\frac{1}{\sqrt{N}}\sum_m iR_m \mathrm{w}_{\nu,m}(x)e^{ik_\ell R_m}. \tag{32}$$

Since the Wannier functions are L periodic, we would conclude that the k derivative of the Bloch wave function is L periodic, i.e., that $\frac{\partial}{\partial k}\varphi^{(\mathrm{vol})}_{\nu k}(x)|_{k=k_\ell}$ equals $\frac{\partial}{\partial k}\varphi^{(\mathrm{vol})}_{\nu k}(x+L)|_{k=k_\ell}$. This, however, cannot be correct, as a direct demonstration shows:

$$\frac{\partial}{\partial k}\varphi^{(\mathrm{vol})}_{\nu k}(x)\bigg|_{k=k_\ell} = \frac{\partial}{\partial k}[e^{ikx}u_{\nu k}(x)]\bigg|_{k=k_\ell} \tag{33}$$

$$= e^{ik_\ell x}\left[ixu_{\nu k_\ell}(x) + \frac{\partial}{\partial k}u_{\nu k}(x)\bigg|_{k=k_\ell}\right]. \tag{34}$$

Since $u_{\nu k}(x)$ and $\partial u_{\nu k}(x)/\partial k$ are lattice periodic, they are also L periodic since L is an integer multiple of the lattice constant. One can then readily arrive at

$$\frac{\partial}{\partial k}\varphi^{(\mathrm{vol})}_{\nu k}(x+L)\bigg|_{k=k_\ell} - \frac{\partial}{\partial k}\varphi^{(\mathrm{vol})}_{\nu k}(x)\bigg|_{k=k_\ell} = iLe^{ik_\ell x}u_{\nu k_\ell}(x), \tag{35}$$

i.e., $\frac{\partial}{\partial k}\varphi^{(\mathrm{vol})}_{\nu k}(x)|_{k=k_\ell}$ is not L periodic.

The point is, for a $k\neq k_\ell$, the Wannier expansion on the right-hand side of Eq. (30) is still L periodic while, in general, $\varphi^{(\mathrm{vol})}_{\nu k}(x)$ is not. This implies that the equality in Eq. (30) is not valid for $k\neq k_\ell$. But evaluating the k derivative,

$$\frac{\partial}{\partial k}\varphi^{(\mathrm{vol})}_{\nu k}(x)\bigg|_{k=k_\ell} = \lim_{\Delta k\to 0}\frac{1}{\Delta k}\left[\varphi^{(\mathrm{vol})}_{\nu k_\ell+\Delta k}(x) - \varphi^{(\mathrm{vol})}_{\nu k_\ell}(x)\right], \tag{36}$$

involves taking the Bloch wave function at $k=k_\ell+\Delta k$ which, for small enough Δk, would not coincide with any k values giving L-periodic plane waves. So using Eq. (30) to evaluate the k derivative of the Bloch wave function is incorrect. One could, in principle, construct Wannier functions with the proper periodicity of $\varphi^{(\mathrm{vol})}_{\nu k_\ell+\Delta k}(x)$, but in that case the Wannier functions become k dependent, and the arguments in Ref. 2 would not apply. We finally note that a relation formally similar to item (b) in Table I (but involving only cell integrals), has been discussed and shown to be incorrect by Zak.[32]

III. NUMERICAL EXAMPLES

In this section, we wish to illustrate the p-r relation for finite crystals, Eq. (15), with numerical examples: (i) bulk GaAs restricted to $\mathbf{k}'=\mathbf{k}$, (ii) a GaAs square-well superlattice (i.e., a Kronig-Penney model), also restricted to $k'=k$, and a GaAs superlattice with δ barriers for arbitrary k and k'. For the first two cases, the limitation to equal k vectors, $\mathbf{k}'=\mathbf{k}$, facilitates the numerical analysis because we can rewrite the p-r relation in terms of integrals over the units cells. To do this, we proceed in the usual manner by writing a volume integral as a sum over cell integrals, $\int_v f(\mathbf{r}) = \sum_{\bar m}\int_{\mathrm{cell}} f(\mathbf{r}+\mathbf{R}_{\bar m})$, where $\mathbf{R}_{\bar m} = m_1\mathbf{a}_1 + m_2\mathbf{a}_1 + m_3\mathbf{a}_1$, $\bar m = (m_1,m_2,m_3)$. Using

$$\frac{1}{N}\sum_{\bar m=-\bar M}^{\bar M} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{\bar m}} = \sum_{\mathbf{G}}\delta_{\mathbf{k}-\mathbf{k}',\mathbf{G}}, \tag{37}$$

with $N_i = 2M_i+1$ being the number of unit cells in direction i, $\bar M = (M_1,M_2,M_3)$, the $\bar m$ sum being a triple sum, $N = N_1N_2N_3$, and $\mathbf{G}$ denoting the reciprocal lattice vectors, we obtain immediately the well-known result for the momentum matrix element,

$$\int_v d^3r\,\varphi^{(\mathrm{vol})*}_{c\mathbf{k}'}(\mathbf{r})\hat{\mathbf{p}}\varphi^{(\mathrm{vol})}_{v\mathbf{k}}(\mathbf{r}) = \delta_{\mathbf{k}\mathbf{k}'}\langle u_{c\mathbf{k}}|\hat{\mathbf{p}}|u_{v\mathbf{k}}\rangle_{\mathrm{cell}}. \tag{38}$$

Here, we have used the fact that both $\mathbf{k}$ and $\mathbf{k}'$ are in the first Brillouin zone, which restricts the $\mathbf{G}$ sum to $\mathbf{G}=0$. We now restrict ourselves to the case $\mathbf{k}=\mathbf{k}'$, in which case the $\mathbf{r}$ matrix element assumes a form similar to that of $\hat{\mathbf{p}}$:

$$\int_v d^3r\,\varphi^{(\mathrm{vol})*}_{c\mathbf{k}'}(\mathbf{r})\mathbf{r}\varphi^{(\mathrm{vol})}_{v\mathbf{k}}(\mathbf{r}) = \delta_{\mathbf{k}\mathbf{k}'}\langle u_{c\mathbf{k}}|\mathbf{r}|u_{v\mathbf{k}}\rangle_{\mathrm{cell}}. \tag{39}$$

Hence, the p-r relation is manifestly independent of the volume in this case:

$$\langle u_{c\mathbf{k}}|\hat{\mathbf{p}}|u_{v\mathbf{k}}\rangle_{\mathrm{cell}} = im\omega_{c\mathbf{k},v\mathbf{k}}\langle u_{c\mathbf{k}}|\mathbf{r}|u_{v\mathbf{k}}\rangle_{\mathrm{cell}} + \mathbf{C}_{c\mathbf{k},v\mathbf{k}}. \tag{40}$$

The cell integrals can be computed easily numerically.

A. Bulk GaAs

As a first example, we look at bulk GaAs. We use a simple Cohen-Bergstresser pseudopotential approach[33] to calculate the band structure and wave functions. The Bloch wave functions are expanded by plane wave functions as

$$\varphi^{(\mathrm{vol})}_{v\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{v,\mathbf{G}}(\mathbf{k})e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}, \tag{41}$$

where $\mathbf{G}$ is reciprocal lattice vector. The coefficients $c_{v,\mathbf{G}}(\mathbf{k})$ and the eigenvalues $\varepsilon_{v\mathbf{k}}$ are determined by

$$\varepsilon_{v\mathbf{k}}c_{v,\mathbf{G}_i} = \sum_{i\neq j}V_p(\mathbf{G}_i-\mathbf{G}_j)c_{v,\mathbf{G}_j} + \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{G}_i)^2c_{v,\mathbf{G}_i}, \tag{42}$$

where m is the electron mass in vacuum and $V_p(\mathbf{G}_i-\mathbf{G}_j)$ are Fourier components of the pseudopotential. The Fourier components are decomposed into symmetric and antisymmetric parts, each consisting of the product of a pseudopotential form factor and a structure factor:

$$V_p(\mathbf{G}_i-\mathbf{G}_j) = V_s(|\mathbf{G}_i-\mathbf{G}_j|a/2\pi)\cos[(\mathbf{G}_i-\mathbf{G}_j)\mathbf{s}] - i\,V_a(|\mathbf{G}_i-\mathbf{G}_j|a/2\pi)\sin[(\mathbf{G}_i-\mathbf{G}_j)\mathbf{s}]. \tag{43}$$

The vector $\mathbf{s}$ in Eq. (43) is the position of the Ga atom inside a Wigner-Seitz cell with the origin chosen to be in the middle of the two basis atoms, i.e., $\mathbf{s} = a/8\,(1,1,1)$ (where a is the lattice constant). These pseudopotential form factors reproduce quite well both the conduction and valence band states (here without spin). Their values for GaAs are taken from Ref. 33. In units of Rydbergs they are $V_s(\sqrt{3}) = -0.23$, $V_s(\sqrt{8}) = 0.01$, $V_s(\sqrt{11}) = 0.06$, $V_a(\sqrt{3}) = 0.07$, $V_a(2) = 0.05$, and $V_a(\sqrt{11}) = 0.01$. Zero values are taken for $|\mathbf{G}_i - \mathbf{G}_j| \geqslant 2\pi/a\sqrt{12}$. The reciprocal lattice of GaAs is a bcc structure. We use $\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$ with $\mathbf{b}_1 = (2\pi/a)(-1,1,1)$, $\mathbf{b}_2 = (2\pi/a)(1,-1,1)$, and $\mathbf{b}_3 = (2\pi/a)(1,1,-1)$. In our calculations, we have included the reciprocal lattice vectors within $-4 \leqslant m_1 \leqslant 4$, $-4 \leqslant m_2 \leqslant 4$, and $-4 \leqslant m_3 \leqslant 4$. Satisfactory convergence has been obtained for the band gap, and the calculated charge distributions are also consistent with the results in Ref. 34.

At the Γ point, the valence band has threefold degenerate solutions that belong to the irreducible representation Γ_{15} of the point group T_d. The numerical solutions of Eq. (42) yield eigenfunctions $|u_{\mathrm{v}_i}\rangle$ that are arbitrary superpositions of commonly used basis eigenfunctions $|u_{x_j}\rangle = \{|u_x\rangle, |u_y\rangle, |u_z\rangle\}$, defined relative to the axes of the conventional unit cell,

$$|u_{\mathrm{v}_i}\rangle = \sum_{j=1}^{3} a_{ji}|u_{x_j}\rangle. \tag{44}$$

To construct the basis functions $|u_{x_j}\rangle$, we calculate the coefficients a_{ji} and invert the matrix a_{ji}. For that, we multiply Eq. (44) by the factor x_n ($n = 1,2,3$) and integrate over a Wigner-Seitz cell with its center chosen to coincide with one of the symmetry points for the point-group symmetry operations of GaAs (these points include the centers of the conventional cells defined with either all Ga atoms or all As atoms at their eight corners, and the positions of the Ga and As atoms). With the center chosen that way, the Wigner-Seitz cell integral (integral over the volume of the shape of a Wigner-Seitz cell) of $x_n|u_{x_j}\rangle$ is proportional to $\delta_{n,j}$ as a result of the fact that, for $n \neq j$, the integrand is odd under the improper rotation S_4 of the point group T_d. By utilizing this relation, we can obtain the basis functions $|u_{x_j}\rangle$.

As mentioned above, both the (Wigner-Seitz) cell dipole matrix element $\langle u_{c\mathbf{k}}|\mathbf{r}|u_{\mathrm{v}\mathbf{k}}\rangle_{\mathrm{cell}}$ and the correction term $\mathbf{C}_{c\mathbf{k},\mathrm{v}\mathbf{k}}$ depend on the location of the cell over which the integrals are taken. We illustrate this in Fig. 1, where we show the variation of the matrix elements as we move the center of the cell along the [111] diagonal of the conventional unit cell (this line is more clearly presented in Fig. 2). (Note that we define directions and Miller indices according to the conventional cubic unit cell, not the primitive cell.) Here, the wave functions and matrix elements are evaluated at $\mathbf{k} = \mathbf{0}$ (we suppress the $\mathbf{k}$ index in the following).

The momentum matrix element $\langle u_c|\hat{\mathbf{p}}|u_{x_j}\rangle_{\mathrm{cell}}$ is independent of the cell center, and furthermore its magnitude $p_{c\mathrm{v}}$ is independent of j. The magnitude of the $\mathbf{r}$-matrix element, $|\langle u_c|\mathbf{r}|u_{x_j}\rangle_{\mathrm{cell}}|$, is independent of j for cell center locations on the [111] line. Note that this independence requires the C_3 rotation symmetry of the group T_d and therefore, in general, does not hold for center locations away from the [111] line. Also note that even on the [111] line, the magnitudes of the three $\mathbf{r}$-matrix elements would in general not be the same had we chosen the arbitrary basis $|u_{\mathrm{v}_i}\rangle$. Cross sections of the conduction band wave function and of one of the three equivalent valence band wave functions in the (110) plane are shown in Fig. 2.

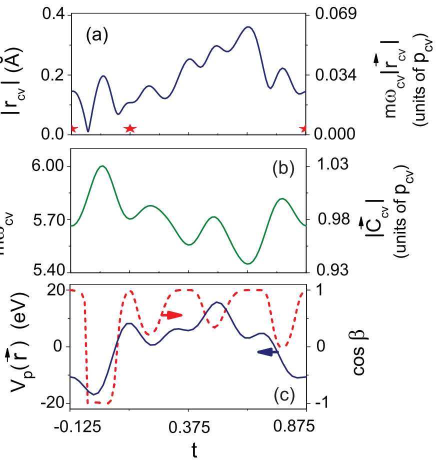

FIG. 1. (Color online) (a) Magnitude of the Γ-point $\mathbf{r}$-matrix element in bulk GaAs. (b) Magnitude of the additional correction term at the Γ point. In (a) and (b), the magnitudes are given in units of Å (left axis) and in units of the momentum matrix element $p_{c\mathrm{v}}$, after appropriate multiplication/division by $m\omega_{c\mathrm{v}}$ (right axis). It is apparent that $|\mathbf{C}_{c\mathrm{v}}|$ is much larger than $m\omega_{c\mathrm{v}}|\mathbf{r}_{c\mathrm{v}}|$. (c) The pseudopotential $V_p(\mathbf{r})$ (solid blue line) and the cosine of the angle β between $\mathbf{r}_{c\mathrm{v}}$ and $-i\mathbf{p}_{c\mathrm{v}}$ (dashed red line). The horizontal axis scans the cell center on the [111] line of the conventional unit cell; the positions of the cell center are given by $t(a,a,a)$. In (a), the red asterisks indicate the positions of the atoms (with the As atoms at $t = -0.125$ and $t = 0.875$).

Figure 1 shows that the magnitude of the $\mathbf{r}$-matrix element is slightly smaller than the distance between the maximum of the s-like wave function and the that of the p_z-like wave function (which is roughly 0.71 Å; see Fig. 2). It is therefore significantly smaller than the magnitude of the appropriately scaled momentum matrix element ($p_{c\mathrm{v}}/m\omega_{c\mathrm{v}} = 5.81$ Å) and also much smaller than the GaAs lattice constant $a = 5.65$ Å. Since the value of the $\mathbf{r}$-matrix element is generally small, that of the additional correction term $\mathbf{C}_{c,\mathrm{v}}$ is rather large (comparable to $p_{c\mathrm{v}}$). The variation of its magnitude reflects roughly that of the pseudopotential, which in turn contains contributions from the atoms on the [111] line as well as atoms in the vicinity of that line. The variation of the pseudopotential on the [111] line can be understood better by looking at its variation in the (110) plane (Fig. 2). The generic form of atomic pseudopotentials comprises a (local or global, depending on the element) maximum at the atom's position, a minimum approximately located at the maximum of the valence electron charge density, and an asymptotic rise to the ionization energy at large radius. In Fig. 1, we see that the two minima from the As atom at $t = -0.125$ and the Ga atom at $t = 0.125$ have merged (this describes the basic Ga-As bond), and the local maximum at the As atom is lower than that of the Ga atom (which reflects the larger electron affinity of As). The remaining features of the pseudopotential in Fig. 1 can be traced back to the shape of the pseudopotential in the (110) plane shown in Fig. 2. Looking at the lower-left-cell cross section of the pseudopotential in Fig. 2, one can identify the minima around the As atoms, which are located at $(z,t) = (-0.125a,-0.125)$, $(-0.125a,0.375)$,

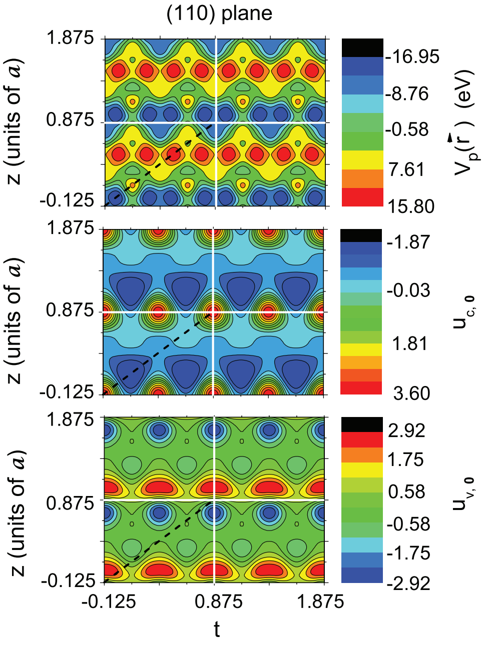

FIG. 2. (Color online) Cross section of the Γ-point pseudopotential (top), conduction band wave function (middle), and valence band wave function $|u_z\rangle$ (bottom) of bulk GaAs. The coordinates on the horizontal axis are given by $t(a,a,0)$. For clarity, the cross sections of four conventional unit cells are shown, which are separated by the white horizontal and vertical lines. One position of the As atoms is $(z,t) = (0.875a,0.875)$; the corresponding s-like orbital of the conduction band and a p_z-like orbital of the valence band can be recognized in the figure. One position of the Ga atoms is $(z,t) = (0.125a,0.125)$; its local pseudopotential maximum is easy to recognize but its underlying atomic orbitals are more difficult to infer from the figure. The diagonal black dashed line in the lower-left-cell cross section indicates the line along which matrix elements are given in Fig. 1.

and $(-0.125a,0.875)$, and the local maxima of the Ga atoms at $(z,t) = (0.125a,0.125)$ and $(0.125a,0.625)$. The four absolute maxima in this cell cross section are on the lines connecting the Ga atoms at $(z,t) = (0.125a,0.125)$ and $(0.125a,0.625)$ on the one hand and the As atoms at $(z,t) = (0.875a,-0.125)$, $(0.875a,0.375)$, and $(0.875a,0.875)$ on the other hand. Along each of these four lines, the atomic pseudopotential minima of the Ga and As atoms are clearly separated (the two atoms are relatively far away from each other) with a maximum nearly at the half point between the two atoms. (The very shallow maxima at the As atoms on these lines cannot be seen in the figure.) Now, the global maximum of the pseudopotential in Fig. 1 can be recognized as the [111] line (dashed black line) crossing the vicinity of the global maximum around $(z,t) \approx (0.5a,0.5)$ in Fig. 2. The basic features in the pseudopotential are reflected in valence and conduction band wave functions, which are also shown in Fig. 2.

From the middle and bottom figures of Fig. 1, we see that the variation of the correction term $|\mathbf{C}_{c,\mathrm{v}}|$ is very similar to that of the pseudopotential and therefore related to the variation of the wave functions. However, the variation of $|\langle u_c|\mathbf{r}|u_{x_j}\rangle_{\mathrm{cell}}|$ is quite different. In a one-dimensional system, the parametric variation of $|\mathbf{C}_{c,\mathrm{v}}|$ and $|\langle u_c|\mathbf{r}|u_{x_j}\rangle_{\mathrm{cell}}|$ would be the same or opposite to each other, as either the sum or the difference of the two quantities would be equal to the constant $|\langle u_c|\hat{\mathbf{p}}|u_{x_j}\rangle_{\mathrm{cell}}|$. In the three-dimensional case, the vectors $\langle u_c|\hat{\mathbf{p}}|u_{x_j}\rangle_{\mathrm{cell}}$, $\langle u_c|\mathbf{r}|u_{x_j}\rangle_{\mathrm{cell}}$, and $\mathbf{C}_{c,\mathrm{v}}$ are generally not parallel. Hence, the variation in $|\langle u_c|\mathbf{r}|u_{x_j}\rangle_{\mathrm{cell}}|$ and $|\mathbf{C}_{c,\mathrm{v}}|$ can differ, if the angles between those vectors vary. We show the variation of the angle between the momentum matrix element and the dipole (i.e., $\mathbf{r}$) matrix element multiplied by $im\omega_{\mathrm{cv}}$ in Fig. 1. For cell centers at the symmetry points ($t = -0.125$, 0.125, 0.375, 0.625, and 0.875), all three vectors are either parallel or antiparallel, but away from the symmetry points this is in general not true. In particular, moving the cell center from the As atom at $t = -0.125$ to the Ga atom at $t = 0.125$ means that the momentum and dipole change from being parallel to antiparallel.

We finally note that the global maximum value for $|\langle u_c|\mathbf{r}|u_{x_j}\rangle_{\mathrm{cell}}|$ is approximately 0.36 Å, which it assumes at the symmetry point $t = 0.625$ in Fig. 1, and correspondingly, at point $(z,t) = (0.625a,0.625)$ in Fig. 2 (this point exhibits a clearly visible local minimum in the pseudopotential). Within a conventional unit cell, there are four equivalent points at which the global maximum is achieved. These points are $(0.625a,0.625a,0.625a)$, $(0.625a,0.125a,0.125a)$, $(0.125a,0.125a,0.625a)$, and $(0.125a,0.625a,0.125a)$. Our results show clearly that, calculating the cell dipole matrix elements from the solution of the Schrödinger equation, rather than treating it as an experimental fit parameter, and using that value in the dipole Hamiltonian, could lead to rather large errors in the strength of the light-matter coupling. We also note that in the one-dimensional example discussed in the next section, the cell can be chosen in a way that the correction term becomes very small and the dipole matrix element essentially as large as momentum matrix element (divided by mass and transition energy), which is quite different from the present bulk GaAs example. It might therefore be conjectured that, more generally, it is difficult in three dimensions to find a cell location such that the wave functions are vanishingly small on its entire surface, whereas in one dimension one just needs to place the cell such that its boundaries are deep inside the barriers.

B. GaAs/AlGaAs superlattice, $k = 0$

We now consider the textbook example of a GaAs/Al$_x$Ga$_{1-x}$As square-well superlattice. The mole fraction is taken as $x = 0.24$ and the conduction band offset at the interface is $V_0 = 0.2$ eV. For simplicity, we take the effective electron mass $m_e = 0.067m$ (m = electron mass in vacuum) to be the same in the well and the barrier (this does not affect the qualitative behavior of the matrix elements and of the p-r relation to be discussed in the following). In a single quantum well, the envelope functions $\xi_{\nu\ell}(z)$ are labeled by the subband index ℓ. In the superlattice, the envelope function $\xi_{\nu\ell}(z)$ itself is a Bloch wave function, and the discrete labels of the quantum well states, ℓ, have to be amended by a superlattice wave vector k, i.e., the envelope function takes the form

$$\xi_{\nu\ell k}(z) = \frac{1}{\sqrt{L}} e^{ikz} u_{\nu\ell k}(z). \tag{45}$$

Here, we use the letter u to denote the lattice-periodic part of the envelope function and denote the length of the superlattice by L and its period by a, and the superlattice wave vector by k. The latter should not be confused with the wave vector in the atomic lattice, which we also denoted by k [for the purpose of this illustration, we will not consider the influence of the lattice-periodic part $u_{\nu\mathbf{k}}(\mathbf{r})$ of the atomic lattice on intersubband transitions]. To be specific, we assume in the following the superlattice states to be the subbands of the conduction band, $\nu = c$, and suppress the band index c. Furthermore, we restrict ourselves to the $k = 0$ superlattice states (i.e., the Γ point of the miniband). We solve the envelope equation

$$\left\{-\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial z^2} + V_{SL}(z)\right\}u_{\ell 0}(z) = \varepsilon_{\ell k}u_{\ell 0}(z), \tag{46}$$

with the periodic potential being zero in the well (of width b) and $V_0 > 0$ in the barrier,

$$V_{SL}(z) = \begin{cases} V_0 & \text{if} \quad b/2 + na < z < a/2 + na, \\ 0 & \text{if} \quad -b/2 + na < z < b/2 + na, \\ V_0 & \text{if} \quad -a/2 + na < z < -b/2 + na, \end{cases} \tag{47}$$

where n is an arbitrary integer, and a is the superlattice lattice constant. In order to make our discussion of the numerical results unambiguous, we briefly summarize the (textbook) results for the wave functions. The even wave functions at $k = 0$, with energies below V_0, are

$$u_{\ell 0}(z) = \begin{cases} \cos q_\ell z & \text{in well,} \\ A_\ell(\cosh \bar{q}_\ell z \mp \tanh \bar{q}_\ell \frac{a}{2} \sinh \bar{q}_\ell z) & \text{in barrier,} \end{cases} \tag{48}$$

where the "−" ("+") indicates the right (left) part of the barriers adjacent to the well. The energy of this wave function is determined by the variable q_ℓ, and given by $\varepsilon_{\ell 0} = \hbar^2 q_\ell^2/2m_e$. Hence, the condition $\epsilon_{\ell 0} < V_0$ is equivalent to $0 \leqslant q_\ell \leqslant \sqrt{2mV_0/\hbar^2}$. The variable $\bar{q}_\ell$ is a function of q_ℓ, $\bar{q}_\ell = \sqrt{|q_\ell^2 - 2mV_0/\hbar^2|}$. The continuity of the wave function and its derivative lead to an equation for q_ℓ,

$$-q_\ell \tan q_\ell \frac{b}{2} = \bar{q}_\ell \left(\frac{\sinh \bar{q}_\ell \frac{b}{2} - \tanh \bar{q}_\ell \frac{a}{2} \cosh \bar{q}_\ell \frac{b}{2}}{\cosh \bar{q}_\ell \frac{b}{2} - \tanh \bar{q}_\ell \frac{a}{2} \sinh \bar{q}_\ell \frac{b}{2}}\right), \tag{49}$$

and the amplitudes A_ℓ are given by

$$A_\ell = \frac{\cos q_\ell \frac{b}{2}}{\cosh \bar{q}_\ell \frac{b}{2} - \tanh \bar{q}_\ell \frac{a}{2} \sinh \bar{q}_\ell \frac{b}{2}}. \tag{50}$$

Similarly, the odd wave functions with energies less than V_0 (i.e., with $0 \leqslant q_\ell \leqslant \sqrt{2mV_0/\hbar^2}$) are

$$u_{\ell 0}(z) = \begin{cases} \sin q_\ell z & \text{in well,} \\ A_\ell \left(\pm \cosh \bar{q}_\ell z - \coth \bar{q}_\ell \frac{a}{2} \sinh \bar{q}_\ell z\right) & \text{in barrier.} \end{cases} \tag{51}$$

The variable q_ℓ must satisfy

$$q_\ell \cot q_\ell \frac{b}{2} = \bar{q}_\ell \left(\frac{\sinh \bar{q}_\ell \frac{b}{2} - \coth \bar{q}_\ell \frac{a}{2} \cosh \bar{q}_\ell \frac{b}{2}}{\cosh \bar{q}_\ell \frac{b}{2} - \coth \bar{q}_\ell \frac{a}{2} \sinh \bar{q}_\ell \frac{b}{2}}\right) \tag{52}$$

and the amplitude coefficient A_ℓ is given by

$$A_\ell = \frac{\sin q_\ell \frac{b}{2}}{\cosh \bar{q}_\ell \frac{b}{2} - \coth \bar{q}_\ell \frac{a}{2} \sinh \bar{q}_\ell \frac{b}{2}}. \tag{53}$$

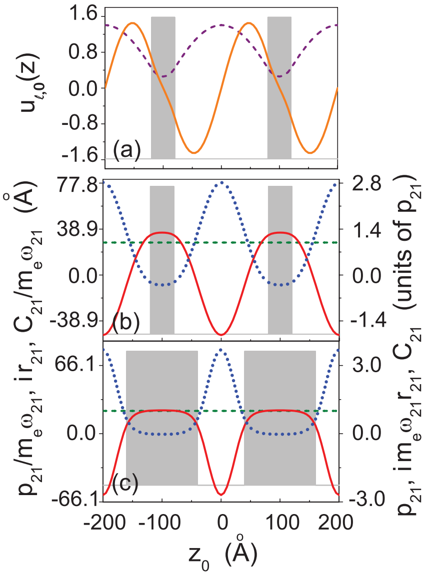

FIG. 3. (Color online) Wave functions and matrix elements for $k = 0$ in a square-well GaAs superlattice with superlattice constant $a = 200$ Å. The barriers are indicated by the solid gray regions. (a) Wave functions $u_{1,0}(z)$ (dashed purple line) and $u_{2,0}(z)$ (solid yellow line). (b) The intersubband matrix element $r_{2,1}$ (solid red line) and the additional correction term $C_{2,1}$ (dotted blue line) as a function of the lower integration limit z_0 (with the unit-cell integration ranging from z_0 to $z_0 + a$). Also shown, as the green dashed line, is the momentum matrix element, $p_{2,1}$. All quantities are given in units of Å (left axis) and in units of $p_{2,1}$ (right axis). The barrier width in (a) and (b) is 40 Å. (c) Same as (b) but for a barrier width of 120 Å.

With these wave functions, we evaluate the matrix elements and correction term $C_{2,1}$ of the transitions between the energetically lowest two states. Integrals are taken over one superlattice unit cell a. In this and in the following, we choose the phase of the wave functions such that the momentum matrix element and the correction term are purely imaginary and the dipole matrix element is real valued.

Figure 3 shows that both the dipole matrix element $r_{2,1} = \langle u_{2,0}|r|u_{1,0}\rangle_{\text{cell}}$ and the correction term $|C_{2,1}|$ vary strongly as the integral's lower limit z_0 changes from $-a$ to $+a$. Unlike in the case of the atomic matrix elements in three-dimensional bulk GaAs, here either $m\omega_{2,1}|r_{2,1}|$ or $|C_{2,1}|$ can be as large as the value of $|p_{2,1}|$, or as small as zero. Interestingly, both $r_{2,1}$ and $iC_{2,1}$ change signs at certain values of z_0. The sign change of $r_{2,1}$ stems from the fact that, for certain z_0, the dipole involves neighboring wells. As a consequence, if z_0 is in the middle of a barrier, the dipole matrix element $r_{2,1}$ is positive while for $z_0 = -a$ it is negative. This is because, if, say, $z_0 = -100$ Å (i.e., at the center of the barrier on the left of the well centered at $z = 0$), then the cell integral involves an even and positive integrand, as the odd wave function $u_{2,0}$ is multiplied by the dipole operator z. The electron motion described by the $r_{2,1}$ is restricted to one well, and $r_{2,1}$ is positive. If, however, $z_0 = 0$ Å (i.e., in the middle of the well centered at $z = 0$), the cell integral is dominated by the negative $u_{2,0}$ in the adjacent well (which is centered at $z = 200$ Å. The negative contribution of the adjacent well dominates because of the factor z (the dipole operator) in the matrix element. In this case, the dipole describes a motion of an electron between two adjacent wells. This analysis shows that $r_{2,1}$ can be negative for certain cell locations, as can be seen from Figs. 3(b) and 3(c).

In order to make the magnitude of $r_{2,1}$ close to $p_{2,1}/m_e\omega_{2,1}$, one simply needs to choose a cell with boundaries deep inside the barriers. That minimizes the role of the additional correction term $C_{2,1}$, as it involves the wave functions at the cell's boundary. Comparing a narrow-barrier case [Fig. 3(b)] with a wide-barrier case [Fig. 3(c)], we see that the wide-barrier case has a wide range of z_0 (almost over the entire barrier) for which $C_{2,1}$ is almost negligible. Moreover, there are points where the correction term vanishes, $C_{2,1} = 0$, which implies $im\omega_{2,1}r_{2,1} = p_{2,1}$. This again is in contrast to the three-dimensional example discussed in the previous section. Depending on the barrier thickness, the zero crossing of $C_{2,1}$ can happen for z_0 inside the well [Fig. 3(b)] or inside the barrier [Fig. 3(c)] (the zero crossing at, for example, $z_0 \approx -75$ Å, is barely noticeable).

C. GaAs/AlGaAs superlattice, *k* dependence

In the previous section, we studied the *p*-*r* relation for realistic well and barrier widths, but restricted the superlattice Bloch wave to $k = 0$. That allowed us to vary the cell boundaries continuously through the well and barrier and to determine the influence of the additional correction term as a function of that variation. In the following, we study the k dependence of the *p*-*r* relation in the superlattice using δ barriers. This allows us to illustrate, within a concrete example, the fact that in the *p*-*r* relation involving volume integrals, $\langle 2,k'|\hat{p}|1,k\rangle_{\text{vol}} = im_e\omega_{2,k';1,k}\langle 2,k'|z|1,k\rangle_{\text{vol}} + C_{2k',1k}$, neither $\langle 2,k'|z|1,k\rangle_{\text{vol}}$ nor $C_{2,k';1,k}$ are diagonal in k ($k = k'$), but of course the momentum matrix element is.

We solve Eq. (46) with

$$V_{SL}(z) = V_0 \sum_{l=-M}^{M} \delta(z - z_n), \tag{54}$$

where $z_n = na$ are the barrier locations. In each interval $z_n < z < z_{n+1}$, the wave function is given by right ("+") and left ("−") traveling waves,

$$\xi_{\ell k}(z) = \alpha_q^{(n,+)} e^{iq(z-z_n)} + \alpha_q^{(n,-)} e^{-iq(z-z_n)}, \tag{55}$$

with energy $\varepsilon_{\ell k} = \hbar^2 q^2/(2m)$. Bloch's theorem, $\xi_{\ell k+a}(z) = e^{ika}\xi_{\ell k}(z)$, yields the dispersion relation with real-valued solutions $q \equiv q_\ell(k)$,

$$e^{ika} = \text{Re}\, A \pm \sqrt{\beta^2 - (\text{Im}\, A)^2}, \tag{56}$$

where $A = e^{iqa}(1 - i\beta)$ and $\beta = mV_0/(q\hbar^2)$. The wave function coefficients are given by

$$\frac{\alpha_q^{(-)}}{\alpha_q^{(+)}} = \frac{1}{\beta}\left(ie^{i(k-q)a} - \beta - i\right), \tag{57}$$

independent of the cell index n.

Figures 4 and 5 show the diagonal momentum matrix element $p_{2,1}(k) = \langle 2,k|(-i\hbar)d/dz|1,k\rangle_{\text{vol}}$, the dipole matrix element $r_{2,1}(k',k) = \langle 2,k'|z|1,k\rangle_{\text{vol}}$, and $C_{2,k';1,k}$ for a fixed sample position ($z_0 = -1$ μm) and a superlattice of length $L = 2$ μm. As we discuss in Sec. IV, the dipole matrix element in an infinite crystal is proportional to $\delta(k' - k)$, which is obviously different from the PBC case shown in Fig. 5, where one can barely see a narrow structure on the diagonal $k' = k$. The appearance of nondiagonal values for the dipole matrix element (i.e., at $k' \neq k$) requires the existence of nondiagonal values for $C_{2,k';1,k}$. The figure shows that, in our example, $C_{2,k';1,k}$ has strong nondiagonal contributions, and is nonzero throughout the entire Brillouin zone.

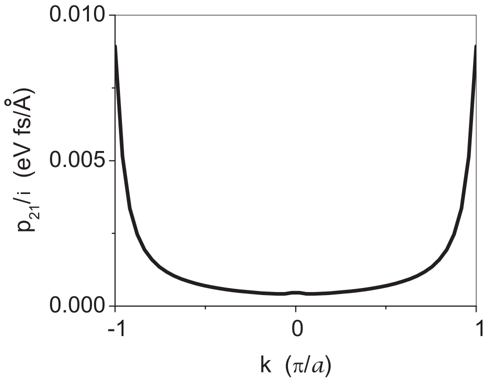

FIG. 4. Diagonal ($k = k'$) momentum matrix element of the 2-1 transition for the GaAs superlattice model with δ barriers.

We note that the matrix elements depend strongly on the value for the effective mass m_e, which is rather small in the present example. Choosing m_e to be close to the electron mass in vacuum, one obtains a relatively strong diagonal contribution for the dipole matrix element and, accordingly, as a smaller correction term (Fig. 5). Also, the feature at $k' = 0$ becomes less pronounced at larger mass values. At small m_e, the kinetic energy dominates, and the behavior is similar to the case without lattice potential, where the dipole matrix element acquires a discontinuity at $k' = 0$.

IV. INFINITE VOLUME (IV), NONVANISHING BOUNDARY CONDITIONS (NVBCs)

We recall from Secs. II and III that the interband dipole matrix element with Bloch wave functions defined in a finite box with periodic boundary conditions is not uniquely defined, and the corresponding *p*-*r* relation must include a correction term. At the same time, with Bloch wave functions defined over the whole (infinite) space $\varphi_{\nu,\mathbf{k}}^{(\infty)}(\mathbf{r})$ and normalized to delta functions, both the momentum matrix element and the dipole matrix element have been shown by Blount[10] to be well-defined $\mathbf{k}$-space distributions (delta functions). For the momentum matrix element,

$$\langle c\mathbf{k}'|\hat{\mathbf{p}}|\mathrm{v}\mathbf{k}\rangle_\infty = \int_{\substack{\text{all}\\ \text{space}}} d^3r\,\varphi_{c\mathbf{k}'}^{(\infty)*}(\mathbf{r})\hat{\mathbf{p}}\varphi_{\mathrm{v}\mathbf{k}}^{(\infty)}(\mathbf{r}) \tag{58}$$

$$= \sum_{\mathbf{G}} \delta(\mathbf{k} - \mathbf{k}' - \mathbf{G})[\langle u_{c\mathbf{k}}|\hat{\mathbf{p}}|u_{\mathrm{v}\mathbf{k}}\rangle_{\text{cell}} + \hbar\mathbf{k}\langle u_{c\mathbf{k}}|u_{\mathrm{v}\mathbf{k}}\rangle_{\text{cell}}] \tag{59}$$

$$= \delta(\mathbf{k} - \mathbf{k}')\langle u_{c\mathbf{k}}|\hat{\mathbf{p}}|u_{\mathrm{v}\mathbf{k}}\rangle_{\text{cell}}, \tag{60}$$

where we used again the usual way of splitting the integral into a sum over cell integrals, the fact that the Bloch functions are periodic in reciprocal space, and the delta function

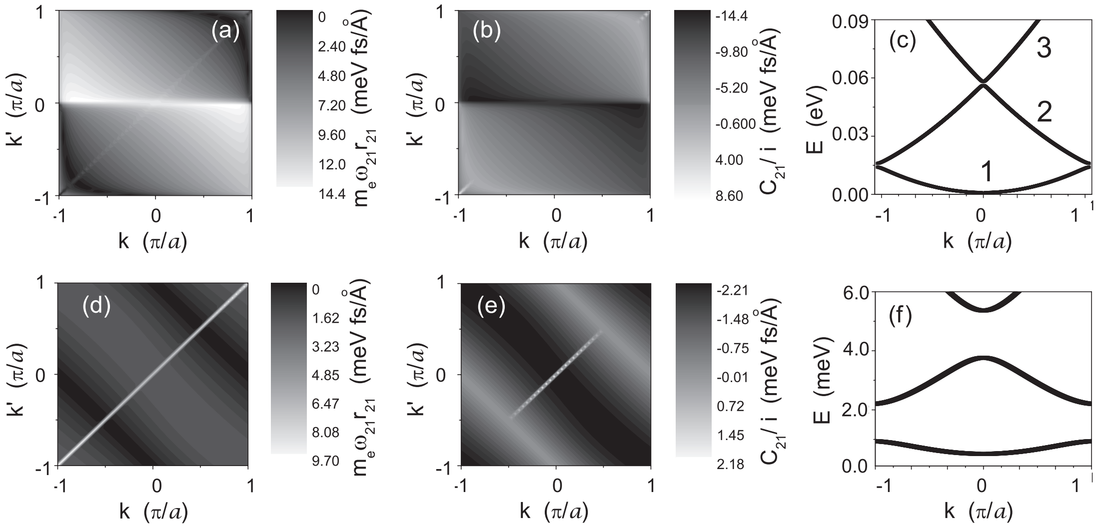

FIG. 5. (a)–(c) The intersubband matrix element $r_{2,1}(k',k)$ and the additional correction term $C_{2,1}(k',k)$ for the δ-barrier model with standard mass $m_e = 0.067m$, with the band structure shown in (c). For comparison, (d)–(f) show the same for $m_e = m$. The intuitive expectation of $r_{2,1}(k',k)$ being dominantly diagonal in k is seen in (d), while in the small-mass result (a) $r_{2,1}$ is not at all dominated by the diagonal ($k = k'$). The small-mass results exhibit an almost discontinuous behavior of $r_{2,1}$ at $k' = 0$ resulting from the almost kinklike feature at $k' = 0$ in subband 2.

representation

$$\frac{1}{(2\pi)^3}\sum_{\bar{m}=-\infty}^{\infty} e^{i\mathbf{k}\cdot\mathbf{R}_{\bar{m}}} = \frac{1}{v_c}\sum_{\mathbf{G}}\delta(\mathbf{k}-\mathbf{G}). \tag{61}$$

Again, since $\mathbf{k}$ and $\mathbf{k}'$ are in the first Brillouin zone, only $\mathbf{G} = 0$ contributes. The proof that the $\mathbf{r}$-matrix element is also a distribution is less trivial; it was given by Blount,[10] who showed

$$\langle c\mathbf{k}'|\mathbf{r}|v\mathbf{k}\rangle_\infty = \int_{\substack{\text{all}\\ \text{space}}} d^3r\,\varphi^{(\infty)*}_{c\mathbf{k}'}(\mathbf{r})\mathbf{r}\varphi^{(\infty)}_{v\mathbf{k}}(\mathbf{r}) \tag{62}$$

$$= \delta(\mathbf{k}-\mathbf{k}')\langle u_{c\mathbf{k}}|i\vec{\nabla}_{\mathbf{k}}|u_{v\mathbf{k}}\rangle_{\text{cell}}. \tag{63}$$

Obviously, the diagonal elements (i.e., $\mathbf{k} = \mathbf{k}'$) of the interband matrix elements taken over all space (both momentum and dipole) are not defined, while, trivially, the equal-k cell-matrix elements exist, provided that the k derivative of $u_{v\mathbf{k}}$ exists (the cell-matrix element is not that of $\mathbf{r}$, but of gradient-k). A detailed analysis of the connection between degeneracy and nonanalytic behavior of $u_{v\mathbf{k}}(\mathbf{r})$ as function of $\mathbf{k}$ has been given in Refs. 9 and 35.

In order to obtain a p-r relation for the IV/NVBC case, we use the p-r relation for cell integrals,

$$\langle u_{c\mathbf{k}}|\hat{\mathbf{p}}|u_{v\mathbf{k}}\rangle_{\text{cell}} = im\omega_{c\mathbf{k},v\mathbf{k}}\langle u_{c\mathbf{k}}|i\vec{\nabla}_{\mathbf{k}}|u_{v\mathbf{k}}\rangle_{\text{cell}}, \tag{64}$$

which was derived by Haug and given as Eq. (42.71) in Ref. 2. Equations (60), (63), and (64) immediately give the "atomlike" p-r relation for infinite crystals, expressed in terms of distributions:

$$\langle c\mathbf{k}'|\hat{\mathbf{p}}|v\mathbf{k}\rangle_\infty = \frac{im}{\hbar}(\varepsilon_{c\mathbf{k}'} - \varepsilon_{v\mathbf{k}})\langle c\mathbf{k}'|\mathbf{r}|v\mathbf{k}\rangle_\infty. \tag{65}$$

One may now ask whether this p-r relation, which does not contain a correction term, can be obtained from a finite-volume p-r relation when the limit of infinite volume is taken. We have seen already that this is not possible if we use finite volume and periodic boundary conditions. In the remainder of this section we proceed in the spirit of the infinite-volume limit, but instead of using the notion of finite "volume" we will interpret Eq. (65) as a limiting case involving wave packets that are of finite extent.

We first note that, since $\mathbf{r}\varphi^{(\infty)}_{v\mathbf{k}}(\mathbf{r})$ not just fails to go to zero, but actually blows up, as $r \to \infty$, the limit at infinity in the evaluation of $\langle c\mathbf{k}'|\mathbf{r}|v\mathbf{k}\rangle_\infty$ must be taken with a great deal of care. A common way to handle issues associated with delta-function-normalized wave functions is to treat them as limits of normalized but increasingly extended functions. In the following, we discuss the interpretation of the p-r relation Eq. (65) in this way. We note that Blount[10] does not follow this route directly. He stresses that the domain of the operator $\mathbf{r}$, i.e., the space of wave functions $\{\phi(\mathbf{r}) : \mathbf{r}\phi(\mathbf{r})\text{ is normalizable}\}$, is smaller than the full Hilbert space of normalizable wave functions. Expanding functions that belong to the domain of $\mathbf{r}$ in the Bloch basis $\{\varphi^{(\infty)}_{\nu\mathbf{k}}(\mathbf{r})\}$, he shows that it is formally correct to make the identification Eq. (63).

It is argued in Appendix A that one can construct a sequence of wave packet states for each band with the following properties. (i) For a given band, each wave packet state is a superposition of Bloch states only from that band (note that an arbitrary wave packet has components in multiple bands). (ii) The wave packets converge pointwise in space to a single Bloch wave function as the packet width in $\mathbf{k}$ space shrinks to zero. That is, the wave packet states are of a form similar to the Weyl's eigendifferentials (e.g., Ref. 36). Using $\varphi_{\nu,\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \varphi_{\nu,\mathbf{k}}(\mathbf{r})$, we write

$$\Psi_{\nu,\mathbf{k}_0}(\mathbf{r}) = \sum_{\mathbf{G}}\int_{BZ}\frac{d^3k}{(2\pi)^3}\xi_\nu(\mathbf{k}+\mathbf{G}-\mathbf{k}_0)\varphi^{(\infty)}_{\nu,\mathbf{k}}(\mathbf{r}), \tag{66}$$

where the envelope functions $\xi_\nu(\mathbf{k})$ are narrowly peaked around $\mathbf{k} = \mathbf{0}$. (iii) Each wave packet state $\Psi_{\nu,\mathbf{k}_0}(\mathbf{r})$ is normalizable and $\mathbf{r}\Psi_{\nu,\mathbf{k}_0}(\mathbf{r})$ is also normalizable. It is straightforward to show, as is done below, that the p-r relation Eq. (65) can be treated as the limit of p-r relations with the wave packet states $\Psi_{\nu,\mathbf{k}_0}(\mathbf{r})$. We recall that in the FV/PBC treatment, the fundamental reason for the presence of the correction terms in the *p-r* relation is that the operator $\mathbf{r}$ maps a Bloch wave function to a function outside the space in which H_0 is hermitian. With the wave packet states here, the mapping images of $\mathbf{r}$ stay within the domain of hermiticity of H_0.

Since $\mathbf{r}\Psi_{\nu,\mathbf{k}_0}(\mathbf{r})$ is square integrable, the *p-r* relation with $\Psi_{\nu,\mathbf{k}_0}(\mathbf{r})$ has the same form as in the atom case (for $\nu \neq \nu'$):

$$\int_{\substack{\text{all}\\\text{space}}} d^3r\,\Psi^*_{\nu'\mathbf{k}'_0}(\mathbf{r})\hat{\mathbf{p}}\Psi_{\nu\mathbf{k}_0}(\mathbf{r}) = \int_{\substack{\text{all}\\\text{space}}} d^3r\,\Psi^*_{\nu'\mathbf{k}'_0}(\mathbf{r})\frac{im}{\hbar}[H_0\mathbf{r}-\mathbf{r}H_0]\Psi_{\nu\mathbf{k}_0}(\mathbf{r}). \tag{67}$$

The wave functions go to zero sufficiently fast at infinity so that the integration by parts does not generate surface terms. Substituting Eq. (66) into Eq. (67), we obtain

$$0 = \sum_{\mathbf{G}\mathbf{G}'}\int_{BZ}\frac{d^3k}{(2\pi)^3}\frac{d^3k'}{(2\pi)^3}\xi^*_{\nu'}(\mathbf{k}'+\mathbf{G}'-\mathbf{k}_0{}')\xi_\nu(\mathbf{k}+\mathbf{G}-\mathbf{k}_0) \times\left\{\int_{\substack{\text{all}\\\text{space}}} d^3r\,\varphi^{(\infty)*}_{\nu'\mathbf{k}'}(\mathbf{r})\hat{\mathbf{p}}\varphi^{(\infty)}_{\nu\mathbf{k}}(\mathbf{r}) - \frac{im}{\hbar}(\varepsilon_{\nu'\mathbf{k}'}-\varepsilon_{\nu\mathbf{k}}) \times\int_{\substack{\text{all}\\\text{space}}} d^3r\,\varphi^{(\infty)*}_{\nu'\mathbf{k}'}(\mathbf{r})\mathbf{r}\varphi^{(\infty)}_{\nu\mathbf{k}}(\mathbf{r})\right\}. \tag{68}$$

If we now perform the limit $\xi_\nu(\mathbf{k}) \to (2\pi)^3\delta(\mathbf{k})$ or, equivalently, $\Psi_{\nu\mathbf{k}_0}(\mathbf{r}) \to \varphi^{(\infty)}_{\nu\mathbf{k}_0}(\mathbf{r})$, then only $\mathbf{G} = \mathbf{G}' = 0$ contribute and we obtain the desired *p-r* relation for Bloch wave functions in an infinite crystal:

$$\langle c\mathbf{k}'_0|\hat{\mathbf{p}}|\mathrm{v}\mathbf{k}_0\rangle_\infty = \frac{im}{\hbar}\big(\varepsilon_{c\mathbf{k}'_0}-\varepsilon_{\mathrm{v}\mathbf{k}_0}\big)\langle c\mathbf{k}'_0|\mathbf{r}|\mathrm{v}\mathbf{k}_0\rangle_\infty. \tag{69}$$

V. ENVELOPE FUNCTION APPROXIMATION IN NANOSTRUCTURES

The envelope function formalism (see, for example, Refs. 37–43) finds widespread application in the theory of nanostructures and quantum confined systems, such as quantum dots, quantum wires, and quantum wells. While the finite extent does not require the use of envelope functions (one could just treat the system as a large, but finite, molecule; see, for example, Ref. 44), it is desirable, when the length scale of variations of the confining potential is much longer than the lattice constant, to write the wave function in terms of lattice-periodic functions $u_{\nu\mathbf{k}}(\mathbf{r})$ (given by the solution of the infinite system) and the envelope $\xi_{\nu\ell}(\mathbf{r})$ (with ℓ labeling the subband), and to ensure vanishing (i.e., zero) boundary conditions using the envelope function, $\xi_{\nu\ell}(\mathbf{r})|_{\mathbf{r}\text{ on boundary}} = 0$. That way, interband transition matrix elements of nanostructures can still be largely reduced to those of the corresponding bulk system. The intersubband transition matrix elements, which we are not concerned with in this paper, are determined by the envelope functions.

As usual in an envelope function theory, we assume that the confining potential varies spatially so slowly that it does not mix the bands. That is, the energy eigenfunctions can be grouped into the same bands as in the bulk. We call these eigenfunctions nanostructure Bloch wave functions and denote them by $\Psi^{(\text{nano})}_{\nu\ell}(\mathbf{r})$, where ν labels the band and ℓ labels the individual states inside a band. Since these eigenfunctions have finite spatial support, it is clear that they satisfy the atomlike *p-r* relation (for $\nu \neq \nu'$)

$$\big\langle\Psi^{(\text{nano})}_{\nu'\ell'}\big|\hat{\mathbf{p}}\big|\Psi^{(\text{nano})}_{\nu\ell}\big\rangle = \frac{im}{\hbar}(\varepsilon_{\nu'\ell'}-\varepsilon_{\nu\ell})\big\langle\Psi^{(\text{nano})}_{\nu'\ell'}\big|\mathbf{r}\big|\Psi^{(\text{nano})}_{\nu\ell}\big\rangle. \tag{70}$$

Note that, written in this form, the conceptual benefits that arise from the fact that the wave functions contain cell-periodic contributions are not yet incorporated. We will discuss in the following how one can interpret Eq. (70) in terms of cell-matrix elements and envelope overlap integrals. One aspect of that discussion will be that, at least for states near the band edges, the dominant contribution to the dipole matrix element $\langle\Psi^{(\text{nano})}_{\nu'\ell'}|\mathbf{r}|\Psi^{(\text{nano})}_{\nu\ell}\rangle$ is given by $\langle u_{c\mathbf{k}}|i\vec{\nabla}_{\mathbf{k}}|u_{\mathrm{v}\mathbf{k}}\rangle_{\text{cell}}|_{\mathbf{k}=\mathbf{0}}$, as could be expected from the previous section.

Under the no-band-mixing approximation stated above, a nanostructure Bloch wave function in band ν can in general be written as a superposition of bulk Bloch wave functions from the same band, weighted by the envelope $\xi(\mathbf{k})$,

$$\Psi^{(\text{nano})}_{\nu\ell}(\mathbf{r}) = \sum_{\mathbf{G}}\int_{BZ}\frac{d^3k}{(2\pi)^3}\xi_{\nu\ell}(\mathbf{k}+\mathbf{G})e^{i\mathbf{k}\cdot\mathbf{r}}u_{\nu\mathbf{k}}(\mathbf{r}), \tag{71}$$

where one assumes the envelope function to be localized around $\mathbf{k} \simeq 0$, which, in turn, implies that only $\mathbf{G} = 0$ contributes to the sum

$$\Psi^{(\text{nano})}_{\nu\ell}(\mathbf{r}) = \int_{BZ}\frac{d^3k}{(2\pi)^3}\xi_{\nu\ell}(\mathbf{k})e^{i\mathbf{k}\mathbf{r}}u_{\nu\mathbf{k}}(\mathbf{r}). \tag{72}$$

Furthermore, in real space $\xi_{\nu\ell}(\mathbf{r})$ is zero at the boundaries of the nanostructure. The spatial Fourier coefficients $\xi_{\nu\ell}(\mathbf{k})$ may be determined by substituting Eq. (72) into the one-electron Hamiltonian eigenvalue equation with the confining potential. Since $\xi_{\nu\ell}(\mathbf{k})$ is peaked around $\mathbf{k} = \mathbf{0}$, the eigenvalue problem can be simplified by the zone-center approximation (zca), $u_{\nu\mathbf{k}}(\mathbf{r}) \simeq u_{\nu\mathbf{0}}(\mathbf{r})$, which allows us to write the eigenfunction as

$$\Psi^{(\text{nano})}_{\nu\ell}(\mathbf{r}) \approx \Psi^{(\text{nano,zca})}_{\nu\ell}(\mathbf{r}) = \xi^{(\text{zca})}_{\nu\ell}(\mathbf{r})u_{\nu\mathbf{0}}(\mathbf{r}), \tag{73}$$

where $\xi^{(\text{zca})}_{\nu\ell}(\mathbf{r})$ is the Fourier transform of $\xi^{(\text{zca})}_{\nu\ell}(\mathbf{k})$. The label "zca" indicates that $\xi^{(\text{zca})}_{\nu\ell}(\mathbf{r})$ is obtained by solving the Hamiltonian eigenvalue problem with the approximate wave function Eq. (73). One might think that the wave functions from two bands of the form Eq. (73) would give the dominant contribution to the dipole matrix element between states in the two bands. But Burt[4] shows that this contribution is actually highly suppressed, i.e., for $\nu \neq \nu'$,

$$\big\langle\Psi^{(\text{nano,zca})}_{\nu'\ell'}\big|\mathbf{r}\big|\Psi^{(\text{nano,zca})}_{\nu\ell}\big\rangle \approx 0, \tag{74}$$

as L_c/a gets large, where L_c is the length scale of variation of $\xi^{(\text{zca})}_{\nu\ell}(\mathbf{r})$. We give an alternative proof of this fact in Appendix B. To obtain the leading contribution to the dipole ($\mathbf{r}$) matrix element, then, one needs to consider corrections to Eq. (73). Burt[4] uses an expansion in terms of $u_{\nu'\mathbf{0}}(\mathbf{r})$ from all bands

$$\Psi^{(\text{nano,Burt})}_{\nu}(\mathbf{r}) = \sum_{\nu'}F_{\nu\nu'}(\mathbf{r})u_{\nu'\mathbf{0}}(\mathbf{r}), \tag{75}$$

of which Eq. (74) is the zeroth-order term. However, Burt[4] does not outline a path towards the cell-envelope factorization as defined in Sec. I.

We stay within one band and introduce a correction by retaining the $\mathbf{k}$ dependence of $u_{\nu\mathbf{k}}(\mathbf{r})$ in the neighborhood of $\mathbf{k}=\mathbf{0}$. The dipole matrix element taken with the general nanostructure Bloch wave functions Eq. (72) between the valence band and the conduction band is

$$\begin{aligned}\langle c\ell'|\mathbf{r}|\text{v}\ell\rangle_{\text{nano}} &= \int_{\substack{\text{all}\\ \text{space}}} d^3r\,\Psi^{(\text{nano})}_{c\ell'}(\mathbf{r})\mathbf{r}\Psi^{(\text{nano})}_{\text{v}\ell}(\mathbf{r})\\ &= \int_{BZ}\frac{d^3k}{(2\pi)^3}\frac{d^3k'}{(2\pi)^3}\xi^*_{c\ell'}(\mathbf{k}')\xi_{\text{v}\ell}(\mathbf{k})(2\pi)^3\\ &\quad\times\int_{\substack{\text{all}\\ \text{space}}} d^3r\,\varphi^{(\infty)*}_{c\mathbf{k}'}(\mathbf{r})\mathbf{r}\varphi^{(\infty)}_{\text{v}\mathbf{k}}(\mathbf{r})\\ &= \int_{BZ}\frac{d^3k}{(2\pi)^3}\frac{d^3k'}{(2\pi)^3}\xi^*_{c\ell'}(\mathbf{k}')\xi_{\text{v}\ell}(\mathbf{k})(2\pi)^3\\ &\quad\times\delta(\mathbf{k}-\mathbf{k}')\langle u_{c\mathbf{k}'}|i\vec{\nabla}_{\mathbf{k}}|u_{\text{v}\mathbf{k}}\rangle_{\text{cell}},\end{aligned}\qquad(76)$$

where we have used the result from Sec. IV. For slowly varying confinement potentials and states close to the band edges, we approximate

$$\langle u_{c\mathbf{k}}|i\vec{\nabla}_{\mathbf{k}}|u_{\text{v}\mathbf{k}}\rangle_{\text{cell}} \simeq \langle u_{c\mathbf{k}}|i\vec{\nabla}_{\mathbf{k}}|u_{\text{v}\mathbf{k}}\rangle_{\text{cell}}|_{\mathbf{k}=0},\qquad(77)$$

which could be labeled the "generalized zone-center approximation" (as it involves the functions $u_{\nu\mathbf{k}}$ and their k derivatives at the zone center), and obtain

$$\begin{aligned}\langle c\ell'|\mathbf{r}|\text{v}\ell\rangle_{\text{nano}} &\simeq \langle u_{c\mathbf{k}}|i\vec{\nabla}_{\mathbf{k}}|u_{\text{v}\mathbf{k}}\rangle_{\text{cell}}|_{\mathbf{k}=0}\\ &\quad\times\int_{BZ}\frac{d^3\mathbf{k}}{(2\pi)^3}\xi^*_{c\ell'}(\mathbf{k})\xi_{\text{v}\ell}(\mathbf{k}).\end{aligned}\qquad(78)$$

Again assuming that the spatial Fourier spectrum of the envelope is fully contained in the Brillouin zone, we find that the nanostructure $\mathbf{r}$-matrix element is given in the form of the cell-envelope factorization, i.e., as a product of the envelope overlap integral and the gradient-k cell-matrix element,

$$\begin{aligned}\langle c\ell'|\mathbf{r}|\text{v}\ell\rangle_{\text{nano}} &\simeq \langle c\ell'|\mathbf{r}|\text{v}\ell\rangle^{\text{zone center}}_{\text{nano}}\\ &= \langle u_{c\mathbf{k}}|i\vec{\nabla}_{\mathbf{k}}|u_{\text{v}\mathbf{k}}\rangle_{\text{cell}}|_{\mathbf{k}=0}\\ &\quad\times\int_{\substack{\text{all}\\ \text{space}}} d^3r\,\xi^{(\text{zca})*}_{c\ell'}(\mathbf{r})\xi^{(\text{zca})}_{\text{v}\ell}(\mathbf{r}),\end{aligned}\qquad(79)$$

where, consistent with the approximation Eq. (77), we have replaced $\xi_{\nu\ell}(\mathbf{r})$ in the overlap integral by $\xi^{(\text{zca})}_{\nu\ell}(\mathbf{r})$. When the envelope function overlap integral is nonzero, Eq. (79) is the dominant contribution to the interband dipole matrix element in nanostructures in which there is a separation of length scales between the whole nanostructure and the unit cell. If the overlap integral vanishes, e.g., for symmetry reasons, the subdominant terms would have to be considered. This problem will not concern us here.

It is now straightforward to derive a p-r relation for the nanostructure that contains only cell-matrix elements and envelope overlap integrals in the form of the cell-envelope factorization. For this, we first note that

$$\begin{aligned}\left\langle\Psi^{(\text{nano,zca})}_{c\ell'}\middle|\hat{\mathbf{p}}\middle|\Psi^{(\text{nano,zca})}_{\text{v}\ell}\right\rangle &\approx \langle u_{c\mathbf{0}}|\hat{\mathbf{p}}|u_{\text{v}\mathbf{0}}\rangle_{\text{cell}}\\ &\quad\times\int_{\substack{\text{all}\\ \text{space}}} d^3r\,\xi^{(\text{zca})*}_{c\ell'}(\mathbf{r})\xi^{(\text{zca})}_{\text{v}\ell}(\mathbf{r}),\end{aligned}\qquad(80)$$

which can readily be verified. Hence, both the momentum [Eq. (80)] and dipole [Eq. (79)] matrix elements are written in the form of the cell-envelope factorization. The relation between the cell-matrix elements (here to be taken at $\mathbf{k}=\mathbf{0}$) in those two quantities has been given by Eq. (64). This yields immediately the zone-center approximation version of the more general Eq. (70),

$$\begin{aligned}&\left\langle\Psi^{(\text{nano,zca})}_{c\ell'}\middle|\hat{\mathbf{p}}\middle|\Psi^{(\text{nano,zca})}_{\text{v}\ell}\right\rangle\\ &\quad= \frac{im}{\hbar}(\varepsilon_{c\mathbf{0}}-\varepsilon_{\text{v}\mathbf{0}})\langle c\ell'|\mathbf{r}|\text{v}\ell\rangle^{\text{zone center}}_{\text{nano}},\end{aligned}\qquad(81)$$

where $(\varepsilon_{c\mathbf{0}}-\varepsilon_{\text{v}\mathbf{0}})$ is the bulk band gap. Note that, just as in the case of an infinite crystal, there is no correction term in the p-r relation, but, also similar to the infinite crystal, the cell-matrix element determining the dipole is that of gradient-k.

Finally, we briefly compare our nanostructure transition dipole Eq. (79) with that obtained by Burt.[4] In Eq. (79), the roles of the bulk unit-cell wave functions and the envelopes are cleanly separated. In contrast, the expressions obtained by Burt [Eqs. (14) and (16) in Ref. 4] contain only the envelope functions. This does not imply that Burt's expressions are independent of the $u_{\nu\mathbf{0}}$'s, since the envelope functions are determined in a diagonalization of the Hamiltonian in a $u_{\nu\mathbf{0}}$ basis. After all, the dipole matrix element in Ref. 4 does satisfy essentially the same p-r relation as Eq. (81). But its dependencies on $u_{\nu\mathbf{0}}$ and the envelopes are entangled. In particular, in the case where $\xi^{(\text{zca})}_{\text{v}\ell}$ and $\xi^{(\text{zca})}_{c\ell'}$ have opposite parities, the overlap integral in Eq. (79), and thus $\langle c\ell'|\mathbf{r}|\text{v}\ell\rangle^{\text{zone center}}_{\text{nano}}$, vanish, implying that the nanostructure transition dipole between the two states is highly suppressed. This is not immediately clear from the expressions in Ref. 4.

VI. CONCLUSION

In conclusion, we have discussed the relation between momentum and dipole (or, equivalently $\mathbf{r}$) matrix elements in semiconductors, including bulk semiconductors with finite volume (treated with periodic boundary conditions), bulk semiconductors with infinite volume, and semiconductor nanostructures. In contrast to many common textbook treatments, we derived a correction term to the p-r relation in the case of periodic boundary conditions. With those boundary conditions, the correction term does not vanish in the limit of infinite volume. On the other hand, the p-r relation for infinite-volume crystals in the distribution sense does not have a correction term. We showed that the absence of the correction term in the infinite-volume case can be understood on the basis of a limiting procedure in which first wave packets of finite extent are constructed and then the limit of infinite extent is taken.

The correction term in the case of periodic boundary conditions was illustrated with several numerical examples. For bulk GaAs, the interband $\mathbf{r}$ matrix element at the Γ point was shown to be much smaller than the lattice constant and its value depends on the choice of the unit-cell center. The correction term was found to be dominant in the *p*-*r* relation for any choice of unit-cell center.

In contrast, the relative importance of the correction term for the transition between the lowest two subbands in a GaAs superlattice depends strongly on the origin of the unit cell. In particular, the correction term becomes small if the unit cell is chosen such that its boundary points lie in the barriers where the wave functions are small.

We also discussed the interband matrix elements in nanostructures. We showed that the cell-envelope factorization of the **r** matrix into a product of cell-matrix element and envelope overlap integrals involves the gradient-*k* cell integral rather than the **r** cell integral, which is consistent with well-known cell-matrix element relations for bulk semiconductors.

We believe that our analysis has some significance for the application of the dipole approximation in the light-matter coupling Hamiltonian. Unlike atomic systems, where the light fields can be assumed to be spatially homogeneous over the spatial extent of the atom, and where, as a consequence, a simple gauge transformation is available that eliminates the vector potential in favor of the electric field (entering the coupling Hamiltonian $-\mathbf{d}\cdot\mathbf{E}$), such a simple transformation is not applicable to extended Bloch wave functions. Practical solutions may include dealing with Wannier or tight-binding functions[45] (which are localized, but unfortunately not energy eigenfunctions of the single-electron Hamiltonian with the lattice-periodic potential). If periodic boundary conditions and Bloch wave functions are used, the matrix elements of the **r** operator are not the same as those of the gradient-*k* operator, and if one wants to use the *p*-*r* relation, one has to account for the additional correction term. A practical alternative to that is to use matrix elements of the gradient-*k* operator in place of those of **r** in a *naive* application of the atomic *p*-*r* relation. Starting from an $\mathbf{A}\cdot\mathbf{p}$ Hamiltonian one can use that atomiclike *p*-*r* to eliminate the momentum matrix elements by a matrix element that one can loosely call **r**-matrix elements (but which is indeed not the **r**-matrix element but the gradient-*k* matrix element), and, together with reformulating the time derivative of the vector potential in terms of the electric field amplitude, one can obtain a coupling Hamiltonian that is formally similar to a dipole Hamiltonian, $-\mathbf{d}\cdot\mathbf{E}$. References 2 and 10 show that, in this practical alternative, the result is valid for both delta-normalized and box-normalized (with periodic boundary conditions) Bloch wave functions. The analysis in this paper shows it is also valid in a cell-envelope approach to nanostructures. Adopting this recipe in the formulation of the dipole electron-light coupling, one need not worry, if one chooses not to, about the pathologies of the **r**-matrix elements with extended wave functions (one just has to be aware that the matrix elements of the gradient-*k* operator are not the same as those of the the **r** operator, even if, in practice, one may be tempted to equate the gradient-*k* with the **r** operator).

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APPENDIX A: WAVE PACKETS OF BLOCH WAVE FUNCTIONS

In this Appendix, we argue that one can construct a sequence of wave packet states for each band which satisfy the conditions laid down above and below Eq. (66): (i) For given band ν, each wave packet state $\Psi_{\nu,\mathbf{k}_0}(\mathbf{r})$ is a superposition of Bloch states only from that band. (ii) The wave packets converge pointwise in space to a single Bloch wave function as the packet width in **k** space shrinks to zero. (iii) Each wave packet state $\Psi_{\nu,\mathbf{k}_0}(\mathbf{r})$ is normalizable and $\mathbf{r}\Psi_{\nu,\mathbf{k}_0}(\mathbf{r})$ is also normalizable.

We begin by arguing that one can construct a sequence of envelope functions $\xi_\nu(\mathbf{k})$ which reside completely in the first Brillouin zone, go to a delta function around $\mathbf{k}=\mathbf{0}$, and have Fourier transforms in **r** space which are suitably normalized. We show this with an example in one dimension. Consider the following sequence of functions, for $m = 1,2,\ldots$:

$$\begin{aligned}\xi_{\nu m}(k) &= 0, \quad k < -K_m,\\ &= \frac{2\pi}{K_m^2}(k+K_m), \quad -K_m \leqslant k < 0,\\ &= \frac{2\pi}{K_m^2}(K_m-k), \quad 0 \leqslant k < K_m,\\ &= 0, \quad k \geqslant K_m,\end{aligned} \tag{A1}$$

where K_m is within the first Brillouin zone for all m and $K_m \to 0$ as $m \to \infty$. Each $\xi_{\nu m}(\mathbf{k})$ is a sequence of triangular "tent" functions of height $2\pi/K_m$ and base length $2K_m$. The area under the curve is the same (=1) for all m, while the base support tends to zero: The sequence tends towards $2\pi\,\delta(k)$. The Fourier transform to x space of $\xi_{\nu m}(k)$ is

$$\xi_{\nu m}(x) = \frac{2}{K_m^2 x^2}[1-\cos(K_m x)]. \tag{A2}$$

It can readily be verified that $\xi_{\nu m}(x)$ is a smooth function of x and both itself and $x\xi_{\nu m}(x)$ are square normalizable. The basic point is that $\xi_{\nu m}(k)$ is not smooth at the points $k=-K_m,0,K_m$, at each of which the first-order derivative is discontinuous. This translates to a $1/x^2$ behavior at large x in $\xi_{\nu m}(x)$. In general, if one desires to bound the large x behavior of $\xi_{\nu m}(x)$ by $1/x^n$, where n is a positive integer larger than 1, one constructs a tent function $\xi_{\nu m}(x)$ in k space with at least $n-2$ continuous derivatives.

We now turn to the wave packet state Eq. (66). Since $\xi_\nu(\mathbf{k})$ is chosen to be completely in the first Brillouin zone, we can limit the **G** sum to $\mathbf{G}=\mathbf{0}$ and formally extend the integration range to all k space,

$$\Psi_{\nu\mathbf{k}_0}(\mathbf{r}) = \int_{\substack{\text{all}\\ k\text{ space}}} \frac{d^3k}{(2\pi)^3}\xi_\nu(\mathbf{k}-\mathbf{k}_0)\varphi^{(\infty)}_{\nu\mathbf{k}}(\mathbf{r}). \tag{A3}$$

Here one might argue that since $\xi_\nu(\mathbf{k}-\mathbf{k}_0)$ is made progressively narrow, we can approximate the lattice-periodic part of the Bloch wave function $u_{\nu\mathbf{k}}(\mathbf{r})$ by $u_{\nu\mathbf{k}_0}(\mathbf{r})$. But, as is shown in Sec. V and Appendix B, there is a pitfall in doing this when the wave packet state is used in a dipole matrix element. To exercise more care, we expand $u_{\nu\mathbf{k}}(\mathbf{r})$ around $\mathbf{k}_0$ [restricting ourselves to points $\mathbf{k}_0$ where $u_{\nu\mathbf{k}}(\mathbf{r})$ is analytic as a function of

k; see Refs. 9 and 35],

$$u_{\nu\mathbf{k}_0+\mathbf{k}}(\mathbf{r}) = \sum_{\ell=0}^{\infty} \frac{1}{\ell!}(\mathbf{k}\cdot\vec{\nabla}_{\mathbf{k}})^{\ell}\, u_{\nu\mathbf{k}_0}(\mathbf{r}), \tag{A4}$$

and using $\mathbf{k}e^{i\mathbf{k}\cdot\mathbf{r}} = -i\vec{\nabla}_{\mathbf{r}}e^{i\mathbf{kr}}$ we can write

$$\Psi_{\nu\mathbf{k}_0}(\mathbf{r}) = \sum_{\ell=\mathbf{0}}^{\infty} \mathbf{c}_{\ell}(\mathbf{r}). \tag{A5}$$

In an unorthodox, but compact, notation, we can write the ℓth term as

$$c_{\ell}(\mathbf{r}) = \frac{1}{(2\pi)^{3/2}} e^{i\mathbf{k}_0\cdot\mathbf{r}} \frac{1}{\ell!}\big(-i\vec{\nabla}^{(\xi)}_{\mathbf{r}}\cdot\vec{\nabla}_{\mathbf{k}}\big)^{\ell}\xi_{\nu}(\mathbf{r})u_{\nu\mathbf{k}_0}(\mathbf{r}), \tag{A6}$$

where it is understood that $\vec{\nabla}^{(\xi)}_{\mathbf{r}}$ operates only on $\xi(\mathbf{r})$ [note that $\xi(\mathbf{r})$, i.e., the Fourier transform of $\xi(\mathbf{k})$, appears because we were able to extend the k integral over all k space]. A formal, but slightly cumbersome, expression is

$$\begin{aligned} c_{\ell}(\mathbf{r}) = {} & \frac{1}{(2\pi)^{3/2}} e^{i\mathbf{k}_0\cdot\mathbf{r}} \frac{1}{\ell!} \sum_{n=0}^{\ell}\sum_{m=0}^{\ell-n}\binom{\ell}{n}\binom{\ell-n}{m} \\ & \times \frac{\partial^{\ell-n-m}\xi_{\nu}(\mathbf{r})}{\partial x^{\ell-n-m}}\frac{\partial^{\ell-n-m}u_{\nu\mathbf{k}}(\mathbf{r})}{\partial k_x^{\ell-n-m}}\bigg|_{\mathbf{k}_0} \\ & \times \frac{\partial^{m}\xi_{\nu}(\mathbf{r})}{\partial y^{m}}\frac{\partial^{m}u_{\nu\mathbf{k}}(\mathbf{r})}{\partial k_y^{m}}\bigg|_{\mathbf{k}_0} \times \frac{\partial^{n}\xi_{\nu}(\mathbf{r})}{\partial z^{n}}\frac{\partial^{n}u_{\nu\mathbf{k}}(\mathbf{r})}{\partial k_z^{n}}\bigg|_{\mathbf{k}_0}, \end{aligned} \tag{A7}$$

where $\binom{n}{m}$ are the binomial coefficients.

It is important to note that the k derivative of the lattice-periodic function is itself lattice periodic,

$$\vec{\nabla}_{\mathbf{k}}u_{\nu\mathbf{k}}(\mathbf{r}+\mathbf{R}_{\bar{m}}) = \vec{\nabla}_{\mathbf{k}}u_{\nu\mathbf{k}}(\mathbf{r}), \tag{A8}$$

and hence does not grow or diverge at infinity, provided it is finite within a unit cell. Since $\xi_{\nu}(\mathbf{r})$ decays sufficiently fast at large $\mathbf{r}$, each $c_{\ell}(\mathbf{r})$ as defined in Eq. (A6) and $\mathbf{r}c_{\ell}(\mathbf{r})$ are square normalizable. The remaining question is whether the series Eq. (A5) retains this property. We provide a rough argument that this is the case with the example of tent functions introduced above. In that example, Eq. (A6) reduces, for each m, to

$$c_{\ell m}(x) = \frac{1}{(2\pi)^{1/2}} e^{ik_0x}\frac{1}{\ell!}(-i)^{\ell}\frac{d^{\ell}\xi_{\nu m}(x)}{dx^{\ell}}\frac{\partial^{\ell}u_{\nu k}(x)}{\partial k^{\ell}}\bigg|_{k=k_0}. \tag{A9}$$

With $\xi_{\nu m}(x)$ given by Eq. (A2), in each derivative $\frac{d^{\ell}\xi_{\nu m}(x)}{dx^{\ell}}$ the leading term as $x\to\infty$ is $O(1/x^2)$ and is bounded by $2K_m^{\ell-2}/x^2$. Therefore the leading term in $\Psi_{\nu\mathbf{k}_0}(\mathbf{r})$ is bounded by the sum

$$\begin{aligned} & \frac{2}{(2\pi)^{1/2}K_m^2x^2}\sum_{\ell=0}^{\infty}\frac{1}{\ell!}K_m^{\ell}\frac{\partial^{\ell}u_{\nu k}(x)}{\partial k^{\ell}}\bigg|_{k=k_0} \\ & = \frac{2}{(2\pi)^{1/2}K_m^2x^2}u_{\nu k_0+K_m}(x), \end{aligned} \tag{A10}$$

which satisfies condition (iii) above.

APPENDIX B: PROOF OF EQ. (74)

In this Appendix, we provide a proof of Eq. (74). We have

$$\begin{aligned} & \big\langle\Psi^{(\mathrm{nano,zca})}_{c\ell'}\big|\mathbf{r}\big|\Psi^{(\mathrm{nano,zca})}_{\mathrm{v}\ell}\big\rangle \\ & = \int_{\substack{\mathrm{all}\\ \mathrm{space}}} d^3r\,\xi^{(\mathrm{zca})*}_{c\ell'}(\mathbf{r})\xi^{(\mathrm{zca})}_{\mathrm{v}\ell}(\mathbf{r})u^{*}_{c\mathbf{0}}(\mathbf{r})\mathbf{r}u_{\mathrm{v}\mathbf{0}}(\mathbf{r}). \end{aligned} \tag{B1}$$

We show now that this is not a product of the envelope overlap integral and a **r**-matrix element taken over the unit cell. In contrast, we show that this is basically zero. To simplify the notation, let us define

$$\xi^{(\mathrm{zca})*}_{c\ell'}(\mathbf{r})\xi^{(\mathrm{zca})}_{\mathrm{v}\ell}(\mathbf{r}) = g(\mathbf{r}), \tag{B2}$$

with the subscripts $c\ell'$,vℓ suppressed to keep the notation simple. Now

$$\begin{aligned} \big\langle\Psi^{(\mathrm{nano,zca})}_{c\ell'}\big|\mathbf{r}\big|\Psi^{(\mathrm{nano,zca})}_{\mathrm{v}\ell}\big\rangle & = \int_{\substack{\mathrm{all}\\ \mathrm{space}}} d^3r\,g(\mathbf{r})u^{*}_{c\mathbf{0}}(\mathbf{r})u_{\mathrm{v}\mathbf{0}}(\mathbf{r}) \\ & = \sum_{\bar{m}}\int_{\mathrm{cell}} d^3r\,g(\mathbf{r}+\mathbf{R}_{\bar{m}})u^{*}_{c\mathbf{0}}(\mathbf{r}) \\ & \quad \times[\mathbf{r}+\mathbf{R}_{\bar{m}}]u_{\mathrm{v}\mathbf{0}}(\mathbf{r}). \end{aligned} \tag{B3}$$

Expanding the envelope functions to first order in **r**,

$$g(\mathbf{r}+\mathbf{R}) \simeq g(\mathbf{R}) + \vec{\nabla}g|_{\mathbf{R}}\cdot\mathbf{r}, \tag{B4}$$

we have

$$\begin{aligned} & \big\langle\Psi^{(\mathrm{nano})(0)}_{c\ell'}\big|\mathbf{r}\big|\Psi^{(\mathrm{nano})(0)}_{\mathrm{v}\ell}\big\rangle \\ & = \sum_{\bar{m}}\int_{\mathrm{cell}} d^3r[g(\mathbf{R}_{\bar{m}})\mathbf{R}_{\bar{m}} + g(\mathbf{R}_{\bar{m}})\mathbf{r} + \mathbf{R}\vec{\nabla}g|_{\mathbf{R}_{\bar{m}}}\cdot\mathbf{r} \\ & \quad + \mathbf{r}\vec{\nabla}g|_{\mathbf{R}_{\bar{m}}}\cdot\mathbf{r}]u^{*}_{c\mathbf{0}}(\mathbf{r})u_{\mathrm{v}\mathbf{0}}(\mathbf{r}). \end{aligned} \tag{B5}$$

The first term in the brackets is zero due to the orthogonality of the u functions, and the last term is a quadrupole term that we neglect (after all, we are evaluating the dipole matrix element and multipole corrections to this element would be an intrinsic conceptual contradiction). Denoting the cell **r**-matrix element by

$$\mathbf{r}^{(\mathrm{cell})}_{c\mathrm{v}} = \frac{1}{v_c}\int_{\mathrm{cell}} d^3r\,u^{*}_{c\mathbf{0}}(\mathbf{r})\mathbf{r}u_{\mathrm{v}\mathbf{0}}(\mathbf{r}), \tag{B6}$$

we have

$$\begin{aligned} & \big\langle\Psi^{(\mathrm{nano})(0)}_{c\ell'}\big|\mathbf{r}\big|\Psi^{(\mathrm{nano})(0)}_{\mathrm{v}\ell}\big\rangle \\ & = \sum_{\bar{m}} v_c\big[g(\mathbf{R}_{\bar{m}})\mathbf{r}^{(\mathrm{cell})}_{c\mathrm{v}} + \mathbf{R}_{\bar{m}}\vec{\nabla}g\big|_{\mathbf{R}_{\bar{m}}}\cdot\mathbf{r}^{(\mathrm{cell})}_{c\mathrm{v}}\big] \\ & \quad + \text{nondipole terms}. \end{aligned} \tag{B7}$$

We have indicated explicitly the nondipole term; in the following we will suppress this. We evaluate the $\bar{m}$ sum approximately by interpreting it as a Riemann sum and taking the limit to an integral,

$$\sum_{\bar{m}} v_c \to \int d^3R, \tag{B8}$$

which yields

$$\big\langle\Psi^{(\mathrm{nano})(0)}_{c\ell'}\big|\mathbf{r}\big|\Psi^{(\mathrm{nano})(0)}_{\mathrm{v}\ell}\big\rangle = \int d^3R\big[g(\mathbf{R})\mathbf{r}^{(\mathrm{cell})}_{c\mathrm{v}} + \mathbf{R}\vec{\nabla}g\big|_{\mathbf{R}}\cdot\mathbf{r}^{(\mathrm{cell})}_{c\mathrm{v}}\big]. \tag{B9}$$

Consider the ith Cartesian component of this equation:

$$\left\langle \Psi_{c\ell'}^{(\mathrm{nano})(0)} \middle| r_i \middle| \Psi_{\mathrm{v}\ell}^{(\mathrm{nano})(0)} \right\rangle = \int d^3R \left[g(\mathbf{R}) r_{\mathrm{cv},i}^{(\mathrm{cell})} + R_i \sum_j \frac{\partial g}{\partial R_j} r_{\mathrm{cv},j}^{(\mathrm{cell})} \right]. \tag{B10}$$

The terms in the j sum with $j \neq i$ vanish since the integral over R_j can be trivially performed, yielding the envelope functions [i.e., $g(\mathbf{R})$] evaluated at the integration boundary (the surface of the nanostructure), and by assumption the envelope functions are zero at that boundary. The $i = j$ contribution in the j sum can be integrated by parts. The surface term again vanishes by the same argument (vanishing envelope functions at the boundary), while the remaining term cancels exactly the first term in Eq. (B10). Hence, except for nondipole corrections,

$$\left\langle \Psi_{c\ell'}^{(\mathrm{nano,zca})} \middle| \mathbf{r} \middle| \Psi_{\mathrm{v}\ell}^{(\mathrm{nano,zca})} \right\rangle = 0. \tag{B11}$$

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