Electromagnetic coupling and gauge invariance in the empirical tight-binding method

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We examine the requirements placed upon the Hamiltonian under the demand of gauge invariance. From these requirements we derive the gauge-invariant form of the tight-binding Hamiltonian with electromagnetic coupling. In our derivation we do not make recourse to a Peierls substitution and hence avoid introducing any ambiguities of path. Our expression transparently reduces to the familiar expression in a complete basis. We apply this Hamiltonian to study resonant magnetotunneling spectroscopy using a simple tight-binding model.

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I. INTRODUCTION

One of the great attractions of the empirical tight-binding method is its close link to atomic and molecular physics through its description of the electronic structure of a crystal in terms of matrix elements of the Hamiltonian between localized atomiclike orbitals centered on neighboring atoms.[1,2] These matrix elements are reduced to a minimal set using symmetries of the crystal, and the resulting set of parameters is chosen to reproduce the observed energy gaps and effective masses.[3–7] Owing to the localized nature of the interactions, the method has proven very useful in models of reduced-dimensional structures as well.[8–10] Deducing interface parameters is not difficult and an applied electrostatic potential is conveniently treated as a same-site, same-orbital only, stepwise-constant interaction.

In contrast to the straightforward treatment of electrostatic potentials, numerous schemes have been proposed for including electromagnetic effects via the vector potential,[11–18] many involving the introduction of new parameters. Graf and Vogl[12] have pointed out that this is unnecessary in their method, which is based upon the Peierls substitution and the two-center approximation. Although their approach is significantly more systematic than most, it is an inescapable fact that the Peierls substitution is, strictly speaking, valid only in one dimension, where there can be no ambiguity of path. The Peierls substitution is also aesthetically unattractive, since it gives a prescription for a matrix element rather than an explicit formula for the Hamiltonian operator in the presence of the vector potential. This situation differs markedly from the formalism of the minimal coupling Hamiltonian familiar from standard quantum mechanics, in which one has an explicit operator and from which considerations of path are completely absent.

Graf and Vogl[12] address this ambiguity by choosing the straight line connecting the two atomic sites involved in a matrix element for their path, quite candidly noting the path dependence of their method. While the straight-line path seems reasonable for a nearest-neighbor model such as the one they employ, the situation is not so clear for models having interactions with more-distant neighbors. For example, a second-near-neighbor matrix element for zinc-blende or diamond crystals presents two obvious competing choices: the straight line between the second-near neighbors, or the two-leg path passing through their common nearest neighbor. (It can be further argued that paths connecting only the second neighbors other than the straight line ought to be considered as well.) The situation rapidly becomes more confusing for more complicated crystals and/or models with more-distant-neighbor interactions.

Here we shall derive the correct expression for the tight-binding Hamiltonian in the presence of the vector potential, thereby overcoming the aesthetic (lack of an explicit operator expression) and practical (ambiguity of path) limitations of the Peierls-substitution approach. Our derivation begins with the observation that the vector potential must enter the equations of motion via the momentum operator and fully takes into account the incompleteness of the tight-binding basis. We introduce no additional parameters into the momentum operator, ensuring that it is the same as the momentum operator used to calculate carrier velocities (band slopes) and inverse effective masses (band curvatures). (Although this treatment of the momentum operator precludes intra-atomic transitions, it avoids altogether ambiguities in defining matrix elements of higher powers of $\mathbf{r}$ in the localized-orbital basis—e.g., $r^{(z)2}$ or $r^{(x)}r^{(y)}$—that arise in even very simple tight-binding models.) As a consequence of the incompleteness of the basis, the familiar textbook commutator $[r^{(\beta)},p^{(\alpha)}]=i\hbar\,\delta_{\alpha,\beta}$ *no longer holds* and multiple commutators such as $[r^{(\gamma)}[r^{(\beta)},p^{(\alpha)}]]$ *do not necessarily vanish*,[3,19] resulting in an infinite series in $\mathbf{A}$. Nevertheless, in a complete basis our expression transparently reduces to the familiar minimal-coupling Hamiltonian.

Following the derivation of the series expression for the Hamiltonian operator in the presence of the vector potential we examine its matrix elements between localized orbitals. Under the most common approximation (treating $\mathbf{A}$ and its spatial derivatives as same-site, same-orbital interactions) we can explicitly sum the power series to obtain a closed-form expression for the matrix elements of the Hamiltonian in the presence of the vector potential. The resulting expression is of the same *form* as that of the Peierls-substitution approach,[12] but there is no arbitrariness of path, our expression being simply that which is demanded by gauge invari-

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ance in an incomplete basis. We thus firmly establish the link between the matrix element and operator expressions of the Hamiltonian in the presence of the vector potential. The paper is organized as follows. In Sec. II we derive the electromagnetic coupling Hamiltonian and demonstrate gauge invariance. In Sec. III we apply it to some cases of interest, and in Sec. IV give our conclusions. The Appendix gives important intermediate results and derivations needed in the development of Secs. II and III.

II. METHOD

A. Basis set and zeroth-order Hamiltonian

The derivation of the electromagnetic coupling Hamiltonian is simplest for a bulk crystal so we begin there. For a perfect crystal in the absence of applied fields we take for the Hamiltonian

$$H_0 = H_{\rm nso} + H_{\rm so}, \tag{1}$$

$$H_{\rm nso} = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}), \tag{2}$$

$$H_{\rm so} = \frac{\hbar}{4m^2c^2}(\boldsymbol{\sigma}\times\boldsymbol{\nabla}V)\cdot\mathbf{p}, \tag{3}$$

where m is the free-electron mass, $\boldsymbol{\sigma}$ are the Pauli spin matrices, and V is the full crystal potential (within the one-electron approximation), which satisfies $V(\mathbf{r}) = V(\mathbf{r}+\mathbf{R})$ for any direct lattice vector $\mathbf{R}$. We adopt Chadi's[20] treatment of the spin-orbit interaction, coupling orbitals on the same site only. We consider a total volume $\mathcal{V}$ consisting of N_i primitive unit cells in the $\mathbf{a}_i$ direction, $i=1,2,3$, where $\mathbf{a}_i$ is a primitive (direct) lattice translation vector, and apply cyclic (Born–von Kármán) boundary conditions in all three directions. Two bases are commonly encountered in tight binding: the Bloch basis and the band basis. The Bloch basis is constructed of localized atomiclike orbitals centered on each atom of the crystal:

$$|\alpha;\mu;\mathbf{k}\rangle = \frac{1}{\sqrt{N}}\sum_{j=1}^{N}\exp[i\mathbf{k}\cdot(\mathbf{R}_j+\mathbf{v}_\mu)]|\alpha;\mu;\mathbf{R}_j+\mathbf{v}_\mu\rangle. \tag{4}$$

In Eq. (4) $\mathbf{k}$ is the three-dimensional wave vector, $\mathbf{R}_j$ is the location of the jth unit cell, $N=N_1N_2N_3$ the total number of cells, μ the atom within the cell, offset by $\mathbf{v}_\mu$ from the cell location, and α the orbital type (including spin). The band basis consists of linear combinations of states (4) that diagonalize H_0:

$$|n;\mathbf{k}\rangle = \sum_{\alpha,\mu} b_{n,(\alpha,\mu)}(\mathbf{k})|\alpha;\mu;\mathbf{k}\rangle, \tag{5}$$

$$H_0|n;\mathbf{k}\rangle = E_n(\mathbf{k})|n;\mathbf{k}\rangle, \tag{6}$$

where n is the band index and the b are expansion coefficients. Both sets of states are orthonormal:

$$\langle\alpha';\mu';\mathbf{k}'|\alpha;\mu;\mathbf{k}\rangle = \delta_{\alpha',\alpha}\delta_{\mu',\mu}\delta_{\mathbf{k}',\mathbf{k}}, \tag{7}$$

$$\langle n';\mathbf{k}'|n;\mathbf{k}\rangle = \delta_{n',n}\delta_{\mathbf{k}',\mathbf{k}}. \tag{8}$$

We represent any cell-periodic operator Ω in the crystal momentum representation,[21]

$$\Omega(\mathbf{k}) = e^{-i\mathbf{k}\cdot\mathbf{r}}\Omega e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{9}$$

where in the direct-space representation $\Omega(\mathbf{r}) = \Omega(\mathbf{r}+\mathbf{R})$ for any direct lattice vector $\mathbf{R}$. Unless otherwise noted we express operators $\Omega(\mathbf{k})$ in the Bloch basis, and all wave vectors in Eqs. (4)–(9) are taken to fall in the first Brillouin zone.

B. Derivation

We expect that in the incomplete basis the electromagnetic coupling Hamiltonian might have contributions to all orders in the vector potential $\mathbf{A}$, so we denote the full Hamiltonian for a particle of charge Q in the presence of applied vector ($\mathbf{A}$) and scalar (Φ) potentials as

$$H = H^{(A)} + U(\mathbf{r},t), \quad H^{(\mathbf{A})} = \sum_{n=0}^{\infty} H_n^{(\mathbf{A})}, \quad U(\mathbf{r},t) = Q\Phi(\mathbf{r},t), \tag{10}$$

where $H_n^{(\mathbf{A})}$ is of nth order in the components of $\mathbf{A}$, $H_0^{(\mathbf{A})} = H_0$, the unperturbed Hamiltonian, and we drop the $\mathbf{s}\cdot\mathbf{B}$ term. As stated in the Introduction, we do not postulate a form for the Hamiltonian; rather, we see what form is demanded by gauge invariance. To that end, observe that the same physical system may be equally well described by H_0 or $H^{(\boldsymbol{\nabla}f)} - Q\partial f/\partial t$, for which $\mathbf{A} = \boldsymbol{\nabla}f$, the solutions of the Shrödinger equation being related solely by a position-dependent phase factor. In other words, H_0 and $H^{(\boldsymbol{\nabla}f)}$ must be related by the unitary transformation[22]

$$H^{(\boldsymbol{\nabla}f)} = e^{iQf/\hbar}H_0e^{-iQf/\hbar}, \tag{11}$$

$$H^{(\boldsymbol{\nabla}f)} = H_0 + \frac{iQ}{\hbar}[f,H_0] + \frac{1}{2!}\left(\frac{iQ}{\hbar}\right)^2[f,[f,H_0]] + \cdots, \tag{12}$$

where f is the gauge function; because the basis is incomplete we use the Baker-Hausdorff identity to expand Eq. (11) yielding Eq. (12).

We deduce the electromagnetic coupling Hamiltonian in the following manner: Observe that in a complete basis with $H_0 = -\hbar^2\nabla^2/2m + V(\mathbf{r})$, we obtain the usual minimal-coupling Hamiltonian, $H^{(\mathbf{A})} = [(\hbar/i)\boldsymbol{\nabla} - Q\mathbf{A}(\mathbf{r},t)]^2/2m + V(\mathbf{r})$, by explicitly calculating the expression $\exp(iQf/\hbar)\{-\hbar^2\nabla^2/2m + V(\mathbf{r})\}\exp(-iQf/\hbar)$ and replacing $\boldsymbol{\nabla}f \to \mathbf{A}$. That is, $\boldsymbol{\nabla}f$ plays the role of $\mathbf{A}$ in the equations of motion, ensuring that the Hamiltonian takes the same *form* regardless of the gauge chosen. As we shall demonstrate below [see the sentences following Eqs. (19) and (24)], our results reduce to the familiar minimal-coupling Hamiltonian in a complete basis.

Here we apply the same procedure, introducing Fourier representations,[19]

$$f = \sum_{\mathbf{q}} f_{\mathbf{q}}e^{i\mathbf{q}\cdot\mathbf{r}}, \tag{13}$$

followed by the analogous substitutions

$$\mathbf{A}=\boldsymbol{\nabla} f \Rightarrow A_{\mathbf{q}}^{(\alpha)}=iq^{(\alpha)}f_{\mathbf{q}}, \quad \left[\frac{\partial A^{(\alpha)}}{\partial r^{(\beta)}}\right]_{\mathbf{q}}=(iq^{(\alpha)})(iq^{(\beta)})f_{\mathbf{q}}, \tag{14}$$

etc. Using Eq. (13) in Eq. (12), then, we find

$$H_1^{(\boldsymbol{\nabla} f)}=\frac{iQ}{\hbar}\sum_{\mathbf{q}} f_{\mathbf{q}}[e^{i\mathbf{q}\cdot\mathbf{r}},H_0], \tag{15}$$

$$H_2^{(\boldsymbol{\nabla} f)}=\frac{1}{2!}\left(\frac{iQ}{\hbar}\right)^2\sum_{\mathbf{q},\mathbf{q}'} f_{\mathbf{q}'}f_{\mathbf{q}}[e^{i\mathbf{q}'\cdot\mathbf{r}}[e^{i\mathbf{q}\cdot\mathbf{r}},H_0]], \tag{16}$$

and so on. Since the Fourier components are completely arbitrary, terms of the Hamiltonian may be isolated by examining matrix elements of the form $\langle\alpha';\mu';\mathbf{k}+\mathbf{q}_1+\mathbf{q}_2+\cdots+\mathbf{q}_n|H_n^{(\boldsymbol{\nabla} f)}|\alpha;\mu;\mathbf{k}\rangle$ and selecting out those subexpressions proportional to the products $f_{\mathbf{q}_1}f_{\mathbf{q}_2}\cdots f_{\mathbf{q}_n}$. Note that there are $n!$ such terms, canceling the global $1/n!$ in Eqs. (15) and (16) and succeeding expressions. We denote the total of all such terms as $[H_n^{(\boldsymbol{\nabla} f)}]_{\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_n}$. Using Eqs. (A8), (A9), (A18), and (A19), we make a fully symmetric Taylor expansion, selecting terms proportional to $f_{\mathbf{q}_1}$ and find for the first-order coupling:

$$[H_1^{(\boldsymbol{\nabla} f)}]_{\mathbf{q}_1}=-\frac{1}{2}\left(\frac{iQ}{\hbar}\right)f_{\mathbf{q}_1}\sum_{\alpha} q_1^{(\alpha)}\left\{\left[\frac{\partial H_0(\mathbf{k})}{\partial k^{(\alpha)}}+\frac{\partial H_0(\mathbf{k}+\mathbf{q}_1)}{\partial k^{(\alpha)}}\right]+\frac{1}{2!}\sum_{\beta} q_1^{(\beta)}\left[\frac{\partial^2 H_0(\mathbf{k})}{\partial k^{(\beta)}\partial k^{(\alpha)}}-\frac{\partial^2 H_0(\mathbf{k}+\mathbf{q}_1)}{\partial k^{(\beta)}\partial k^{(\alpha)}}\right]\right.$$
$$\left.+\frac{1}{3!}\sum_{\beta,\gamma} q_1^{(\beta)}q_1^{(\gamma)}\left[\frac{\partial^3 H_0(\mathbf{k})}{\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}}+\frac{\partial^3 H_0(\mathbf{k}+\mathbf{q}_1)}{\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}}\right]+\cdots\right\}. \tag{17}$$

Now, making use of Eq. (14) along with Eqs. (A3)–(A7) to rewrite Eq. (17) in terms of the vector potential, and observing from Eqs. (A1) and (A2) that the arguments of the functions involved show the relative positions of the exponentials, we find

$$[H_1^{(\mathbf{A})}]_{\mathbf{q}_1}=-\frac{Q}{2\hbar}\left(\sum_{\alpha}\frac{\hbar}{m}[e^{i\mathbf{q}_1\cdot\mathbf{r}}A_{\mathbf{q}_1}^{(\alpha)}p^{(\alpha)}+p^{(\alpha)}e^{i\mathbf{q}_1\cdot\mathbf{r}}A_{\mathbf{q}_1}^{(\alpha)}]+\frac{1}{2!}\sum_{\alpha,\beta}\left(-\frac{\hbar}{m}\right)\right.$$
$$\times\left\{e^{i\mathbf{q}_1\cdot\mathbf{r}}\left[\frac{\partial A^{(\alpha)}}{\partial r^{(\beta)}}\right]_{\mathbf{q}_1}[r^{(\beta)},p^{(\alpha)}]-[r^{(\beta)},p^{(\alpha)}]e^{i\mathbf{q}_1\cdot\mathbf{r}}\left[\frac{\partial A^{(\alpha)}}{\partial r^{(\beta)}}\right]_{\mathbf{q}_1}\right\}+\frac{1}{3!}\sum_{\alpha,\beta,\gamma}\left(\frac{\hbar}{m}\right)$$
$$\left.\times\left\{e^{i\mathbf{q}_1\cdot\mathbf{r}}\left[\frac{\partial^2 A^{(\alpha)}}{\partial r^{(\gamma)}\partial r^{(\beta)}}\right]_{\mathbf{q}_1}[r^{(\gamma)},[r^{(\beta)},p^{(\alpha)}]]+[r^{(\gamma)},[r^{(\beta)},p^{(\alpha)}]]e^{i\mathbf{q}_1\cdot\mathbf{r}}\left[\frac{\partial^2 A^{(\alpha)}}{\partial r^{(\gamma)}\partial r^{(\beta)}}\right]_{\mathbf{q}_1}\right\}+\cdots\right). \tag{18}$$

Equation (18) is now easily translated back from Fourier space to real space:

$$H_1^{(A)}=-\frac{Q}{2m}\left\{\sum_{\alpha}[A^{(\alpha)}p^{(\alpha)}+p^{(\alpha)}A^{(\alpha)}]+\frac{1}{2!}\sum_{\alpha,\beta}\left[M_2^{(\alpha,\beta)}\frac{\partial A^{(\alpha)}}{\partial r^{(\beta)}}-\frac{\partial A^{(\alpha)}}{\partial r^{(\beta)}}M_2^{(\alpha,\beta)}\right]\right.$$
$$\left.+\frac{1}{3!}\sum_{\alpha,\beta,\gamma}\left[\frac{\partial^2 A^{(\alpha)}}{\partial r^{(\gamma)}\partial r^{(\beta)}}M_3^{(\alpha,\beta,\gamma)}+M_3^{(\alpha,\beta,\gamma)}\frac{\partial^2 A^{(\alpha)}}{\partial r^{(\gamma)}\partial r^{(\beta)}}\right]+\cdots\right\}. \tag{19}$$

Note that in a complete basis only the single sum in Eq. (19) survives since $M_2^{(\alpha,\beta)}=i\hbar\,\delta_{\alpha,\beta}$, $M_j=0$, $j\geqslant 3$ and we recover the usual expression for the first-order coupling to the vector potential.

For the second-order coupling we select out subexpressions proportional to $f_{\mathbf{q}_1}f_{\mathbf{q}_2}$ using the same procedures as employed with the first-order coupling. The leading term (that without any derivatives of the vector potential) is shown below:

$$[H_2^{(\mathbf{A})}]_{\mathbf{q}_1,\mathbf{q}_2}=\left(-\frac{Q}{2\hbar}\right)^2\left(\frac{-i\hbar}{m}\right)\left\{\frac{1}{2!}\sum_{\alpha,\beta}\left[\binom{2}{1,1}\{e^{i(\mathbf{q}_1+\mathbf{q}_2)\cdot\mathbf{r}}A_{\mathbf{q}_1}^{(\alpha)}A_{\mathbf{q}_2}^{(\beta)}[r^{(\beta)},p^{(\alpha)}]+[r^{(\beta)},p^{(\alpha)}]e^{i(\mathbf{q}_1+\mathbf{q}_2)\cdot\mathbf{r}}A_{\mathbf{q}_1}^{(\alpha)}A_{\mathbf{q}_2}^{(\beta)}\}\right.\right.$$
$$\left.\left.+\binom{2}{1,1}\{A_{\mathbf{q}_2}^{(\alpha)}e^{i\mathbf{q}_2\cdot\mathbf{r}}[r^{(\beta)},p^{(\alpha)}]e^{i\mathbf{q}_1\cdot\mathbf{r}}A_{\mathbf{q}_1}^{(\beta)}+e^{i\mathbf{q}_1\cdot\mathbf{r}}A_{\mathbf{q}_1}^{(\alpha)}[r^{(\beta)},p^{(\alpha)}]A_{\mathbf{q}_2}^{(\beta)}e^{i\mathbf{q}_2\cdot\mathbf{r}}\}\right]+\cdots\right\}. \tag{20}$$

In translating Eq. (20) back to real space there is one complication, for when there are n identical-order Fourier components together (e.g., $e^{i(\mathbf{q}_1+\mathbf{q}_2)\cdot\mathbf{r}}A_{\mathbf{q}_1}^{(\alpha)}A_{\mathbf{q}_2}^{(\beta)}$ above, for which $n=2$), we must divide the resulting real-space expression by $n!$, since there

are this many permutations of the real-space functions that contribute to the same term. Likewise, a single real-space term gives rise to the last two terms shown in Eq. (20). Taking these observations into account, we obtain the second-order coupling Hamiltonian:

$$
\begin{aligned}
H_2^{(\mathbf{A})} = &-\frac{1}{m}\left(\frac{Q}{2}\right)^2\left(\frac{i}{\hbar}\right)^{2-1}\Bigg(\frac{1}{2!}\sum_{\alpha,\beta}\binom{2}{1,1}\left(\frac{1}{2!}[A^{(\alpha)}A^{(\beta)}M_2^{(\alpha,\beta)}+M_2^{(\alpha,\beta)}A^{(\alpha)}A^{(\beta)}]+A^{(\alpha)}M_2^{(\alpha,\beta)}A^{(\beta)}\right)\\
&+\frac{1}{3!}\sum_{\alpha,\beta,\gamma}\binom{3}{2,1}\left(M_3^{(\alpha,\beta,\gamma)}A^{(\alpha)}\frac{\partial A^{(\beta)}}{\partial r^{(\gamma)}}-A^{(\alpha)}\frac{\partial A^{(\beta)}}{\partial r^{(\gamma)}}M_3^{(\alpha,\beta,\gamma)}+A^{(\beta)}M_3^{(\alpha,\beta,\gamma)}\frac{\partial A^{(\alpha)}}{\partial r^{(\gamma)}}-\frac{\partial A^{(\beta)}}{\partial r^{(\gamma)}}M_3^{(\alpha,\beta,\gamma)}A^{(\alpha)}\right)\\
&+\frac{1}{4!}\sum_{\alpha,\beta,\gamma,\delta}\Bigg\{\binom{4}{3,1}\left(A^{(\beta)}\frac{\partial^2 A^{(\alpha)}}{\partial r^{(\delta)}\partial r^{(\gamma)}}M_4^{(\alpha,\beta,\gamma,\delta)}+M_4^{(\alpha,\beta,\gamma,\delta)}\frac{\partial^2 A^{(\alpha)}}{\partial r^{(\delta)}\partial r^{(\gamma)}}A^{(\beta)}\right)\\
&+\binom{4}{3,1}\left(A^{(\beta)}M_4^{(\alpha,\beta,\gamma,\delta)}\frac{\partial^2 A^{(\alpha)}}{\partial r^{(\delta)}\partial r^{(\gamma)}}+\frac{\partial^2 A^{(\beta)}}{\partial r^{(\delta)}\partial r^{(\gamma)}}M_4^{(\alpha,\beta,\gamma,\delta)}A^{(\alpha)}\right)+\binom{4}{2,2}\Bigg[\frac{1}{2!}\Bigg(\frac{\partial A^{(\alpha)}}{\partial r^{(\gamma)}}\frac{\partial A^{(\beta)}}{\partial r^{(\delta)}}M_4^{(\alpha,\beta,\gamma,\delta)}\\
&+M_4^{(\alpha,\beta,\gamma,\delta)}\frac{\partial A^{(\alpha)}}{\partial r^{(\gamma)}}\frac{\partial A^{(\beta)}}{\partial r^{(\delta)}}\Bigg)-\frac{\partial A^{(\beta)}}{\partial r^{(\delta)}}M_4^{(\alpha,\beta,\gamma,\delta)}\frac{\partial A^{(\alpha)}}{\partial r^{(\gamma)}}\Bigg]\Bigg\}+\cdots\Bigg).
\end{aligned}
\tag{21}
$$

Together the first- and second-order expressions, Eqs. (19) and (21), demonstrate general patterns that may be employed to simply write down the third-order (and higher-order) couplings.

First, note that the nth-order coupling leads with the multiple commutator M_n and has a global factor 2^{-n} due to the n-fold averaging. Second, the nth-order coupling involves only n-nomial coefficients whose n lower indices tell the order of the derivatives involved (1 for no derivative, 2 for a first derivative, 3 for a second derivative, etc.) and whose upper index n' (as well as prefactor $1/n'!$) is the sum of n and the total order of the derivatives in the term. We see this explicitly in Eq. (21), where we have the associations between multinomial coefficients and derivatives of the vector potential such as

$$
\binom{4}{3,1} \leftrightarrow A^{(\beta)}\frac{\partial^2 A^{(\alpha)}}{\partial r^{(\delta)}\partial r^{(\gamma)}}M_4^{(\alpha,\beta,\gamma,\delta)},
$$

$$
A^{(\beta)}M_4^{(\alpha,\beta,\gamma,\delta)}\frac{\partial^2 A^{(\alpha)}}{\partial r^{(\delta)}\partial r^{(\gamma)}},\ \ldots, \tag{22}
$$

$$
\binom{4}{2,2} \leftrightarrow \frac{\partial A^{(\alpha)}}{\partial r^{(\gamma)}}\frac{\partial A^{(\beta)}}{\partial r^{(\delta)}}M_4^{(\alpha,\beta,\gamma,\delta)},
$$

$$
\frac{\partial A^{(\beta)}}{\partial r^{(\delta)}}M_4^{(\alpha,\beta,\gamma,\delta)}\frac{\partial A^{(\alpha)}}{\partial r^{(\gamma)}},\ \ldots, \tag{23}
$$

where in Eq. (22) the lower indices 3 and 1 indicate a second derivative and no derivative, respectively, while each of the identical lower indices 2 in Eq. (23) indicates a first derivative. We employ the term ''order'' in a generalized fashion, and say that both Eqs. (22) and (23) above are ''second-order derivative terms'' since Eq. (22) involves products of A and its second (partial) derivative, while Eq. (23) involves products of two first (partial) derivatives of A. Third, as derivatives accumulate, a sign change occurs when the order of a derivative on the *left-hand* side of the operator M_j is incremented over the preceding term, but *not* on the right. This is illustrated by Eq. (21), where we see that the first two terms of the triple sum lead to the first, second, fifth, and sixth terms of the quadruple sum, while the last two terms of the triple sum give rise to the third, fourth, and last terms of the quadruple sum. Fourth, when there are fully symmetric expressions in identical A's (or derivatives) on the same side of the operator M_j, we divide by the number of permutations of the identical A's. This occurs in Eq. (21) in the first two terms of the double sum and the fifth and sixth terms of the quadruple sum. Finally, all unique permutations of n factors of A appear in Hermitian combinations (the A and the M_j do not commute). For example, in the quadruple sum of Eq. (21) the term with an A to the left of the (anti-Hermitian) M_4 and a second derivative of A to the right is added to the term with the A and second derivative transposed. The terms with the A and second derivative on the same side of the M_4 are of course distinct and appear in a separate combination. Note too that the last term of this sum is already symmetric. In the triple sum of Eq. (21) paired terms are subtracted since there is a global factor of i and the M_{2n+1} are Hermitian.

We emphasize that there is no mystery to the above-noted patterns—they arise quite naturally from the Taylor expansions and the Baker-Hausdorff identity. We discuss them simply to provide a mnemonic for writing down subsequent terms in the expansion of $H_2^{(\mathbf{A})}$, as well as writing down $H_3^{(\mathbf{A})}$ and higher-order coupling Hamiltonians. With these observations, we can simply write down the third-order Hamiltonian,

$$H_3^{(\mathbf{A})}=-\frac{1}{m}\left(\frac{Q}{2}\right)^3\left(\frac{i}{\hbar}\right)^{3-1}\left(\frac{1}{3!}\sum_{\alpha,\beta,\gamma}\binom{3}{1,1,1}\left(\frac{1}{3!}[A^{(\alpha)}A^{(\beta)}A^{(\gamma)}M_3^{(\alpha,\beta,\gamma)}+M_3^{(\alpha,\beta,\gamma)}A^{(\alpha)}A^{(\beta)}A^{(\gamma)}]\right.\right.$$
$$\left.+\frac{1}{2!}[A^{(\gamma)}M_3^{(\alpha,\beta,\gamma)}A^{(\alpha)}A^{(\beta)}+A^{(\beta)}A^{(\gamma)}M_3^{(\alpha,\beta,\gamma)}A^{(\alpha)}]\right)+\frac{1}{4!}\sum_{\alpha,\beta,\gamma,\delta}\binom{4}{2,1,1}\left\{\frac{1}{2!}\left[\left(M_4^{(\alpha,\beta,\gamma,\delta)}\frac{\partial A^{(\alpha)}}{\partial r^{(\delta)}}A^{(\beta)}A^{(\gamma)}\right.\right.\right.$$
$$\left.-\frac{\partial A^{(\alpha)}}{\partial r^{(\delta)}}A^{(\beta)}A^{(\gamma)}M_4^{(\alpha,\beta,\gamma,\delta)}\right)+\left(A^{(\beta)}A^{(\gamma)}M_4^{(\alpha,\beta,\gamma,\delta)}\frac{\partial A^{(\alpha)}}{\partial r^{(\delta)}}-\frac{\partial A^{(\gamma)}}{\partial r^{(\delta)}}M_4^{(\alpha,\beta,\gamma,\delta)}A^{(\beta)}A^{(\alpha)}\right)\Big]$$
$$\left.\left.+\left(A^{(\gamma)}M_4^{(\alpha,\beta,\gamma,\delta)}A^{(\beta)}\frac{\partial A^{(\alpha)}}{\partial r^{(\delta)}}-A^{(\gamma)}\frac{\partial A^{(\beta)}}{\partial r^{(\delta)}}M_4^{(\alpha,\beta,\gamma,\delta)}A^{(\alpha)}\right)\right\}+\cdots\right). \tag{24}$$

Succeeding terms of Eq. (24) as well as the fourth-, fifth-, and higher-order couplings in the vector potential can be deduced using these same patterns. Observe that in a complete basis (21) becomes the familiar second-order coupling and Eq. (24) and all higher-order couplings vanish.

C. Gauge invariance

To close this section we establish gauge invariance of the electromagnetic coupling Hamiltonian whose leading terms are given in Eqs. (19), (21), and (24). This involves showing that under a gauge transformation g, for which $\mathbf{A}'=\mathbf{A}+\boldsymbol{\nabla}g$, $U'=U-Q\partial g/\partial t$, the equality

$$H^{(\mathbf{A}+\boldsymbol{\nabla}g)}=e^{iQg/\hbar}H^{(\mathbf{A})}e^{-iQg/\hbar}$$
$$=H^{(\mathbf{A})}+\frac{iQ}{\hbar}[g,H^{(\mathbf{A})}]+\frac{1}{2!}\left(\frac{iQ}{\hbar}\right)^2[g,[g,H^{(\mathbf{A})}]]+\cdots \tag{25}$$

holds to all orders. (The scalar potential U poses no difficulty as it is a function of $\mathbf{r}$, not $\mathbf{p}$, and thus commutes with g.) That is, the left-hand side of Eq. (25) is to be computed simply by substituting $A^{(\alpha)}+\partial g/\partial r^{(\alpha)}$ for $A^{(\alpha)}$ in Eqs. (19), (21), and (24) and succeeding coupling terms, while the right-hand side is to be found by direct computation of the multiple commutators. Gauge invariance is established then, by demonstrating that the term with n factors of A and m of g is the same in the left- and right-hand expressions in Eq. (25). On the left-hand side this term comes from the expansion of $H_{n+m}^{(\mathbf{A}+\boldsymbol{\nabla}g)}$ while on the right-hand side this term comes from the m-fold commutator of g with $H_n^{(\mathbf{A})}$.

The demonstration is not difficult when done in the Fourier representation; as usual we concentrate on a single matrix element between states of wave vector $\mathbf{k}$ and $(\mathbf{k}+\mathbf{q}_1+\mathbf{q}_2+\cdots+\mathbf{q}_{(m+n)})$. From the discussion in Sec. 4 of the Appendix it is clear that the Taylor expansion resulting from $(n+m)$ commutators applied to H_0 must be the same as that which comes from n commutators applied to H_0, subsequently subjected to a further m commutators. Thus, the terms will be equal if they have identical coefficients; the averaging coefficients are obviously the same, being $2^{-(m+n)}$ for $H_{n+m}^{(\mathbf{A}+\boldsymbol{\nabla}g)}$ and $(2^{-m})(2^{-n})$ for the m-fold commutator of g with $H_n^{(\mathbf{A})}$. For the left-hand side of Eq. (25), $(n+m)$ commutators applied to H_0, the $(n+m)!$ permutations of the $f_{\mathbf{q}}q^{(\alpha)}$ cancel the leading $1/(n+m)!$ and we have renamed all terms as

$$if_{\mathbf{q}_j}q_j^{(\alpha_j)}\rightarrow[A_{\mathbf{q}_j}^{(\alpha_j)}+iq_j^{(\alpha_j)}g_{\mathbf{q}_j}],\quad j=1,2,...,(n+m). \tag{26}$$

In the product of $(n+m)$ factors, Eq. (26), it is clear (using the equality of mixed partial derivatives) that there is but one term $A_{\mathbf{q}_1}A_{\mathbf{q}_2}\cdots A_{\mathbf{q}_n}g_{\mathbf{q}_{n+1}}g_{\mathbf{q}_{n+2}}\cdots g_{\mathbf{q}_{n+m}}$. Likewise, for the right-hand side of Eq. (25) there is a leading $1/n!$ due to $H_n^{(\mathbf{A})}$ and a further factor of $1/m!$ associated with the m-fold commutator with g. The $(n+m)$ Fourier sums now run over the dummy indices $\mathbf{s}_1,\mathbf{s}_2,\ldots,\mathbf{s}_{(n+m)}$ and here we have renamed n leading factors

$$if_{\mathbf{s}_j}s_j^{(\alpha_j)}\rightarrow A_{\mathbf{s}_j}^{(\alpha_j)},\quad j=1,2,\ldots,n \tag{27}$$

leaving the remaining m as $g_{\mathbf{g}}s^{(\alpha)}$. Computing the matrix element, we see that there are $n!$ terms in which $\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_n$ are distributed among the $A_{\mathbf{q}}$ and for each of these there are $m!$ terms in which the $\mathbf{q}_{n+1},\mathbf{q}_{n+2},\ldots,\mathbf{q}_{n+m}$ are distributed amongst the $g_{\mathbf{q}}$, for a total factor $(m!)(n!)$, canceling the leading $(1/m!)(1/n!)$ and giving once again one term $A_{\mathbf{q}_1}A_{\mathbf{q}_2}\cdots A_{\mathbf{q}_n}g_{\mathbf{q}_{n+1}}g_{\mathbf{q}_{n+2}}\cdots g_{\mathbf{q}_{n+m}}$. Thus the left- and right-hand sides of Eq. (25) yield the same result and gauge invariance is established.

D. Closed-form expression in the usual tight-binding approximation

Thus far in the development of the gauge-invariant electromagnetic coupling Hamiltonian we have not specified how the components of $\mathbf{A}$ and their spatial derivatives are to be treated. The advantages of this procedure are that it establishes the correct form for $H^{(\mathbf{A})}$ free of any assumptions beyond the requirement of formal gauge invariance (demonstrated in Sec. II C above) and that it leads to an operator that transparently reduces to the usual minimal-coupling Hamiltonian in a complete basis. The obvious disadvantages of the method are that it produces an infinite series of increasingly cumbersome terms that might fail to converge (at least in certain cases) and that truncating the series entails sacrificing gauge invariance.

We can, however, avoid these problems by treating the components of **A** and their derivatives in the customary manner: as same-site-, same-orbital-only interactions. Under this approximation there exists a closed-form expression for the matrix elements of $H^{(\mathbf{A})}$ in the localized-orbital basis. We remark that this approximation entails no additional reduction in accuracy, for it is *exactly* the same treatment applied to the matrix elements of the scalar potential:[12] indeed, consistency demands it. The closed-form expression, the details and mathematical justification of which are discussed at length in Sec. 6 of the Appendix is

$$\langle \alpha;\mu;\mathbf{R}_j+\mathbf{v}_\mu|H^{(\mathbf{A})}|\alpha';\mu';\mathbf{R}_{j'}+\mathbf{v}_{\mu'}\rangle = \exp\left[i\frac{Q}{\hbar}\int_{\boldsymbol{\sigma};\mathbf{R}_{j'}+\mathbf{v}_{\mu'}}^{\boldsymbol{\sigma};\mathbf{R}_j+\mathbf{v}_\mu}\mathbf{A}\cdot d\mathbf{l}\right] \times\langle \alpha;\mu;\mathbf{R}_j+\mathbf{v}_\mu|H_0|\alpha';\mu';\mathbf{R}_{j'}+\mathbf{v}_{\mu'}\rangle, \quad (28)$$

where the path of integration, $\boldsymbol{\sigma}$, is the straight line connecting the two sites. Although Eq. (28) resembles the result given in Ref. 12, there are several important differences. First, in terms of its derivation neither the *form* of Eq. (28)—a bare Hamiltonian matrix element weighted by a path-integral-dependent phase—nor the straight-line path for the integral therein are *chosen* by us. Both apply *only* because the closed-form expression gives the same matrix elements as does $H^{(\mathbf{A})}$ in this approximation. Second, the line integral in Eq. (28) must be carried out *exactly*; we do not approximate the integral using the trapezoidal rule. (For uniform magnetic fields the two methods will give the same result since the trapezoidal approximation is exact for linear **A**, and in this case our result confirms the assumptions of Ref. 12.) Third, the straight-line path in Eq. (28) applies for both nearest- and more-distant-neighbor interactions. For a more-distant-neighbor matrix element, then, the correct path is always the straight line, the common nearer neighbors notwithstanding.

Beyond the mathematics, which is the final arbiter, there are sound physical reasons for the straight-line path that appears in Eq. (28). From the development in Sec. 6 in the Appendix it is not difficult to see that only the straight-line path guarantees a balanced treatment of the components of **A** and their derivatives. That is, coefficients of like terms ($A^{(\alpha)}$, $\partial A^{(\alpha)}/\partial r^{(\beta)}$, etc.) sampled at the two atomic sites must be equal in magnitude for the expression to have come from a Hermitian operator. Furthermore, it follows from the derivative of the straight-line path (A32) that in the usual tight-binding approximation the right-hand side of Eq. (28) becomes a series of multiple commutators of the bare Hamiltonian and position to which are coupled **A** and its derivatives. This is exactly the same coupling manifested in the expression for the gauge-invariant electromagnetic coupling Hamiltonian, $H^{(\mathbf{A})}$, developed in Sec. II B above. (In a complete basis, too, **A** couples into H via **p**; even the $\mathbf{A}^2$ term can be regarded as arising from the commutators $[r^{(\beta)},p^{(\alpha)}]=i\hbar\delta_{\alpha,\beta}$.) Thus Eq. (28) in some sense reflects the tight-binding representations of the momentum operator and its multiple commutators with position.

III. RESULTS

A. General

The electromagnetic coupling Hamiltonian derived in Sec. II differs markedly from both the standard prescription and that of Ref. 12 in that it includes terms involving derivatives of the vector potential. To employ it in the usual tight-binding approximation the line integral in Eq. (28) must therefore be carried out exactly. Previously we employed the standard prescription for the first-order coupling in calculating the absorption of bulk GaAs,[19] where we found only small differences with the electric dipole approximation (in which **A** is assumed to be spatially uniform). The problem of finding electronic states in a large magnetic field is another matter entirely and it is here that we focus our attention. Rather than treating bulk effects such as Landau levels or the magnetic band structure[23] we discuss a quantum well in a magnetic field parallel to the heterointerfaces, similar to resonant magnetotunneling spectroscopy[24–27] (RMS) and other experiments carried out in a transverse magnetic field.[28] In such experiments it is argued that a charge Q tunneling along z a distance $\overline{z}$ in a transverse magnetic field $\mathbf{B}=B_0\mathbf{e}_y$ experiences a change in its in-plane (kinetic) crystal momentum $\hbar\mathbf{k}_\parallel\rightarrow(\hbar\mathbf{k}_\parallel-QB_0\overline{z}\mathbf{e}_x)$. Hence varying the applied magnetic field should allow carriers tunneling into a quantum well to probe the subband dispersions. Earlier,[29] we derived a completely general condition on the validity of this semiclassical interpretation, namely, that the distance tunneled into the center of the well (from, say, an accumulation region), $\overline{z}$, must be larger than the quantum well width, w (i.e., $w/\overline{z}<1$). Here we shall see the explicit manifestation of these conditions.

We consider a quantum well oriented along the z direction (interfaces parallel to the x-y plane), so that the crystal potential is translationally symmetric only in the plane: $V(\mathbf{r}+\mathbf{R}_\parallel)=V(\mathbf{r})$, where the subscript $\parallel$ denotes a vector lying in the x-y plane and $\mathbf{R}_\parallel$ is a direct lattice vector lying in the plane. The most natural basis for this problem in the planar-orbital basis (i.e., Bloch sums in the plane),

$$|\alpha;\mu;L;\mathbf{k}_\parallel\rangle=\frac{1}{\sqrt{N_\parallel}}\sum_{j=1}^{N_\parallel}\exp[i\mathbf{k}_\parallel\cdot(\mathbf{R}_{j\parallel}+\mathbf{v}_{\mu\parallel}+\boldsymbol{\Delta}_{L,\parallel})] \times|\alpha;\mu;L;\mathbf{R}_{j\parallel}+\mathbf{v}_{\mu\parallel}+\boldsymbol{\Delta}_{L,\parallel}\rangle, \quad (29)$$

where $N_\parallel$ is the number of cells in the plane, L is the layer index (adjacent layers are separated by a distance a_z and we assume a layer is one bulk unit cell thick), and $\boldsymbol{\Delta}_{L,\parallel}$ is a layer-dependent in-plane offset vector, necessary for some lattices such as fcc in which lattice sites in adjacent layers are shifted in the plane. The other symbols have the same meanings as in Eq. (4). We place the quantum well in a uniform magnetic field $\mathbf{B}=B_0\mathbf{e}_y$ and take for the vector potential,

$$\mathbf{A}=B_0z\mathbf{e}_x. \quad (30)$$

For an electron we have $Q=-e$, where e is the magnitude of the electronic charge, and we can directly compute the matrix element by substituting Eq. (30) into Eq. (28). How-

ever, explicit summation of the terms $H_n^{(\mathbf{A})}$ is a helpful illustration of Eq. (28) and its link to the series form, so we substitute Eq. (30) into Eqs. (19), (21), and (24), finding that all derivative terms vanish. The first three terms of the series form of the electromagnetic coupling Hamiltonian thus become

$$H_1^{(\mathbf{A})}=\frac{eB_0}{2m}[zp^{(x)}+p^{(x)}z], \tag{31}$$

$$H_2^{(\mathbf{A})}=-\frac{1}{2!}\frac{i}{m\hbar}\left(\frac{eB_0}{2}\right)^2[z^2M_2^{(x,x)}+2zM_2^{(x,x)}z+M_z^{(x,x)}z^2], \tag{32}$$

$$H_3^{(\mathbf{A})}=\frac{1}{3!}\frac{1}{m\hbar^2}\left(\frac{eB_0}{2}\right)^3[z^3M_3^{(x,x,x)}+3z^2M_3^{(x,x,x)}z+3zM_3^{(x,x,x)}z^2+M_3^{(x,x,x)}z^3]. \tag{33}$$

The pattern, of course, continues for higher-order couplings.

Since we employ the planar-orbital basis and do not impose cyclic boundary conditions along the z direction the matrix elements appearing in Eqs. (31)–(33) are well behaved. This is usually the case in nanostructure applications in which the extent in the dimension(s) along which the matrix elements of $\mathbf{r}$ are evaluated is limited by hard walls (our case), bulklike boundaries of space-charge layers, and the like. The only difficulty is that the only matrix elements we know are those of *commutators* such as $[z,M_3^{(\alpha,\beta,\gamma)}]$. The simplest expression for z consistent with the multiple commutators is the diagonal approximation,

$$z\rightarrow\sum_{\alpha'',\mu'',j''}|\alpha'';\mu'';\mathbf{R}_{j''}+\mathbf{v}_{\mu''}\rangle(\mathbf{R}_{j''}+\mathbf{v}_{\mu''})^{(z)}\times\langle\alpha'';\mu'';\mathbf{R}_{j''}+\mathbf{v}_{\mu''}|, \tag{34}$$

where the superscript z denotes the z component of the vector and we index the atomic sites with three-dimensional vectors as in Eq. (4) to simplify the notation. This is the customary tight-binding approximation, used in deriving Eq. (28), wherein functions of the position operator are treated as same-site, same-orbital-only interactions. With the diagonal approximation (34) and using Eq. (A28) to evaluate the M_j, we calculate matrix elements of Eqs. (31)–(33) between localized orbitals:

$$\langle\alpha;\mu;\mathbf{R}_j+\mathbf{v}_\mu|H_1^{(A)}|\alpha';\mu';\mathbf{R}_{j'}+\mathbf{v}_{\mu'}\rangle=\left(\frac{ieB_0\overline{z}_{(j',\mu'),(j,\mu)}d^{(x)}_{(j',\mu'),(j,\mu)}}{\hbar}\right)\times\langle\alpha;\mu;\mathbf{R}_j+\mathbf{v}_\mu|H_0|\alpha';\mu';\mathbf{R}_{j'}+\mathbf{v}_{\mu'}\rangle, \tag{35}$$

$$\langle\alpha;\mu;\mathbf{R}_j+\mathbf{v}_\mu|H_2^{(A)}|\alpha';\mu';\mathbf{R}_{j'}+\mathbf{v}_{\mu'}\rangle=\frac{1}{2!}\left(\frac{ieB_0\overline{z}_{(j',\mu'),(j,\mu)}d^{(x)}_{(j',\mu'),(j,\mu)}}{\hbar}\right)^2\times\langle\alpha;\mu;\mathbf{R}_j+\mathbf{v}_\mu|H_0|\alpha';\mu';\mathbf{R}_{j'}+\mathbf{v}_{\mu'}\rangle, \tag{36}$$

$$\langle\alpha;\mu;\mathbf{R}_j+\mathbf{v}_\mu|H_3^{(A)}|\alpha';\mu';\mathbf{R}_{j'}+\mathbf{v}_{\mu'}\rangle=\frac{1}{3!}\left(\frac{ieB_0\overline{z}_{(j',\mu'),(j,\mu)}d^{(x)}_{(j',\mu'),(j,\mu)}}{\hbar}\right)^3\times\langle\alpha;\mu;\mathbf{R}_j+\mathbf{v}_\mu|H_0|\alpha';\mu';\mathbf{R}_{j'}+\mathbf{v}_{\mu'}\rangle, \tag{37}$$

where in Eqs. (35)–(37) we define the average z position and the x displacement of the right site with respect to the left, respectively, as

$$\overline{z}_{(j',\mu'),(j,\mu)}=\tfrac{1}{2}[\mathbf{R}_{j'}+\mathbf{v}_{\mu'}+\mathbf{R}_j+\mathbf{v}_\mu]\cdot\mathbf{e}_z=\tfrac{1}{2}[\mathbf{R}_{j'}+\mathbf{v}_{\mu'}+\mathbf{R}_j+\mathbf{v}_\mu]^{(z)}, \tag{38}$$

$$d^{(x)}_{(j',\mu'),(j,\mu)}=[\mathbf{R}_{j'}+\mathbf{v}_{\mu'}-\mathbf{R}_j-\mathbf{v}_\mu]\cdot\mathbf{e}_x=[\mathbf{R}_{j'}+\mathbf{v}_{\mu'}-\mathbf{R}_j-\mathbf{v}_\mu]^{(x)}. \tag{39}$$

Continuing this pattern, we see that to all orders, including the zeroth-order Hamiltonian, we have

$$\langle\alpha;\mu;\mathbf{R}_j+\mathbf{v}_\mu|H^{(A)}|\alpha';\mu';\mathbf{R}_{j'}+\mathbf{v}_{\mu'}\rangle=\exp\left[i\left(\frac{eB_0\overline{z}_{(j',\mu'),(j,\mu)}}{\hbar}\right)d^{(x)}_{(j',\mu'),(j,\mu)}\right]\times\langle\alpha;\mu;\mathbf{R}_j+\mathbf{v}_\mu|H_0|\alpha';\mu';\mathbf{R}_{j'}+\mathbf{v}_{\mu'}\rangle. \tag{40}$$

Equation (40) is of course, the answer we would have obtained via direct computation of Eq. (28). As noted in Sec. II D, for this constant field we obtain the same result as do Graf and Vogl,[12] since the trapezoidal rule is exact for linear $\mathbf{A}$. Our result will obviously differ from theirs for a nonuniform magnetic field, as seen from the perspective of either the series formulation or closed-form expression for the matrix elements of $H^{(\mathbf{A})}$. In the former the derivative terms do not generally vanish; likewise in the latter the exact line integral gives a result different from the trapezoidal rule. A result similar to Eq. (40) but for pseudopotentials, in which a region is subdivided into many layers, has been obtained by Inkson, Tan, and Edwards.[30]

Equation (40) shows that in the planar-orbital basis (29) the net effect is to introduce a layer-dependent shift of the wave vector:

$$\langle\alpha;\mu;L;\mathbf{k}_\parallel|H^{(A)}|\alpha';\mu';L';\mathbf{k}_\parallel\rangle=\sum_{j'=1}^{N_\parallel}\exp[i\mathbf{k}_\parallel\cdot\mathbf{d}^{(\parallel)}_{(j',\mu'',L'),(0,\mu,L)}]\langle\alpha;\mu;L;\mathbf{v}_{\mu,\parallel}+\mathbf{\Delta}_{L,\parallel}|H^{(A)}|\alpha';\mu';L';\mathbf{R}_{j'\parallel}+\mathbf{v}_{\mu'\parallel}+\mathbf{\Delta}_{L',\parallel}\rangle$$

$$= \sum_{j'=1}^{N_\parallel} \exp[i(\mathbf{k}_\parallel + \mathbf{b}^{(L',L)}_{(\mu',\mu)}) \cdot \mathbf{d}^{(\parallel)}_{(j',\mu',L')(0,\mu,L)}] \langle \alpha;\mu;L;\mathbf{v}_{\mu\parallel} + \mathbf{\Delta}_{L,\parallel} | H_0 | \alpha';\mu';L';\mathbf{R}_{j'\parallel} + \mathbf{v}_{\mu'\parallel} + \mathbf{\Delta}_{L',\parallel} \rangle, \quad (41)$$

$$\mathbf{d}^{(\parallel)}_{(j',\mu'L'),(0,\mu,L)} = (\mathbf{R}_{j'\parallel} + \mathbf{v}_{\mu'\parallel} + \mathbf{\Delta}_{L',\parallel} - \mathbf{v}_{\mu\parallel} - \mathbf{\Delta}_{L,\parallel}), \quad (42)$$

$$\mathbf{b}^{(L',L)}_{(\mu',\mu)} = \frac{eB_0 \overline{z}^{(L',L)}_{(\mu',\mu)}}{\hbar} \mathbf{e}_x,$$

$$\overline{z}^{(L',L)}_{(\mu',\mu)} = \tfrac{1}{2}[(L'+L)a_z + \mathbf{v}^{(z)}_{\mu'} + \mathbf{v}^{(z)}_{\mu}], \quad (43)$$

where we recognize that the x component of Eq. (42) is merely the x vector displacement (39) and the second of equations (43) gives the average z position.

Equations (41)–(43) are fairly general so we present a specific application: matrix elements for a nearest-neighbor model in the zinc-blende crystal structure (e.g., sp^3, sp^3s^*, sp^3d^5, $sp^3d^5s^*$). Matrix elements of H_0 take one of the forms

$$\langle \alpha;\mu;L;\mathbf{k}_\parallel | H_0 | \alpha';\mu';L';\mathbf{k}_\parallel \rangle = \begin{cases} \nu^{(L,L')}_{(\alpha\mu,\alpha'\mu')} & \cos[(k_x \pm k_y)a/4] \\ i\nu^{(L,L')}_{(\alpha\mu,\alpha'\mu')} & \sin[(k_x \pm k_y)a/4] \end{cases} \quad (44)$$

where a is the conventional unit cell cube edge, the ν are real (of either sign), and μ and μ' differ, one being a (anion) the other c (cation). In Eq. (43) $a_z = a/2$, and the anions occupy the Bravais lattice sites with the cations displaced by $(a/4)(1,1,1)$ from them. Thus, from Eqs. (41) and (44),

$$\overline{z}^{(L',L)}_{(\mu',\mu)} = \tfrac{1}{2}[(L'+L)(a/2) + (\delta_{\mu,c} + \delta_{\mu',c})(a/4)], \quad (45)$$

$$\langle \alpha;\mu;L;\mathbf{k}_\parallel | H_0 | \alpha';\mu';L';\mathbf{k}_\parallel \rangle = \begin{cases} \nu^{(L,L')}_{(\alpha\mu,\alpha'\mu')} & \cos\left[\left(k_x + \dfrac{eB_0 \overline{z}^{(L',L)}_{(\mu',\mu)}}{\hbar} \pm k_y\right)\dfrac{a}{4}\right] \\ i\nu^{(L,L')}_{(\alpha\mu,\alpha'\mu')} & \sin\left[\left(k_x + \dfrac{eB_0 \overline{z}^{(L',L)}_{(\mu',\mu)}}{\hbar} \pm k_y\right)\dfrac{a}{4}\right]. \end{cases} \quad (46)$$

In Eqs. (45) and (46) note that since we include only nearest-neighbor interactions there are but two distinct possibilities: $\overline{z} = La/2 \pm a/8$. The positive sign holds for the anion and cation both in layer L, the negative sign for an anion in layer L and the cation in layer $L-1$.

B. Two simple models

Figure 1 is a schematic depiction of the simulated RMS experiment considered here. Carriers emerge from a reservoir (striped) at the origin and tunnel a distance aL_c to the center of an unbiased quantum well, width w. Thus they feel the effect of the applied transverse magnetic field B over this distance in traveling to the center of the well. The semiclassical interpretation of this experiment asserts that they undergo a shift in wave vector $\Delta\mathbf{k}_\parallel = (eBL_ca/\hbar)\mathbf{e}_x$. Below we compare results calculated with two simple models that have identical equations of motion in the absence of an applied magnetic field: the single s-band, nearest-neighbor tight-binding model on a simple-cubic lattice and the discretized effective mass model.

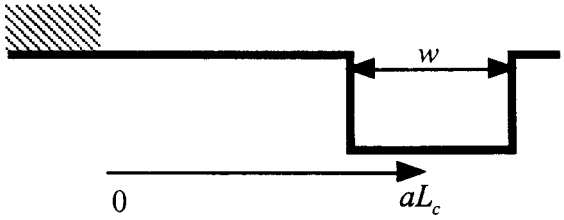

FIG. 1. Schematic depiction of the simulated RMS experiment considered here. Carriers emerge from a reservoir (striped) at the origin and tunnel a distance aL_c to the center of an unbiased quantum well, width w. The semiclassical interpretation of this experiment asserts that they undergo a shift in wave vector $\Delta\mathbf{k}_\parallel = (eBL_ca/\hbar)\mathbf{e}_r$. In the simplified calculations the results of which are plotted in Figs. 2 and 3 we apply hard-wall (infinite well) boundary conditions and offset the well center by aL_c from the origin of the vector potential.

For the single s-orbital tight-binding model the vectors $\mathbf{v}_{\mu\parallel}$ and $\mathbf{\Delta}_{L,\parallel}$ in Eq. (29) are zero, and the same-site and nearest-neighbor couplings, chosen to reproduce a conduction band of effective mass m^* whose minimum coincides with the zero of energy, are

$$\langle s;\mathbf{0} | H_0 | s;\pm a\mathbf{e}_\alpha \rangle = -V_s = -\frac{\hbar^2}{2m^*a^2}, \quad \alpha \in \{x,y,z\} \quad (47)$$

$$\langle s;\mathbf{0} | H_0 | s;\mathbf{0} \rangle = E_s = 6V_s = \frac{3\hbar^2}{m^*a^2}, \quad (48)$$

where a is the unit-cell cube edge. We write the wave function in the planar-orbital basis as

$$|\Psi_{\mathbf{k}_\parallel}\rangle = \sum_{L'} C_{L'} |s;L';\mathbf{k}_\parallel\rangle \quad (49)$$

so that the Schrödinger equation for the (unbiased) quantum well reads:

$$-V_sC_{L-1} + \left\{E_s - 2V_s\cos(k_ya) - 2V_s \times \cos\left[\left(k_x + \frac{eB_0La}{\hbar}\right)a\right] - E\right\}C_L - V_sC_{L+1} = 0, \quad (50)$$

where the symmetric quantum well extends over the $(2n+1)$ layers $-n + L_c \leq L \leq n + L_c$. We apply hard-wall boundary conditions at $L = L_c \pm n$: $C_{L_c-n-1} = C_{L_c+n+1} = 0$.

For the effective-mass calculation, we discretize the Schrödinger equation,

$$-\frac{\hbar^2}{2m^*}\nabla^2\psi(\mathbf{r})+\frac{(eB_0z)^2}{2m^*}\psi(\mathbf{r})+\frac{\hbar}{im^*}eB_0z\frac{d\psi(\mathbf{r})}{\partial x}=E\psi(\mathbf{r}), \tag{51}$$

using the standard central difference expressions on a uniform (three-dimensional) mesh of spacing a for the Laplacian and partial derivative. Since Eq. (51) is separable, we write

$$\psi(\mathbf{r})=\phi(x,y)\zeta(z), \tag{52}$$

and impose Bloch conditions in the plane

$$\psi(x\pm a,y,z)=e^{\pm ik_xa}\psi(x,y,z),$$
$$\psi(x,y,\pm a,z)=e^{\pm ik_ya}\psi(x,y,z) \tag{53}$$

to obtain

$$-V_s\zeta_{L-1}+\left[E_s-2V_s\cos(k_ya)-2V_s\cos(k_xa)+\frac{2V_sLa^2}{z_0^2}\sin(k_xa)+\frac{V_sL^2a^4}{z_0^4}-E\right]\zeta_L-V_s\zeta_{L+1}=0, \tag{54}$$

where V_s and E_s are the same as in Eqs. (47)–(48) and

$$\zeta_L=\zeta(aL), \tag{55}$$

$$\frac{1}{z_0^2}=\frac{eB_0}{\hbar}. \tag{56}$$

As before we apply hard-wall boundary conditions: $\zeta_{L_c-n-1}=\zeta_{L_c-n+1}=0$. Observe that for $B_0=0$ Eqs. (50) and (54) are identical so that any discrepancies in the results will be solely due to the different treatments of the electromagnetic coupling in the two models.

Figures 2 and 3 show calculations for three different cases: single *s*-band tight-binding, $\mathbf{k}_\parallel=\mathbf{0}$, Eq. (50), solid curve; effective-mass, $\mathbf{k}_\parallel=\mathbf{0}$, Eq. (54), dash-dotted curve; and single *s*-band tight-binding, Eq. (50), with zero magnetic field, but $\mathbf{k}_\parallel=(eBL_ca/\hbar)\mathbf{e}_x$, where B is taken from the abscissa of the graph (i.e., the $\mathbf{k}_\parallel$ shift is *fixed* for all layers at its midwell value in the nonzero-field case), dotted curve. This last calculation is just the semiclassical approximation[29] often used to interpret RMS experiments. For all calculations we take $a=2.8\,\text{Å}$, $m^*=0.07m_0$, and the well is $27a=75.6\,\text{Å}$ wide. In Fig. 2 the center of the well is placed at $179a=501.2\,\text{Å}$, while in Fig. 3 it is at $25a=70\,\text{Å}$. In Fig. 2 the two tight-binding calculations agree quite well differing by about 4.85% at 90 T, but the effective-mass result disagrees significantly with both: about 32% at 90 T versus the solid curve. On the other hand, in Fig. 3 the tight-binding and effective-mass results agree well (within about 0.32% at 90 T) but differ significantly from the RMS tight-binding result (dashed curve), a discrepancy of about 18.5% at 90 T.

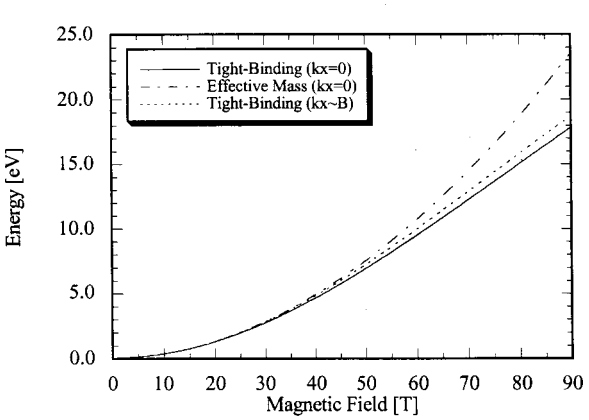

FIG. 2. Ground-state subband for a 75.6-Å quantum well (see text); the center of the well is at layer $L_c=179$ (501.2 Å). We take B_0 as indicated on the abscissa and $k_x=k_y=0$ for two of the curves, using Eq. (50) for the solid curve and Eq. (54) for the dash-dotted curve. For the dashed curve we use Eq. (54) with $B_0=0$ and $k_y=0$ but set $k_x=eBL_ca/\hbar$, where B is given by the abscissa.

The relatively close agreement of the tight-binding results in Fig. 2 and their large relative disagreement in Fig. 3 is exactly what we expect in light of our earlier, general results,[29] for Fig. 2 simulates a case in which the distance from the accumulation layer to the center of the quantum well is much greater than the quantum-well width, while Fig. 3 simulates a case in which this distance is slightly less than the quantum-well width. Likewise, the different treatments of the electromagnetic coupling in the tight-binding and effective-mass results show most dramatically when the carriers are subject to the effect of the magnetic field over a greater distance.

IV. CONCLUSIONS

In summary, we have derived a gauge-invariant electromagnetic coupling Hamiltonian for tight-binding models. We demand of the electromagnetic coupling Hamiltonian abso-

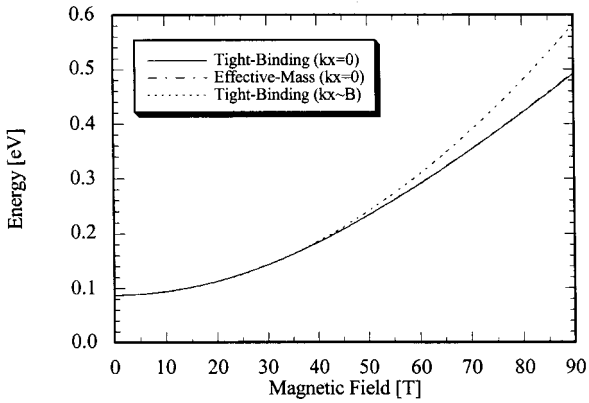

FIG. 3. Ground-state subband for a 75.6-Å quantum well (see text); the center of the well is at layer $L_c=25$ (70 Å). We take B_0 as indicated on the abscissa and $k_x=k_y=0$ for two of the curves, using Eq. (50) for the solid curve and Eq. (54) for the dash-dotted curve. For the dashed curve we use Eq. (54) with $B_0=0$ and $k_y=0$ but set $k_x=eBL_ca/\hbar$, where B is given by the abscissa.

lute consistency with the underlying tight-binding model and hence we neither make an external ansatz in developing our results nor do we introduce additional parameters into the momentum operator. Instead, we simply require the Hamiltonian to be gauge invariant, and it is this requirement alone that produces the equation from which we deduce the electromagnetic coupling terms. Unlike methods based directly upon the Peierls substitution, our results naturally and transparently reduce to the usual minimal-coupling Hamiltonian in a complete basis. Furthermore, under the customary tight-binding approximation the resulting series can be summed and the result an expression of the same form as that assumed in the Peierls substitution derivation. However, in this case there are differences: the path (a straight line) is *imposed*, since it is the only one that will permit a matrix element in this form to agree with the series and the integral must be carried out exactly. This settles the question of how to handle matrix elements in more-distant-neighbor tight-binding models: the straight line connecting the two sites involved in the matrix element, nearer neighbors notwithstanding. We have shown how to calculate matrix elements with our method and have applied it to a simulated resonant magnetotunneling experiment, comparing the results of two simple models.

ACKNOWLEDGMENTS

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APPENDIX

1. Matrix elements

From Ref. 19 the matrix elements of a cell-periodic operator Ω in the Bloch sum basis (4) are

$$\langle \alpha';\mu';\mathbf{k}+\mathbf{q}_1|e^{i\mathbf{q}\cdot\mathbf{r}}\Omega|\alpha;\mu;\mathbf{k}\rangle=\delta_{(\mathbf{k}+\mathbf{q}_1),(\mathbf{k}+\mathbf{q})}\times[\Omega(\mathbf{k})]_{(\alpha',\mu'),(\alpha,\mu)}=\delta_{\mathbf{q}_1,\mathbf{q}}[\Omega(\mathbf{k})]_{(\alpha',\mu'),(\alpha,\mu)}, \tag{A1}$$

$$\begin{aligned}\langle \alpha';\mu';\mathbf{k}+\mathbf{q}_1|\Omega e^{i\mathbf{q}\cdot\mathbf{r}}|\alpha;\mu;\mathbf{k}\rangle&=\delta_{(\mathbf{k}+\mathbf{q}_1),(\mathbf{k}+\mathbf{q})}[\Omega(\mathbf{k}+\mathbf{q})]_{(\alpha',\mu'),(\alpha,\mu)}\\&=\delta_{\mathbf{q}_1,\mathbf{q}}[\Omega(\mathbf{k}+\mathbf{q}_1)]_{(\alpha',\mu'),(\alpha,\mu)},\end{aligned} \tag{A2}$$

where in Eq. (A1) and (A2) $\mathbf{k}$, $\mathbf{q}$, and $\mathbf{q}_1$ all lie within the first Brillouin zone and any sum of wave vectors that falls outside the first zone is to be translated back inside it.

2. Incompleteness and multiple commutators of position and momentum

Due to the incompleteness of the tight-binding basis, multiple commutators of position and momentum exist.[3] Because we employ Chadi's[20] treatment of the spin-orbit coupling, the momentum and velocity operators are proportional:[19]

$$p^{(\alpha)}(\mathbf{k})=-\frac{im}{\hbar}[r^{(\alpha)},H_0](\mathbf{k})=\frac{m}{\hbar}\frac{\partial H_0(\mathbf{k})}{\partial k^{(\alpha)}}. \tag{A3}$$

We list below the several of the succeeding commutators (with our shorthand notation for them) for reference:

$$M_2^{(\alpha,\beta)}(\mathbf{k})=[r^{(\beta)},p^{(\alpha)}](\mathbf{k})=\frac{im}{\hbar}\frac{\partial^2 H_0(\mathbf{k})}{\partial k^{(\beta)}\partial k^{(\alpha)}}, \tag{A4}$$

$$M_3^{(\alpha,\beta,\gamma)}(\mathbf{k})=[r^{(\gamma)},[r^{(\beta)},p^{(\alpha)}]](\mathbf{k})=-\frac{m}{\hbar}\frac{\partial^3 H_0(\mathbf{k})}{\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}}, \tag{A5}$$

$$\begin{aligned}M_4^{(\alpha,\beta,\gamma,\delta)}(\mathbf{k})&=[r^{(\delta)}[r^{(\gamma)},[r^{(\beta)},p^{(\alpha)}]]](\mathbf{k})\\&=-\frac{im}{\hbar}\frac{\partial^4 H_0(\mathbf{k})}{\partial k^{(\delta)}\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}},\end{aligned} \tag{A6}$$

$$\begin{aligned}M_5^{(\alpha,\beta,\gamma,\delta,\epsilon)}(\mathbf{k})&=[r^{(\epsilon)},[r^{(\delta)}[r^{(\gamma)},[r^{(\beta)},p^{(\alpha)}]]]](\mathbf{k})\\&=\frac{m}{\hbar}\frac{\partial^5 H_0(\mathbf{k})}{\partial k^{(\epsilon)}\partial k^{(\delta)}\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}},\end{aligned} \tag{A7}$$

where for n even (odd) M_n is anti-Hermitian (Hermitian) and M_n is obviously invariant under permutation of the indices α, β, γ, δ, etc.

3. Multiple commutators involving complex exponentials

Consider the commutator involving $\alpha(\mathbf{k})$,

$$\begin{aligned}[e^{i\mathbf{q}\cdot\mathbf{r}},e^{i\mathbf{q}'\cdot\mathbf{r}}\alpha(\mathbf{k})]&=e^{i(\mathbf{q}+\mathbf{q}')\cdot\mathbf{r}}\alpha(\mathbf{k})-e^{i\mathbf{q}'\cdot\mathbf{r}}\alpha(\mathbf{k})e^{i\mathbf{q}\cdot\mathbf{r}}\\&=e^{i(\mathbf{q}+\mathbf{q}')\cdot\mathbf{r}}[\alpha(\mathbf{k})-\alpha(\mathbf{k}+\mathbf{q})].\end{aligned} \tag{A8}$$

Defining

$$\alpha^{(n+1)}(\mathbf{k})=\alpha^{(n)}(\mathbf{k})-\alpha^{(n)}(\mathbf{k}+\mathbf{q}_{n+1}),\quad n=0,1,2,\ldots \tag{A9}$$

we repeatedly employ Eq. (A9) to reduce multiple commutators such as

$$\begin{aligned}&[e^{i\mathbf{q}_3\cdot\mathbf{r}},[e^{i\mathbf{q}_2\cdot\mathbf{r}},[e^{i\mathbf{q}_1\cdot\mathbf{r}},\alpha^{(0)}(\mathbf{k})]]]\\&\quad=[e^{i\mathbf{q}_3\cdot\mathbf{r}},[e^{i\mathbf{q}_2\cdot\mathbf{r}},e^{i\mathbf{q}_1\cdot\mathbf{r}}\alpha^{(1)}(\mathbf{k})]],\end{aligned} \tag{A10}$$

$$\begin{aligned}&[e^{i\mathbf{q}_3\cdot\mathbf{r}},[e^{i\mathbf{q}_2\cdot\mathbf{r}},[e^{i\mathbf{q}_1\cdot\mathbf{r}},\alpha^{(0)}(\mathbf{k})]]]\\&\quad=[e^{i\mathbf{q}_3\cdot\mathbf{r}},e^{i(\mathbf{q}_1+\mathbf{q}_2)\cdot\mathbf{r}},\alpha^{(2)}(\mathbf{k})],\end{aligned} \tag{A11}$$

$$[e^{i\mathbf{q}_3\cdot\mathbf{r}},[e^{i\mathbf{q}_2\cdot\mathbf{r}},[e^{i\mathbf{q}_1\cdot\mathbf{r}},\alpha^{(0)}(\mathbf{k})]]]=e^{i(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3)\cdot\mathbf{r}}\alpha^{(3)}(\mathbf{k}). \tag{A12}$$

In this progression, note that each successive commutator produces two terms, so that $\alpha^{(n)}(\mathbf{k})$ consists of 2^n terms when reduced to components $\alpha^{(0)}$. For example, repeated application of Eq. (A9) yields for $\alpha^{(3)}(\mathbf{k})$,

$$\alpha^{(3)}(\mathbf{k})=\alpha^{(2)}(\mathbf{k})-\alpha^{(2)}(\mathbf{k}+\mathbf{q}_3), \tag{A13}$$

$$\alpha^{(3)}(\mathbf{k})=[\alpha^{(1)}(\mathbf{k})-\alpha^{(1)}(\mathbf{k}+\mathbf{q}_2)] -[\alpha^{(1)}(\mathbf{k}+\mathbf{q}_3)-\alpha^{(1)}(\mathbf{k}+\mathbf{q}_2+\mathbf{q}_3)], \tag{A14}$$

$$\alpha^{(3)}(\mathbf{k})=\alpha^{(0)}(\mathbf{k})-\alpha^{(0)}(\mathbf{k}+\mathbf{q}_1)-\alpha^{(0)}(\mathbf{k}+\mathbf{q}_2)-\alpha^{(0)}(\mathbf{k}+\mathbf{q}_3) +\alpha^{(0)}(\mathbf{k}+\mathbf{q}_1+\mathbf{q}_2)+\alpha^{(0)}(\mathbf{k}+\mathbf{q}_1+\mathbf{q}_3) +\alpha^{(0)}(\mathbf{k}+\mathbf{q}_2+\mathbf{q}_3)-\alpha^{(0)}(\mathbf{k}+\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3). \tag{A15}$$

4. Taylor expansions of multiple commutators involving complex exponentials

Consider a Taylor expansion of $\Omega^{(1)}(\mathbf{k})$, defined as in Eq. (A9) above. It is clear that the only way to ensure a fully symmetric expansion and treat all wave vectors on an equal footing is to average the expansions of the $\Omega^{(0)}$ about $\mathbf{k}$ and $\mathbf{k}+\mathbf{q}_1$. This is essential in order to obtain a Hermitian electromagnetic coupling Hamiltonian, since Eqs. (A1) and (A2) show that it is the position of $\exp(i\mathbf{q}\cdot\mathbf{r})$ relative to Ω that determines the argument, $\mathbf{k}$ or $\mathbf{k}+\mathbf{q}_1$. The two Taylor expansions are

$$\Omega^{(0)}(\mathbf{k})-\Omega^{(0)}(\mathbf{k}+\mathbf{q}_1) =-\sum_\alpha q_1^{(\alpha)}\frac{\partial\Omega^{(0)}(\mathbf{k})}{\partial k^{(\alpha)}}-\frac{1}{2!}\sum_{\alpha,\beta}q_1^{(\alpha)}q_1^{(\beta)}\frac{\partial^2\Omega^{(0)}(\mathbf{k})}{\partial k^{(\beta)}\partial k^{(\alpha)}} -\frac{1}{3!}\sum_{\alpha,\beta,\gamma}q_1^{(\alpha)}q_1^{(\beta)}q_1^{(\gamma)}\frac{\partial^3\Omega^{(0)}(\mathbf{k})}{\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}}-\cdots, \tag{A16}$$

$$\Omega^{(0)}(\mathbf{k})-\Omega^{(0)}(\mathbf{k}+\mathbf{q}_1) =-\sum_\alpha q_1^{(\alpha)}\frac{\partial\Omega^{(0)}(\mathbf{k}+\mathbf{q}_1)}{\partial k^{(\alpha)}} +\frac{1}{2!}\sum_{\alpha,\beta}q_1^{(\alpha)}q_1^{(\beta)}\frac{\partial^2\Omega^{(0)}(\mathbf{k}+\mathbf{q}_1)}{\partial k^{(\beta)}\partial k^{(\alpha)}} -\frac{1}{3!}\sum_{\alpha,\beta,\gamma}q_1^{(\alpha)}q_1^{(\beta)}q_1^{(\gamma)}\frac{\partial^3\Omega^{(0)}(\mathbf{k}+\mathbf{q}_1)}{\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}}-\cdots. \tag{A17}$$

Averaging Eqs. (A16) and (A17), we have

$$\Omega^{(0)}(\mathbf{k})-\Omega^{(0)}(\mathbf{k}+\mathbf{q}_1)=-\tfrac{1}{2}\sum_\alpha q_1^{(\alpha)}X_{(\alpha)}^{(1)}(\mathbf{k}), \tag{A18}$$

$$X_{(\alpha)}^{(1)}(\mathbf{k})=\left[\frac{\partial\Omega^{(0)}(\mathbf{k})}{\partial k^{(\alpha)}}+\frac{\partial\Omega^{(0)}(\mathbf{k}+\mathbf{q}_1)}{\partial k^{(\alpha)}}\right]+\frac{1}{2!}\sum_\beta q_1^{(\beta)} \times\left[\frac{\partial^2\Omega^{(0)}(\mathbf{k})}{\partial k^{(\beta)}\partial k^{(\alpha)}}-\frac{\partial^2\Omega^{(0)}(\mathbf{k}+\mathbf{q}_1)}{\partial k^{(\beta)}\partial k^{(\alpha)}}\right]+\frac{1}{3!}\sum_{\beta,\gamma}q_1^{(\beta)}q_1^{(\gamma)} \times\left[\frac{\partial^3\Omega^{(0)}(\mathbf{k})}{\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}}+\frac{\partial^3\Omega^{(0)}(\mathbf{k}+\mathbf{q}_1)}{\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}}\right]+\cdots. \tag{A19}$$

It is apparent from Eq. (A19) that the $X_{(\alpha)}^{(1)}$ are cell-periodic operators. Thus we may use Eqs. (A8) and (A9) to reduce multiple commutators such as

$$[e^{i\mathbf{q}_2\cdot\mathbf{r}},[e^{i\mathbf{q}_1\cdot\mathbf{r}},\Omega^{(0)}(\mathbf{k})]]=-\tfrac{1}{2}\sum_\alpha q_1^{(\alpha)}[e^{i\mathbf{q}_2\cdot\mathbf{r}},e^{i\mathbf{q}_1\cdot\mathbf{r}}X_{(\alpha)}^{(1)}(\mathbf{k})], \tag{A20}$$

$$[e^{i\mathbf{q}_2\cdot\mathbf{r}},[e^{i\mathbf{q}_1\cdot\mathbf{r}},\Omega^{(0)}(\mathbf{k})]] =e^{i(\mathbf{q}_1+\mathbf{q}_2)\cdot\mathbf{r}}(-\tfrac{1}{2})^2\sum_{\alpha,\beta}q_1^{(\alpha)}q_2^{(\beta)}X_{(\alpha,\beta)}^{(2)}(\mathbf{k}), \tag{A21}$$

$$X_{(\alpha)}^{(1)}(\mathbf{k})-X_{(\alpha)}^{(1)}(\mathbf{k}+\mathbf{q}_2)=-\tfrac{1}{2}\sum_\beta q_2^{(\beta)}X_{(\alpha,\beta)}^{(2)}(\mathbf{k}), \tag{A22}$$

where $X_{(\alpha,\beta)}^{(2)}(\mathbf{k})$ is again a symmetric, averaged Taylor expansion, obtained by applying Eq. (A19) twice:

$$X^{(2)}_{(\alpha,\beta)}(\mathbf{k})=\left[\frac{\partial X^{(1)}_{(\alpha)}(\mathbf{k})}{\partial k^{(\beta)}}+\frac{\partial X^{(1)}_{(\alpha)}(\mathbf{k}+\mathbf{q}_2)}{\partial k^{(\beta)}}\right]+\frac{1}{2!}\sum_{\gamma} q_2^{(\gamma)}\left[\frac{\partial^2 X^{(1)}_{(\alpha)}(\mathbf{k})}{\partial k^{(\gamma)}\partial k^{(\beta)}}-\frac{\partial^2 X^{(1)}_{(\alpha)}(\mathbf{k}+\mathbf{q}_2)}{\partial k^{(\gamma)}\partial k^{(\beta)}}\right]$$
$$+\frac{1}{3!}\sum_{\gamma,\delta} q_2^{(\gamma)}q_2^{(\delta)}\left[\frac{\partial^3 X^{(1)}_{(\alpha)}(\mathbf{k})}{\partial k^{(\delta)}\partial k^{(\gamma)}\partial k^{(\beta)}}+\frac{\partial^3 X^{(1)}_{(\alpha)}(\mathbf{k}+\mathbf{q}_2)}{\partial k^{(\delta)}\partial k^{(\gamma)}\partial k^{(\beta)}}\right]+\cdots, \tag{A23}$$

$$X^{(2)}_{(\alpha,\beta)}(\mathbf{k})=\left[\frac{\partial^2\Omega^{(0)}(\mathbf{k})}{\partial k^{(\beta)}\partial k^{(\alpha)}}+\frac{\partial^2\Omega^{(0)}(\mathbf{k}+\mathbf{q}_1)}{\partial k^{(\beta)}\partial k^{(\alpha)}}+\frac{\partial^2\Omega^{(0)}(\mathbf{k}+\mathbf{q}_2)}{\partial k^{(\beta)}\partial k^{(\alpha)}}+\frac{\partial^2\Omega^{(0)}(\mathbf{k}+\mathbf{q}_1+\mathbf{q}_2)}{\partial k^{(\beta)}\partial k^{(\alpha)}}\right]$$
$$+\frac{1}{3!}\binom{3}{2,1}\sum_{\gamma}\left\{(q_1^{(\gamma)}+q_2^{(\gamma)})\left[\frac{\partial^3\Omega^{(0)}(\mathbf{k})}{\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}}-\frac{\partial^3\Omega^{(0)}(\mathbf{k}+\mathbf{q}_1+\mathbf{q}_2)}{\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}}\right]\right.$$
$$\left.+(q_1^{(\gamma)}-q_2^{(\gamma)})\left[\frac{\partial^3\Omega^{(0)}(\mathbf{k}+\mathbf{q}_2)}{\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}}-\frac{\partial^3\Omega^{(0)}(\mathbf{k}+\mathbf{q}_1)}{\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}}\right]\right\}+\frac{1}{4!}\left\{\binom{4}{3,1}\sum_{\gamma,\delta}(q_1^{(\gamma)}q_1^{(\delta)}+q_2^{(\gamma)}q_2^{(\delta)})\right.$$
$$\times\left[\frac{\partial^4\Omega^{(0)}(\mathbf{k})}{\partial k^{(\delta)}\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}}+\frac{\partial^4\Omega^{(0)}(\mathbf{k}+\mathbf{q}_1)}{\partial k^{(\delta)}\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}}+\frac{\partial^4\Omega^{(0)}(\mathbf{k}+\mathbf{q}_2)}{\partial k^{(\delta)}\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}}+\frac{\partial^4\Omega^{(0)}(\mathbf{k}+\mathbf{q}_1+\mathbf{q}_2)}{\partial k^{(\delta)}\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}}\right]$$
$$+\binom{4}{2,2}\sum_{\gamma,\delta}(q_1^{(\gamma)}q_2^{(\delta)})\left[\frac{\partial^4\Omega^{(0)}(\mathbf{k})}{\partial k^{(\delta)}\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}}+\frac{\partial^4\Omega^{(0)}(\mathbf{k}+\mathbf{q}_1+\mathbf{q}_2)}{\partial k^{(\delta)}\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}}-\frac{\partial^4\Omega^{(0)}(\mathbf{k}+\mathbf{q}_1)}{\partial k^{(\delta)}\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}}\right.$$
$$\left.\left.-\frac{\partial^4\Omega^{(0)}(\mathbf{k}+\mathbf{q}_2)}{\partial k^{(\delta)}\partial k^{(\gamma)}\partial k^{(\beta)}\partial k^{(\alpha)}}\right]\right\}+\cdots. \tag{A24}$$

Several important features of the Taylor expansions are apparent from Eqs. (A18)–(A24). First, $X^{(n)}$ starts with the nth derivatives of $\Omega^{(0)}$, with leading factor $q_1^{(\alpha)}q_2^{(\beta)}\cdots q_n^{(\nu)}$. Second, the $q_1^{(\alpha)}$ and $q_2^{(\beta)}$ pulled out in Eq. (A21) have no effect on subsequent Taylor expansions—this is clear in the progression from Eqs. (A20)–(A22). Thus, we could replace them by anything, say, $q_j^{(\xi)}\to A^{(\xi)}_{\mathbf{q}_j}/if_{\mathbf{q}_j}$, and further Taylor expansions (due to application of additional commutators) would be unchanged. Third, the symmetric form chosen treats all wave vectors on an equal footing, as required.

5. Decomposition of Bloch-basis matrix elements

Matrix elements in the Bloch basis (4) of commutator $[r^{(\alpha)},\Omega]$, where Ω is a cell-periodic operator, are readily decomposed into matrix elements between localized orbitals. Since we apply cyclic boundary conditions, we have from Eq. (4),

$$\langle\alpha;\mu;\mathbf{k}|\Omega|\alpha';\mu';\mathbf{k}\rangle=\sum_{m=1}^{N}\exp[i\mathbf{k}\cdot(\mathbf{R}_m+\mathbf{v}_{\mu'}-\mathbf{v}_{\mu})]$$
$$\times\langle\alpha;\mu;\mathbf{v}_{\mu}|\Omega|\alpha';\mu';\mathbf{R}_m+\mathbf{v}_{\mu'}\rangle, \tag{A25}$$

where we have placed the unit cell of the left-hand orbital at the origin. From Eq. (9) it follows that

$$[r^{(\beta)},\Omega](\mathbf{k})=i\frac{\partial\Omega(\mathbf{k})}{\partial k^{(\beta)}}, \tag{A26}$$

so that

$$\langle\alpha;\mu;\mathbf{k}[r^{(\beta)},\Omega]\alpha';\mu';\mathbf{k}\rangle$$
$$=-\sum_{m=1}^{N}(\mathbf{R}_m+\mathbf{v}_{\mu'}-\mathbf{v}_{\mu})^{(\beta)}\exp[i\mathbf{k}\cdot(\mathbf{R}_m+\mathbf{v}_{\mu'}-\mathbf{v}_{\mu})]$$
$$\times\langle\alpha;\mu;\mathbf{v}_{\mu}|\Omega|\alpha';\mu';\mathbf{R}_m+\mathbf{v}_{\mu'}\rangle, \tag{A27}$$

and we may make the general identification

$$\langle\alpha;\mu;\mathbf{R}+\mathbf{v}_{\mu}|r^{(\beta)},\Omega|\alpha';\mu'\mathbf{R}_{j'}+\mathbf{v}_{\mu'}\rangle$$
$$=-(\mathbf{R}_{j'}+\mathbf{v}_{\mu'}-\mathbf{R}_j-\mathbf{v}_{\mu})^{(\beta)}$$
$$\times\langle\alpha;\mu;\mathbf{R}_j+\mathbf{v}_{\mu}|\Omega|\alpha';\mu';\mathbf{R}_{j'}+\mathbf{v}_{\mu'}\rangle, \tag{A28}$$

where the quantity in parentheses is simply the β component of the vector displacement of the orbital (α',μ') relative to the orbital (α,μ). Matrix elements of multiple commutators such as Eqs. (A3)–(A7) in the localized-orbital basis can be obtained through repeated application of Eq. (A28).

6. Closed-form expression for localized-orbital matrix elements

Here we give the derivation of the compact expression for the matrix elements of $H^{(\mathbf{A})}$ in the localized-orbital basis. We demonstrate that, within the approximation that the matrix elements of $\mathbf{A}$ and its derivatives are same-site; same-orbital-only interactions (consistent with the treatment of the scalar potential),

$$\langle \omega;\mu;\mathbf{R}_{j,\mu}|H^{(\mathbf{A})}|\omega';\mu';\mathbf{R}_{j',\mu'}\rangle = \exp\left[i\frac{Q}{\hbar}\int_{\boldsymbol{\sigma}\cdot\mathbf{R}_{j',\mu'}}^{\boldsymbol{\sigma}\cdot\mathbf{R}_{j,\mu}} \mathbf{A}\cdot d\boldsymbol{l}\right] \times\langle \omega;\mu;\mathbf{R}_{j,\mu}|H_0|\omega';\mu';\mathbf{R}_{j',\mu'}\rangle, \quad \text{(A29)}$$

where the path of integration, $\boldsymbol{\sigma}$, is the straight line connecting the two sites and we introduce the shorthand

$$\mathbf{R}_{l,\nu}=\mathbf{R}_l+\mathbf{v}_\nu \quad \text{(A30)}$$

by expanding both sides in a Taylor series after performing the integral.

To compute the integral, we parametrize the path as

$$\boldsymbol{\sigma}(\lambda)=(1-\lambda)\mathbf{R}_{j',\mu'}+\lambda\mathbf{R}_{j,\mu}=\mathbf{R}_{j',\mu'}+\lambda(\mathbf{R}_{j,\mu}-\mathbf{R}_{j',\mu'}), \quad \lambda:\ 0\to 1 \quad \text{(A31)}$$

$$\boldsymbol{\sigma}'(\lambda)=\mathbf{d}_{(j,\mu),(j',\mu')}=(\mathbf{R}_{j,\mu}-\mathbf{R}_{j',\mu'}), \quad \text{(A32)}$$

then employ the average of the two Taylor series of $\mathbf{A}(\boldsymbol{\sigma})$, one expansion taken about each of the end points. The result is

$$\begin{aligned}\int_{\boldsymbol{\sigma}:\mathbf{R}_{j',\mu'}}^{\boldsymbol{\sigma}:\mathbf{R}_{j,\mu}}\mathbf{A}\cdot d\boldsymbol{l} =&\frac{1}{2}\Bigg\{\sum_\alpha d^{(\alpha)}_{(j,\mu),(j',\mu')}A^{(\alpha)}_{(j',\mu'),(j,\mu)} \\ &+\frac{1}{2!}\sum_{\alpha,\beta} d^{(\alpha)}_{(j,\mu),(j',\mu')}d^{(\beta)}_{(j,\mu),(j',\mu')}\left[\frac{\partial A^{(\alpha)}}{\partial r^{(\beta)}}\right]_{(j',\mu'),(j,\mu)} \\ &+\frac{1}{3!}\sum_{\alpha,\beta,\gamma} d^{(\alpha)}_{(j,\mu)(j',\mu')}d^{(\beta)}_{(j,\mu),(j',\mu')}d^{(\gamma)}_{(j,\mu),(j',\mu')} \\ &\times\left[\frac{\partial^2 A^{(\alpha)}}{\partial r^{(\beta)}\partial r^{(\gamma)}}\right]_{(j',\mu'),(j,\mu)}+\cdots\Bigg\}, \end{aligned} \quad \text{(A33)}$$

where we introduce the shorthand notation

$$A^{(\alpha)}_{(j',\mu'),(j,\mu)}=[A^{(\alpha)}(\mathbf{R}_{j,\mu})+A^{(\alpha)}(\mathbf{R}_{j',\mu'})], \quad \text{(A34)}$$

$$\left[\frac{\partial A^{(\alpha)}}{\partial r^{(\beta)}}\right]_{(j',\mu'),(j,\mu)}=\left\{\left[\frac{\partial A^{(\alpha)}}{\partial r^{(\beta)}}\right]_{\mathbf{R}_{j',\mu'}}-\left[\frac{\partial A^{(\alpha)}}{\partial r^{(\beta)}}\right]_{\mathbf{R}_{j,\mu}}\right\}, \quad \text{(A35)}$$

$$\left[\frac{\partial^2 A^{(\alpha)}}{\partial r^{(\beta)}\partial r^{(\gamma)}}\right]_{(j',\mu'),(j,\mu)} =\left\{\left[\frac{\partial^2 A^{(\alpha)}}{\partial r^{(\beta)}\partial r^{(\gamma)}}\right]_{\mathbf{R}_{j',\mu'}}+\left[\frac{\partial^2 A^{(\alpha)}}{\partial r^{(\beta)}\partial r^{(\gamma)}}\right]_{\mathbf{R}_{j,\mu}}\right\}, \quad \text{(A36)}$$

and so forth. Observe the convention that terms in *even*-order partials are *added* while those in *odd*-order partials are *subtracted*.

The first few terms of the exponential in Eq. (A29) are readily evaluated with the aid of the multinomial theorem. Writing the exponential as a power series in $\mathbf{A}$ as in Eq. (10) for the Hamiltonian,

$$\exp\left[i\frac{Q}{\hbar}\int_{\boldsymbol{\sigma}:\mathbf{R}_{j',\mu'}}^{\boldsymbol{\sigma}:\mathbf{R}_{j,\mu}}\mathbf{A}\cdot d\boldsymbol{l}\right]=\sum_{n=0}^{\infty}\mathcal{I}_n, \quad \mathcal{I}_0=1 \quad \text{(A37)}$$

we find for the first several terms,

$$\mathcal{I}_1=i\frac{Q}{2\hbar}\Bigg\{\sum_\alpha d^{(\alpha)}_{(j,\mu),(j',\mu')}A^{(\alpha)}_{(j',\mu'),(j,\mu)}+\frac{1}{2!}\sum_{\alpha,\beta} d^{(\alpha)}_{(j,\mu),(j',\mu')}d^{(\beta)}_{(j,\mu),(j'\mu')}\left[\frac{\partial A^{(\alpha)}}{\partial r^{(\beta)}}\right]_{(j',\mu'),(j,\mu)} +\frac{1}{3!}\sum_{\alpha,\beta,\gamma} d^{(\alpha)}_{(j,\mu),(j',\mu')}d^{(\beta)}_{(j,\mu),(j',\mu')}d^{(\gamma)}_{(j,\mu),(j',\mu')}\left[\frac{\partial^2 A^{(\alpha)}}{\partial r^{(\beta)}\partial r^{(\gamma)}}\right]_{(j',\mu'),(j,\mu)}+\cdots\Bigg\}, \quad \text{(A38)}$$

$$\begin{aligned}\mathcal{I}_2=&-\frac{1}{2!}\left(\frac{Q}{2\hbar}\right)^2\Bigg\{\sum_{\alpha,\beta} d^{(\alpha)}_{(j,\mu),(j',\mu')}d^{(\beta)}_{(j,\mu),(j',\mu')}A^{(\alpha)}_{(j',\mu'),(j,\mu)}A^{(\beta)}_{(j',\mu'),(j,\mu)} \\ &+\left(\frac{1}{2!}\right)^2\sum_{\alpha,\beta,\gamma,\delta} d^{(\alpha)}_{(j,\mu),(j',\mu')}d^{(\beta)}_{(j,\mu),(j',\mu')}d^{(\gamma)}_{(j,\mu),(j',\mu')}d^{(\delta)}_{(j,\mu),j',\mu'}\left[\frac{\partial A^{(\alpha)}}{\partial r^{(\beta)}}\right]_{(j',\mu'),(j,\mu)}\left[\frac{\partial A^{(\gamma)}}{\partial r^{(\delta)}}\right]_{(j',\mu'),(j,\mu)}+\cdots \\ &+\sum_{\alpha,\beta,\gamma} d^{(\alpha)}_{(j,\mu),(j',\mu')}d^{(\beta)}_{(j,\mu),(j',\mu')}d^{(\gamma)}_{(j,\mu),(j',\mu')}A^{(\alpha)}_{(j',\mu'),(j,\mu)}\left[\frac{\partial A^{(\beta)}}{\partial r^{(\gamma)}}\right]_{(j',\mu'),(j,\mu)} \\ &+\frac{2!}{3!}\sum_{\alpha,\beta,\gamma,\delta} d^{(\alpha)}_{(j,\mu),(j',\mu')}d^{(\beta)}_{(j,\mu),(j',\mu')}d^{(\gamma)}_{(j,\mu),(j',\mu')}d^{(\delta)}_{(j,\mu),(j',\mu')}A^{(\alpha)}_{(j',\mu'),(j,\mu)}\left[\frac{\partial^2 A^{(\beta)}}{\partial r^{(\gamma)}\partial r^{(\delta)}}\right]_{(j',\mu',(j,\mu)}+\cdots\Bigg\}, \end{aligned} \quad \text{(A39)}$$

$$\mathcal{I}_3 = -\frac{i}{3!}\left(\frac{Q}{2\hbar}\right)^3\Bigg\{\sum_{\alpha,\beta,\gamma} d^{(\alpha)}_{(j,\mu),(j',\mu')} d^{(\beta)}_{(j,\mu),(j',\mu')} d^{(\gamma)}_{(j,\mu),(j',\mu')} A^{(\alpha)}_{(j',\mu'),(j,\mu)} A^{(\beta)}_{(j',\mu'),(j,\mu)} A^{(\gamma)}_{(j',\mu'),(j,\mu)} + \cdots$$

$$+\frac{3!}{(2!)^2}\sum_{\alpha,\beta,\gamma,\delta} d^{(\alpha)}_{(j,\mu),(j',\mu')} d^{(\beta)}_{(j,\mu),(j',\mu')} d^{(\gamma)}_{(j,\mu),(j',\mu')} d^{(\delta)}_{(j,\mu),(j',\mu')} A^{(\alpha)}_{(j',\mu'),(j,\mu)} A^{(\beta)}_{(j',\mu'),(j,\mu)} \left[\frac{\partial A^{(\gamma)}}{\partial r^{(\delta)}}\right]_{(j',\mu'),(j,\mu)}$$

$$+\frac{3!}{(2!)^3}\sum_{\alpha,\beta,\gamma,\delta,\varepsilon} d^{(\alpha)}_{(j,\mu),(j',\mu')} d^{(\beta)}_{(j,\mu),(j',\mu')} d^{(\gamma)}_{(j,\mu),(j',\mu')} d^{(\delta)}_{(j,\mu),(j',\mu')} d^{(\varepsilon)}_{(j,\mu),(j',\mu')} A^{(\alpha)}_{(j',\mu'),(j,\mu)} \left[\frac{\partial A^{(\beta)}}{\partial r^{(\gamma)}}\right]_{(j',\mu'),(j,\mu)}$$

$$\times\left[\frac{\partial A^{(\delta)}}{\partial r^{(\varepsilon)}}\right]_{(j',\mu'),(j,\mu)} + \frac{1}{2!}\sum_{\alpha,\beta,\gamma,\delta,\varepsilon} d^{(\alpha)}_{(j,\mu),(j',\mu')} d^{(\beta)}_{(j,\mu),(j',\mu')} d^{(\gamma)}_{(j,\mu),(j',\mu')} d^{(\delta)}_{(j,\mu),(j',\mu')} d^{(\varepsilon)}_{(j,\mu),(j',\mu')}$$

$$\times A^{(\alpha)}_{(j',\mu'),(j,\mu)} A^{(\beta)}_{(j',\mu'),(j,\mu)} \left[\frac{\partial^2 A^{(\gamma)}}{\partial r^{(\delta)}\partial r^{(\varepsilon)}}\right]_{(j',\mu'),(j,\mu)} + \cdots\Bigg\}. \tag{A40}$$

We now compare these terms, when substituted into Eq. (A29), to the corresponding ones obtained from our gauge-invariant Hamiltonian. In so doing we will find it helpful to make repeated use of Eq. (A28) to obtain expressions such as

$$\langle \omega;\mu;\mathbf{R}_{j,\mu}|r^{(\beta)},[r^{(\alpha)},\Omega]|\omega';\mu';\mathbf{R}_{j',\mu'}\rangle$$

$$= d^{(\alpha)}_{(j,\mu),(j',\mu')} d^{(\beta)}_{(j,\mu),(j',\mu')} \langle \omega;\mu;\mathbf{R}_{j,\mu}|\Omega|\omega';\mu';\mathbf{R}_{j',\mu'}\rangle \tag{A41}$$

to evaluate the multiple commutators appearing in Eqs. (19), (21), and (24). Our only use of the diagonal approximation for the position operator, Eq. (34), is with respect to **A** and its derivatives. This is consistent with the usual treatment of the scalar potential as a same-site, same-orbital interaction[12] and results in expressions such as

$$\langle \omega;\mu;\mathbf{R}_{j,\mu}|p^{(\alpha)}A^{(\alpha)}|\omega';\mu';\mathbf{R}_{j',\mu'}\rangle$$

$$= -\frac{im}{\hbar}A^{(\alpha)}(\mathbf{R}_{j',\mu'}) d^{(\alpha)}_{(j,\mu),(j',\mu')} \times\langle \omega;\mu;\mathbf{R}_{j,\mu}|H_0|\omega';\mu';\mathbf{R}_{j',\mu'}\rangle, \tag{A42}$$

where we have used Eq. (A3) for p.

Carrying out this procedure on the first-order coupling term, Eq. (19), we find immediately

$$\langle \omega;\mu;\mathbf{R}_{j,\mu}|H_1^{(A)}|\omega';\mu';\mathbf{R}_{j',\mu'}\rangle$$

$$= i\frac{Q}{2\hbar}\Bigg\{\sum_{\alpha} d^{(\alpha)}_{(j,\mu),(j',\mu')} A^{(\alpha)}_{(j',\mu'),(j,\mu)} + \frac{1}{2!}\sum_{\alpha,\beta} d^{(\alpha)}_{(j,\mu),(j',\mu')} d^{(\beta)}_{(j,\mu),(j',\mu')} \left[\frac{\partial A^{(\alpha)}}{\partial r^{(\beta)}}\right]_{(j',\mu'),(j,\mu)}$$

$$+\frac{1}{3!}\sum_{\alpha,\beta,\gamma} d^{(\alpha)}_{(j,\mu),(j',\mu')} d^{(\beta)}_{(j,\mu),(j',\mu')} d^{(\gamma)}_{(j,\mu),(j',\mu')} \times\left[\frac{\partial^2 A^{(\alpha)}}{\partial r^{(\beta)}\partial r^{(\gamma)}}\right]_{(j',\mu'),(j,\mu)} + \cdots\Bigg\}$$

$$\times\langle \omega;\mu;\mathbf{R}_{j,\mu}|H_0|\omega';\mu';\mathbf{R}_{j',\mu'}\rangle, \tag{A43}$$

which agrees with the first-order term of the exponential, Eq. (A38), substituted into Eq. (A29). For the second-order [Eq. (21)] and third-order [Eq. (24)] terms we change the dummy indices of summation to rewrite terms such as

$$\sum_{\alpha,\beta} d^{(\alpha)}_{(j,\mu),(j',\mu')} d^{(\beta)}_{(j,\mu),(j',\mu')} [A^{(\alpha)}(\mathbf{R}_{j,\mu})A^{(\beta)}(\mathbf{R}_{j,\mu}) + A^{(\alpha)} \times(\mathbf{R}_{j',\mu'})A^{(\beta)}(\mathbf{R}_{j',\mu'}) + 2A^{(\alpha)}(\mathbf{R}_{j,\mu})A^{(\beta)}(\mathbf{R}_{j',\mu'})]$$

$$= \sum_{\alpha,\beta} d^{(\alpha)}_{(j,\mu),(j',\mu')} d^{(\beta)}_{(j,\mu),(j',\mu')} \times[A^{(\alpha)}(\mathbf{R}_{j,\mu}) + A^{(\alpha)}(\mathbf{R}_{j',\mu'})] \times[A^{(\beta)}(\mathbf{R}_{j,\mu}) + A^{(\beta)}(\mathbf{R}_{j',\mu'})]$$

$$= \sum_{\alpha,\beta} d^{(\alpha)}_{(j,\mu),(j',\mu')} d^{(\beta)}_{(j,\mu),(j',\mu')} A^{(\alpha)}_{(j',\mu'),(j,\mu)} A^{(\beta)}_{(j',\mu'),(j,\mu)}. \tag{A44}$$

After a few manipulations of this type we obtain agreement for the second- and third-order terms as well:

$$\langle \omega;\mu;\mathbf{R}_{j,\mu}|H_2^{(\mathbf{A})}|\omega';\mu';\mathbf{R}_{j',\mu'}\rangle$$
$$= -\frac{1}{2!}\left(\frac{Q}{2\hbar}\right)^2\Bigg\{\sum_{\alpha,\beta} d^{(\alpha)}_{(j,\mu),(j',\mu')}d^{(\beta)}_{(j,\mu),(j',\mu')}A^{(\alpha)}_{(j',\mu')}A^{(\beta)}_{(j',\mu'),(j,\mu)}$$
$$+\left(\frac{1}{2!}\right)^2\sum_{\alpha,\beta,\gamma,\delta} d^{(\alpha)}_{(j,\mu),(j',\mu')}d^{(\beta)}_{(j,\mu),(j',\mu')}d^{(\gamma)}_{(j,\mu),(j',\mu')}d^{(\delta)}_{(j,\mu),(j',\mu')}\left[\frac{\partial A^{(\alpha)}}{\partial r^{(\beta)}}\right]_{(j',\mu'),(j,\mu)}\left[\frac{\partial A^{(\gamma)}}{\partial r^{(\delta)}}\right]_{(j',\mu'),(j,\mu)}+\cdots$$
$$+\sum_{\alpha,\beta,\gamma} d^{(\alpha)}_{(j,\mu),(j',\mu')}d^{(\beta)}_{(j,\mu),(j',\mu')}d^{(\gamma)}_{(j,\mu),(j',\mu')}A^{(\alpha)}_{(j',\mu'),(j,\mu)}\left[\frac{\partial A^{(\beta)}}{\partial r^{(\gamma)}}\right]_{(j',\mu'),(j,\mu)}$$
$$+\frac{2!}{3!}\sum_{\alpha,\beta,\gamma,\delta} d^{(\alpha)}_{(j,\mu),(j',\mu')}d^{(\beta)}_{(j,\mu),(j',\mu')}d^{(\gamma)}_{(j,\mu),(j',\mu')}d^{(\delta)}_{(j,\mu),(j',\mu')}A^{(\alpha)}_{(j',\mu'),(j,\mu)}\left[\frac{\partial^2 A^{(\beta)}}{\partial r^{(\gamma)}\partial r^{(\delta)}}\right]_{(j',\mu'),(j,\mu)}+\cdots\Bigg\}$$
$$\times\langle \omega;\mu;\mathbf{R}_{j,\mu}|H_0|\omega';\mu';\mathbf{R}_{j',\mu'}\rangle, \tag{A45}$$

$$\langle \omega;\mu;\mathbf{R}_{j,\mu}|H_3^{(A)}|\omega';\mu';\mathbf{R}_{j',\mu'}\rangle$$
$$= -\frac{i}{3!}\left(\frac{Q}{2\hbar}\right)^3\Bigg\{\sum_{\alpha,\beta,\gamma} d^{(\alpha)}_{(j,\mu),(j',\mu')}d^{(\beta)}_{(j,\mu),(j',\mu')}d^{(\gamma)}_{(j,\mu),(j',\mu')}A^{(\alpha)}_{(j',\mu'),(j,\mu)}A^{(\beta)}_{(j',\mu'),(j,\mu)}A^{(\gamma)}_{(j',\mu'),(j,\mu)}+\cdots$$
$$+\frac{3!}{(2!)^2}\sum_{\alpha,\beta,\gamma,\delta} d^{(\alpha)}_{(j,\mu),(j',\mu')}d^{(\beta)}_{(j,\mu),(j',\mu')}d^{(\gamma)}_{(j,\mu),(j',\mu')}d^{(\delta)}_{(j,\mu),(j',\mu')}A^{(\alpha)}_{(j',\mu'),(j,\mu)}A^{(\beta)}_{(j',\mu'),(j,\mu)}\left[\frac{\partial A^{(\gamma)}}{\partial r^{(\delta)}}\right]_{(j',\mu'),(j,\mu)}$$
$$+\frac{3!}{(2!)^3}\sum_{\alpha,\beta,\gamma,\delta,\varepsilon} d^{(\alpha)}_{(j,\mu),(j',\mu')}d^{(\beta)}_{(j,\mu),(j',\mu')}d^{(\gamma)}_{(j,\mu),(j',\mu')}d^{(\delta)}_{(j,\mu),(j',\mu')}d^{(\varepsilon)}_{(j,\mu),(j',\mu')}A^{(\alpha)}_{(j',\mu'),(j,\mu)}$$
$$\times\left[\frac{\partial A^{(\beta)}}{\partial r^{(\gamma)}}\right]_{(j',\mu'),(j,\mu)}\left[\frac{\partial A^{(\delta)}}{\partial r^{(\varepsilon)}}\right]_{(j',\mu'),(j,\mu)}+\frac{1}{2!}\sum_{\alpha,\beta,\gamma,\delta,\varepsilon} d^{(\alpha)}_{(j,\mu),(j',\mu')}d^{(\beta)}_{(j,\mu),(j',\mu')}d^{(\gamma)}_{(j,\mu),(j',\mu')}d^{(\delta)}_{(j,\mu),(j',\mu')}d^{(\varepsilon)}_{(j,\mu),(j',\mu')}$$
$$\times A^{(\alpha)}_{(j',\mu'),(j,\mu)}A^{(\beta)}_{(j',\mu'),(j,\mu)}\left[\frac{\partial^2 A^{(\gamma)}}{\partial r^{(\delta)}\partial r^{(\varepsilon)}}\right]_{(j',\mu'),(j,\mu)}+\cdots\Bigg\}\langle \omega;\mu;\mathbf{R}_{j,\mu}|H_0|\omega';\mu';\mathbf{R}_{j',\mu'}\rangle. \tag{A46}$$

Some aspects of this compact representation merit further comment. First, note that the straight-line path specified in Eqs. (A29)–(A32) is not *chosen* by us, but rather is *imposed* upon us by the requirement that Eq. (A29) give the same result as the Hamiltonian derived in Sec. II above. Second, observe that Eq. (A29) makes the proof of formal gauge invariance transparent, for the line integral of ∇f along *any* path connecting the two points is simply $f(\mathbf{R}_{j,\mu})-f(\mathbf{R}_{j',\mu'})$.

Finally, we conclude with a brief discussion of integrals along a general path that provides a physical justification for the straight line beyond the mathematical agreement of Eq. (A29) with the development of Sec. II above. A general path between two atomic sites may be parametrized as

$$\boldsymbol{\rho}(\lambda)=\sum_\alpha \mathbf{e}_\alpha[R^{(\alpha)}_{j',\mu'}+f^{(\alpha)}(\lambda)(R^{(\alpha)}_{j,\mu}-R^{(\alpha)}_{j',\mu'})],\quad \lambda:\quad 0\to 1 \tag{A47}$$

$$f^{(\alpha)}(0)=0,\quad f^{(\alpha)}(1)=1,\quad \alpha\in\{x,y,z\} \tag{A48}$$

$$\frac{d\boldsymbol{\rho}(\lambda)}{d\lambda}=\sum_\alpha \mathbf{e}_\alpha\frac{df^{(\alpha)}(\lambda)}{d\lambda}(R^{(\alpha)}_{j,\mu}-R^{(\alpha)}_{j',\mu'}), \tag{A49}$$

where the $\mathbf{e}_\alpha$ are Cartesian unit vectors and the functions $f^{(\alpha)}(\lambda)$ are arbitrary. Note that for the special case of a straight line we have $f^{(x)}(\lambda)=f^{(y)}(\lambda)=f^{(z)}(\lambda)=f(\lambda)$ and that in this case the parameter λ is superfluous since it is clear from Eqs. (A47)–(A49) that $\boldsymbol{\rho}$ really depends (linearly) upon the single parameter f, so that we may simplify the equations by using just f. Integrating the average of the two Taylor series of $\mathbf{A}(\boldsymbol{\rho})$, one expansion taken about each of the endpoints, we find:

$$\int_{\boldsymbol{\rho}:\mathbf{R}_{j',\mu'}}^{\boldsymbol{\rho}:\mathbf{R}_{j,\mu}} \mathbf{A}\cdot d\boldsymbol{l} = \frac{1}{2}\Bigg(\sum_{\alpha} d^{(\alpha)}_{(j,\mu),(j',\mu')}[A^{(\alpha)}(\mathbf{R}_{j,\mu})+A^{(\alpha)}(\mathbf{R}_{j',\mu'})] + \sum_{\alpha,\beta} d^{(\alpha)}_{(j,\mu),(j',\mu')} d^{(\beta)}_{(j,\mu),(j',\mu')}$$
$$\times\left\{F_1^{(\alpha,\beta)}\left[\frac{\partial A^{(\alpha)}}{\partial r^{(\beta)}}\right]_{\mathbf{R}_{j',\mu'}} - G_1^{(\alpha,\beta)}\left[\frac{\partial A^{(\alpha)}}{\partial r^{(\beta)}}\right]_{\mathbf{R}_{j,\mu}}\right\} + \frac{1}{2!}\sum_{\alpha,\beta,\gamma} d^{(\alpha)}_{(j,\mu),(j',\mu')} d^{(\beta)}_{(j,\mu),(j',\mu')} d^{(\gamma)}_{(j,\mu),(j',\mu')}$$
$$\times\left\{F_2^{(\alpha,\beta,\gamma)}\left[\frac{\partial^2 A^{(\alpha)}}{\partial r^{(\beta)}\partial r^{(\gamma)}}\right]_{\mathbf{R}_{j',\mu'}} + G_2^{(\alpha,\beta,\gamma)}\left[\frac{\partial^2 A^{(\alpha)}}{\partial r^{(\beta)}\partial r^{(\gamma)}}\right]_{\mathbf{R}_{j,\mu}}\right\} + \cdots\Bigg), \tag{A50}$$

where

$$F_1^{(\alpha,\beta)} = \int_0^1 f^{(\beta)}(\lambda)\frac{df^{(\alpha)}}{\delta\lambda}d\lambda, \quad G_1^{(\alpha,\beta)} = \int_0^1 [1-f^{(\beta)}(\lambda)]\frac{df^{(\alpha)}}{d\lambda}d\lambda, \tag{A51}$$

$$F_2^{(\alpha,\beta,\gamma)} = \int_0^1 f^{(\gamma)}(\lambda)f^{(\beta)}(\lambda)\frac{df^{(\alpha)}}{d\lambda}d\lambda, \quad G_2^{(\alpha,\beta,\gamma)} = \int_0^1 [1-f^{(\gamma)}(\lambda)][1-f^{(\beta)}(\lambda)]\frac{df^{(\alpha)}}{d\lambda}d\lambda, \tag{A52}$$

and so forth. For the straight-line path we immediately obtain $F_nG_n = 1/(n+1)$, in agreement with Eq. (A33). Observe that this ensures equal weights for corresponding components of **A** (and their derivatives) evaluated at the two endpoints, and therefore can be the end result of an Hermitian operator. If, however, the path is not straight, we find unequal weights. For example, if we choose the path paramtrized by

$$f^{(x)}(\lambda) = f^{(y)}(\lambda) = \lambda, \quad f^{(z)}(\lambda) = \lambda^2, \tag{A53}$$

we obtain

$$F_1^{(z,x)} = \int_0^1 2\lambda^2 d\lambda = \tfrac{2}{3},$$

$$G_1^{(z,x)} = \int_0^1 (1-\lambda)2\lambda\, d\lambda = (\lambda^2 - \tfrac{2}{3}\lambda^3|_0^1) = \tfrac{1}{3}, \tag{A54}$$

which are obviously unequal. No Hermitian operator could sample $\partial A^{(z)}/\partial r^{(x)}$ with different weights on the two sites. Thus the straight-line path ensures that the line integral may come from a Hermitian operator. Equation (A50) reveals one more interesting fact: the trapezoidal rule (i.e., the single sum) discards *all* path information so that within it all paths are identical.

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