Second-order k·p perturbation theory with Vanderbilt pseudopotentials and plane waves

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The **k·p** expressions for the gradient and curvature (and hence effective masses) of electronic energy bands in reciprocal space are presented for calculations involving nonlocal and non-normconserving Vanderbilt ultrasoft pseudopotentials [D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990)]. The expressions have been implemented, and comparison with numerically calculated gradients and curvatures show that they are practical, accurate, and useful in the calculation of electronic densities-of-states.

I. AN INTRODUCTION TO k·p PERTURBATION THEORY

The central idea behind **k·p** perturbation theory also lies at the heart of any attempt to understand the electronic band structure of a periodic system. As a result **k·p** perturbation theory has been taught for many years to students of solid-state physics.[1] This idea is that the knowledge of the wave functions and energy levels at any given point in the Brillouin zone implies knowledge of the band structure in the region surrounding that point. It resurfaces in modern day approaches to efficient electronic structure calculations.[2] Implicit in this is the concept that quantities such as band energies and matrix elements vary smoothly throughout the Brillouin zone. This behavior is crucial to any attempt to calculate properties that require integrations over the Brillouin zone.

k·p perturbation theory has a long history, stretching back to the early days of electronic structure theory of the solid state.[3] It was initially used partly as a pedagogical tool—for learning about the form of the electronic bands before calculated band structures became widely available. But by far the most important use of the method was as a tool in the parameterization of bands using, as data, experimental observables such as effective masses, oscillator strengths, and band gaps. The hope was to learn about as much of the band structure as possible from the restricted experimental data available, and also to produce a compact representation of the band structure.[4,5] Recently **k·p** perturbation theory has not been so widely used, but it has, however, found a home in the transport theory of heterostructures (it enables effective masses to be calculated) and Robertson and Payne[6] applied it to total-energy calculations using local pseudopotentials.

Possibly it is now time to return to the original spirit in which the theory was used. The output of the relatively expensive plane-wave pseudopotential calculations can be thought of in the same way as restricted experimental data — data from which the maximum information about the band structure is to be extracted, and a compact representation is to be produced. Kane[4] may have predicted this when he wrote:

"... Perhaps a judicious combination of the **k·p** and pseudopotential methods will nevertheless provide the ultimate in accuracy. ..."

In pursuit of this end, we present here the **k·p** expressions to be used in the case of a Hamiltonian based on Vanderbilt's nonlocal and non-normconserving ultrasoft pseudopotentials.[7,8] The use of these potentials, while leading to efficient and accurate results, introduces some complications in comparison to a purely local Hamiltonian— namely, the Hamiltonian no longer commutes with the position operator and the eigenproblem is generalized.

In Sec. II we derive the required expressions for the **k·p** perturbation theory, and in Secs. III and IV we describe the details of their practical implementation. In Sec. V we present some tests of our implementation. Finally, in Sec. VI, **k·p** perturbation theory is discussed in terms of its utility and a desirable future development is outlined.

II. THE k·p APPROACH TO THE QUADRATIC REPRESENTATION OF A BAND

The Taylor expansion of an energy band around a point $\mathbf{k}_0$ in the first Brillouin zone is

$$E_n(\mathbf{k}_0+\mathbf{q}) = E_n(\mathbf{k}_0) + \mathbf{A}_n^T\mathbf{q} + \frac{1}{2}\mathbf{q}^T\mathbf{B}_n\mathbf{q} + \cdots, \quad (1)$$

where **A** and **B** are given by

$$A_{n,\alpha} = \frac{\partial E_n(\mathbf{k})}{\partial k_\alpha}\bigg|_{\mathbf{k}_0} \quad B_{n,\alpha\beta} = \frac{\partial^2 E_n(\mathbf{k})}{\partial k_\alpha \partial k_\beta}\bigg|_{\mathbf{k}_0}. \quad (2)$$

We wish to find **A** and **B** in terms of the eigenspectrum of the Hamiltonian evaluated at $\mathbf{k}_0$.

A. Generalized first- and second-order perturbation theory

In order to find the variation of band energies in the vicinity of a given **k** point we turn to the first- and second-order perturbation theory for the generalized eigenproblem; $\hat{H}|\Psi\rangle = E\hat{S}|\Psi\rangle$. Since this generalized perturbation theory has not been widely published, a brief derivation is presented below. We shall write the perturbation to second order as

$$\hat{H} \rightarrow \hat{H} + \lambda\Delta\hat{H}^{(1)} + \lambda^2\Delta\hat{H}^{(2)}, \quad (3)$$

$$\hat{S} \rightarrow \hat{S} + \lambda\Delta\hat{S}^{(1)} + \lambda^2\Delta\hat{S}^{(2)}.$$

The perturbed wave function may be written as

$$|\Psi_n\rangle = |\phi_n^{(0)}\rangle + \sum_{k\neq n} C_{nk}(\lambda)|\phi_k^{(0)}\rangle, \qquad (4)$$

where $C_{nk}(\lambda) = \lambda C_{nk}^{(1)} + \lambda^2 C_{nk}^{(2)} + \cdots$ and $\{|\phi_n^{(0)}\rangle\}$ are the eigenfunctions of the unperturbed Hamiltonian, $\hat{H}|\phi_n^{(0)}\rangle = E_n^{(0)}\hat{S}|\phi_n^{(0)}\rangle$. The perturbed eigenvalue is $E_n(\lambda) = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots$. We may now write the perturbed eigenexpression as:

$$[\hat{H} + \lambda \Delta \hat{H}^{(1)} + \lambda^2 \Delta \hat{H}^{(2)}]$$

$$\times \left[|\phi_n^{(0)}\rangle + \sum_{k\neq n} \lambda C_{nk}^{(1)}|\phi_k^{(0)}\rangle + \lambda^2 C_{nk}^{(2)}|\phi_k^{(0)}\rangle + \cdots \right]$$

$$= [E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots]$$

$$\times [\hat{S} + \lambda \Delta \hat{S}^{(1)} + \lambda^2 \Delta \hat{S}^{(2)}]$$

$$\times \left[|\phi_n^{(0)}\rangle + \sum_{k\neq n} \lambda C_{nk}^{(1)}|\phi_k^{(0)}\rangle + \lambda^2 C_{nk}^{(2)}|\phi_k^{(0)}\rangle + \cdots \right].$$
$$(5)$$

Equating powers of λ and using $\hat{H}|\phi_n^{(0)}\rangle = E_n^{(0)}\hat{S}|\phi_n^{(0)}\rangle$ we obtain:

$$\sum_{k\neq n} C_{nk}^{(1)} E_k^{(0)} \hat{S}|\phi_k^{(0)}\rangle + \Delta \hat{H}^{(1)}|\phi_n^{(0)}\rangle$$

$$= E_n^{(0)} \sum_{k\neq n} C_{nk}^{(1)} \hat{S}|\phi_k^{(0)}\rangle + E_n^{(1)}\hat{S}|\phi_n^{(0)}\rangle + E_n^{(0)} \Delta \hat{S}^{(1)}|\phi_n^{(0)}\rangle.$$
$$(6)$$

If we now apply $\langle\phi_n^{(0)}|$ to the left, using $\langle\phi_n^{(0)}|\hat{S}|\phi_m^{(0)}\rangle = \delta_{nm}$, we are left with

$$E_n^{(1)} = \langle\phi_n^{(0)}|\Delta\hat{H}^{(1)} - E_n^{(0)}\Delta\hat{S}^{(1)}|\phi_n^{(0)}\rangle. \qquad (7)$$

Similarly, operating on the left with $\langle\phi_m^{(0)}|$, where $m\neq n$, gives the coefficients $C_{nm}^{(1)}$:

$$C_{nm}^{(1)} = \langle\phi_m^{(0)}|\Delta\hat{H}^{(1)} - E_n^{(0)}\Delta\hat{S}^{(1)}|\phi_n^{(0)}\rangle/(E_n^{(0)} - E_m^{(0)}). \quad (8)$$

And now, for the second-order change in the energy, we must equate powers of λ^2, again using $\hat{H}|\phi_n^{(0)}\rangle = E_n^{(0)}\hat{S}|\phi_n^{(0)}\rangle$.

$$\sum_{k\neq n} C_{nk}^{(2)} E_k^{(0)} \hat{S}|\phi_k^{(0)}\rangle + \sum_{k\neq n} C_{nk}^{(1)} \Delta\hat{H}^{(1)}|\phi_k^{(0)}\rangle + \Delta\hat{H}^{(2)}|\phi_n^{(0)}\rangle$$

$$= E_n^{(0)} \sum_{k\neq n} C_{nk}^{(2)} \hat{S}|\phi_k^{(0)}\rangle + E_n^{(0)} \sum_{k\neq n} C_{nk}^{(1)} \Delta\hat{S}^{(1)}|\phi_k^{(0)}\rangle$$

$$+ E_n^{(0)} \Delta\hat{S}^{(2)}|\phi_n^{(0)}\rangle + E_n^{(1)} \sum_{k\neq n} C_{nk}^{(1)} \hat{S}|\phi_k^{(0)}\rangle$$

$$+ E_n^{(1)} \Delta\hat{S}^{(1)}|\phi_n^{(0)}\rangle + E_n^{(2)} \hat{S}|\phi_n^{(0)}\rangle. \qquad (9)$$

If we apply $\langle\phi_n^{(0)}|$ to the left we obtain an expression for the second-order change in the energy:

$$E_n^{(2)} = \sum_{k\neq n} C_{nk}^{(1)}\langle\phi_n^{(0)}|\Delta\hat{H}^{(1)} - E_n^{(0)}\Delta\hat{S}^{(1)}|\phi_k^{(0)}\rangle$$

$$- E_n^{(1)}\langle\phi_n^{(0)}|\Delta\hat{S}^{(1)}|\phi_n^{(0)}\rangle$$

$$+ \langle\phi_n^{(0)}|\Delta\hat{H}^{(2)} - E_n^{(0)}\Delta\hat{S}^{(2)}|\phi_n^{(0)}\rangle. \qquad (10)$$

B. The k·p perturbation

In order to use these expressions we must now find the effective perturbation due to taking a small step in reciprocal space $\delta\mathbf{k}$. A Bloch wave function may be written as,

$$|\Psi_n^{\mathbf{k}}\rangle = e^{i\mathbf{k}\cdot\mathbf{r}}|U_n^{\mathbf{k}}\rangle, \qquad (11)$$

where $|U_n^{\mathbf{k}}\rangle$ is a cell periodic function. If $\hat{H}|\Psi_n^{\mathbf{k}}\rangle = E_n^{\mathbf{k}}\hat{S}|\Psi_n^{\mathbf{k}}\rangle$ then $e^{-i\mathbf{k}\cdot\mathbf{r}}\hat{H}e^{i\mathbf{k}\cdot\mathbf{r}}|U_n^{\mathbf{k}}\rangle = E_n^{\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{r}}\hat{S}e^{i\mathbf{k}\cdot\mathbf{r}}|U_n^{\mathbf{k}}\rangle$ and so the k-dependent Hamiltonian and overlap matrices are

$$\hat{H}(\mathbf{k}) = e^{-i\mathbf{k}\cdot\mathbf{r}}\hat{H}e^{i\mathbf{k}\cdot\mathbf{r}}, \qquad (12)$$

$$\hat{S}(\mathbf{k}) = e^{-i\mathbf{k}\cdot\mathbf{r}}\hat{S}e^{i\mathbf{k}\cdot\mathbf{r}}. \qquad (13)$$

The perturbation is given by Taylor expanding the exponentials to second order for small $\delta\mathbf{k}$,

$$\Delta\hat{H}(\mathbf{k}) = \hat{H}(\mathbf{k}+\delta\mathbf{k}) - \hat{H}(\mathbf{k})$$

$$= e^{-i\mathbf{k}\cdot\mathbf{r}}\left(i[\hat{H}, \delta\mathbf{k}\cdot\hat{\mathbf{r}}] - \frac{1}{2}[[\hat{H}, \delta\mathbf{k}\cdot\hat{\mathbf{r}}], \delta\mathbf{k}\cdot\hat{\mathbf{r}}] \right.$$

$$\left. + O(\delta\mathbf{k}^3) \right) e^{i\mathbf{k}\cdot\mathbf{r}}. \qquad (14)$$

And similarly,

$$\Delta\hat{S}(\mathbf{k}) = \hat{S}(\mathbf{k}+\delta\mathbf{k}) - \hat{S}(\mathbf{k})$$

$$= e^{-i\mathbf{k}\cdot\mathbf{r}}\left(i[\hat{S}, \delta\mathbf{k}\cdot\hat{\mathbf{r}}] - \frac{1}{2}[[\hat{S}, \delta\mathbf{k}\cdot\hat{\mathbf{r}}], \delta\mathbf{k}\cdot\hat{\mathbf{r}}] \right.$$

$$\left. + O(\delta\mathbf{k}^3) \right) e^{i\mathbf{k}\cdot\mathbf{r}}. \qquad (15)$$

Thus, to second order in the step $\delta\mathbf{k}$, we can identify the terms in Eqs. (7) and (10) as

$$\Delta\hat{H}^{(1)} - E_n^{(0)}\Delta\hat{S}^{(1)} = i[\hat{H} - E_n^{(0)}\hat{S}, \hat{\mathbf{q}}\cdot\hat{\mathbf{r}}],$$

$$\Delta\hat{H}^{(2)} - E_n^{(0)}\Delta\hat{S}^{(2)} = -\frac{1}{2}[[\hat{H} - E_n^{(0)}\hat{S}, \hat{\mathbf{q}}\cdot\hat{\mathbf{r}}], \hat{\mathbf{q}}\cdot\hat{\mathbf{r}}]. \quad (16)$$

In the above, $\delta\mathbf{k}$ has been written as $\lambda\hat{\mathbf{q}}$, where $\hat{\mathbf{q}}$ is a unit vector in reciprocal space.

C. The band gradients and curvatures

The gradients and curvatures of the bands may now be evaluated since we have, in Eqs. (7), (10), and (16), an expression for the band energy up to second order in small steps about $\mathbf{k}_0$. If we use the notation,

$$P_{nm}^\alpha = \langle\phi_m^{(0)}|i[\hat{H} - E_n^{(0)}\hat{S}, \hat{r}_\alpha]|\phi_n^{(0)}\rangle, \qquad (17)$$

then the band gradient in reciprocal space may be written as,

$$\frac{\partial E_n}{\partial k_\alpha} = P_{nn}^\alpha, \tag{18}$$

and the curvature as,

$$\frac{\partial^2 E_n}{\partial k_\beta \partial k_\alpha} = -\langle \phi_n^{(0)} | i[[\hat{H} - E_n^{(0)}\hat{S}, \hat{r}_\alpha], \hat{r}_\beta] | \phi_n^{(0)} \rangle$$
$$- P_{nn}^\alpha \langle \phi_n^{(0)} | i[\hat{S}, \hat{r}_\beta] | \phi_n^{(0)} \rangle$$
$$- P_{nn}^\beta \langle \phi_n^{(0)} | i[\hat{S}, \hat{r}_\alpha] | \phi_n^{(0)} \rangle$$
$$+ \sum_{k \neq n} \frac{P_{nk}^\alpha P_{nk}^{\beta*} + P_{nk}^\beta P_{nk}^{\alpha*}}{E_n^{(0)} - E_k^{(0)}}. \tag{19}$$

Equations (18) and (19) are derived by simply taking the reciprocal space derivatives of the second-order energy expression.

III. THE COMMUTATORS

The electronic Hamiltonian $\hat{H}$ may be written as,

$$\hat{H} = -\frac{\hbar^2 \nabla^2}{2m} + \hat{V}, \tag{20}$$

where $\hat{V}$ is the self-consistently calculated potential. Assuming for the moment that $[\hat{V}, \hat{\mathbf{r}}] = 0$, which is the case for a purely local potential, then we need to evaluate the following commutators that appear in the expressions for the band gradients and curvatures above:

$$i[\hat{H}, \hat{r}_i] = i\left[-\frac{\hbar^2}{2m}\nabla^2, \hat{r}_i\right] = \frac{\hbar}{m}\hat{p}_i,$$

$$[[\hat{H}, \hat{r}_i], \hat{r}_j] = \left[\left[-\frac{\hbar^2}{2m}\nabla^2, \hat{r}_i\right], \hat{r}_j\right] = -\frac{\hbar^2}{m}\delta_{ij}. \tag{21}$$

The operator $\hat{\mathbf{p}}$ is the momentum operator, from which the name "**k · p**" is derived. Using these expressions for the commutators, the **k · p** expansion agrees with standard expressions found elsewhere.[1] There are however two situations in which the commutators are not so straightforward. One is in the case of incomplete of basis sets, which has been examined by Boykin.[9] In the plane-wave basis the basis functions are eigenstates of the momentum operator, and these complications disappear. The other source of complication is more obvious, and concerns the use of nonlocal pseudopotentials. The effect of nonlocal pseudopotentials on the **k · p** expansion does not appear to have been treated previously, although the first-order correction is closely connected to the correction required for the calculation of dipole optical transition matrix elements in reciprocal space.[10] This is an important omission given the prevalence of such potentials in modern electronic structure calculations. In general the pseudopotential can be divided into local and nonlocal components,

$$\hat{V} = \hat{V}_l + \hat{V}_{nl}, \tag{22}$$

and so the full expressions for the commutators will be,

$$i[\hat{H}, \hat{r}_i] = \frac{\hbar}{m}\hat{p}_i + i[\hat{V}_{nl}, \hat{r}_i], \tag{23}$$

or what is known as the velocity operator, and the double commutator,

$$[[\hat{H}, \hat{r}_i], \hat{r}_j] = -\frac{\hbar^2}{m}\delta_{ij} + [[\hat{V}_{nl}, \hat{r}_i], \hat{r}_j]. \tag{24}$$

The modifications due to the nonlocality of the potential are generally nonzero, and there are similar expressions for the commutators of the $\hat{S}$ operator, which deviates from the identity in the ultrasoft pseudopotential case and is nonlocal in the same manner as the potential.

IV. EVALUATION OF THE **k · p** MATRIX ELEMENTS

The matrix elements of the form $\langle \Psi_n^{\mathbf{k}} | \hat{p}_i | \Psi_m^{\mathbf{k}} \rangle$ can be efficiently evaluated in reciprocal space since the plane waves making up the basis are eigenstates of the the momentum operator, and hence the operator $\hat{\mathbf{p}}$ is diagonal. If the nonlocal part of the potential is in separable form (which is common due to its computational efficiency) then it may be written, following Vanderbilt,[7] as,

$$\hat{V}_{nl} = \sum_{n,m} |\beta_n\rangle D_{nm}\langle \beta_m|, \tag{25}$$

and the $\hat{S}$ operator is,

$$\hat{S} = 1 + \sum_{n,m} |\beta_n\rangle q_{nm}\langle \beta_m|. \tag{26}$$

The $|\beta_n\rangle$ are atomiclike projectors localized within the so-called core radius of the pseudopotential. In the case of Vanderbilt's pseudopotentials, they are constructed so that $\langle \beta_n | \phi_m^{ps} \rangle = \delta_{nm}$, where $|\phi_m^{ps}\rangle$ are the atomic pseudowave-functions. The D_{nm} can be thought of as the strength of the nonlocal potential in each angular momentum channel, and the q_{nm} are related to the charge deficiency within the core radius due to the decision not to apply the norm conservation constaint during the construction of the Vanderbilt pseudopotentials. Clearly, if the q_{nm} are set to zero, the form of the nonlocal potential is just that of standard separable nonlocal norm-conserving pseudopotentials since $\hat{S}$ reduces to the identity operator.

This means that we must evaluate matrix elements of the form $\langle \beta | \hat{r}_i | \Psi_n^{\mathbf{k}} \rangle$ and $\langle \beta | \hat{r}_i \hat{r}_j | \Psi_n^{\mathbf{k}} \rangle$. These matrix elements may also be evaluated in reciprocal space in the following way. Consider the matrix element $\langle \beta | e^{i\mathbf{q}\cdot\hat{r}} | \Psi_n^{\mathbf{k}} \rangle$, for small $\mathbf{q}$:

$$\langle \beta | e^{i\mathbf{q}\cdot\hat{r}} | \Psi_n^{\mathbf{k}} \rangle = \langle \beta | \Psi_n^{\mathbf{k}} \rangle + i\langle \beta | \mathbf{q} \cdot \hat{r} | \Psi_n^{\mathbf{k}} \rangle - \frac{1}{2}\langle \beta | |\mathbf{q} \cdot \hat{r}|^2 | \Psi_n^{\mathbf{k}} \rangle$$
$$+ O(q^3). \tag{27}$$

Now, let $\mathbf{q} = (q, 0, 0)$, then

$$\langle \beta | e^{iq\hat{r}_1} | \Psi_n^{\mathbf{k}} \rangle - \langle \beta | e^{-iq\hat{r}_1} | \Psi_n^{\mathbf{k}} \rangle = 2iq\langle \beta | \hat{r}_1 | \Psi_n^{\mathbf{k}} \rangle + O(q^3), \tag{28}$$

TABLE I. The electronic band gradients of the first four bands of diamond at the **k** point (0.48,0.23,0.38) in reciprocal lattice vectors. The calculations were performed for the primitive cell, at a plane-wave cutoff of 600 eV and 360 bands in the normconserving case and 280 eV and 116 bands in the ultrasoft case. The units of the band gradients are in eV Å.

Gradient		Band	Normconserving			Ultrasoft		
	Direction		x	y	z	x	y	z
Numerical derivative		1	6.2053	3.1345	1.2353	6.1550	3.1181	1.2363
		2	−3.8210	−5.3539	−6.8463	−3.8193	−5.3681	−6.8659
		3	−4.6409	−3.0813	5.9605	−4.6426	−3.0900	5.9874
		4	−6.6917	1.6231	0.6623	−6.7471	1.6312	0.6532
Perturbation theory		1	6.2053	3.1345	1.2353	6.1550	3.1181	1.2363
		2	−3.8210	−5.3539	−6.8463	−3.8193	−5.3681	−6.8659
		3	−4.6409	−3.0813	5.9605	−4.6426	−3.0900	5.9874
		4	−6.6917	1.6231	0.6623	−6.7471	1.6312	0.6532

and so on. In a similar way, the matrix elements required for the double commutator may be found. Again, let $\mathbf{q} = (q,0,0)$, then

$$\langle\beta|e^{iq\hat{r}_1}|\Psi_n^{\mathbf{k}}\rangle + \langle\beta|e^{-iq\hat{r}_1}|\Psi_n^{\mathbf{k}}\rangle - 2\langle\beta|\Psi_n^{\mathbf{k}}\rangle$$
$$= -q^2\langle\beta|\hat{r}_1^2|\Psi_n^{\mathbf{k}}\rangle + O(q^4), \tag{29}$$

and so on. The cross terms (i.e., $\hat{r}_1\hat{r}_2$ etc.) are obtained as follows. Let $\mathbf{q}=(q,q,0)$, then

$$\langle\beta|e^{iq(\hat{r}_1+\hat{r}_2)}|\Psi_n^{\mathbf{k}}\rangle + \langle\beta|e^{-iq(\hat{r}_1+\hat{r}_2)}|\Psi_n^{\mathbf{k}}\rangle - 2\langle\beta|\Psi_n^{\mathbf{k}}\rangle$$
$$= -q^2(\langle\beta|\hat{r}_1^2|\Psi_n^{\mathbf{k}}\rangle + \langle\beta|\hat{r}_2^2|\Psi_n^{\mathbf{k}}\rangle + 2\langle\beta|\hat{r}_1\hat{r}_2|\Psi_n^{\mathbf{k}}\rangle)$$
$$+ O(q^4), \tag{30}$$

and so, using Eq. (29), $\langle\beta|\hat{r}_1\hat{r}_2|\Psi_n^{\mathbf{k}}\rangle$ can be extracted. Given that the electronic structure method used must already have routines for evaluating $\langle\beta|\Psi_{\mathbf{k}}^n\rangle$, the advantage of this method is that evaluating $\langle\beta|e^{i\mathbf{q}\cdot\hat{r}}|\Psi_n^{\mathbf{k}}\rangle$ simply involves small shifts in the grid in reciprocal space on which $|\beta\rangle$ is calculated. This avoids tiresome evaluation of new spherical harmonic projectors, and this approach is readily extended to higher order. The size of q is chosen to be small enough for the

$O(q^3)$ and $O(q^4)$ terms to be negligible, but large enough to avoid errors due to precision limitations.

V. TESTS OF THE k·p METHOD

After deriving expressions for the electronic band gradients and curvatures, it remains to show that these expressions can be implemented practically. To demonstrate this, two tests are presented. The first is a straightforward comparison with numerically calculated derivatives, and the second demonstrates a practical application of the theory.

A. Numerical evaluation of gradients and curvatures

The electronic band gradients and curvatures may be calculated numerically by simply taking small steps in reciprocal space. However, such numerical derivatives can be difficult to converge with respect to the step size. Accuracy requires small step sizes, but this, in turn, leads to small energy differences and an extreme sensitivity to errors in these energies. This is a particular problem for the iterative, rather than direct, diagonalization techniques commonly used in plane-wave codes. A further problem is that of band crossing.[11] If the derivatives are sought about a **k** point for which some bands are degenerate, the numerical derivatives

TABLE II. As in Table I, but here the curvature in the direction of the three principal axes of the curvature tensor is presented. The units of curvature are eV Å^2, and the curvature for a free-electron band in the same units is 7.62 eV Å^2.

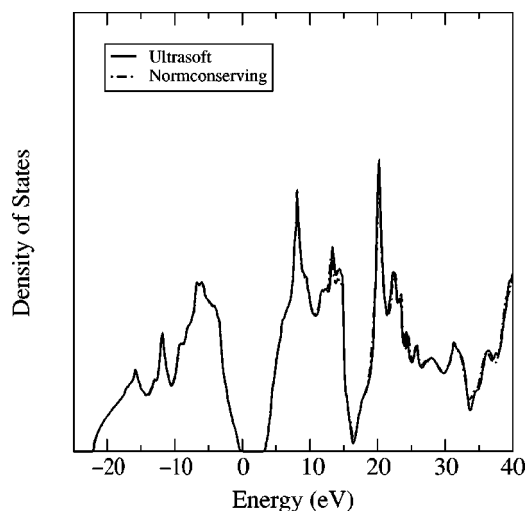| Curvature		Band	Normconserving			Ultrasoft		
	Direction		1	2	3	1	2	3
Numerical derivative		1	3.40	5.41	5.67	3.49	5.37	5.62
		2	−3.68	3.71	5.54	−3.57	3.75	5.58
		3	−20.35	2.17	6.03	−20.22	2.16	6.00
		4	−6.72	−0.67	12.04	−6.70	−0.69	11.95
Perturbation theory		1	3.40	5.41	5.67	3.49	5.37	5.61
		2	−3.68	3.71	5.53	−3.57	3.76	5.58
		3	−20.33	2.16	6.03	−20.20	2.15	6.00
		4	−6.70	−0.67	12.01	−6.67	−0.68	11.93

FIG. 1. The valence and conduction-band density-of-states for diamond, calculated for normconserving and ultrasoft pseudopotentials using plane-wave cutoffs of 600 and 280 eV, respectively. A total of 40 bands were included in the perturbation summation and the Fermi energy is 0 eV.

become ill defined. For this reason, the test case of diamond presented here in Tables I and II is a calculation performed about a *non*special **k** point. In order to test that the numerical and **k · p** derivatives are equivalent—as they should be — almost the entire eigenspectrum has been included in the perturbation summation of Eq. (19). In practical applications such accuracy will be rarely required. The result of this test is positive, in that the deviations between the numerically and perturbationally calculated derivatives presented in Tables I and II might reasonably be assigned to numerical imprecisions rather than some error in Eqs. (18) and (19), or in the implementation. In fact, to the number of significant figures presented, the gradients are identical.

B. Calculation of electronic density-of-states

The motivation for this extension of **k · p** perturbation theory was the generation of a piecewise quadratic representation of electronic bands for use in the second-order extrapolative Brillouin-zone integration scheme described previously.[11] In Fig. 1 we show the total density-of-states of diamond, using gradients and curvatures calculated with the expressions presented here and the extrapolative integration scheme. A fairly low number of **k** points (16 in the irreducible wedge of the primitive cell of diamond) have been used in order to emphasize any differences in the gradients and curvatures in the normconserving and ultrasoft cases. It is

clear that the normconserving and ultrasoft pseudopotential results are practically identical within the valence band. The small differences in the conduction band are due to the different higher energy scattering properties of the pseudopotentials. This is expected, since the pseudopotentials are constructed to give accurate results in the valence-band energy range only.

VI. DISCUSSION

As a crude indication of the usefulness of this extension of **k · p** perturbation theory to ultrasoft nonlocal pseudopotentials, we found that the calculation of the density-of-states shown in Fig. 1 was some three and a half times quicker in the ultrasoft case, compared to the calculation using normconserving pseudopotentials. Even greater efficiency gains have been found in larger systems—a factor of 7 for the carbon polymorph described in Winkler *et al.*[12]

While the band gradients are essentially computationally cost free, the **k · p** perturbation theory presented here for the band curvatures requires a summation over the entire eigenspectrum. Given the typically large size of plane-wave bases, this is impractical in general. Currently the evaluation of these many eigenstates dominates the computational cost of the method. While it is often possible to use a set of eigenstates restricted to the lower portion of the eigenspectrum, it would be desirable to reformulate this theory in terms of only those states for which we are interested in the electronic structure. It is likely that such a formulation would be similar to that employed by Mauri *et al.*[13] in which the perturbation theory including the summation is recast as a linear system and solved using conjugate gradients minimization.[14] This reformulation would result in an efficient and accurate approach to the calculation of band curvatures (and hence effective masses) and would be of great interest to those who model the transport properties of heterostructures.

In conclusion, we have derived the **k · p** expressions for the gradients and curvature of the electronic energy bands for a generalized Hamiltonian, and implemented these expressions in the case of the widely used Vanderbilt ultrasoft pseudopotentials and plane waves. The results are found to be accurate, and in combination with an extrapolative Brillouin-zone integration scheme,[11] the approach is shown to be efficient and useful in the calculation of electronic densities-of-states.

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