Calculation of momentum matrix elements using the Green's-function method

A.-B. Chen

Department of Physics, Auburn University, Auburn, Alabama 36830
(Received 24 February 1976)

A method for calculating the interband momentum matrix elements in the Green's-function method has been obtained, which is applicable to the l- and E-dependent potentials. This method is convenient in that it requires only the knowledge of wave functions inside the muffin-tin spheres. Numerical results calculated from this method are used to study the dependence of the matrix elements on the number of angular momentum components included. It is found that $l > 2$ components are important for the matrix elements.

The Green's-function method[1] (GFM) of Korringa,[2] Kohn and Rostoker[3] (KKR) has been shown to be a very useful band scheme even if the simple muffin-tin-potential approximation is used. However, the use of this method for the calculation of the momentum matrix elements and related physical quantities has been relatively new. One reason for this is that the diagonalization of the GFM matrix only yields the non-normalized wave functions inside the muffin-tin spheres. Extra work and further approximations are needed to obtain the wave functions in the interstitial regions.[4] In a recent paper Janak *et al.*[5] pointed out a convenient way to calculate the proper normalizations and the momentum matrix elements $\vec{p}_{nm}$. Their formula for the $\vec{p}_{nm}$ is based on the simple form of the commutator between the $\vec{p}$ and the muffin-tin potential V and has the form

$$\vec{p}_{nm} = -i\hbar \int_{r < r_0} \frac{\Psi_n^*(\vec{r}) \nabla V \Psi_m(\vec{r}) \, d^3 r}{E_m - E_n}. \tag{1}$$

Since the ∇V is only nonvanishing inside the muffin-tin radius r_0, the calculation only requires the ∇V and wave functions for $r \leq r_0$. However, Eq. (1) cannot be used to deal with potentials which are E (energy) and l (angular momentum) dependent,[5-7] because the states involved have different l components and different energies. This paper presents a different approach in which only the wave functions are involved in the calculation. Hence, the difficulties associated with the l- and E-dependent potentials can be circumvented.

We note that the effective crystal potential, as it is to describe the electron excitations in a solid, is expected to be E and l dependent due to the non-local nature of the self-energy associated with the one-particle Green's function in the many-body theory. This fact was born out in a detailed parametrization study of the energy bands of Cu and Ag by Chen and Segall.[7] It was found that in order to achieve accurate bands in agreement with the empirical data each l component requires a smooth but different E dependence in the potential correc-

tion to the *ab initio* form. Means for obtaining wave functions from this GFM parametrization scheme has also been implemented.[8] In order to apply the above results for the study of physical properties such as the $\epsilon_2(\omega)$ spectra, one has to have a method for calculating the momentum matrix elements using these l- and E-dependent interactions. The present paper addresses itself to this problem.

The trial wave functions $\Psi_n(\vec{r})$ in the KKR muffin-tin form can be expanded in terms of real spherical harmonics $\mathcal{Y}_{lj}$:

$$\Psi_n(\vec{r}) = \sum_{lj} i^l C_{lj} R_l(E_n, r) \mathcal{Y}_{lj}(\vec{r}), \tag{2}$$

where the radial function R_l satisfies the equation

$$-\frac{1}{r^2} \frac{dr}{dr} \left(r^2 \frac{dR_l}{dr} \right) + \left(\frac{l(l+1)}{r^2} + V_l(E, r) - E \right) R_l(E, r) = 0. \tag{3}$$

The muffin-tin potential in Eq. (3) is assumed to be l and E dependent. The non-normalized coefficients C_{lm} in Eq. (3) can be obtained from the GFM matrix which determines the E_n. To obtain the properly normalized Ψ_n we use a procedure suggested by Ham and Segall.[4] If small constant muffin-tin potentials, say v_0 and $-v_0$, are added to every muffin-tin potential, then E_n will have small shifts, say δ^+ and δ^-, respectively. Since v_0 is small, δ^+ and δ^- can be obtained from the perturbation series

$$\delta^+ = \frac{1}{N} \langle \Psi_n | v_0 | \Psi_n \rangle + \frac{1}{N^2} {\sum_m}' \frac{|\langle \Psi_m | v_0 | \Psi_n \rangle|^2}{E_n - E_m} + \cdots, \tag{4}$$

and

$$\delta^- = \frac{-1}{N} \langle \Psi_n | v_0 | \Psi_n \rangle + \frac{1}{N^2} {\sum_m}' \frac{|\langle \Psi_m | v_0 | \Psi_n \rangle|^2}{E_n - E_m} + \cdots. \tag{5}$$

In Eqs. (4) and (5) we have assumed that Ψ_n is

normalized to unity in a unit cell so the factor $1/N$ appears, where N being the number of unit cells in the crystal. Equations (4) and (5) can be used to obtain σ_n, the normalization inside the muffin-tin radius r_0, correct to the second order in v_0:

$$\sigma_n \equiv \int_{r<r_0} |\Psi_n(\vec{r})|^2 d^3r = \frac{1}{2} \frac{(\delta^+ - \delta^-)}{v_0}. \tag{6}$$

Since v_0 can be chosen reasonably small, σ_n can be determined with reasonable accuracy.[9]

To obtain $\vec{p}_{nm}$, first we decompose the integration into two parts:

$$\vec{p}_{nm} = \frac{1}{N} \int_{\text{in}} \Psi_n^*(\vec{r}) \vec{p}\Psi_m(\vec{r}) d^3r + \frac{1}{N} \int_{\text{out}} \Psi_n^*(\vec{r}) \vec{p}\Psi_m(\vec{r}) d^3r, \tag{7}$$

where in and out indicate, respectively, the regions inside and outside the muffin-tin spheres. The first term can be integrated directly. For the second term we note that $\vec{p}$ commutes with the Hamiltonian $(V=0)$, i.e.,

$$0 = \int_{\text{out}} \Psi_n^*(\vec{r})(\vec{p}H - H\vec{p})\Psi_m(\vec{r}) d^3r = E_m \int_{\text{out}} \Psi_n^*(\vec{r}) \vec{p}\Psi_m(\vec{r}) d^3r - \int_{\text{out}} \Psi_n^*(\vec{r}) \frac{p^2}{2m} \vec{p}\Psi_m(\vec{r}) d^3r. \tag{8}$$

Letting $\phi \equiv -i\hbar\nabla\Psi_m$ and making use of the Green's theorem, we can cast Eq. (8) into

$$0 = E_m \int_{\text{out}} \Psi_n^*(\vec{r}) \vec{p}\Psi_m(\vec{r}) d^3r + \frac{\hbar^2}{2m} \oint (\Psi_n^*\nabla\phi - \phi\nabla\Psi_n^*) \cdot d\vec{s} + \frac{\hbar^2}{2m} \int_{\text{out}} \phi\nabla^2\Psi_n^*(\vec{r}) d^3r$$

$$= (E_m - E_n) \int_{\text{out}} \Psi_n^*(\vec{r}) \vec{p}\Psi_m(\vec{r}) d^3r + \frac{\hbar^2}{2m} \oint (\Psi_n^*\nabla\phi - \phi\nabla\Psi_n^*) \cdot d\vec{s}.$$

In the above, the surface integrations are over the surfaces of all the muffin-tin spheres in the crystal. The periodic surface integrations can then be represented by that on the central muffin-tin surface so finally the whole outside contribution takes the form

$$\int_{\text{out}} \Psi_n^*(\vec{r}) \vec{p}\Psi_m(\vec{r}) d^3r = \frac{-iN\hbar^3 r_0^2}{2m(E_m - E_n)} \sum_\alpha \hat{e}_\alpha \int_{r=r_0} \left(\Psi_n^* \frac{\partial^2\Psi_m}{\partial r \partial x_\alpha} - \frac{\partial\Psi_n^*}{\partial r} \frac{\partial\Psi_m}{\partial x_\alpha}\right) d\Omega. \tag{9}$$

Now, the explicit expansion of Ψ of Eq. (2) can be used to obtain the following explicit formula for the $\vec{p}_{nm}$ (in units of $\hbar/a_0$, a_0 being the Bohr radius of the H atom):

$$\vec{p}_{nm} = \sum_{\substack{lj \\ l'j'}} \sum_\alpha \hat{e}_\alpha i^{(l'-l-1)} C_{lj}^* C_{l'j'} \left(\mathcal{F}_{nm}^{ll'} \int \mathcal{Y}_{lj} \frac{x_\alpha}{r} \mathcal{Y}_{l'j'} d\Omega + \mathcal{G}_{nm}^{ll'} \int \mathcal{Y}_{lj} r \frac{\partial\mathcal{Y}_{l'j'}}{\partial x_\alpha} d\Omega\right), \tag{10}$$

where

$$\mathcal{F}_{nm}^{ll'} \equiv \frac{1}{E_m - E_n} \left(\left[l'(l'+1) - E_m r_0^2\right]R_l R_{l'} - 2r_0 R_l \frac{dR_{l'}}{dr} - r_0^2 \frac{dR_l}{dr} \frac{dR_{l'}}{dr}\right)_{r=r_0} + \int_0^{r_0} r^2 R_l \frac{dR_{l'}}{dr} dr, \tag{11}$$

and

$$\mathcal{G}_{nm}^{ll'} \equiv \frac{1}{E_m - E_n} \left[r_0\left(R_l \frac{dR_{l'}}{dr} - R_{l'} \frac{dR_l}{dr}\right) - R_l R_{l'}\right]_{r=r_0} + \int_0^{r_0} r R_l R_{l'} dr. \tag{12}$$

The indices with a prime in the above equations are those for the state Ψ_m.

Except for the two radial integrations all the quantities appearing in Eqs. (10) to (12) are calculated in the process of determining the band energies. We note that $\int \mathcal{Y}_{lj}(x_\alpha/r)\mathcal{Y}_{l'j'}$ behaves as $\int \mathcal{Y}_{lj} \mathcal{Y}_{1\alpha}\mathcal{Y}_{l'j'} d\Omega$, which is needed for the formation of the KKR matrix, and that $\int \mathcal{Y}_{lj} r(\partial\mathcal{Y}_{l'j'}/\partial x_\alpha) d\Omega$ can be related to it by[10]

$$\int \mathcal{Y}_{lj} r \frac{\partial\mathcal{Y}_{l'j'}}{\partial x_\alpha} d\Omega$$

$$= \left[-l'\delta_{l+1,l'} + (l'+1)\delta_{l-1,l'}\right] \int \mathcal{Y}_{lj} \frac{x_\alpha}{r}\mathcal{Y}_{l'j'} d\Omega. \tag{13}$$

Thus the computation of $\vec{p}_{nm}$ using Eqs. (10)–(12) is straightforward. Since the GFM is valid for l- and E-dependent potentials and since the potential

TABLE I. Normalizations σ_n and σ_m [defined in Eq. (6)], magnitudes of the interband momentum matrix elements p_{nm} (in $\hbar/a_0$), and band energies E_n and E_m (in Ry relative to the constant muffin-tin potential) for some states at X and L for the Cu Chodorow potential and for the Al Snow's self-consistent potential. The l_{max} indicates the maximum l value used. The labels Eq. (1) and Eq. (10) indicate the equations used for computing the p_{nm}.

| | $l_{max}=2$ | | | | | | $l_{max}=4$ | | | | | |
| | E_n | E_m | σ_n | σ_m | p_{nm} | | E_n | E_m | σ_n | σ_m | p_{nm} | |
$n \to m$					Eq. (1)	Eq. (10)					Eq. (1)	Eq. (10)
Cu Chodorow potential												
$L_1^l \to L_2'$	0.158	0.516	0.911	0.656	0.140	0.134	0.158	0.512	0.917	0.665	0.214	0.220
$L_3^l \to L_2'$	0.289	0.516	0.976	0.656	0.006	0.007	0.288	0.512	0.982	0.665	0.081	0.104
$L_3^l \to L_2'$	0.399	0.516	0.996	0.656	0.385	0.384	0.399	0.512	0.997	0.665	0.302	0.384
$L_2' \to L_1^u$	0.516	0.854	0.656	0.879	0.673	0.659	0.512	0.853	0.665	0.880	0.857	0.843
$X_1^l \to X_4'$	0.156	0.717	0.894	0.718	0.178	0.175	0.156	0.709	0.896	0.740	0.201	0.203
$X_5 \to X_4'$	0.411	0.717	0.998	0.718	0.071	0.071	0.411	0.709	0.998	0.740	0.350	0.350
$X_4' \to X_1^u$	0.717	1.104	0.718	0.798	0.790	0.776	0.709	1.103	0.740	0.802	0.977	0.963
Al Snow potential (Ref. 11)												
$L_2' \to L_1$	0.260	0.271	0.705	0.833	2.186	2.165	0.259	0.271	0.712	0.834	0.571	0.562
$X_4' \to X_1$	0.392	0.461	0.761	0.765	1.247	1.240	0.389	0.461	0.778	0.767	0.773	0.767

does not enter in this procedure, the present results are applicable to the more general interactions.

We have compared the values of p_{nm} calculated according to Eq. (10) with those obtained by Eq. (1) as well as σ_n and σ_m for the Chodorow Cu potential and Snow's Al potential.[11] It should be noted that neither of these potentials has any l and E dependents. These numerical results along with the band energies for some of the states at X and L are given in Table I. Two sets of numbers are presented: one is for $l_{max}=2$ and the other for $l_{max}=4$, where l_{max} is the maximum value for the l included in the calculation. It can be seen that the two methods give nearly the same values for the p_{nm}. Significant differences, however, are found between the values calculated for the $l_{max}=2$ and $l_{max}=4$ with the differences for Al being particular larger.

All significant differences in the tabulated matrix elements arise from the fact that while exact Ψ and E are assumed in the derivation of Eqs. (1) and (10) approximate wave functions and energies are used in the calculation. In general, the errors in Ψ are more significant than those in E since by the variational principle the former is accurate to the first order while the latter is correct to second order. (This is, of course, manifested by the slower convergence of Ψ than E.) These errors are most serious for both of these methods when the energy differences between the states involved, $E_n - E_m$, become very small as is the case for Al, especially for the $L_2' \to L_1$ transition. For then the numerators in Eqs. (1) and (9) must become correspondingly small presumably by cancellations of various terms.

ACKNOWLEDGMENT

[1]For a review of the GFM see B. Segall and F. S. Ham, in *Methods in Computational Physics*, edited by B. Alder (Academic, New York, 1968), Vol. 8, p. 251. In the present note the potential is assumed to have the muffin-tin form.

[2]J. Korringa, Physica (Utr.) XIII, 392 (1947).

[3]W. Kohn and N. Rostoker, Phys. Rev. 94, 1111 (1954).

[4]F. S. Ham and B. Segall, Phys. Rev. 124, 1786 (1961), where the procedures for obtaining the normalizations and the wave functions in the interstitial region are derived.

[5]J. F. Janak, A. R. Williams, and V. L. Moruzzi, Phys. Rev. B 11, 1522 (1975).

[6]B. Segall, Phys. Rev. 125, 109 (1962), where a l-dependent Cu potential is used.

[7]A.-B. Chen and B. Segall, Phys. Rev. B 12, 600 (1975).

[8]A.-B. Chen and B. Segall (unpublished).

[9]The δ^+ and δ^- can be computed at least to an accuracy of 10^{-5} Ry. Thus, if $v_0 = 0.05$ Ry is used, $v_0^3 \approx 10^{-4}$ and the σ_n should be accurate to 10^{-3}.

[10]This can be verified using Eqs. (5.9.16) and (5.9.17) in *Angular Momentum in Quantum Mechanics*, edited by A. R. Edmonds (Princeton U.P., Princeton, N.J., 1960), p. 84.

[11]E. C. Snow, Phys. Rev. 158, 683 (1967).