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Energy-band theory of Auger line shapes: Silicon $L_{2,3}VV$ and lithium KVV

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It is shown that one-electron band theory predicts the experimentally observed $L_{2,3}VV$ Auger line shape of silicon and the KVV line shape of lithium, provided that the partial densities of states are properly normalized for the atomic orbital (AO) basis used to calculate the matrix elements. This normalization, when combined with matrix-element effects, is responsible for the dominance of p-p hole final states in the experimental spectra. The effect is equivalent to noting that with the atomic-orbital basis, the electronic charge is divided into atomic and overlap populations. Due to matrix-element effects, the latter does not contribute to the Auger process. Thus, Auger-electron spectroscopy is sensitive to the variation of the *local* atomic charge density across the valence band. Since the s AO contributes more to the overlap (bonding) charge than the p AO does, the s-like contribution is suppressed in the Auger line shape. The quality of the agreement with experiment suggests that the combined effects of the surface, many-body phenomena, and the distortion of the valence band in response to the core hole are small for the above spectra.

I. INTRODUCTION

Recently there has been growing interest in Auger-electron spectroscopy (AES) as a probe not only of surface elemental composition, but as a probe of the local chemical environment of the target atomic species. The latter information is provided through the analysis of the Auger line shape. Houston[1] has shown that solid-state Auger line shapes of high quality may be generated by deconvoluting an electron loss function, taken at the appropriate energy, from the measured Auger spectrum. Using this procedure, line shapes of sufficient quality to permit a detailed comparison to theory have been generated for several materials.[1-4] However, the naive theory of Auger core-valence-valence (CVV) line shapes, which ignores matrix-element effects and simply self-convolutes the total valence density of states (DOS), works poorly, if at all.[3,5] Auger-line-shape analysis may provide an additional and potentially powerful technique for the analysis of the chemical environment of chemisorbed molecules. Recent experimental work by Rye *et al.*[6] on both gas- and condensed-phase molecules has been very encouraging in this respect. Recent work by the author[7] has provided a basis for the calculation of the CVV Auger spectra of chemisorbed molecules using a cluster approach to simulate the surface. This work has also shown that one may interpret the spectra of molecules that are considerably larger than those previously analyzed[8] in terms of the canonical molecular orbitals. These results strongly suggest that the CVV Auger spectra of covalent solids may be analyzed in terms of the canonical Bloch functions. The author has recently demonstrated that this approach is indeed valid for the Si $L_{2,3}VV$ spectrum.[9] Following the work of Feibelman, McGuire, and Pandey[5] and of Feibelman and McGuire,[10] who showed the importance of matrix-element effects in the Auger spectra of s-p band materials, it was stated[9] that the partial densities of states (PDOS's), obtained from the band structure, must be properly normalized for the local basis functions used to calculate the atomic-like Auger matrix elements. One purpose of the present paper is to explain this result in greater detail and show that this correction places the solid-state theory in direct correspondence with the molecular theory which has proved successful.[7]

Work on lithium metal by Madden and Houston[3] has shown, as for covalent solids, that the Auger KVV spectrum of this simple metal cannot be reproduced simply by self-folding the DOS (the SFDOS). The author also has confirmed this with a recent band-structure calculation.[11] Madden and Houston were able to show that the KVV Auger line was quite closely a self-fold of the p-like DOS as empirically determined by K-shell x-ray emission data. They thus hypothesized that s-like contributions to the Auger line shape were negligibly small. This surprising result for what many (wrongly) consider to be an "s-band material" has led to the proposal that this disagreement between the measured peak position and that obtained by the SFDOS is due to a many-body effect.[12] The second purpose of this paper is to show that, as with the Si $L_{2,3}VV$ spectrum, one-electron energy band theory can indeed account for the Li KVV line shape and that many-body effects, if present, are negligibly small. We will see, however, that there is substantial s-like contribution to the Li KVV line, but it is almost entirely of the sp type,[13] which can only with difficulty be distinguished from the pp contributions due to a great similarity in shape and peak position. Thus the observation by Madden and Houston that the *KVV* Auger line may be reproduced simply by self-folding the *K*-shell x-ray emission line is something of an accident and, as has recently been confirmed on beryllium by Madden and Zehner,[4] is not expected to be true in general.

The lithium *KVV* line shape was calculated from an *ab initio* band structure that used the Kohn-Sham exchange and correlation approximation and a linear-combination-of-atomic-orbitals (LCAO) basis set of 3*s* and 3*p* Slater functions.[1] Thus this paper also presents the first nonempirical Auger line shape that is in excellent agreement with experiment, and illustrates the utility of the LCAO method for the calculation of solid-state Auger spectra.

II. THEORY

A thorough analysis of the band theory of Auger line shapes was reported by Feibelman *et al.*[5] In the present work, however, surface effects have been neglected. For this reason and in order to define notation for the analysis that follows, the above theory is recalled here in a somewhat simplified form.

We assume that we may write the total wave function of both the initial state (with the core hole) and the final state (with two valence holes and a continuum electron) as single Slater determinants. Then if relaxation (i.e., valence-band distortion) effects are neglected, the initial and final states differ by just two spin orbitals, and we may express the Auger intensity $I(E_f)$ in terms of Auger matrix elements $(\mu\nu|cf)$ of the form

$$(\mu\nu|cf) \equiv \int\int d(1)\,d(2)\,\Phi_\mu^*(1)\Phi_\nu^*(2)\frac{e^2}{r_{12}}\,\Phi_c(1)\Phi_f(2), \tag{1}$$

where the subscripts $\mu \equiv n\vec{k}$ and $\nu \equiv n'\vec{k}'$ refer to the valence Bloch orbitals which are depopulated, and where the subscripts c and f refer to the localized core orbital and the continuum wave function, respectively, which are populated by the transition. Now, if μ and ν are holes of the same spin (i.e., the solid is left in a triplet state), then μ, ν, c, and f all have the same spin and, assuming Fermi's golden rule, we have

$${}^3I_{\mu\nu} \propto |(\mu\nu|cf) - (\nu\mu|cf)|^2, \tag{2}$$

where ${}^3I_{\mu\nu}$ is the transition probability for creating a triplet final state with holes in the μ and ν spin orbitals. However, if μ and ν are singlet coupled (i.e., are of different spin), one of the two terms in Eq. (2) vanishes and we have

$${}^1I_{\mu\nu} \propto |(\mu\nu|cf)|^2 + |(\nu\mu|cf)|^2 \tag{3}$$

if we sum over all possibilities for spin assignment. If we now further assume that hole-hole interaction[14] and static-relaxation[15] effects are negligibly small for the solid state *CVV* process, then we may combine the above expressions into a total amplitude for creating an Auger electron at energy $E_f = -E_c + E_\mu + E_\nu$, i.e.,

$$\begin{aligned} I_{\mu\nu} \propto {} & 2|(\mu\nu|cf)|^2 + 2|(\nu\mu|cf)|^2 \\ & - (\mu\nu|cf)^*(\nu\mu|cf) - (\mu\nu|cf)(\nu\mu|cf)^*, \end{aligned} \tag{4}$$

where E_c, E_μ, and E_ν refer to the negative of the ionization potentials of the c, μ, and ν orbitals, respectively. Summing now over all ways to create an Auger electron of energy E_f, we have

$$I(E_f) \propto \sum_\mu^{\text{occ}} \sum_\nu I_{\mu\nu}\,\delta(E_f + E_c - E_\mu - E_\nu). \tag{5}$$

We now expand the Bloch functions in the LCAO form

$$\Phi_\mu \equiv \Phi_{n\vec{k}} = \sum_{ai} C_{\mu,ai}\,e^{i\vec{k}\cdot\vec{R}_a}\,\Phi_{ai}\,, \tag{6}$$

where ai refers to the ith basis function on atomic site a at position $\vec{R}_a$. Noting that in all but highly ionic solids the interatomic Auger matrix elements are truly negligible,[16] we may restrict the sum to the same site as the core hole. Dropping the subscript a, we have, upon substituting Eqs. (6) and (4) in (5),

$$\begin{aligned} I(E_f) \propto \sum_{ijkl} \Bigg(& \sum_{\mu\nu}^{\text{occ}} C_{\mu,i}^* C_{\nu,j}^* C_{\mu,k} C_{\nu,l} \\ & \times \delta(E_f + E_c - E_\mu - E_\nu)\Bigg) M_{ijkl}, \end{aligned} \tag{7}$$

where

$$\begin{aligned} M_{ijkl} \equiv {} & 2(ij|cf)^*(kl|cf) + 2(ji|cf)^*(lk|cf) \\ & - (ij|cf)^*(lk|cf) - (ij|cf)(lk|cf)^*. \end{aligned} \tag{8}$$

The total DOS, $D(E)$, may be written as a sum of PDOS, $F_{ai,bj}(E)$, by writing

$$\begin{aligned} D(E) &= \sum_\mu \delta(E - E_\mu) = \sum_\mu \langle\mu|\mu\rangle\delta(E - E_\mu) \\ &= \sum_{ai,bj} F_{ai,bj}(E) S_{ai,bj}\,, \end{aligned} \tag{9}$$

where

$$F_{ai,bj}(E) \equiv \sum_\mu C_{\mu,ai}^* C_{\mu,bj}\,e^{i\vec{k}\cdot(\vec{R}_b - \vec{R}_a)}\,\delta(E - E_\mu), \tag{10}$$

where $S_{ai,bj}$ is the overlap matrix between basis functions ai and bj, and where we recall $\mu \equiv n\vec{k}$. Expressing the convolution of two functions as

$$\{F * G\}(E) \equiv \int dE'\,F(E')G(E - E'), \tag{11}$$

we note that Eq. (7) may be written

$$I(E_f) \propto \sum_{ijkl} \{F_{ik} * F_{jl}\}(E_f + E_c) M_{ijkl}, \tag{12}$$

where the site subscripts on F have been dropped and where F is restricted, of course, to occupied energies.

The areas under the PDOS may be interpreted in terms of the distribution of valence electron charge density. Defining

$$A_{ai,bj} \equiv \int_{\text{occ}} dE\, F_{ai,bj}(E) S_{ai,bj}, \tag{13}$$

we note that the valence charge density may be expressed as

$$\begin{aligned} N = \int d\vec{r}\, \rho(\vec{r}) &= \sum_{\mu} \int d\vec{r}\, \Phi_{\mu}^{*} \Phi_{\mu} \\ &= \sum_{ai,bj} \sum_{\mu} C_{\mu,ai}^{*} C_{\mu,bj} e^{i\vec{k}_0 \cdot (\vec{R}_a - \vec{R}_b)} S_{ai,bj} \\ &= \sum_{ai,bj} A_{ai,bj}\,. \end{aligned} \tag{14}$$

Thus the total charge density may be broken into atomic $(A_{ai,aj})$ and overlap $(A_{ai,bj},\ b \neq a)$ populations, as is often done in LCAO molecular-orbital calculations.[17] Due to the above-mentioned matrix-element effects, it is clear that except in highly ionic materials, only the atomic charge contributes to the Auger current, and that the Auger line shape is sensitive to the variation in the local atomic charge density across the valence bands. Thus valence orbitals which contribute mostly to the bonding charge (e.g., Γ_1 in Si) will have their contribution to the Auger current suppressed, while the opposite is true of orbitals that contribute little to the bonding (e.g., Γ_{25}' in Si).[9]

The Auger lines were calculated using Eq. (12). The PDOS were calculated with a histogram method using Eq. (10) and 152 regularly spaced points in the irreducible wedge of the Brillouin zone in the case of Si, and 285 points in the case of Li. Although this method of Brillouin-zone integration is crude, considerable smoothing results from the convolution. The Si calculation used as a basis set Hartree-Fock atomic orbitals and details may be found in the Appendix. The Li basis set and details of the band structure calculation were previously reported.[11] Further information on Li may also be found in the Appendix, together with a discussion on the calculation of the atomic Auger matrix elements [the $(ij|cf)$ in Eq. (8)].

III. RESULTS AND DISCUSSION

A comparison of the present $L_{2,3}VV$ Si results with experiment and previous theory has already been reported.[9] It was shown that there were large differences between the PDOS found from a Wannier basis and those found with the present atomic-orbital basis. It was thus established that one must be consistent, and calculate the PDOS with the same basis set used to calculate the atomic Auger matrix elements. Similar problems would be encountered if one attempted to calculate an Auger spectrum from a cluster calculation that used a theory [e.g., Hückel theory or CNDO (Ref. 17)] that did not explicitly account for atomic-orbital overlap and hence did not divide the charge density into atomic and bonding components.

The Si $L_{2,3}VV$ spectrum is presented in Fig. 1, and is compared to the previous theory and to experiment in Fig. 2. No attempt has been made to smooth or broaden the present result, and it is obvious that better agreement with the experimental results may be obtained by broadening. Since surface effects have been neglected, it is tempting to blame them for the remaining small disagreement. However, experimental resolution and noise introduced by the deconvolution of the loss processes[1] are certainly not negligible. Thus, at least in the present case, the combined effect of the surface, many-body phenomena, and initial-state valence-band distortion (i.e., polarization in response to the core hole) appear to be small.

The Li KVV spectrum is compared to experiment[3] and analyzed in Fig. 3. We see excellent agreement, except on the low-energy side. Madden has indicated that much of this discrepancy could be explained by slight oxygen contamination.[18] It is seen that the pp contribution is indeed dominant, as was suggested by Madden and Houston.[3] However, it is also noted that the sp contribution is about half the pp, and would have been visible had its peak position and line shape not been so similar to those of the pp contribution. Thus the agreement between the self-fold of the

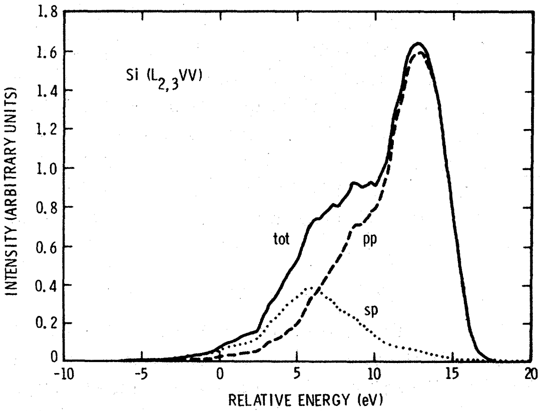

FIG. 1. The theoretical Si ($L_{2,3}VV$) Auger line is broken into pp and sp components. The ss component is so small that it has been neglected.

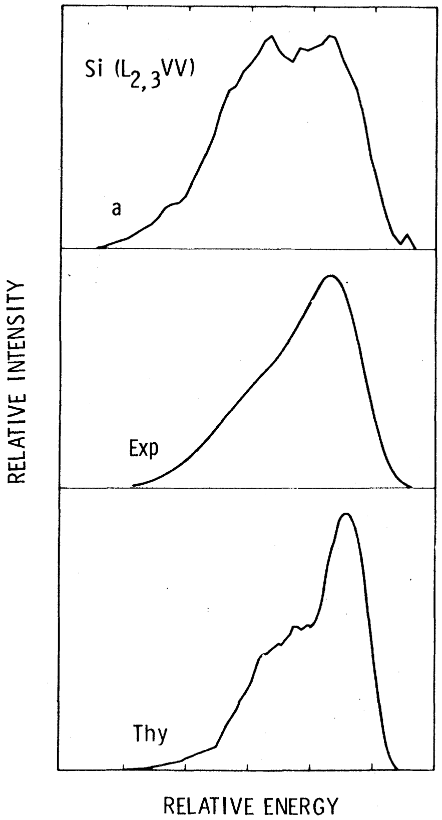

FIG. 2. Theoretical-experimental comparison of the Si ($L_{2,3}VV$) line. The top curve, labeled (a), is the previous theoretical result from Ref. 10. The experimental result is from Ref. 27.

K-shell x-ray emission data and the KVV line is somewhat fortuitous. Indeed, recent work by Madden and Zehner[4] on beryllium has shown that the Auger KVV line is not the same as the self-fold of the p-like PDOS. The ratio of the pp to sp convoluted PDOS's, determined by the atomic matrix elements [M_{ijkl} in Eq. (12)], should be very similar in Li and Be. However, the cross fold of the s and p PDOS does not resemble the self-fold of the p PDOS as it does in Li, and thus the sp contribution becomes visible. In Li we see once again that other effects, if present, appear to be small. One expects that initial-state polarization should be more important in Li than in Si; however, this screening charge effect would only change the sp vs pp amplitudes. The author is currently exploring this aspect of the problem in Be, where it should be more visible.

The theoretical development above is similar to the theory of molecular and cluster Auger spectra[7] with several exceptions. The amplitude analysis of H. Siegbahn *et al.*[19] used a proper spin-dependent multideterminental expression for the initial and final states, and thus obtained different numerical coefficients in Eqs. (2) and (3) that also depended upon whether $\mu=\nu$ or not. It N is the number of molecular orbitals, these differences vanish as $1/N$ when $N\rightarrow\infty$. A more serious difference between the solid-state and molecular theory is the neglect of hole-hole interaction[14] and static relaxation[15] in the former. The author's recent work on molecules[7] has shown that for delocalized orbitals, e.g., those composing covalent or metallic bonds, static relaxation has a negligible effect. Hole-hole interaction, which provides the singlet-triplet splittings that prevent one in the molecular case from combining Eqs. (2) and (3) into Eq. (4), does vanish for these orbitals in the limit of the infinite solid. However, the author's recent work indicates, not unexpectedly, that static relaxation is very important and hole-hole interaction never vanishes if localized states (e.g., so-called lone-pair electrons in molecules) are present. A question worthy of further investigation, then, is where in the solid-state case, for example, as one proceeds across the transition-metal series, the present theory fails due to the presence of localized states. The present work, showing that one may indeed reproduce the Auger CVV line shapes in these somewhat prototypic covalent and metallic systems, should make the onset of localized behavior quite visible from a theoretical point of view.

IV. CONCLUSIONS

The Si $L_{2,3}VV$ and Li KVV Auger line shapes may be reproduced from a one-electron band-structure calculation. Many-body and surface effects, if present, are quite small in the present cases. There is great utility in calculating these line shapes from an LCAO expansion of the Bloch functions. However, one must not only include matrix-element effects, but one must ensure that the partial DOS are properly normalized for the local basis functions. This normalization leads to the interesting interpretation that AES is sensitive to the variation of the *local* atomic (as opposed to bonding) charge populations across the valence bands, and is thus an inherently local probe of the chemical environment of the target atom.

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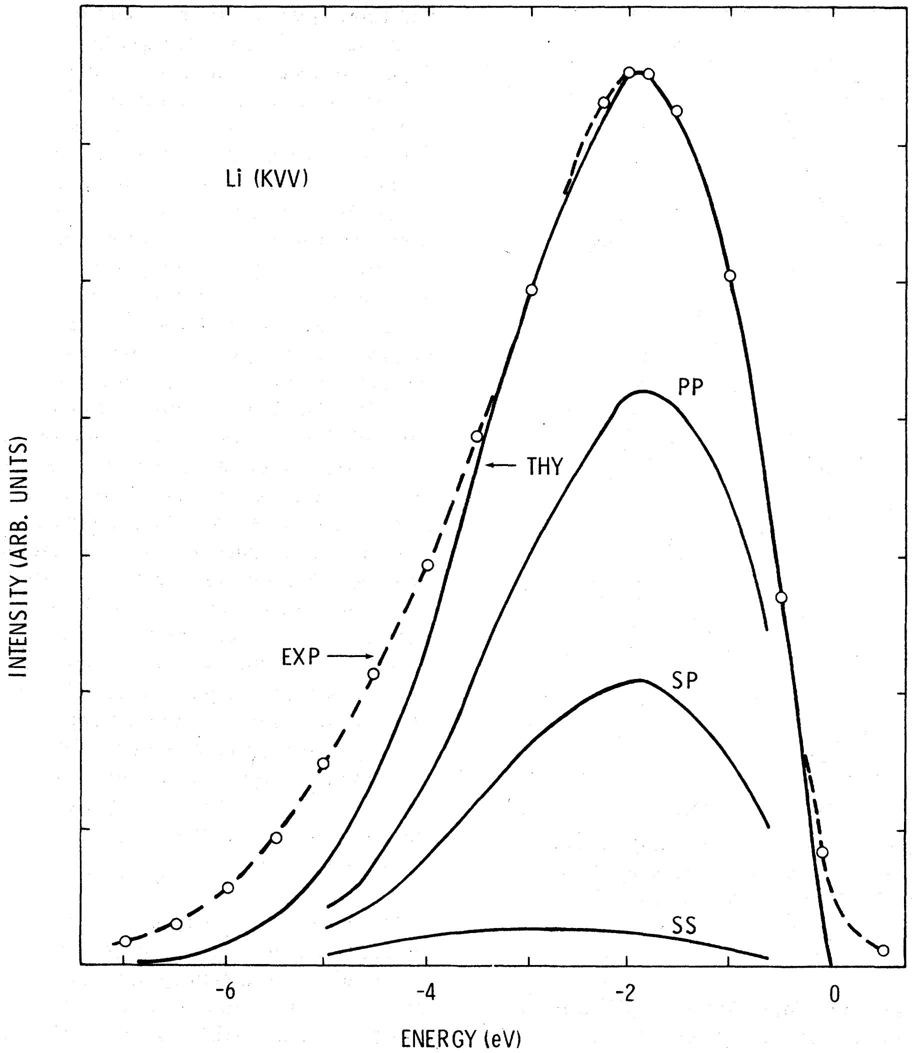

FIG. 3. Theoretical-experimental comparison of the Li (*KVV*) line. The experimental curve is from Ref. 3. The theoretical curve has been broken into *pp*, *sp*, and *ss* components. A comparison of the experimental curve to the self-fold of the total density of states may be found in Refs. 3 and 11.

APPENDIX: DETAILS OF THE CALCULATION

By referring to Eq. (12), one notes that two types of information are required before one can calculate the Auger line shape: the atomiclike Auger matrix elements and the intra-atomic PDOS for the local basis functions. These basis functions may be numerical atomic orbitals (AO's), AO's or other basis functions expressed in terms of Gaussian or Slater functions (so called contracted functions), or the Gaussian or Slater functions themselves (so called primitive functions). Equation (12) is quite general, and a minimal AO basis was used for the Si $L_{2,3}VV$ line, while six primitive Slater functions were used for the Li KVV line. Although AO overlaps are large in Li, the compact basis set of Ref. 11 still permits interatomic terms to be neglected.

The atomiclike Auger matrix elements used here were generated by the method of McGuire[20] with some notable differences. McGuire generated continuum wave functions as numerical solutions to the Coulomb wave equation for the potential of a Herman-Skillman[21] ion with the appropriate core hole. Thus the potential used was a sum of the actual ionic Coulomb potential and the Slater statistical exchange potential. However, it is well known in atomic theory that by far the largest portion of the exchange potential is self-exchange and intrashell exchange. Thus the continuum electron sees very little exchange interaction with the other electrons and a better potential to use for

TABLE I. A comparison of Si atomic Auger matrix elements. The present results were found using a continuum wave function generated from a Hartree-Fock Coulomb potential of the Si^+ $2p^{-1}$ ion. The results from Ref. 10 were found using both Coulomb and statistical exchange potential. The matrix elements are of the form $\int\int dr_1 dr_2\, \phi_i^*(1)\phi_j^*(2)(r_<^\kappa / r_>^{\kappa+1})\phi_c(1)\phi_f(2)$, where here f may be an s or p partial wave.

i	j	c	f	κ	This work	Reference 10
$3s$	$3s$	$2p$	p	1	0.402×10^{-2}	0.625×10^{-2}
$3s$	$3p$	$2p$	s	0	0.709	0.770
$3p$	$3s$	$2p$	s	1	0.436	0.613
$3p$	$3p$	$2p$	p	0	0.742	0.788

its generation is just the Coulomb potential alone. The magnitude of this difference may be seen in Table I, where the AO matrix elements of Si are compared for the two approaches. The Coulomb potential was generated by self-consistently solving the Hartree-Fock problem for the ion with the appropriate core-hole using the symmetry and equivalence restrictions of Nesbet[22] and the basis functions of Bagus *et al.*[23] It may be seen that while the differences in Table I are noticeable, they make a small difference (~10% in relative *sp*, *pp* amplitudes) in the present case. However, in the molecular case, where occasionally a triplet state is resolved, it may be seen from Eq. (2) and Table I that the Coulomb versus Coulomb and statistical exchange cases differ in *sp* triplet amplitude by over 300%. Experience with the methane molecule[7] indicates that the use of the Coulomb potential alone is *much* closer to the experimental amplitudes, and thus this procedure was followed in the solid-state case.

The Coulomb potential was expressed on a 161 point radial mesh whose point spacings increase exponentially with distance from the nucleus. Following McGuire,[20] the continuum wave functions for the appropriate partial waves were then found in terms of regular and irregular Whittaker functions with the normal asymptotic forms. The solutions were expressed numerically, as were the core wave function and the basis functions, on the same mesh that was then used to perform the radial integration,

$$e^2 \int\int dr_1\, dr_2\, \Phi_i(r_1)\Phi_j(r_2)\frac{r_<^\kappa}{r_>^{\kappa+1}}\Phi_c(r_1)\Phi_{\mathrm{pw}}(r_2),$$

where pw indicates that the continuum radial wave function is partial-wave dependent. The angular part of the matrix element[24] was found using the usual analysis of the integral in terms of Clebsch-Gordan coefficients, the latter being generated using the Racah formula.[25] The resulting nonvanishing integrals were stored along with the partial-wave index, the latter used to generate the M_{ijkl} by summing over the individual partial-wave contributions.

The text gave references for the Li band structure, and described the computation of the PDOS's therefrom. However, the Si band structure was not generated from first principles, but from the empirical band theory of Pandey and Phillips.[26] The latter work parametrized the Hamiltonian matrix elements for the $3s$ and $3p$ "AO's" to fit experimental data, but ignored the actual AO overlap matrix, setting the latter to the identity matrix (i.e., an orthonormal "Wannier" basis was actually assumed). Thus the Bloch function coefficients could not be used directly in the present theory. For consistency with the atomiclike Auger matrix elements, a minimal basis set consisting of AO's from Bagus *et al.*[23] was assumed. These were transformed to the normal Bloch basis set, and the overlap matrix was determined. Since rather high symmetry exists in silicon, the AO coefficients could then be found unless there was *s-p* mixing in the band. However, those bands that produce the large peaks in the DOS are largely *s or p* like. Thus rather than recalculate the *s-p* mixing (which would require an entire LCAO band structure calculation), the author assumed the mixing predicted by the semiempirical theory of Pandey and Phillips.[26] This approximation, while quite sound here, would not be as appropriate for solids with less symmetry such as the heteropolar semiconductors.

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