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Crystal Potential and Energy Bands of Semiconductors. I. Self-Consistent Calculations for Diamond*

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Approximate self-consistent potentials are constructed for diamond, first with exchange ignored, and then with exchange included according to the Slater free-electron approximation and according to a refined momentum-dependent free-electron approximation. The Hartree charge densities and energy gap are in fair agreement with experiment. Inclusion of valence exchange by the Slater approximation shows that Herman's earlier calculation was nearly self-consistent in this approximation. Agreement with experiment on charge densities and energy gap is greatly improved in comparison with the Hartree results. Further inclusion of the momentum dependence of the exchange potential does not greatly improve the charge densities and the energy gap but does alter the valence band width.

1. INTRODUCTION

WITH the exception of a few especially simple cases, the object of most energy-band papers may be said to have been the calculation of wave functions and energy bands in a crystal grated a certain crystal potential. Ofter great emphasis is placed on the exactness with which this mathematical problem is solved while no estimate is made of the uncertainties in the assumed crystal potential. It has appeared for some time that (for any but the simplest crystals) the physical uncertainties are as large as the mathematical ones. Our primary interest in this series of papers lies in the calculation of experimental features of the energy bands of diamond- and zinc-blende-type semiconductors; for the reasons discussed above we begin with a consideration of the crystal potential of diamond, which is the simplest of these crystals.

A secondary object of the calculations presented below is to test the exactness of the "effective potential" method proposed recently by us.[1] The method is quite similar to the orthogonalized plane wave (OPW) method which has already been used on diamond with much success by Herman.[2] Using the same potential we find results in close agreement with his; changes in the potential itself lead to larger differences, in agreement with the above remarks.

Herman's diamond potential is obtained from a superposition of free atom Hartree-Fock charge densities. These are used to calculate the Coulomb potential to which is added an exchange potential taken from the Slater[3] free-electron approximation. (According to the Slater approximation, exchange terms can be represented by an exchange potential which is the same at a given point as the average exchange potential in a free-electron gas having the same local density.)

At first sight there is no reason to expect that free-atom charge densities would yield more than a qualitatively correct charge distribution in the crystal. In the case of diamond, however, Herman was able to compare his charge densities with those calculated by Brill[4] from x-ray diffraction; good agreement was obtained, thus justifying the Coulomb potential.

In principle, of course, the crystal charge density should be calculated self-consistently. Again, in principle, this requires the calculation of valence wave functions throughout the reduced zone and in diamond, where convergent wave functions are easily obtained only at points of high symmetry of the Brillouin zone, this appears to be prohibitively laborious. An advantage of the "effective potential" method is that it shows that all valence charge densities should be similar, which greatly reduces the amount of calculation required to obtain a good approximation to the valence electron charge density. In this way we are able to demonstrate in Sec. 2 that granted his exchange potential, Herman's original calculation is nearly self-consistent.

We are therefore left with the exchange potential which is obtained from Slater's heuristic approximation. We may omit exchange among the valence electrons altogether, thus doing a self-consistent Hartree calculation. This materially worsens the agreement with experiment for the charge densities and energy gap, as is shown in Sec. 3. On the other hand, we may say that even in diamond the wave functions often closely resemble plane waves so that an improvement might be made by including the momentum dependence of the local-density free-electron exchange potential. The results of this refinement are presented in Sec. 3 also; it turns out that only the valence band width is appreciably changed.

It might be felt that if the valence electron charge density is sufficiently simple to make self-consistent calculations of the Coulomb potential feasible, somewhat more effort should yield an exchange potential. The importance of this point has led us to include our

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[1] J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959).

[2] F. Herman, Phys. Rev. **93**, 1214 (1954).

[3] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[4] R. Brill, Acta Cryst. **3**, 333 (1950).

reasons for being unable to obtain such a potential in the Appendix.

2. SELF-CONSISTENCY OF HERMAN'S MODEL

The Fourier coefficients of Herman's crystal potential V_c are listed in Table I, where the contributions of the core and valence Coulomb and exchange terms are listed separately. The numbers in parenthesis represent a small correction to Herman's potential whose effect would be to reduce the energy gap by 0.4 ev. This is omitted here to facilitate comparison with Herman's results. Also listed are the Fourier coefficients of

$$[1s]=\left[\int \psi_{1s}^*(r)d^3r\right]\psi_{1s}(r), \qquad (1)$$

where ψ_{1s} is the normalized Hartree-Fock $1s$ wave function for neutral atomic carbon calculated by Jucys.[5] (This is the wave function used by Herman.) It was shown in reference 1 that s states see an effective potential

$$V_{\text{eff}}=V_c+V_r, \qquad (2)$$

$$V_r=(E-E_{1s})[1s]. \qquad (3)$$

Here we have taken Jucys' value, $E_{1s}=-22.7$ ry.

TABLE I. Fourier transforms of various terms in the effective crystal potential. Here $h^2=(a/2\pi)^2k^2$ and the form factor $\cos(\mathbf{k}\cdot\boldsymbol{\tau})$ with $\boldsymbol{\tau}=\frac{1}{8}a(111)$ has been omitted. The numbers in parenthesis in the fourth row represent corrections to Herman's potential which were not included in the calculations of Secs. 2 and 3.

h^2	$V_{\text{core}}^{\text{coul}}$	$V_{\text{val}}^{\text{coul}}$	V^{exch}	V^{total}	$[1s]$
0				2.87	0.0320
3	1.030	−0.286	0.166	0.905	0.0270
8	0.398	−0.013	0.034	0.419	0.0205
11	0.294	0.001	−0.010(0.025)	0.284(0.319)	0.0175
16	0.209	0.0	0.018	0.227	0.0140

The effective potential in Eq. (2) is l-dependent; in particular, in diamond, states having no s atomic character see no repulsive potential. Prescriptions for determining the atomic character of a given wave function were described in reference 1. When applied to diamond these lead to particularly simple results because of the small size of the $1s$ core. The atomic characters of the diamond wave functions of interest to us are listed in Table II. The notation for irreducible representations is that of Herring.[6]

We now compare the results obtained by our method with those obtained by Herman. For p states these are necessarily the same. For an s state like Γ_1, small differences result from the approximate nature of the repulsive potential as compared with the orthogonalization terms it replaces. We have therefore calculated the energy associated with the lowest Γ_1 state by the OPW method including 9 plane waves, and the results are compared with ours in Table III. The Γ_1 energy has converged quite well at this point, as can be seen from Table III for our case or from Herman's graph of the OPW results.[7] The agreement here turns out to be especially good; however even less favorable cases should agree to within a few hundredths of a Rydberg.

TABLE II. Atomic characters of wave functions calculated for diamond.

Term	s	p
Γ_1, $\Gamma_{2'}$	1.0	0.0
$\Gamma_{25'}$, Γ_{15}	0.0	1.0
X_1	1.0	0.0
X_4	0.0	1.0
L_1, $L_{2'}$	1.0	0.0
L_3, $L_{3'}$	0.0	1.0

A criticism of the OPW method which also applies here is that p states such as $\Gamma_{25'}$ converge slowly and, from Herman's results for 162 plane waves (16th order secular equation), it is not clear that his result is convergent. (Actually Herman checked that his energy was convergent to within 0.1 ry.) To settle this point we calculated the $\Gamma_{25'}$ energy to 469 plane waves; the results are also listed in Table III. Herman's value was convergent to within 0.01 ry. With this result in hand, we felt justified in limiting our calculation to 90 plane waves; s levels are convergent at this point and the similar convergence of p levels enables us to use the $\Gamma_{25'}$ results to extrapolate other p levels to convergent values with an uncertainty of less than 0.05 ry. The results of our calculation of the energy levels at Γ, X and L using Herman's potential are listed in Table IV: these represent extrapolated values.

We now turn to a self-consistent calculation of the valence electron charge density. A systematic procedure for doing this is the following. Reciprocal space is divided into similar volumes resembling the first Brillouin zone. The first division uses the Brillouin zone about each reciprocal lattice point. The second division refines the first by introducing new points ("sub-reciprocal-lattice points") midway between the lattice points of the first division; new "subzones" are now drawn about each of the points of the new lattice (which

TABLE III. Energies of $\Gamma_1^{(1)}$ and $\Gamma_{25'}^{(1)}$ in ry at various stages of convergence. E_n is obtained from an nth order secular equation. We have used $V_{000}=-2.8700$ in each case.

	$\Gamma_1^{(1)}$		$\Gamma_{25'}^{(1)}$
	OPW	Eff. potential	
E_1	−2.2200	−2.2200	0.170
E_2	−2.4027	−2.4027	−0.431
E_6		−2.4142	−0.731
E_{15}			−0.797
E_{34}			−0.803

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[5] A. Jucys, Proc. Roy. Soc. (London) **A173**, 59 (1939).

[6] C. Herring, J. Franklin Inst. **233**, 525 (1942).

[7] F. Herman, Ph.D. thesis, Columbia University, 1953 (unpublished).

TABLE IV. Energies in ry of various terms in diamond using self-consistent potentials. In column 2 the Slater free-electron exchange potential is used; in column 3 exchange is omitted altogether, and in column 4 the momentum dependence of the free-electron exchange potential is included approximately. The last row lists the indirect energy gap to within 0.02 ry.

Term	Herman	Hartree	k-dependent
Γ_1	−2.41	−2.19	−2.97
$\Gamma_{2'}$	0.35	0.40	0.94
$\Gamma_{25'}$	−0.80	−0.60	−0.23
Γ_{15}	−0.35	−0.25	0.19
$X_1^{(1)}$	−1.64	−1.52	−2.21
X_4	−1.29	−1.07	−0.75
$X_1^{(2)}$	−0.28	−0.32	0.20
$L_1^{(1)}$	−1.55	−1.54	−2.08
$L_{2'}$	−1.97	−1.89	−2.54
$L_{3'}$	−1.14	−0.87	−0.56
$L_1^{(2)}$	−0.14	−0.05	0.34
L_3	−0.14	−0.09	0.39
E_g	~0.40	~0.25	~0.37

includes all the points of the previous lattice). The subzones will clearly be similar to the original zones, but have 2^{-3} the volume. This process can be used to obtain an arbitrarily fine covering of reciprocal space.

The valence electron charge density is now represented in the first approximation as the average of the charge densities associated with the lattice points in each occupied zone. (For the diamond lattice the problem of partially occupied zones is easily solved by considering the subzones projected back into the reduced zone.) Thus in the case of diamond the first approximation to the valence electron charge density is $\{\Gamma_1\}+3\{\Gamma_{25'}\}$. Here the brackets denote $\psi^*\psi$ for a nondegenerate level and the average of $\psi^*\psi$ for degenerate levels; ψ denotes the symmetrized OPW eigenfunction.

This process can now be continued to higher approximations. In the second approximation it is necessary to know wave functions at Γ, X and L. The third approximation requires wave functions of symmetry Γ, X, L, Λ, Δ and the twofold point $2\pi a^{-1}(\frac{3}{4},\frac{1}{4},\frac{1}{4})$. Thus in the third approximation, the reduced secular equation at the last point will be about half as large as the number of plane waves included in the over-all expansion; in our case this would be 45×45. Calculation of the charge density associated with such a case is tedious but feasible.

Such calculations do not appear to be necessary, however, since the charge density appears to have converged fairly well in the second approximation. It is perhaps well to emphasize at this point that our chief concern in obtaining self-consistency is the accurate calculation of the first few nonzero Fourier coefficients of the crystal potential. (We take V_{000} from Herman's calculations; it can be shown that small changes in this quantity do not affect the relative positions of the bands.) The nonzero Fourier coefficients of the potential can be obtained directly from those of the charge density by Poisson's equation:

$$V_k=+(64\pi/k^2a^3)\rho_k. \tag{4}$$

Thus the (111) Fourier coefficient of the Coulomb potential of the valence electrons is 0.416 ry in the first approximation and 0.316 ry in the second.

From Table V which lists our results from various parts of the zone, several important conclusions can be deduced. All terms contribute approximately the same amount to V_{111} and all have the same sign. (The only exceptions are L_1 and $L_{2'}$ which because of their strong mixing should be grouped together.) This is a result of the effect mentioned in the introduction; all charge densities respond to similar effective potentials. Furthermore, it is clear why the second approximation differs appreciably from the first: $\Gamma_{25'}$, being at the top of the valence band, has the largest V_{111} and compared to the rest of the zone it is weighted too heavily compared to Γ_1 (3 to 1; at X and L the ratio is 2 to 2 for higher to lower levels). Both these errors are corrected in the second approximation which weights $\Gamma_{25'}$ only in proportion to the subzone it represents. It is difficult to estimate the accuracy of the second approximation but considering the small variation of the charge densities throughout the zone and the fact that the second sampling is 8 times finer than the first, we estimate the results from the second approximation should be accurate to within 10%, or 0.03 ry on V_{111}. We have also calculated V_{220}; the results are listed in Table V and, to within our accuracy, it is zero. Presumably all other higher Fourier coefficients are zero.

Herman's results for the Coulomb potential of the valence electrons are listed in Table I. The valence electrons are seen to make an appreciable contribution only to V_{111} whether free atom or crystal charge densities are used. It is interesting to see how this comes about for the crystal charge density. The (111) coefficient of the effective crystal potential is much larger than the other coefficients, especially for s states where the repulsive potential makes the remaining coefficients quite small. Thus the charge density arranges itself to favor constructively the [111]

TABLE V. The contribution of charge densities representing different subzones in the valence band to the Fourier coefficients of the crystal potential using the Slater free-electron approximation for exchange. The last line lists the total $=\{\Gamma\}+\{X\}+\{L\}$. Each of the latter represents the contribution of each term multiplied by the degeneracy and weighting factors listed in columns 2 and 3.

Term	Degeneracy	Weight	V_{111}	V_{220}
Γ_1	1		0.0074	0.0002
$\Gamma_{25'}$	3		0.0149	−0.0012
$\{\Gamma\}$		1	0.0520	−0.0034
X_1	2		0.0103	0.0000
X_4	2		0.0099	−0.0005
$\{X\}$		3	0.1210	−0.0030
L_1	1		0.0036	0.0005
$L_{2'}$	1		0.0106	0.0004
$L_{3'}$	2		0.0108	−0.0006
$\{L\}$		4	0.1432	−0.0003
$8\{\Gamma\}$ (alone)			0.416	−0.027
Total			0.316	−0.007

directions, and contributions to other directions add only destructively.

From Table I we see that Herman's (111) Fourier coefficient of the Coulomb potential of the valence electrons is 0.286 ry as compared to our value of 0.316 ry; thus his valence electron charge density is very nearly self-consistent. The self-consistent charge density is also in good agreement with Brill's x-ray data, which gives the value 0.349 ry when the core terms have been subtracted.

Note added in proof.—The (111) x-ray intensity has recently been carefully remeasured by Brill and Zandy [Nature **183**, 1387 (1959)]. Their result leads to $V_{111}^{\text{val coul}}=0.299\pm0.025$ ry, in good agreement with our calculated value.

As Herman[7] has shown, the minimum in the conduction band should lie along Δ. This leads to an energy gap of about 5.4 ev, in good agreement with the experimental value of 5.6 ev.[7]

While Slater[3] has given plausible physical arguments for the correctness of the local-density free-electron expression for exchange, the approximation remains a heuristic one. We therefore now consider the results obtained from other exchange potentials.

3. HARTREE AND NONLOCAL POTENTIALS

The simplest approximation is a Hartree one in which exchange is neglected altogether. From Table I we see that the largest change occurs in V_{111} which affects both the energy gap and the valence electron charge density. To facilitate comparison with the results of the last section we have retained the value $V_{000}=-2.87$ ry but otherwise omitted exchange terms. The resulting term values are shown in Table IV; the energy gap is now about 3.4 ev. The (111) Fourier coefficient of the self-consistent Coulomb potential of the valence electrons is now 0.270 ry. It follows that the omission of exchange leads to poorer results for both the energy gap and the charge density.

The Slater approximation assumes that each electron sees an average exchange potential appropriate to a free-electron gas having the same local density. In a free-electron gas the exchange potential is momentum-dependent[8] with the strength of the potential at the Fermi surface half its value at $\mathbf{k}=0$. In a free-electron gas of the density of diamond $V_{000}^{\text{exch}}=+1.4$ ry. Also the valence-electron contribution to V_{111}^{exch} can be seen from Table I to be about 0.12 ry. (We neglect the momentum-dependence of exchange with 1s electrons. This should be very small.) The momentum-dependent effects will be increased slightly if we arbitrarily assume that $L_1^{(1)}$, $L_{2'}$, $X_1^{(1)}$ and $\Gamma_1^{(1)}$ all experience an exchange potential appropriate to $\mathbf{k}=0$ ($V_{000}^{\text{exch}}=1.9$ ry, $V_{111}^{\text{exch}}=0.206$ ry) while the remaining states listed in Table IV experience the potential appropriate to k_F ($V_{000}^{\text{exch}}=0.9$ ry, $V_{111}^{\text{exch}}=0.126$ ry).

The term levels resulting from this potential are also listed in Table IV. The energy gap is 5.0 ev, which is practically the same as is obtained from the momentum-independent potential. The self-consistent valence-electron charge density is unaltered. The chief effect is to increase the valence band width from 21 ev to 36 ev. Soft x-ray values range from 16 to 30 ev.[7]

Most of the effects of a momentum-dependent potential are therefore small. In addition, the effect of correlation is to reduce the momentum dependence by about a factor of 2 for the value $r_s=1.3$ appropriate to diamond.[9] This will lead to even smaller changes in term levels, so that it appears that except for the valence band width, one is usually justified in neglecting the momentum dependence of the valence contribution to the potential.

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APPENDIX

Analysis of $\rho_k=\psi_k^*\psi_k$ at various points in the valence band shows that for each $\mathbf{k}$ the charge density ρ_k contains a large (111) component in addition to higher Fourier components. The (111) terms for different $\mathbf{k}$ all add in phase while the higher components have random phases. This has a simple physical interpretation: the (111) terms are a response to the large attractive value of the (111) coefficient of the effective potential. Higher terms result from the symmetrization of a given set of plane waves; this varies from one irreducible representation to another and so adds randomly. As was mentioned in Sec. 2, this leads to a simple valence-electron charge density and hence Coulomb potential.

For a free electron gas[8] the exchange potential is straightforward because

$$A\psi_k=-C_k\psi_k, \tag{A.1}$$

where A is the exchange operator and

$$C_k=e^2k_0\left(2+\frac{k_0^2-k^2}{k_0k}\ln\left|\frac{k+k_0}{k-k_0}\right|\right), \tag{A.2}$$

where k_0 is the Fermi wave number. Now if

$$\psi_k=V^{-\frac{1}{2}}e^{i\mathbf{k}\cdot\mathbf{r}}u_k(\mathbf{r})$$

and we assume

$$u_k(\mathbf{r})=u_{k'}(\mathbf{r}) \tag{A.3}$$

for k and k' labeling states in the occupied band, a

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[8] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 340.

[9] J. G. Fletcher and D. C. Larson, Phys. Rev. **111**, 455 (1958).

similar result can be obtained. Let $\mathbf{K}$ be a reciprocal lattice vector and

$$u_k^2(\mathbf{r})=u_{k'}^2(\mathbf{r})=\sum_{\mathbf{K}}\lambda_{\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{r}}. \tag{A.4}$$

A simple calculation following Seitz[8] gives

$$A\psi_k(\mathbf{r})=-\{\sum_{\mathbf{K}}\lambda_{\mathbf{K}}C_{\mathbf{k}-\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{r}}\}\psi_k(\mathbf{r}), \tag{A.5}$$

which is similar to (A.1) except that the exchange potential now has nonzero Fourier coefficients $\lambda_{\mathbf{K}}C_{\mathbf{k}-\mathbf{K}}$. In deriving this result, however, it was necessary to assume (A.3) whereas actually only (A.4) is a good approximation. In fact (A.3) does not appear to be even approximately correct for the diamond lattice. This is reasonable since only charge densities, not wave function amplitudes, respond to the large (111) effective potential.

The situation is not materially improved if we examine the arguments for the Slater $\rho^{\frac{1}{3}}$ approximation more closely. The approximation here is a Thomas-Fermi one and assumes that the charge density varies slowly over the radius of the exchange hole. More precisely the radius of the exchange hole should be small compared with the wavelength of the Fourier coefficient of the potential being calculated. The largest term in the exchange potential which affects the relative position of the bands is V_{111}, which has a wavelength somewhat smaller than the radius of the exchange hole. Thus a Thomas-Fermi approximation is not justified. The chief conclusion which can be drawn from the calculations presented in Secs. 2 and 3 is that *a posteriori* the approximation seems to yield about the right answer for valence charge densities corresponding to $r_s\approx 1.3$ (diamond).

Since the above was written, we have seen unpublished work of Brooks which treats the nonlocal exchange and correlation hole. Brooks assumes that charge densities of both spins are affected equally and that the hole has an exponential form

$$\rho_h=\rho_1 e^{-|\mathbf{r}-\mathbf{r}_1|/r_0}. \tag{A.6}$$

Now if ρ_1 has the form

$$\rho_1=\frac{3e}{4\pi r_s^3}\{1+\lambda_\kappa\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_1)\}, \tag{A.7}$$

and r_0 is normalized so that the hole contains unit charge,

$$\frac{1}{r_0}=\frac{6^{\frac{1}{3}}}{r_s}\left\{1+\tfrac{1}{3}\lambda_\kappa\frac{\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_1)}{1+\kappa^2 r_0^2}\right\}, \tag{A.8}$$

then the nonzero Fourier coefficient of the potential is

$$V_h^\kappa=\frac{0.908e}{r_s}\lambda_\kappa\left[\frac{1}{1+\kappa^2\rho_0^2}-\frac{2}{3}\frac{1}{(1+\kappa^2\rho_0^2)^2}\right] \tag{A.9}$$

(where $\rho_0=\bar{r}_0=0.55r_s$), the second term in the brackets resulting from the spacial variation of r_0. By comparison the Slater approximation for the exchange hole yields, by formal expansion of the cube root [compare (A.9) with $r_0=0$],

$$V_e^\kappa=\frac{0.916e}{r_s}\lambda_\kappa[\tfrac{1}{3}]. \tag{A.10}$$

For diamond $\rho_0\simeq 0.72$ and for $\boldsymbol{\kappa}=2\pi a^{-1}(111)$ [the term of greatest interest] $\kappa\rho_0\simeq 1.05$. Substituting this into (A.9) we find a result almost identical to (A.10), which has been used for the calculations of this paper. Further (A.9) is insenstive to κ for $\kappa\rho_0\lesssim 1$, so that the nonlocal character of the exchange hole can be neglected under these conditions.

The coincidence of these two results still does not justify the quite different approximations which have been made in deriving either:

1. The derivation leading to (A.9) necessarily omits momentum-dependent effects. These can be treated only by assuming (A.3).
2. Correlation effects are weaker than exchange effects and should be distinguished. Indeed it is not clear that the plasma energy can be represented as a one-electron potential.

Finally there is a qualitative objection which we feel is as serious as either of these. The expressions (A.9) and (A.10) for V_h^κ are taken from rough approximations to the total exchange energy, which consists predominantly of V_h^{000} (which is 10 times larger than V_h^{111}). Thus the value of V_h^{111} derived from a density- (but not momentum-) dependent exchange hole replaces the factor $C_{\mathbf{k}-\kappa}$ in (A.5) by approximately $\langle C_{\mathbf{k}}\rangle$ where the brackets denote an average over the Fermi sea. For $\kappa\simeq k_0$ [which is the case for $\boldsymbol{\kappa}=2\pi a^{-1}(111)$] these quantities may differ by a factor of 2. Differences between $u_{k'}$ and u_k make the momentum average even more suspect. Thus "physical intuition" about V_h^κ cannot be relied upon for $\boldsymbol{\kappa}\neq 0$.

Hence we conclude, as before, that a simple treatment of the nonzero Fourier coefficients of the exchange potential can be given only when (A.3) holds. For monovalent metals $u_k\simeq u_{k'}\simeq u_0$, providing k is sufficiently small. Even for polyvalent metals the approximation $u_k=u_{k'}=1$ is still available. For semiconductors, however, the most difficult terms in the crystal potential arise from exchange and correlation among the valence electrons.