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Crystal Potential and Energy Bands of Semiconductors. IV. Exchange and Correlation*

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The contribution of exchange and correlation to one-electron self-energies in a periodic potential is treated using the generalized Koopmans' theorem. Numerical estimates are made for effects due to covalent bonds in Si. In the random phase approximation, matrix elements of the valence exchange and correlation operators are found to be weakly momentum dependent and spatially similar to the valence Coulomb potential. Near the energy gap the combined exchange and correlation "potential" in Si is remarkably similar to the Slater free-electron exchange potential.

1. INTRODUCTION

WE are concerned here with the contribution of exchange and correlation to one-electron self-energies in real crystals. A method for calculating these contributions in the random-phase approximation has been proposed.[1] We apply the method to a covalently bonded semiconductor Si.

Although the importance of exchange and correlation is frequently emphasized, all rigorous calculations have so far been confined to the free electron gas. Only in this case does the exchange operator A, defined by

$$A\psi_i(\mathbf{r}_1) = -\frac{e^2}{2}\sum_j N_j \int \frac{\psi_j^\dagger(\mathbf{r}_2)\psi_i(\mathbf{r}_2)}{r_{12}} d\tau_2\, \psi_j(\mathbf{r}_1), \qquad (1.1)$$

reduce to a scalar (momentum-dependent) potential which can be evaluated analytically.[2] Here N_j is the occupation number of the jth state. In general, (1.1) is difficult to evaluate because of the sum over occupied band states.

Slater has suggested[3] a generalization of the free-electron exchange potential which can be used to treat nonuniform charge densities. He has shown that the effect of exchange is to introduce a hole in the charge density of $(N-1)$ electrons exchanging with electron i. The total charge in this hole is just e. The interaction of the hole with an electron at $\mathbf{r}$ gives the average, over the occupied band, exchange energy. The size of the hole, and hence the exchange energy, is determined by the charge density $\rho(\mathbf{r})$. In this way Slater proposes a Thomas-Fermi approximation to the exchange operator which replaces it by the local potential of a free-electron gas with charge density $\rho(\mathbf{r})$.

There are several disquieting aspects to this approach. The free-electron exchange potential is momentum-dependent (nonlocal) and varies by a factor of 2 from $k=0$ to k_F. We know that it is the long-range character of the Coulomb interaction $1/r_{12}$ in (1.1) that produces analytic singularities in the exchange potential at $k=k_F$. These are eliminated by inclusion of correlation[4] which makes the effective interaction short range. The Thomas-Fermi-Slater exchange potential makes no mention of correlation screening. It turns out that in the limit that $\rho(\mathbf{r})$ is slowly varying, when the Slater approximation should be most accurate, correlation effects due to plasma screening produce quite different one-electron potentials.

In spite of these objections the Slater potential has generally led to satisfactory results, even in semiconductors where the covalent bonding produces a charge density that is far from uniform.[5] Semiconductors are particularly interesting because we should expect the exchange potential to be quite different for antibonding (conduction band) states as compared to bonding (valence band) states.

Consider, then, the calculation of the self-consistent exchange potential (1.1). The calculation of the valence Coulomb potential must also be carried out by summing over valence states. We have previously shown[6,7] that because the effective potential for valence states can be represented almost entirely by the coefficients V_{111}^{eff} in the Fourier expansion

$$V^{\mathrm{eff}}(\mathbf{r}) = \textstyle\sum_{\mathbf{K}} V_{\mathbf{K}}^{\mathrm{eff}} e^{i\mathbf{K}\cdot\mathbf{r}}, \qquad (1.2)$$

the Fourier coefficients $\rho_{\mathbf{K}}$ in the valence charge density

$$\rho(\mathbf{r}) = \rho_0 + \textstyle\sum_{K\neq 0} \rho_{\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}} \qquad (1.3)$$

will be dominated by ρ_{111}, apart from terms which come

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

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

[4] J. J. Quinn and R. A. Ferrell, Phys. Rev. **112**, 812 (1958).

[5] L. Kleinman and J. C. Phillips, Phys. Rev. **125**, 819 (1962).

[6] L. Kleinman and J. C. Phillips, Phys. Rev. **116**, 880 (1959) (I).

[7] L. Kleinman and J. C. Phillips, Phys. Rev. **118**, 1153 (1960) (III).

from orthogonalization to core states.[8] Also, the contributions to ρ_{111} from different $\mathbf{k}$'s in the valence band will be similar and will vary smoothly throughout the band. Thus, to calculate the valence Coulomb potential it is sufficient to replace the sum over the entire band by a sample of 32 points.

The calculation of each of the matrix elements of the valence exchange operator proves to be similar to the calculation of the valence Coulomb potential. It is discussed in Sec. 2. Numerical results for exchange and correlation in Si are given in Sec. 3. In Sec. 4 we summarize the results of the calculation and make simple semiclassical comparisons with the Thomas-Fermi-Slater model. A critical summary of numerical approximations is given in the Appendix.

2. EXCHANGE AND CORRELATION MATRICES

We are concerned here solely with valence-valence exchange and correlation. Valence-core exchange has been treated carefully by Heine for Al.[9] The valence wave functions are written as

$$\psi_{\mathbf{k}}=\phi_{\mathbf{k}}-\sum\nolimits_n b_n\psi_n, \qquad (2.1)$$

where the ψ_n are core functions, and b_n is chosen so that $(\psi_{\mathbf{k}},\psi_n)=0$. Here $\phi_{\mathbf{k}}$ is the "smooth" part of the wave function, which we represent as a linear combination of plane waves. Covalent bonding introduces constructive interference[5,7] between the plane waves making up $\phi_{\mathbf{k}}$. The valence Coulomb potential coefficients $V_{111}{}^{\mathrm{coul}}$ in Si derived mainly from $\phi_{\mathbf{k}}{}^\dagger\phi_{\mathbf{k}}$, with a small reduction from core terms involving ψ_n. Because it turns out that "smooth" exchange and correlation terms are similar to Coulomb terms, we assume the same holds true for the small core terms and confine our attention to terms involving only ϕ's. These terms are the ones associated with covalent bonding.

In this manner evaluation of the exchange integral (1.1) is reduced to summing terms of the form

$$(a_j{}^{\mathbf{k}'})^\dagger a_i{}^{\mathbf{k}}/|\mathbf{k}-\mathbf{k}'|^2, \qquad (2.2)$$

where $a_i{}^{\mathbf{k}}$ is the coefficient of $e^{i\mathbf{k}\cdot\mathbf{r}}$ in the expansion of ϕ_i in plane waves. This is similar to calculating an exchange charge density and should be contrasted with the labor required to calculate 2-, 3-, and 4-center exchange integrals in an atomic orbital representation.

According to the discussion of (1.2) and (1.3), bonding effects are described largely by ρ_{111}. Valence-valence exchange would be simplest if the exchange operator in a plane wave representation could be separated into a diagonal, momentum-dependent potential

$$A(\mathbf{k}), \qquad (2.3)$$

and an exchange matrix whose off-diagonal part was approximately proportional to the off-diagonal part of the Coulomb matrix resulting from $V_{111}{}^{\mathrm{coul}}$. In that case one could describe the off-diagonal parts of the exchange matrix as resulting from the potential $A_{111}{}^{\mathrm{exch}}$.

Although $A(\mathbf{k})$ is the natural generalization of the diagonal free-electron exchange potential, it is inadequate because of degeneracies. It is easy to show that at a symmetry point in the Brillouin zone, where irreducible representations are labeled by α,

$$A\psi_{\mathbf{k}\alpha}=-\frac{e^2}{2}\sum_j N_j\int\psi_j{}^\dagger(\mathbf{r}_2)\frac{1}{r_{12}}\psi_{\mathbf{k}\alpha}(\mathbf{r}_2)d^3r_2\,\psi_j(\mathbf{r}_1) \qquad (2.4)$$

transforms like α. Thus, A has no off-diagonal matrix elements between different irreducible representations. For this reason it is convenient to calculate matrix elements of A between symmetrized combinations of plane waves belonging to irreducible representations α of the group of the wave vector. By adding the index α to (2.3) we have

$$A_\alpha(\mathbf{k}), \qquad (2.5)$$

which enables us to distinguish between valence and conduction band states. It turns out that A_{111} and $A_\alpha(\mathbf{k})$ describe all the matrix elements that we have calculated quite accurately.

According to the generalized Koopmans' theorem,[1] we can now add correlation to off-diagonal matrix elements by replacing $|\mathbf{k}-\mathbf{k}'|^{-2}$ in (2.2) by

$$1/\epsilon(|\mathbf{k}-\mathbf{k}'|)|\mathbf{k}-\mathbf{k}'|^2 \qquad (2.6)$$

Here, $\epsilon(q)$ is the static, wave-number dependent dielectric function. Strictly speaking, the screening factor ϵ in (2.6) should be evaluated at the exchange frequency $\omega=(E_j-E_i)/\hbar$. We have found that this changes our results by about 5%, so we have approximated the screening factor by its static value. A calculation of $\epsilon(q)$ for a model semiconductor approximating Si has been given by Penn.[10] His results have been used to evaluate correlation effects in Sec. 3.

3. EXCHANGE AND CORRELATION IN Si

In order to examine the validity of the simplified picture of an exchange operator A described by $A_\alpha(\mathbf{k})$ and A_{111} we have calculated 10 matrix elements of A. These calculations have been carried out for the representations $\Gamma_{25'}$ (top of valence band, p atomic symmetry), Γ_{15} (conduction band, p symmetry), and X_1 (valence and conduction bands, mostly s symmetry). Because of degeneracy we have basis functions consisting of symmetrized combinations of plane waves. The first two basis functions have $\mathbf{k}a/2\pi=(1,1,1)$ and $(2,0,0)$ for $\Gamma_{25'}$, $(1,1,1)$ and $(2,2,0)$ for Γ_{15}, and $(1,0,0)$ and $(0,1,1)$ for X_1. With these basis functions we have calculated $A_\alpha{}^{11}$, $A_\alpha{}^{12}$ and $A_\alpha{}^{22}$ for $\alpha=\Gamma_{25'}$, Γ_{15}, and X_1. We have also calculated $A_\alpha{}^{11}$ for $\alpha=\Gamma_1$, whose first basis function had $k=0$. This basis function gives a good

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[8] An approximate treatment of such terms, which can be extended to give exchange terms, is given in reference 7.

[9] V. Heine, Proc. Roy. Soc. (London) **A240**, 340 (1957).

[10] D. Penn, preceding paper [Phys. Rev. **128**, 2093 (1962)].

TABLE I. The contribution of different subzones to the (12) matrix element for $\Gamma_{25'}$ in Ry for Hartree-Fock exchange (HF) and Hartree-Fock-Hubbard screened exchange (HFH). In the first approximation Γ alone is sampled and in the second Γ, X, and L are sampled. In each case the product of the degeneracy and weighting factors is listed with the term value, and the contribution listed is the product of this factor with the contribution of an individual term.

	HF	HFH
Γ alone:		
Γ_1	-0.024	-0.017
$3\Gamma_{25'}$	-0.432	-0.165
Total	-0.456	-0.182
Γ, X, and L:		
Γ_1	-0.003	0.003
$3\Gamma_{25'}$	-0.188	-0.031
$6X_1$	-0.030	-0.017
$6X_4$	-0.031	-0.016
$4L_1$	-0.006	-0.003
$4L_{2'}$	-0.018	-0.011
$8L_{3'}$	-0.075	-0.028
Total	-0.351	-0.109

approximation to ϕ at the bottom of the valence band. The other matrix elements can be used to study $A_\alpha(\mathbf{k})$. If our simple model is correct, A_{111} should describe all the off-diagonal matrix elements A_α^{12}.

As an example, consider A_α^{12} for $\alpha=\Gamma_{25'}$. The matrix element H_α^{12} is responsible for the large drop in $\Gamma_{25'}$, which makes Si a semiconductor (see Fig. 3 in reference 6). The energy gap is most sensitive to A_α^{12}. The contribution of states at Γ, X, and L to the matrix element, properly weighted according to degeneracy, is listed in column one of Table I.

A typical entry in this table (such as the exchange with X_4) is proportional to

$$h_1h_2[(012)^{-2}+(112)^{-2}+(122)^{-2}+(103)^{-2}+2(100)^{-2}+2(110)^{-2}], \quad (3.1)$$

where h_1 and h_2 are the coefficients of the expansion of X_4 in SCPW (h_3, h_4, $\cdots$ are negligible). Because of interference between SCPW various terms appear in (3.1): $(012)^{-2}$ is an abbreviation for k^{-2}, where where $\mathbf{k}=2\pi a^{-1}(0,1,2)$.

One point deserves special attention. In the exchange of $\Gamma_{25'}$ with itself, a term proportional to $(000)^{-2}$ appears. Evidently for this singular term numerical sampling breaks down. In this case we return to (1.1) and replace the sum by an integral, so that the term is proportional to

$$\int_{\text{subzone}} \frac{1}{k^2} d^3k = \frac{4\pi}{m^{1/3}} k_{BZ}, \quad (3.2)$$

where k_{BZ} is the radius of a sphere having the same volume as the Brillouin zone and m is the number of subzones (of equal volume) into which the Brillouin zone has been divided by the sampling process.

It is interesting to note that no singular terms appear for $\alpha=\Gamma_{15}$. It is easy to show that this is so because Γ_{15} is orthogonal by symmetry to all valence band states.

We note from Table I that except for the singular term the contributions to the off-diagonal matrix element from Γ, X, and L are roughly in the proportion 1, 3, 4, as would be expected if each valence state contributed roughly the same amount. This means that the sampling should be a good approximation. In Table II we have listed in column one the values for the 10 exchange matrix elements that we have calculated.

It is now easy to calculate the screened exchange matrix B: we need only replace k^{-2} by $\epsilon^{-1}k^{-2}$ in contributions of the form (3.1). Again except for the singular term variations in the contributions from one part of the zone to another seem small, as can be seen from column two of Table I. There is, however, a dramatic reduction (by about a factor of 3) in the one-electron matrix elements as a result of dielectric screening.

It is evident that a special discussion of the suitability of the sampling method is required for the singular terms. In effect we assume in evaluating these terms that for $\mathbf{k}'$ in the subzone of $\mathbf{k}$, $u_{\mathbf{k}'}=u_{\mathbf{k}}$. This approximation causes little error in the nonsingular terms, but it can lead to overestimates of the valence singular terms. For example, for $\Gamma_{25'}(k=0)$ by $\mathbf{k}\cdot\mathbf{p}$ perturbation theory we know that the $u_{\mathbf{k}'}$ contributing to the singular term has for small k' the form

$$u_{\mathbf{k}'} \simeq u_{\mathbf{k}}^{\Gamma_{25'}} + \frac{\langle \Gamma_{15}|\hbar\mathbf{k}'\cdot\mathbf{p}/m|\Gamma_{25'}\rangle}{E_{\Gamma_{25'}}-E_{\Gamma_{15}}} u_{\mathbf{k}}^{\Gamma_{15}} + \cdots \quad (3.3)$$

and, as we have remarked, $u_{\mathbf{k}}^{\Gamma_{15}}$ does not contribute singular terms in exchanging with $\Gamma_{25'}$. A detailed graphical analysis based on (3.3) shows that $u_{\mathbf{k}'}=u_{\mathbf{k}}$ overestimates the valence singular terms by about 20%. From Table I it is seen that A_{12} is overestimated by about 0.04 Ry, and B_{12} by about 0.004 Ry. The former error would be important if we were to make much use of unscreened exchange (which we shall not), while the latter error can be neglected: It is somewhat smaller than the error inherent in the sampling of the rest of the zone.

Let us now examine these matrix elements and compare the exchange terms in the presence of covalent bonds with those of a free electron gas.

The diagonal matrix elements of A show the same qualitative behavior, as one would expect. There is a sharp dependence of $A_\alpha(\mathbf{k})$ on $\mathbf{k}$ for $k\sim k_F$. (cf. A_{11} vs A_{22} for $\Gamma_{25'}$ and Γ_{15}.) A feature not present in the free electron gas is the difference between a conduction band and a valence band matrix element for the same value of $\mathbf{k}$ (A_{11} for $\Gamma_{25'}$ and Γ_{15}). This feature is also not present in the Thomas-Fermi-Slater model. It alone would increase the energy gap between valence and conduction bands by about 0.3 Ry; it is the semicon-

TABLE II. Matrix elements (in Ry) of various irreducible representations using SCPW basis functions, for exchange (HF) and screened exchange (HFH).

Rep.	(i,j)	HF	HFH
$\Gamma_{25'}$	(11)	-0.67	-0.25
$\Gamma_{25'}$	(12)	-0.35	-0.11
$\Gamma_{25'}$	(22)	-0.38	-0.19
Γ_{15}	(11)	-0.35	-0.21
Γ_{15}	(12)	-0.07	-0.05
Γ_{15}	(22)	-0.12	-0.10
X_1	(11)	-0.86	-0.29
X_1	(12)	-0.34	-0.11
X_1	(22)	-0.39	-0.20
Γ_1	(11)	-1.10	-0.35

ductor analog of the analytic singularity[4] in the free-electron exchange potential for $k=k_F$.

The off-diagonal elements are, of course, new. By comparison the off-diagonal matrix element of the valence Coulomb potential V_{12}^{val} for $\Gamma_{25'}$ is 0.21 Ry. Because of spin, one expects exchange interactions to be about half of Coulomb interactions, but $A_{12}=-0.35$ Ry for $\Gamma_{25'}$. According to Table I most of this comes from exchange with nearby states in k space (long-range $1/r$ interaction again). It turns out that such strong covalent exchange would also increase the energy gap by about 0.3 Ry. The combined diagonal and off-diagonal effects of unscreened exchange completely destroy agreement[7] between theory and experiment for the energy gap in Si.

The inclusion of correlation screening clears up all the difficulties resulting from bare exchange. In the diagonal matrix elements the average energy of $\Gamma_{25'}$ (the top of the valence band) is about $0.6B_{11}+0.4B_{22}=-0.21$ Ry. This is to be compared with the diagonal energy for X_1 (the bottom of the conduction band), which is given accurately by $B_{22}=-0.20$ Ry, so that the energy gap is practically the same as one would calculate from an ordinary potential.

Note added in proof. We notice that the diagonal matrix elements of the screened exchange operator B are less negative than those of A. This is because we have not included the lowering of energy due to suppression of plasma oscillations. It was suggested[1] that because the latter is practically constant if all electrons have energy $E_{\mathbf{k}}<\hbar\omega_p$, that it be added as a constant B_0 to all diagonal elements with unperturbed energy below the plasma energy. The constant B_0 cancels in computing energy differences near the energy gap.

Numerical computation of B_0 requires knowledge of $\epsilon(q,\omega)$ for $\omega\lesssim\omega_p$ and $q\lesssim q_c$, where q_c is the Bohm-Pines cutoff, which task is beyond the scope of this paper. We may estimate B_0 empirically as follows. The average diagonal exchange potential for valence states is from Table II of order -0.9 Ry. The average diagonal B for valence states is -0.3 Ry. Correlation lowers the total energy of silicon by about 1 eV per valence electron, or 0.15 Ry of potential. This gives $B_0\simeq-0.75$ Ry.

The situation is also satisfactory for the off-diagonal elements B_{12}^{α}, $\alpha=\Gamma_{25'}$, Γ_{15}, and X_1. The Thomas-Fermi-Slater value for these matrix elements is 0.11 Ry in all cases. This is in surprisingly good agreement for $\Gamma_{25'}$ and X_1 (see also the next section) and is a slight overestimate for Γ_{15}. Because the second basis function for Γ_{15} has very high kinetic energy (about 30 eV) this correction has little effect on the lowest Γ_{15} eigenvalue.

4. CONCLUSIONS

We have examined the physical content of the modern theory of exchange and correlation, which has hitherto been studied in detail only for the free-electron gas, when it is applied to covalently bonded Si. We have found that in many respects the true exchange operator does resemble an exchange potential, but that because of the long-range interaction bare exchange potentials would destroy the agreement between theory and experiment for semiconductor band structures.

Actual band calculations have used the Thomas-Fermi-Slater approximation based on the picture of an exchange hole. Because the interaction of an electron with its exchange hole is a short-range one, this approximation inadvertently includes (in a qualitative way) effects of correlation. Surprisingly enough, our values of B_{12} were in good *quantitative* agreement with the Thomas-Fermi-Slater values.

The reason for this agreement can be found by examining Table II. The off-diagonal exchange matrix elements for $\Gamma_{25'}$ and X_1 are reduced by a factor of 3 by screening. If one defines

$$\frac{1}{\epsilon(r)r}=\frac{1}{(2\pi)^3}\int\frac{1}{\epsilon(q)q^2}e^{i\mathbf{q}\cdot\mathbf{r}}d^3q, \tag{4.1}$$

and uses (4.1) to compute $\epsilon(r)$, it turns out that $\epsilon(r_s)\simeq3$. The effect of screening is to replace the bare exchange energy, of order

$$A_K=-(e^2/r_s)\rho_K, \tag{4.2}$$

by the screened interaction, of order

$$B_K=[-e^2/\epsilon(r_s)r_s]\rho_K. \tag{4.3}$$

By contrast the Thomas-Fermi-Slater expression is

$$V_{\mathrm{TFS}}(r)=-(0.92/r_s)e^2(\rho_1)^{1/3}, \tag{4.4}$$

where ρ_1 has the form

$$\rho_1=1+\sum_{\mathbf{K}\neq0}\rho_{\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{r}}. \tag{4.5}$$

If we, now, linearize (4.4) by expanding the cube root we find

$$V_{\mathrm{TFS}}{}^{\mathbf{K}}\simeq-(e^2/r_s)(\rho_{\mathbf{K}}/3), \tag{4.6}$$

where the factor of 3 comes from the cube root. Fortuitously, this factor is nearly equal to the mean screening factor $\epsilon(r_s)$ given by Penn's wave-number-dependent dielectric function $\epsilon(q)$.

This screening function is, of course, only approximate. In spite of the large number of approximations we have made (see the Appendix), we feel that the most serious one is the use of an approximate $\epsilon(q)$. Further progress requires a more accurate evaluation of this complicated function. On the other hand, the present work resolves, at least partly, the objections to the Thomas-Fermi-Slater approximation raised in the introduction, and suggests that it is good to a few hundredths of a Ry for calculating term differences in real crystals.

Several self-consistent band calculations for Si and Ge using the Slater exchange potential have been reported.[11] We have demonstrated that near the energy gap the momentum dependence of exchange and correlation shifts term values by about 0.01 Ry. By interpolating between $\Gamma_{25'}$ and Γ_1 we see that for states deeper in the valence band (such as $L_{3'}$ or X_4) the shift may be of order 0.03–0.05 Ry. It would be of considerable theoretical interest if such differences could be observed as discrepancies between the ultraviolet term differences[12] and local potential band values.

Part of this work was done by one of us (J.C.P.) during a visit to the Royal Society Mond Laboratory, Cambridge. He is grateful to the staff, particularly Professor A. B. Pippard, for stimulating discussions and kind hospitality. We are also grateful to Professor M. H. Cohen and Dr. V. Heine for several conversations.

Note added in proof. After this paper was submitted, a letter appeared discussing the application of the free electron Slater exchange potential to the tight binding method [J. E. Robinson, F. Bassani, R. S. Knox, and J. R. Schrieffer, Phys. Rev. Letters **9**, 215 (1962)]. This Letter proposes to use a screened interaction similar to (4.1), and states that the interaction will always be closer to true exchange and correlation than the Slater approximation. While it is not surprising that our conclusions, which have been obtained in a nearly free electron representation, differ from theirs, it appears desirable to clarify several points.

The principal difference of approach lies in the replacement by these authors of the total charge density ρ_1 in (4.4) by a superposition of atomic charge densities $\sum\rho_i$, and the subsequent replacement of $\rho^{1/3}$ by $\sum\rho_i^{1/3}$. The first of these approximations is a good one, the second is not. All their criticism of the Slater approximation is based on the deficiencies of this latter atomic approximation, which runs directly counter to the Thomas-Fermi-Slater method. The atomic approximation gives especially poor results for the average part of the crystal screened exchange potential. As we emphasize, the average part must be calculated separately, and to it must be added B_0, which these authors neglect entirely.

APPENDIX

We summarize here the various approximations that were made in evaluating the matrix elements of the exchange operator A and the screened exchange operator B.

(1) The sum over occupied band states throughout the Brillouin zone was replaced by a sample of the 32 states at Γ, X, and L. (The same sample was used to evaluate the Coulomb potential in reference 7.) Except for the singular terms coming from the self subzone this sample should give results accurate to 10%. The singular terms are estimated to be accurate to 20%. As they constitute about half of the contribution to A, the error from this source is estimated to be about 15%.

(2) Each wave function at the symmetry point Γ, X, or L was expanded only to the first two symmetrized combinations of plane waves. The cross terms between these SCPW had been found[7] to give the Coulomb V_{111} to within about 15%. Because of the great similarity between the Coulomb and exchange potentials, we believe this approximation causes an error of only 15%.

(3) The most serious approximation lies in replacing the dielectric matrix $\epsilon(q/q+K)$ by its diagonal element $\epsilon(q/q)=\epsilon(q)$, and then evaluating $\epsilon(q)$ by an isotropic band model which contains only the average energy gap.[10] The off-diagonal matrix elements of ϵ represent (speaking semiclassically) the periodic variation of the Debye screening length because of the variation in charge density in the unit cell. This is quite large in a diamond-type lattice (Fig. 3 of reference 5). We now show that terms of this sort are not so large as they, at first, appear.

It is well known that the Debye screening length λ is proportional to $r_s^{1/2}$, that is, to $\rho^{-1/6}$. Inserting ρ_1 from (4.6) and linearizing, we see that

$$\Delta\lambda/\lambda \simeq -\tfrac{1}{6}\Delta\rho/\rho, \tag{A.1}$$

and, with $\Delta\rho/\rho=1$, $\Delta\lambda/\lambda$ gives errors of order 20% arising from the neglected off-diagonal elements.

The isotropic band model replaces the energy gap throughout the zone (which varies[12] from about 3 to 6 eV in Si) by an average band gap (about 4.5 eV). This may also lead to errors of order 20%.

We conclude that the approximations made to the dielectric matrix are the most drastic, and they may produce an error of order 30% in our final estimate of the screened exchange matrix B. On the other hand, errors of this sort would probably change the magnitude of the off-diagonal elements B_{12} in the same way for $\Gamma_{25'}$, Γ_{15}, and X_1. Thus, they would remain approximately equal. Our chief conclusion, that the screened exchange operator resembles a nonlocal potential for states near the energy gap, would be unchanged.

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[12] H. Ehrenreich, H. R. Philipp, and J. C. Phillips. Phys. Rev. Letters **8**, 59 (1962).