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Exchange and correlation effects on the quasiparticle band structure of semiconductors

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The influence of the nonlocal exchange and electron correlations on the quasiparticle band structure of semiconductors is investigated in a simple and transparent way. The starting point is a determinantal wave function in the bond-orbital approximation. In a model with hopping between neighboring bonds the main effects of the nonlocal exchange on the band structure, especially the band gap, can be extracted. Electronic correlations are taken into account by applying a variational ansatz. Analytical expressions for the different correlation-energy contributions to the quasiparticle energy are obtained and physically interpreted. The theory is applied to diamond, silicon, and germanium. It provides a good understanding of the exchange-correlation effects on the band gaps and bandwidths.

I. INTRODUCTION

Energy-band calculations of semiconductors have attracted considerable interest over the last years, mainly because for that particular problem the limitations of the local-density approximation (LDA) to exchange and correlation have become obvious. The band gaps and bandwidths come out much too small in LDA calculations.[1-5] It is now clear[5-13] that this failure is due to the use of a local, energy-independent exchange-correlation potential $V_{xc}(\mathbf{r})$ in the effective single-particle Schrödinger equation which cannot describe correctly the energy-dependent self-energy.

This suggests taking an alternative approach to the calculation of the quasiparticle band structure, namely by using a Hartree-Fock (HF) calculation as a starting point for the many-body or correlation calculation. Recent work along this line has been done by using a Green's-function technique[10-15] or by applying the local approach (LA), a variational ansatz.[16] The LA has also been successfully applied to make transparent the physics of electronic correlations in the ground state of covalent semiconductors.[17] The use of a variational ansatz was motivated by the fact that from quantum chemistry it is known that variational calculations of correlation effects are preferable to perturbation expansions.[18]

In this work we want to give a simple and transparent picture of exchange and correlation effects concerning the quasiparticle band structure using the LA. In order to be able to perform analytical calculations some approximations have to be made. The basic approximation which leads to the required simplification is the bond-orbital approximation (BOA).[19,20] It enables us to derive expressions for those correlation-energy contributions to the quasiparticle band structure which can be described within a minimal basis set. It also allows for good insight into the role of the nonlocal exchange and its influence on the band structure, e.g., the energy gap.

The present paper is organized as follows. In Sec. II the basic equations are written down, and in Sec. III the role of the nonlocal exchange is discussed in a simple model which allows a straightforward discussion of the exchange part of the self-energy. In Sec. IV the treatment of electron correlations is described. The matrix elements which appear in the theory are evaluated in Sec. V using the BOA. A physical interpretation of the various correlation-energy contributions to the quasiparticle energy is given in Sec. VI. The theory is applied to the elemental semiconductors diamond (C) and silicon (Si) in Sec. VII. Thereby we use *ab initio* HF energy bands as input for the correlation-energy contributions to the quasiparticle energies. Finally, Sec. VIII contains a brief summary and the conclusions.

II. BASIC EQUATIONS

The basic equations which we need for a discussion of exchange and correlation effects on the quasiparticle band structure of covalent semiconductors are summarized in this section. Let us consider a system with a diamond lattice structure built up from atomiclike (sp^3) hybrid orbitals. We assume that our starting hybrid functions have been orthogonalized with respect to each other by a Löwdin orthogonalization. The resulting functions are denoted by $h_i(\mathbf{r})$. The corresponding electron creation and annihilation operators $a_{i\sigma}^\dagger$ and $a_{j\sigma}$, respectively, fulfill the usual anticommutation relations.

The Hamiltonian H expressed in terms of the hybrid creation and annihilation operators is given by

$$\begin{aligned} H &= H_0 + H_{\text{int}} , \\ H_0 &= \sum_{i,j,\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} , \\ H_{\text{int}} &= \frac{1}{2} \sum_{\substack{i,j,k,l \\ \sigma,\sigma'}} V_{ijkl} a_{i\sigma}^\dagger a_{k\sigma'}^\dagger a_{l\sigma'} a_{j\sigma} . \end{aligned} \tag{1}$$

Here

$$t_{ij} = \int d^3r h_i^*(\mathbf{r}) [-\tfrac{1}{2}\Delta + V(\mathbf{r})] h_j(\mathbf{r}) \tag{2}$$

is the bare hopping matrix element between hybrid orbitals i and j, $V(\mathbf{r})$ is the electrostatic potential due to the nuclei and core electrons, and

$$V_{ijkl}=\int d^3r\, d^3r' h_i^*(\mathbf{r})h_j(\mathbf{r})\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}h_k^*(\mathbf{r}')h_l(\mathbf{r}') \qquad (3)$$

are the interaction matrix elements.

In the HF approximation the effective one-particle Hamiltonian is given by

$$H_{\mathrm{HF}}=\sum_{i,j,\sigma} f_{ij}a^{\dagger}_{i\sigma}a_{j\sigma} , \qquad (4)$$

where f_{ij} denotes the Fock matrix which consists of a Hartree part f^H_{ij} and an exchange part f^x_{ij}, that is

$$f_{ij}=f^H_{ij}+f^x_{ij} , \qquad (5)$$

where

$$f^H_{ij}=t_{ij}+\sum_{k,l,\sigma'} V_{ijkl}\langle a^{\dagger}_{k\sigma'}a_{l\sigma'}\rangle \qquad (6a)$$

and

$$f^x_{ij}=-\tfrac{1}{2}\sum_{k,l,\sigma'} V_{ilkj}\langle a^{\dagger}_{k\sigma'}a_{l\sigma'}\rangle . \qquad (6b)$$

The one-particle density matrix $\langle a^{\dagger}_{k\sigma'}a_{l\sigma'}\rangle$ is evaluated with respect to the HF ground state $|\Phi_{\mathrm{HF}}\rangle$ which has to be determined self-consistently from Eqs. (4)–(6). Here and in the following

$$\langle \cdots \rangle=\langle\Phi_{\mathrm{HF}}| \cdots |\Phi_{\mathrm{HF}}\rangle .$$

The HF ground-state energy is given by

$$\begin{aligned} E_{\mathrm{HF}}&=\langle H_0+H_{\mathrm{int}}\rangle+E_{\mathrm{NN}} \\ &=\langle H_{\mathrm{HF}}\rangle-\tfrac{1}{2}\langle H_{\mathrm{int}}\rangle+E_{\mathrm{NN}} , \end{aligned} \qquad (7)$$

where E_{NN} denotes the interaction energy of the nuclei and core electrons.

The eigenvalues $\varepsilon^{\mathrm{HF}}_{n\sigma}(\mathbf{k})$ of the HF Hamiltonian form the HF energy bands. Their interpretation is given by Koopmans's theorem, which states that

$$\varepsilon^{\mathrm{HF}}_{n\sigma}(\mathbf{k})=E_{\mathrm{HF}}(N)-E_{\mathrm{HF}}(N-1) \qquad (8a)$$

for a one-electron state which is occupied in the ground state of the system, and

$$\varepsilon^{\mathrm{HF}}_{n'\sigma'}(\mathbf{k}')=E_{\mathrm{HF}}(N+1)-E_{\mathrm{HF}}(N) \qquad (8b)$$

for a one-electron state which is vacant in the ground state of the system. Here $E_{\mathrm{HF}}(N)$ is the total energy of the N-electron system calculated in the HF approximation. In Eqs. (8), the assumption is made that during the removal or addition of an electron to the N-electron system, the HF one-particle eigenfunctions do not change appreciably. Whereas this assumption is not valid for "localized" states like electronic core states or electron states in atoms or small molecules, it is valid for, e.g., valence- and conduction-band states of infinite systems.

The electron correlations are, by definition, determined by the residual electron-electron interaction Hamiltonian H_{res} which is given by

$$H_{\mathrm{res}}=H_{\mathrm{int}}-\sum_{\substack{i,j,k,l\\ \sigma,\sigma'}} (V_{ijkl}-\delta_{\sigma,\sigma'}V_{ilkj})\langle a^{\dagger}_{k\sigma'}a_{l\sigma'}\rangle a^{\dagger}_{i\sigma}a_{j\sigma} . \qquad (9)$$

An investigation of the influence of electron correlations on ground-state properties of covalent semiconductors has been given recently by the authors.[17] In this work we will discuss the effects of electron correlations— and exchange—on the quasiparticle band structure of covalent semiconductors. For that purpose we introduce bonding and antibonding functions

$$\begin{aligned} B^{\dagger}_{I\sigma}&=2^{-1/2}(a^{\dagger}_{I1\sigma}+a^{\dagger}_{I2\sigma}) , \\ A^{\dagger}_{I\sigma}&=2^{-1/2}(a^{\dagger}_{I1\sigma}-a^{\dagger}_{I2\sigma}) . \end{aligned} \qquad (10)$$

The operators $a^{\dagger}_{I1\sigma}$ and $a^{\dagger}_{I2\sigma}$ refer to the hybrid orbitals 1 and 2 which form bond I. This construction applies to elemental semiconductors. The transformation from the hybrid functions to bonding and antibonding functions can be made irrespective of whether or not a bond-orbital approximation (BOA) is made. The simplifications of the BOA come in when the HF ground-state wave function $|\Phi_{\mathrm{HF}}\rangle$ is derived. In that case it has the simple form

$$|\Phi_{\mathrm{HF}}\rangle=\prod_{I,\sigma} B^{\dagger}_{I\sigma}|0\rangle , \qquad (11)$$

where $|0\rangle$ is the vacuum state. The one-particle density matrix is then of the simple diagonal form

$$\langle a^{\dagger}_{i\sigma}a_{j\sigma'}\rangle=\begin{cases}\tfrac{1}{2}\delta_{\sigma,\sigma'}, & i,j \text{ in } I\\ 0, & \text{otherwise} .\end{cases} \qquad (12)$$

This diagonal form which follows directly from the BOA allows firstly for a simple discussion of the exchange effects on the band structure and secondly for an analytical treatment of the many-body or correlation corrections.

III. ROLE OF NONLOCAL EXCHANGE

In this section we want to discuss the influence of the nonlocal exchange on the energy gaps and valence-band widths of covalent semiconductors. A summary of the results has been published recently by the authors.[21] The dispersion relation for the state

$$|\phi_{\mathbf{k}n\sigma}\rangle=c^{\dagger}_{\mathbf{k}n\sigma}|\Phi_{\mathrm{HF}}\rangle , \qquad (13)$$

where $c^{\dagger}_{\mathbf{k}n\sigma}$ creates an additional electron (or hole) in the HF Bloch state specified by $\mathbf{k}$, band index n, and spin σ, is given by

$$\varepsilon^{\mathrm{HF}}_{n\sigma}(\mathbf{k})=\varepsilon^{H}_{n\sigma}(\mathbf{k})+\varepsilon^{x}_{n\sigma}(\mathbf{k}) . \qquad (14)$$

The (non-self-consistent) Hartree part $\varepsilon^{H}_{n\sigma}(\mathbf{k})$ is determined by f^H_{ij} while the exchange part $\varepsilon^{x}_{n\sigma}(\mathbf{k})$ is determined by f^x_{ij}.

For the sake of transparency only matrix elements within a bond and between neighboring bonds will be considered. For a definition of the hopping matrix elements f_{ij} see Fig. 1. In spite of its drawbacks, concerning especially the conduction bands, this simple model is sufficient to describe the essential physics of the exchange corrections to the Hartree band structure. For that reason

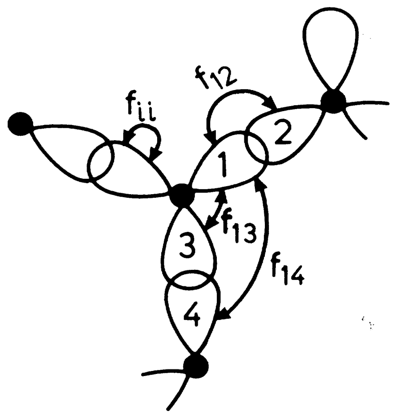

FIG. 1. Schematic representation of different bonds in a diamond lattice and the definition of different Fock matrix elements f_{ij}.

we don't investigate a more elaborate model.

We now want to discuss how the Hartree energy bands, especially how the direct band gap $E^{H}_{\mathrm{gap}}(\Gamma)$ and the valence-band width W^{H}_{val} are changed when the nonlocal exchange is taken into account. In the present model one finds for the exchange contributions $\varepsilon^{x}_{v\sigma}(\mathbf{k})$ and $\varepsilon^{x}_{c\sigma}(\mathbf{k})$ to the dispersion relations of the valence and conduction bands, e.g., along the Γ-X direction

$$\varepsilon^{x}_{v\sigma}(\mathbf{k})=\begin{cases}-f^{x}_{0}-t^{x}_{0}+2f^{x}_{B}, & v=1,2\\ -f^{x}_{0}-t^{x}_{0}-2f^{x}_{B}[1\pm 2\cos(k)], & v=3,4\end{cases} \tag{15}$$

and

$$\varepsilon^{x}_{c\sigma}(\mathbf{k})=\begin{cases}-f^{x}_{0}+t^{x}_{0}+2f^{x}_{A}, & c=1,2\\ -f^{x}_{0}+t^{x}_{0}-2f^{x}_{A}[1\pm 2\cos(k)], & c=3,4\ .\end{cases} \tag{16}$$

In these equations the following abbreviations have been used

$$f^{x}_{0}=-f^{x}_{ii}=\tfrac{1}{2}U+\tfrac{3}{2}V_{1331}+\tfrac{1}{2}V_{1221}+\cdots\ , \tag{17a}$$

$$t^{x}_{0}=-f^{x}_{12}=\tfrac{1}{2}K+\tfrac{1}{2}V_{1221}+\cdots\ , \tag{17b}$$

$$f^{x}_{B}=-\tfrac{1}{2}f^{x}_{13}-f^{x}_{14}=\tfrac{1}{2}V_{1113}+V_{1114}+\cdots\ , \tag{17c}$$

$$f^{x}_{A}=-\tfrac{1}{2}f^{x}_{13}+f^{x}_{14}=\tfrac{1}{2}V_{1113}-V_{1114}+\cdots\ . \tag{17d}$$

Here $U=V_{1111}$ and $K=V_{1122}$ are the Coulomb interactions of two electrons in the same hybrid orbitals and in the two different hybrid orbitals 1 and 2 forming a bond, respectively. The meaning of the other interaction matrix elements can be easily understood from Fig. 1. The second equality in Eqs. (17a)–(17d) is approximate only because we have neglected terms like V_{1222}, V_{1441}, etc. For diamond the values $U=22.5$, $K=13.3$, $V_{1331}=1.9$, $V_{1221}=0.3$, $V_{1113}=0.7$, and $V_{1114}=0.4$ eV, respectively, were obtained in an approximate HF calculation.[22]

Combining Eqs. (15)–(17) we arrive at the following expressions for the direct band gap $E^{\mathrm{HF}}_{\mathrm{gap}}(\Gamma)$ and the valence-band width $W^{\mathrm{HF}}_{\mathrm{val}}$ in the HF approximation

$$\begin{aligned}E^{\mathrm{HF}}_{\mathrm{gap}}(\Gamma)&=E^{H}_{\mathrm{gap}}(\Gamma)+2t^{x}_{0}-2(f^{x}_{B}-f^{x}_{A})\\ &\cong E^{H}_{\mathrm{gap}}(\Gamma)+K-4V_{1114}\ ,\end{aligned} \tag{18}$$

$$\begin{aligned}W^{\mathrm{HF}}_{\mathrm{val}}&=W^{H}_{\mathrm{val}}+8f^{x}_{B}\\ &\cong W^{H}_{\mathrm{val}}+4V_{1113}+8V_{1114}\ .\end{aligned} \tag{19}$$

First of all we note that the exchange leads to downward shift of the bands by $f^{x}_{0}\cong U/2$. This results from the cancellation of the self-interaction in the Hartree part, as given by Eq. (6a), due to the nonlocal exchange. The exchange energy contribution K to the direct HF bandgap results from the nonlocal exchange interaction within a bond as can be seen from Eq. (17b). Stated differently, the exchange contribution $K/2$ to the effective HF hopping matrix element between the two hybrids forming a bond leads to a drastic increase, K, in the bonding-antibonding splitting. This is the main effect of the exchange on the gap, which demonstrates why the HF gaps are so large in these materials. The same situation is expected to occur in other semiconductors. In the simple model used here the exchange part of the quasiparticle energy has a discontinuity

$$\Delta_{x}(\Gamma)=2t^{x}_{0}-2(f^{2}_{B}-f^{x}_{A})\cong K-4V_{1114} \tag{20}$$

across the direct gap [compare with Eq. (18)].

From Eq. (19) we see that in general the HF valence-band width will be larger than the Hartree valence-band width. This is due to the fact that the exchange contribution f^{x}_{ij} to the HF hopping matrix element f_{ij} enters with the same sign as the bare hopping matrix element t_{ij} which is negative in general. In diamond it is $W^{\mathrm{HF}}_{\mathrm{val}}=30$ eV as compared to $W^{H}_{\mathrm{val}}=24$ eV.[23]

In Fig. 2 the exchange part of the quasiparticle energy is plotted as a function of the exact quasiparticle energy

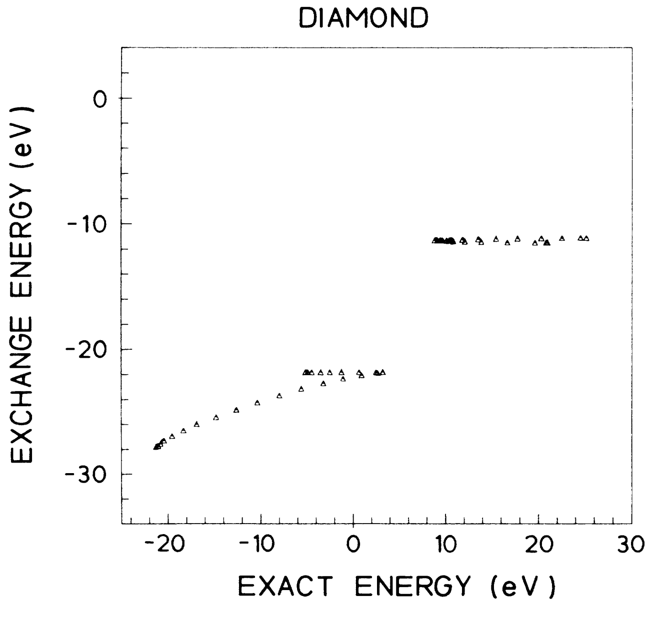

FIG. 2. Exchange contribution to the quasiparticle energy as function of the quasiparticle energy for diamond.

for the case of diamond. Here Eqs. (15)–(17) have been used to calculate the exchange part with the interaction parameters listed above. The exact energies have been taken from Sec. VII. Because, in general, the dispersion relations for the valence bands can be rather well described by the BOA (Refs. 19 and 20) the energy dependence of the exchange part of the valence-band energies should be realistic. In principle one also expects the conduction-band exchange energy to increase with increasing energy.[24] The fact that in Fig. 2 the conduction-band exchange energy is nearly energy independent is due to our simple model and the fact that the conduction bands are poorly described by the BOA.[19,20] Nevertheless we think that the simple model discussed in this section gives a qualitative understanding of the effects of the nonlocal exchange on the quasiparticle band structure of semiconductors.

A more realistic discussion of the exchange self-energy for semiconductors and insulators, starting from a Penn model, has been given recently by Horsch.[24]

IV. TREATMENT OF ELECTRON CORRELATIONS

In the following we will consider the case where an electron is added to the system. In that case the HF excited state is given by

$$|\phi_{\mathbf{k}c\sigma}\rangle = A^\dagger_{\mathbf{k}c\sigma}|\Phi_{\mathrm{HF}}\rangle , \tag{21}$$

where

$$A^\dagger_{\mathbf{k}c\sigma} = N_B^{-1/2}\sum_I \alpha_{\mathbf{k}c\sigma}(I) A^\dagger_{I\sigma} \tag{22}$$

creates an electron in the conduction-band specified by the momentum $\mathbf{k}$, band index $n=c$, and spin σ. The positions of the N_B different bonds are denoted by I. The coefficients $\alpha_{\mathbf{k}c\sigma}(I)$ follow from the solution of the HF eigenvalue problem.

In order to describe the effect of electron correlations we use the ansatz

$$|\Psi_{\mathbf{k}c\sigma}\rangle = e^S A^\dagger_{\mathbf{k}c\sigma}|\Phi_{\mathrm{HF}}\rangle \tag{23}$$

for the correlated excited state, in analogy to the correlated ground-state wave function.[17] The operator S is expressed directly in terms of bonding and antibonding functions

$$S = S^\pi + S^\eta = -\sum_{I,J}\pi_{IJ}S^\pi_{IJ} - \sum_{I,J}\eta_{IJ}S^\eta_{IJ} , \tag{24}$$

where

$$S^\pi_{IJ} = \tfrac{1}{4}\sum_{\sigma,\sigma'} A^\dagger_{J\sigma'}B_{J\sigma'}A^\dagger_{I\sigma}A_{I\sigma} \tag{25a}$$

and

$$S^\eta_{IJ} = \tfrac{1}{4}\sum_{\sigma,\sigma'} A^\dagger_{J\sigma'}B_{J\sigma'}A^\dagger_{I\sigma}B_{I\sigma} . \tag{25b}$$

The π_{IJ} and η_{IJ} are variational parameters.

In order to understand the implications of this form of S let us assume first that the extra electron would not be present, that means $\exp(S)$ acts on the HF ground state $|\Phi_{\mathrm{HF}}\rangle$. In that case $S^\pi_{IJ}|\Phi_{\mathrm{HF}}\rangle = 0$ because $A^\dagger_{I\sigma}A_{I\sigma}|\Phi_{\mathrm{HF}}\rangle = 0$. The ansatz

$$e^{S^\eta}|\Phi_{\mathrm{HF}}\rangle = \exp\left[-\sum_{I,J}\eta_{IJ}S^\eta_{IJ}\right]|\Phi_{\mathrm{HF}}\rangle \tag{26}$$

is then identical to that for the correlated ground-state function of Ref. 17. The operator S^η_{IJ} describes electron correlations within a bond ($I=J$) and between different bonds ($I\neq J$) and the η_{IJ} are determined by minimizing the total energy.

When an electron is added to $|\Phi_{\mathrm{HF}}\rangle$, i.e., when we start from $A^\dagger_{\mathbf{k}c\sigma}|\Phi_{\mathrm{HF}}\rangle$, states of the form

$$e^{S^\eta}A^\dagger_{I\sigma}|\Phi_{\mathrm{HF}}\rangle \tag{27}$$

and

$$e^{S^\pi}A^\dagger_{I\sigma}|\Phi_{\mathrm{HF}}\rangle \tag{28}$$

must be considered instead of Eq. (26). The operator $\exp(S^\eta)$ introduces again electron correlations within and between bonds like in the ground state but with one modification. Due to the presence of the additional electron some of the ground-state correlations are blocked resulting in a *loss* of ground-state correlation energy.

When the operator S^π is applied on $A^\dagger_{I\sigma}|\Phi_{\mathrm{HF}}\rangle$ one obtains

$$S^\pi A^\dagger_{I\sigma}|\Phi_{\mathrm{HF}}\rangle = -\tfrac{1}{4}\sum_{J,\sigma'}\pi_{IJ}A^\dagger_{J\sigma'}B_{J\sigma'}A^\dagger_{I\sigma}|\Phi_{\mathrm{HF}}\rangle . \tag{29}$$

By generating particle-hole excitations (or dipoles) $A^\dagger_{J\sigma'}B_{J\sigma'}$ in bonds J around bond I, a long-range polarization cloud is created around the extra electron. It reduces considerably the energy which is required for adding an extra electron into the conduction band.

The variational parameters π_{IJ} and η_{IJ} are determined by minimizing the total energy

$$E_{\mathbf{k}c\sigma}(N+1) = \frac{\langle\Psi_{\mathbf{k}c\sigma}|H|\Psi_{\mathbf{k}c\sigma}\rangle}{\langle\Psi_{\mathbf{k}c\sigma}|\Psi_{\mathbf{k}c\sigma}\rangle} \tag{30}$$

of the $(N+1)$-electron system. By making use of a linked cluster theorem[16] it follows that

$$E_{\mathbf{k}c\sigma}(N+1) = \varepsilon_{c\sigma}(\mathbf{k}) + E(N) . \tag{31}$$

Here

$$E(N) = \langle e^{S^\eta}He^{S^\eta}\rangle_c \tag{32a}$$

is the total energy of the N-electron system and the subscript c means that only connected diagrams have to be taken into account in evaluating the expectation value. Furthermore

$$\varepsilon_{c\sigma}(\mathbf{k}) = \frac{\langle A_{\mathbf{k}c\sigma}e^{S^\dagger}He^{S}A^\dagger_{\mathbf{k}c\sigma}\rangle_c}{\langle A_{\mathbf{k}c\sigma}e^{S^\dagger}e^{S}A^\dagger_{\mathbf{k}c\sigma}\rangle_c} . \tag{32b}$$

From Eq. (31) it is seen that $\varepsilon_{c\sigma}(\mathbf{k})$ plays the role of a quasiparticle energy. It should be stressed that like in the HF problem (see Sec. II) we do not have to calculate $E(N+1)$. Instead we can directly calculate the quasiparticle energy from Eq. (32b).

The variational parameters π_{IJ} and η_{IJ} are determined by requiring that $E(N+1)$ is minimized. This implies

$$\frac{d\varepsilon_{c\sigma}(\mathbf{k})}{d\pi_{IJ}}=0 \tag{33a}$$

and

$$\frac{d\varepsilon_{c\sigma}(\mathbf{k})}{d\eta_{IJ}}+\frac{dE(N)}{d\eta_{IJ}}=0 \ . \tag{33b}$$

Because $E(N)$ is the total energy of N electrons and $\varepsilon_{c\sigma}(\mathbf{k})$ is that of a single one, the last equation reduces to

$$\frac{dE(N)}{d\eta_{IJ}}=0 \ . \tag{33c}$$

The η_{IJ} are therefore the same parameters as in the ground-state correlation calculation. They remain unchanged when excited states are considered.

The correlation contribution to the quasiparticle energy is by definition

$$\varepsilon_{c\sigma}^{\text{corr}}(\mathbf{k})=\varepsilon_{c\sigma}(\mathbf{k})-\varepsilon_{c\sigma}^{\text{HF}}(\mathbf{k}) \ . \tag{34}$$

In order to calculate $\varepsilon_{c\sigma}^{\text{corr}}(\mathbf{k})$ we replace in Eq. (32b) $\exp(S)$ by $1+S$.[16,17] It follows that

$$\varepsilon_{c\sigma}^{\text{corr}}(\mathbf{k})=\frac{\langle A_{\mathbf{k}c\sigma}(S^{\dagger}H+HS+S^{\dagger}HS)A_{\mathbf{k}c\sigma}^{\dagger}\rangle_c-\varepsilon_{c\sigma}^{\text{HF}}(\mathbf{k})\langle A_{\mathbf{k}c\sigma}S^{\dagger}SA_{\mathbf{k}c\sigma}^{\dagger}\rangle_c}{1+\langle A_{\mathbf{k}c\sigma}S^{\dagger}SA_{\mathbf{k}c\sigma}^{\dagger}\rangle_c} \ . \tag{35}$$

Minimizing with respect to π_{IJ} we obtain the equation

$$\langle A_{\mathbf{k}c\sigma}H_{\text{res}}S_{IJ}^{\pi}A_{\mathbf{k}c\sigma}^{\dagger}\rangle_c+\langle A_{\mathbf{k}c\sigma}S^{\dagger}[H-\varepsilon_{c\sigma}(\mathbf{k})]S_{IJ}^{\pi}A_{\mathbf{k}c\sigma}^{\dagger}\rangle_c=0 \tag{36}$$

for the determination of these parameters. Note that the exact quasiparticle energy $\varepsilon_{c\sigma}(\mathbf{k})$ appears on the right-hand side of Eq. (36). Due to the fact that $A_{\mathbf{k}c\sigma}^{\dagger}$ is an eigenstate of the Hamiltonian H_{HF}, only the residual Hamiltonian H_{res} appears on the left-hand side of this equation. Using the π_{IJ} from Eq. (36) and the parameters η_{IJ} from the ground-state calculation, the quasiparticle correlation energy finally can be written as

$$\varepsilon_{c\sigma}^{\text{corr}}(\mathbf{k})=\varepsilon_{c\sigma}^{\pi}(\mathbf{k})+\varepsilon_{c\sigma}^{\eta}(\mathbf{k}) \ . \tag{37}$$

Here

$$\begin{aligned}\varepsilon_{c\sigma}^{\pi}(\mathbf{k})&=\langle A_{\mathbf{k}c\sigma}H_{\text{res}}S^{\pi}A_{\mathbf{k}c\sigma}^{\dagger}\rangle_c\\&=-\sum_{I,J}\pi_{IJ}\langle A_{\mathbf{k}c\sigma}H_{\text{res}}S_{IJ}^{\pi}A_{\mathbf{k}c\sigma}^{\dagger}\rangle_c\end{aligned} \tag{38}$$

represents the energy *gain* due to the polarization of the bonds by the extra electron while

$$\begin{aligned}\varepsilon_{c\sigma}^{\eta}(\mathbf{k})&=\langle A_{\mathbf{k}c\sigma}H_{\text{res}}S^{\eta}A_{\mathbf{k}c\sigma}^{\dagger}\rangle_c\\&=-\sum_{I,J}\eta_{IJ}\langle A_{\mathbf{k}c\sigma}H_{\text{res}}S_{IJ}^{\eta}A_{\mathbf{k}c\sigma}^{\dagger}\rangle_c\end{aligned} \tag{39}$$

is the *loss* of ground-state correlation energy due to the extra electron. What remains is the evaluation of the various expectation values.

V. EVALUATION OF MATRIX ELEMENTS

In this section we want to compute the matrix elements which appear in Eq. (36) for the determination of the variational parameters π_{IJ}. Because the Bloch state $A_{\mathbf{k}c\sigma}^{\dagger}$ can be expressed in terms of the antibonding functions $A_{I\sigma}^{\dagger}$ [see Eq. (22)] we have to calculate the various matrix elements with respect to the $A_{I\sigma}^{\dagger}$. In the following all matrix elements will be expressed in terms of the bonding and antibonding functions. The corresponding interaction matrix elements are denoted by $\widetilde{V}_{A_IB_JA_KB_L}$, etc. If necessary they can be transformed back to the hybrid representation by using Eq. (10).

One finds for $J\neq I$

$$\begin{aligned}\langle A_{T'\sigma}H_{\text{res}}S_{IJ}^{\pi}A_{T\sigma}^{\dagger}\rangle_c&=\delta_{TT'}\delta_{TI}(\widetilde{V}_{A_IA_IA_JB_J}-\tfrac{1}{2}\widetilde{V}_{A_IB_JA_JA_I})\\&=\delta_{TT}\delta_{TI}V_{|I-J|}^{P} \ .\end{aligned} \tag{40}$$

Equation (40) represents the interaction of a charge in bond I with an induced-dipole in bond $J\neq I$ of the polarized medium. There is no contribution for $I=J$ because $\widetilde{V}_{A_IA_IA_IB_I}=0$ due to symmetry.

The corresponding matrix element for the operator S_{IJ}^{η} is given by

$$\begin{aligned}\langle A_{T'\sigma}H_{\text{res}}S_{IJ}^{\eta}A_{T\sigma}^{\dagger}\rangle_c&=-\delta_{TT'}\delta_{TI}(\widetilde{V}_{A_IB_IA_JB_J}-\tfrac{1}{2}\widetilde{V}_{A_IB_JA_JB_I})\\&=-\delta_{TT'}\delta_{TI}V_{|I-J|}^{D} \ .\end{aligned} \tag{41}$$

$V_{|I-J|}^{D}$ represents the van der Waals interaction between electron-hole pairs in bonds I and $J\neq I$.[17] For $I=J$ the corresponding interaction parameter V_0^D for the interaction of two electron-hole pairs (of opposite spin) within the same bond is[17]

$$\begin{aligned}V_0^D&=\widetilde{V}_{A_IB_IA_IB_I}\\&=\langle\Phi_{\text{HF}}|H_{\text{res}}|A_{I\sigma}^{\dagger}B_{I\sigma}A_{I,-\sigma}^{\dagger}B_{I,-\sigma}\Phi_{\text{HF}}\rangle\\&=\tfrac{1}{2}(U-K) \ .\end{aligned} \tag{42}$$

Due to the missing spin summation V_0^D appears with a prefactor $\frac{1}{2}$ in Eq. (41).

The evaluation of the various matrix elements is facilitated by the use of diagrams which can be associated with them. The diagrams are shown in Fig. 3. Solid lines running up correspond to antibonding states while solid lines running down correspond to bonding states. A wavy line denotes the operator S_{IJ}^{π} if one of the incoming lines comes from below [see, e.g., diagram (1a)]. It corresponds to S_{IJ}^{η} if both incoming lines come from above [see, e.g., diagram (1c)]. A dashed line denotes the interaction matrix element $\widetilde{V}_{IJKL}$, where the indices I,J,K,L refer hereby to bonding or antibonding states. A cross represents the Fock matrix element f_{IJ}. For a detailed description of the diagrammatic rules we refer to Ref. 16.

Using the identifications given above each expectation

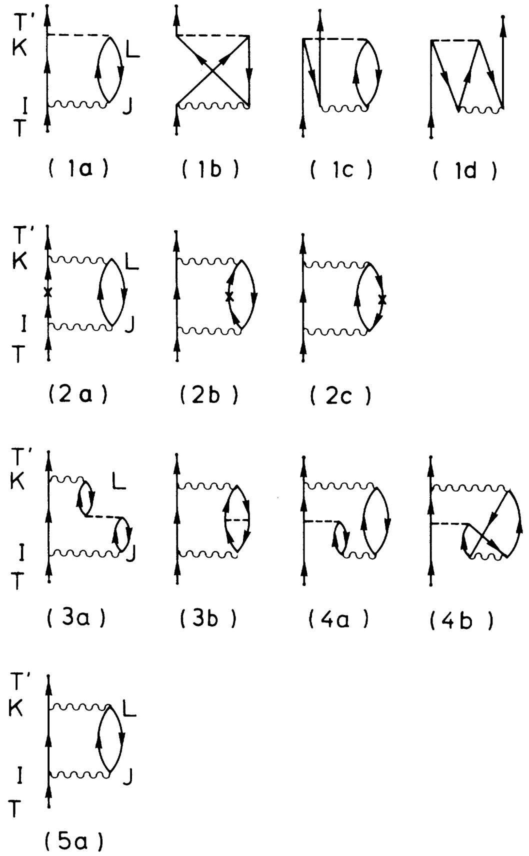

FIG. 3. Diagrams contributing to the quasiparticle energy. An upward running solid line symbolizes an electron in an antibonding state and a downward running line a hole in a bonding state. A cross stands for a Fock matrix element f_{IJ}. Dashed lines denote interaction matrix elements $\widetilde{V}_{IJKL}$, while wavy lines denote operators S_{IJ}^{π} or $S_{IJ}^{\bar{\pi}}$, depending on whether the incoming lines come from below or above, respectively.

value can be represented in terms of diagrams and is thereby easily interpreted. In Fig. 3 those diagrams are shown which correspond to the nonvanishing expectation values we have to calculate. The expectation value Eq. (40) has associated with it the two diagrams, (1a) and (1b), where the first one is the direct term and the second one is the exchange diagram. Similarly diagrams (1c) and (1d) correspond to Eq. (41).

In order to calculate the expectation value

$$\langle A_{T'\sigma} S^{\dagger} H S_{IJ}^{\pi} A_{T\sigma}^{\dagger} \rangle_c$$

which enters Eq. (36) we use the fact that

$$H = H_{\mathrm{HF}} + H_{\mathrm{res}} .$$

We first find

$$-\langle A_{T'\sigma} S^{\dagger} H_{\mathrm{HF}} S_{IJ}^{\pi} A_{T\sigma}^{\dagger} \rangle_c = \delta_{TT'} \delta_{TI} \pi_{IJ} \tfrac{1}{2} (\bar{E}_A + 2T_0) + C_{T \neq T'} . \tag{43}$$

Here

$$\bar{E}_A = \langle A_{J\sigma} H_{\mathrm{HF}} A_{J\sigma}^{\dagger} \rangle = -f_0 + T_0 \tag{44a}$$

is the mean energy of the extra conduction electron. Similarly

$$\bar{E}_B = \langle B_{J\sigma} H_{\mathrm{HF}} B_{J\sigma}^{\dagger} \rangle = -f_0 - T_0 \tag{44b}$$

is the mean energy or center of gravity of the valence bands. The HF bonding-antibonding splitting $2T_0$ is given by

$$2T_0 = 2(t_0^H + t_0^x) = \bar{E}_A - \bar{E}_B . \tag{44c}$$

Furthermore $C_{T \neq T'}$ denotes all those contributions to the expectation value which are not diagonal in T,T'. They correspond to hopping processes between different bonds and lead to an explicit momentum dependence of the correlation energy.[16] In the following we will neglect the term $C_{T \neq T'}$. This approximation is the better, the larger the energy difference $2T_0$ between the centers of the conduction and valence bands is as compared to the energy dispersion within the bands (see Sec. VII). The diagrams corresponding to Eq. (43) are (2a)—(2c) of Fig. 3. The corresponding exchange diagrams vanish due to symmetry if we keep only the diagonal terms $T=T'$ in Eq. (43).

Next we have to calculate the expectation value with respect to H_{res}. It is

$$-\langle A_{T'\sigma} S^{\dagger} H_{\mathrm{res}} S_{IJ}^{\pi} A_{T\sigma}^{\dagger} \rangle_c = \delta_{TT'} \delta_{TI} [-\pi_{IJ} V_{\mathrm{sc}} + V^{P}_{|I-J|} (\tfrac{1}{2} \eta_0 + \delta)] . \tag{45}$$

Here the first term on the right-hand side is represented by the diagrams (3a) and (3b). If in diagrams (3a) and (3b) only the contribution with $L=J$ is taken into account if follows that

$$\begin{aligned} V_{\mathrm{sc}} &= -(\widetilde{V}_{A_I B_I A_I B_I} - \tfrac{1}{2} \widetilde{V}_{A_I A_I B_I B_I}) \\ &\cong \tfrac{1}{2} (K - V_0^D) \end{aligned} \tag{46}$$

Due to the fact that the induced dipoles (or electron-hole pairs) point into different directions the diagrams with $L \neq J$ enter with different signs and therefore give only a negligible contribution. The first term in V_{sc}, i.e., $\widetilde{V}_{A_I B_I A_I B_I}$, represents the electron-hole pair interaction while the exchange term $\widetilde{V}_{A_I A_I B_I B_I}$ represents the electron-hole attraction. These terms also enter the Green's-function theory.[9,10,15]

The second term on the right-hand side of Eq. (45) corresponds to the diagrams (4a) and (4b). It represents the influence of the ground-state correlations. A detailed discussion is given in Sec. VI. η_0 is the variational parameter for the ground-state correlations within a bond (see also Ref. 17). It represents the contributions of diagrams (4a) and (4b) with $L=J$. The parameter δ represents the contributions from the same diagrams but with $L \neq J$ and was found to be numerically approximately equal to the variational parameter η_1 which describes the ground-state correlations between neighboring bonds.[17]

We finally have

$$\langle A_{T'\sigma} S^{\dagger} \varepsilon_{c\sigma}(\mathbf{k}) S_{IJ}^{\pi} A_{T\sigma}^{\dagger} \rangle_c = \delta_{TT'} \delta_{TI} \pi_{IJ} \tfrac{1}{2} \varepsilon_{c\sigma}(\mathbf{k}) \tag{47}$$

which corresponds to diagram (5) in Fig. 3. The exchange term vanishes in the $T = T'$ approximation. This completes the evaluation of the expectation values.

VI. PHYSICAL INTERPRETATION

We are now able to evaluate the correlation contribution $\varepsilon_{c\sigma}^{\text{corr}}(\mathbf{k})$ to the quasiparticle energy of an extra electron with the help of Eqs. (37)—(39). The variational parameters π_{IJ} have to be determined from Eq. (36). Using all the expectation values calculated in the last section in the $T = T'$ approximation we find from Eq. (36)

$$V^P_{|I-J|} = \pi_{IJ}[\tfrac{1}{2}(\bar{E}_A + 2T_0) - V_{\text{sc}} - \tfrac{1}{2}\varepsilon_{c\sigma}(\mathbf{k})] + V^P_{|I-J|}(\tfrac{1}{2}\eta_0 + \eta_I) \tag{48}$$

or

$$\pi_{IJ} = \frac{2V^P_{|I-J|}(1 - \frac{1}{2}\eta_0 - \eta_1)}{\bar{E}_A + 2T_0 - 2V_{\text{sc}} - \varepsilon_{c\sigma}(\mathbf{k})} . \tag{49}$$

Note that π_{IJ} depends on the exact quasiparticle energy $\varepsilon_{c\sigma}(\mathbf{k})$.

The energy of an additional electron in the conduction band or an additional hole in the valence band, i.e., the quasiparticle energy, is given by

$$\begin{aligned} \varepsilon_{n\sigma}(\mathbf{k}) &= \varepsilon_{n\sigma}^{\text{HF}}(\mathbf{k}) + \varepsilon_{n\sigma}^{\text{corr}}(\mathbf{k}) \\ &= \varepsilon_{n\sigma}^{\text{HF}}(\mathbf{k}) + \varepsilon_{n\sigma}^{\pi}(\mathbf{k}) + \varepsilon_{n\sigma}^{\eta}(\mathbf{k}) . \end{aligned} \tag{50}$$

For an extra electron in the conduction band ($n = c$) we obtain finally

$$\varepsilon_{c\sigma}^{\pi}(\mathbf{k}) = -\frac{\Pi_c^2(1 - \frac{1}{2}\eta_0 - \eta_1)}{\bar{E}_A + 2T_0 - 2V_{\text{sc}} - \varepsilon_{c\sigma}(\mathbf{k})} \tag{51}$$

and

$$\varepsilon_{c\sigma}^{\eta}(\mathbf{k}) = -\tfrac{1}{4}(-2V_0^D\eta_0 - 24V_1^D\eta_1) . \tag{52}$$

Here V_1^D is the van der Waals interaction between dipoles (or electron-hole pairs) in neighboring bonds I and J [see Eq. (41)]. Furthermore

$$\begin{aligned} \Pi_c^2 &= 2\sum_{J(\neq I)} (V^P_{|I-J|})^2 \\ &= 2\sum_{J(\neq I)} (\tilde{V}_{A_I A_I A_J B_J} - \tfrac{1}{2}\tilde{V}_{A_I B_J A_J A_I})^2 . \end{aligned} \tag{53}$$

The factor 2 results from the fact that in every bond two electron-hole pairs can be excited. Equations (50)—(52) represent the final result of our correlation energy calculation. In order to calculate the quasiparticle energy of an extra conduction electron these equations have to be solved self-consistently because $\varepsilon_{c\sigma}(\mathbf{k})$ appears in the denominator on the right-hand side of Eq. (51).

The correlation contribution $\varepsilon_{c\sigma}^{\eta}(\mathbf{k})$ describes the *loss* of ground-state correlation energy in the presence of the extra electron. Physically this contribution results from the blocking of two-particle excitations which were possible without the extra electron.[16] It is equal to $-E_{\text{corr}}(N)/4 > 0$, where

$$E_{\text{corr}}(N) = -2V_0^D\eta_0 - 24V_1^D\eta_1 \tag{54}$$

is the ground-state correlation energy per unit cell of the N-particle system which was calculated within the same model in Ref. 17. The factor $\frac{1}{4}$ follows from the fact that there are four bonds in a unit cell. Note that $\varepsilon_{c\sigma}^{\eta}(\mathbf{k})$ is independent of the wave vector $\mathbf{k}$. This is due to the short-range nature of the van der Waals interactions which represent the physical origin of $E_{\text{corr}}(N)$. Because $\varepsilon_{c\sigma}^{\eta}(\mathbf{k})$ is positive it will lead to an upward shift (in energy) of the conduction bands and therefore to an *increase* of the energy gap. Because $V_0^D\eta_0 \cong (U-K)^2/2t_0$,[17] T_0 being the bare hopping matrix element between two hybrids within a bond, the onsite Coulomb interaction U will lead to a larger band gap when only $\varepsilon_{c\sigma}^{\eta}(\mathbf{k})$ is taken into account.

We now come to the interpretation of $\varepsilon_{c\sigma}^{\pi}(\mathbf{k})$ as given by Eq. (51). It describes the energy *gain* due to the interaction energy of the extra electron with the induced polarization cloud (of electron-hole pairs) which follows its motion through the solid. The quantity Π_c^2 in the numerator is the sum of squared polarization matrix elements $V^P_{|I-J|}$. The polarizability of a bond is reduced when ground-state correlations are taken into account. This leads to the prefactor $1 - \eta_0/2 - \eta_1$ which comes physically simply from the fact that it is more difficult to polarize correlated electrons in bonds than uncorrelated ones. In the denominator there appears first the mean HF energy $\bar{E}_A$ of the extra electron [see Eq. (44a)]. The bonding-antibonding splitting $2T_0 = \bar{E}_A - \bar{E}_B$ is the energy required to create a HF electron-hole pair. This energy, however, is reduced by the electron-hole attraction, i.e., the second term in V_{sc}. It should be pointed out that

$$2T_0 - 2V_{\text{sc}} \cong 2t_0^H + V_0^D . \tag{55}$$

From Eq. (6a) we obtain

$$t_0^H \cong t_0 - 2V_{1221} , \tag{56}$$

where 1 and 2 denote the two hybrids of a bond (see Sec. III). In diamond it is $t_0 = 10.7$ eV,[17] and therefore $t_0^H \cong 10.1$ eV. The final energy splitting $2t_0^H + V_0^D$ ($\cong 25$ eV in diamond) entering the denominator is comparable to the experimental bonding-antibonding splitting but much smaller than the HF value $2T_0$($\cong 35$ eV in diamond). This feature demonstrates that in our theory the polarization cloud is built up from interacting (correlated) electron-hole pairs and not from bare HF electron-hole pairs. The last term entering the denominator is the exact quasiparticle energy $\varepsilon_{c\sigma}(\mathbf{k})$. The form of the denominator in Eq. (51) reminds one of self-consistent Brillouin-Wigner perturbation theory.

The calculation which we have performed for the case of an extra electron can be done in a completely analogous way for the case of an extra hole in the valence bands. Instead of Eqs. (51) and (52) we obtain ($n = v$)

$$\varepsilon_{v\sigma}^{\pi}(\mathbf{k}) = -\frac{\Pi_v^2(1 - \frac{1}{2}\eta_0 - \eta_1)}{\bar{E}_B - 2T_0 + 2V_{\text{sc}} - \varepsilon_{v\sigma}(\mathbf{k})} \tag{57}$$

and

$$\varepsilon_{v\sigma}^{\eta}(\mathbf{k}) = \tfrac{1}{4}(-2V_0^D\eta_0 - 24V_1^D\eta_1) . \tag{58}$$

The sum Π_v^2 of the polarization matrix elements squared is given by

$$\Pi_v^2 = 2 \sum_{J(\neq I)} (\tilde{V}_{B_I B_I A_J B_J} - \tfrac{1}{2} \tilde{V}_{B_I B_J A_J B_I})^2 \; . \tag{59}$$

instead of Eq. (53). The sign changes in Eqs. (57) and (58), as compared to Eqs. (51) and (52), are due to the fact that in one case an additional hole in the valence band and in the other case an additional electron in the conduction band were considered.

In principle one can calculate Π_c^2 and Π_v^2, provided all required interaction matrix elements for the bonding and antibonding functions are known. In the following, however, we will neglect the difference between these two quantities and calculate classically $\Pi^2 = \Pi_c^2 = \Pi_v^2$ for a diamond lattice. For that purpose we write for the interaction for an elementary charge in bond 0 with a dipole $\mathbf{p}_R$ in bond R

$$\tilde{V}_R = \tilde{V}_{A_0 A_0 A_R B_R} = \tfrac{1}{2} p_R E_0(R) \cos(\hat{\mathbf{p}}_R \cdot \hat{\mathbf{E}}_0(\mathbf{R})) \; . \tag{60}$$

The dipole $\mathbf{p}_R$ represents the electron-hole pair in bond R. We set $p_R = ep$ where $p = \lambda d$ can be considered as a classical effective dipole length when d denotes the bond length and λ is a yet undetermined parameter. Furthermore, $E_0(R)$ is the size of the electric field generated by the change e at a distance R, i.e., $E_0(R) = e/R^2$. Distances R are measured with respect to the midpoints of the bonds. The (negligible) exchange contributions have no classical analogue. They will be absorbed in the effective dipole length. With the given form for the monopole-dipole interaction $\tilde{V}_R$ one finds

$$\begin{aligned} \Pi^2 &= 2 \sum_{\mathbf{R}(\neq 0)} \tfrac{1}{4} p_R^2 E_0^2(R) \cos^2(\hat{\mathbf{p}}_R \cdot \hat{\mathbf{E}}_0(\mathbf{R})) \\ &= \tfrac{1}{2} e^4 p^2 \gamma \; , \end{aligned} \tag{61}$$

with

$$\gamma = \sum_{\mathbf{R}(\neq 0)} \frac{1}{R^4} \cos^2(\hat{\mathbf{p}}_R \cdot \hat{\mathbf{R}}) \; . \tag{62a}$$

In order to obtain the accurate result

$$\gamma = \frac{13.247}{d^4} \tag{62b}$$

for the diamond lattice it was necessary to include more than 2×10^6 bonds even when convergence acceleration was used. This slow convergence is of course connected with the long-ranged nature of the polarization. The situation is completely different in the ground state. There the electron correlations are short ranged.[17] We finally obtain

$$\Pi^2 = \lambda^2 \frac{1373.4}{d^2} (\text{eV})^2 \quad (d \text{ in Å}) \tag{63}$$

for the diamond lattice.

At this point we wish to comment on possible basis-set effects. The above calculations were done by using a minimal basis set, i.e, by working with sp^3 hybrid functions. If one allows for larger basis sets by including d functions and several different sets of s and p functions, the correlation energy associated with an extra electron (hole) added to the system will change. For example, the polarizability of the bonds will increase and the loss of ground-state correlations will decrease.

Previous investigations of the dielectric function[25] and optical properties[15,26] suggest that basis set effects are not very large and in the 1–2 eV regime. Correlations which cannot be described within a minimal basis set but require a larger one are conventionally called "intra-atomic." In Ref. 17 it was shown how they can be reliably determined for the ground state of an elemental semiconductor. A similar estimate for excited states is more complex but has been done on a molecular level.[27] Instead of trying to carry over these considerations to the present case we take here a more pragmatic point of view. We shall assume that their effect can be incorporated in the quantity λ, for which we have to make an appropriate choice.

VII. NUMERICAL RESULTS

We want to apply the theory to diamond, silicon, germanium and calculate the quasiparticle band structure $\varepsilon_{n\sigma}(\mathbf{k})$ for these materials. According to Eq. (50) $\varepsilon_{n\sigma}(\mathbf{k})$ consists of a HF part and a correlation part. The HF energies $\varepsilon_{n\sigma}^{\text{HF}}(\mathbf{k})$ are taken from the recent HF calculations of von der Linden and Horsch.[28] They are shown for silicon by the dashed lines in Fig. 5. The correlation energies $\varepsilon_{n\sigma}^{\text{corr}}(\mathbf{k})$ are calculated according to Eqs. (51) and (52) and Eqs. (57) and (58) for the conduction bands and valence bands, respectively. By using the *ab initio* HF results and inserting them into the denominators of Eqs. (51) and (57) we go beyond the BOA. The parameters η_0, η_1, and $\varepsilon_{n\sigma}^{\eta}(\mathbf{k}) = E_{\text{corr}}(N)/4$ are taken from the ground-state correlation energy calculations of Ref. 17. The interaction matrix element V_{sc} was calculated according to Eq. (46) with V_0^D from Ref. 17 and assuming a $1/d$ scaling for the Coulomb integral K.

The mean energies $\bar{E}_B$ and $\bar{E}_A$ of the HF valence and conduction bands, respectively, have been chosen to be the mean energies of the HF bands at the X point, e.g.,

$$\bar{E}_B = \tfrac{1}{2} [\varepsilon^{\text{HF}}(X_4) + \varepsilon^{\text{HF}}(X_1)] \; . \tag{64}$$

The zero of the energy is at the top of the HF valence bands. Numerical values were obtained from the HF calculations of Ref. 28.

The sum Π^2 of the polarization matrix elements squared depends sensitively on the parameter λ which determines the effective dipole length $p = \lambda d$ [see Eq. (63)]. As pointed out above, λ is supposed to contain also the effects of intraatomic correlations which are not contained in a minimal basis set. We set $p = a_0/4$, where a_0 is the lattice constant. This implies $\lambda = 3^{-1/2}$. This choice of λ yields sensible results but is, of course, not free of arbitrariness. The same value of p has been used in Ref. 15.

TABLE I. Numerical values for various parameters entering the theory. Energies are given in eV.

	C	Si	Ge
η_0	0.20	0.24	0.25
η_l	0.029	0.030	0.032
$E_{\mathrm{corr}}(N)$	-2.6	-1.6	-1.6
$\overline{E}_A$	21.8	12.8	11.7
$\overline{E}_B$	-13.3	-8.6	-8.3
V_{sc}	8.7	6.2	6.0
λ^2	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$

Numerical results for the parameters which are required for the computation of $\varepsilon^{\pi}_{n\sigma}(\mathbf{k})$ are given in Table I for diamond, silicon and germanium. The calculated correlation energy for diamond is plotted in Fig. 4 as a function of the quasiparticle energy. One notices a considerable energy dependence, which results in a reduction of the band widths as compared with the HF band widths. In agreement with general considerations given in Ref. 29 the correlation energy is found to be larger at the bottom of the valence band than at the top. Because we have neglected the $C_{T\neq T'}$ terms in Eq. (43), the correlation energy depends on the energy only and does not differ for different $\mathbf{k}$ values belonging to the same excitation energy. The discontinuity of the correlation energy across the gap has a simple reason. Due to the dominant correlation contribution, i.e.,the build up of a polarization cloud around an added electron or hole, the ionization energy decreases while the electron affinity increases. Therefore a discontinuity across the gap must exist. The quasiparticle band structures for Si are shown in Fig. 5. They can be compared for example with the ones of Ref. 10.

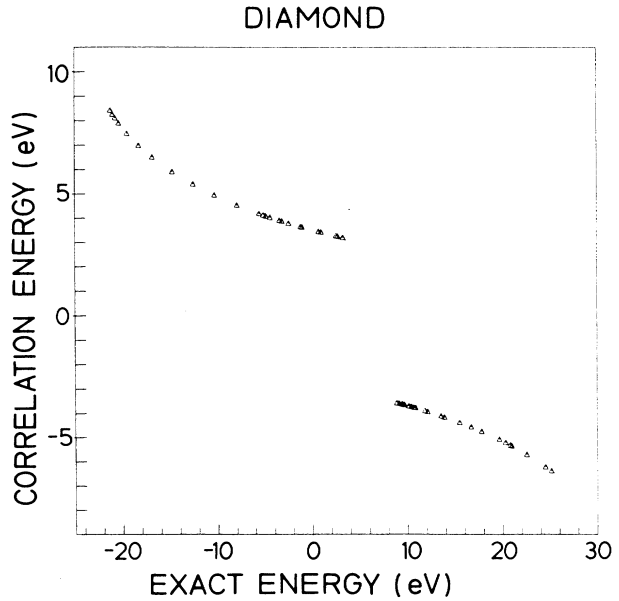

FIG. 4. Correlation contribution to the quasiparticle energy as function of the quasiparticle energy for diamond.

TABLE II. Comparison of the experimental direct gaps and valence-band widths with results from HF calculations and our theory (in eV).

	C	Si	Ge
$W^{\mathrm{HF}}_{\mathrm{val}}$	29.9[a]	18.9[a]	18.2[a]
$E^{\mathrm{HF}}_{\mathrm{gap}}(\Gamma)$	14.2[a]	8.0[a]	5.1[a]
$W^{\mathrm{theor}}_{\mathrm{val}}$	24.6	15.2	14.4
$E^{\mathrm{theor}}_{\mathrm{gap}}(\Gamma)$	7.2	3.0	0.44
$W^{\mathrm{expt}}_{\mathrm{val}}$	24.2 ± 1[b]	12.5 ± 0.6[c] 14.7 ± 0.5	13.0 ± 0.5[d]
$E^{\mathrm{expt}}_{\mathrm{gap}}(r)$	7.4[c]	3.4[c], 3.3[e]	0.9[c]

[a] Reference 28.
[b] Reference 33.
[c] Reference 31.
[d] Reference 30.
[e] Reference 32.

The direct band gaps as well as the valence-band widths for diamond, Si, and Ge are shown in Table II. For comparison also the corresponding HF values and the experimental data are listed. The overall agreement with the experiments is good. One notices that for Si and Ge the calculated gaps are somewhat smaller, while the band widths are somewhat larger than the experimental values. This is due to the omission of the terms $C_{T\neq T'}$ in Eq. (43). These terms introduce an additional $\mathbf{k}$ dependence into the denominators of Eqs. (51) and (57), which has the effect of decreasing the band widths. Since the centers of gravity of the different bands remain unchanged, the gap increases therefore. In any case it is seen how the correlation effects described by the present theory reduce the

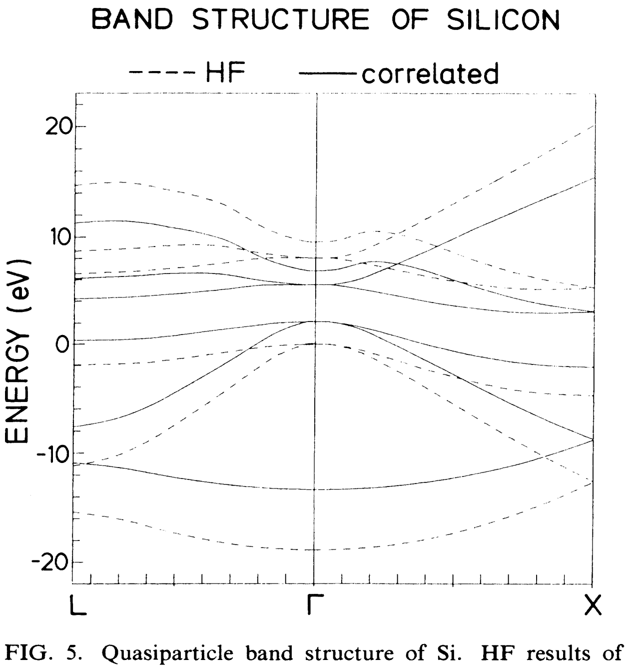

FIG. 5. Quasiparticle band structure of Si. HF results of Ref. 28 are shown by dashed lines. One notices that the correlation energy contribution is larger for the bottom of the valence band than for the top of it.

gaps and band widths from the large HF values to the observed size.

VIII. SUMMARY AND CONCLUSIONS

We have shown that the exchange and correlation contributions to the quasiparticle energies of elemental semiconductors can be computed in a way which makes them very transparent. This was made possible by the use of the bond-orbital approximation. It enabled us to derive simple expressions [see Eqs. (15) and (16)] for the exchange contribution to the quasiparticle energies. The main part of the paper dealt with the discussion of correlation energies. The main part of the paper dealt with the discussion of correlation effects on the quasiparticle band structure. For the calculation of the correlation energy contribution a variational local ansatz was applied. Due to the BOA the correlation-energy calculations could be done analytically. It was pointed out that there are two competing effects of correlations on the quasiparticle energy. One is the *gain* in polarization energy while the other is a *loss* in ground-state correlation energy. The energy gain is of course dominant and results in a reduction of the energy gaps and band widths as compared with the HF values. When plotted against the quasiparticle energy both the exchange energy and correlation energy contributions to the quasiparticle dispersions show a considerable energy dependence and a discontinuity across the band gap. The origin of the discontinuities was pointed out. It is very instructive to add the exchange and correlation energy contributions. Thereby one must take into account that both quantities are calculated with different accuracies. The exchange energy is certainly not very accurate for the conduction bands, but it is reasonably reliable for the valence bands. The correlation energy is based on accurate HF calculations [they enter into Eqs. (51) and (57)] and is quite reliable. One notices that, when the sum of exchange and correlation energy is taken, the energy dependence of the two contributions cancels almost completely for the valence bands. For the conduction bands the cancellation is less good because of the poor accuracy of the exchange part in that regime. Also the discontinuity across the gap cancels to some extent. Therefore the sum of exchange and correlation is only weakly dependent on energy *except* for a discontinuity across the gap. The local density approximation (LDA) to the density functional theory replaces exchange and correlation by an energy *independent* quantity. It neglects therefore the discontinuity across the gap and the remaining energy dependence in the valence- and conduction-band regime. For that reason energy gaps and band widths are inadequately described by the LDA. The present theory gives good insight into which physical processes are responsible for the large HF gaps and band widths and which correlation effects result in their reductions to the experimental values. When one is interested in the energy gap only and not in more detailed quasiparticle dispersions the present theory can be reduced even further (see Ref. 21).

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