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Electronic excitations in semiconductors. General theory

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A general theory is presented that allows for the computation of excitation energies in semiconductors with proper inclusion of electron correlations. It is a natural extension to excited states of a local approach to the electron-correlation problem that has been formulated and tested before for ground-state calculations. The electronic correlations can be treated thereby with the same accuracy as is customary in quantum-chemistry calculations for small molecules. The formulation does not have the shortcomings that prevent conventional quantum-chemistry methods to be carried over to a treatment of delocalized excited states in solids. The theory is formulated in terms of a set of basis functions. Computation of the correlation energy is reduced to the computation of a number of expectation values. They are explicitly evaluated by applying a set of rules which are described in detail. By means of a simple model, special aspects of the correlation problem are discussed, such as electronic polarizations, local-field effects, the dependence of the correlation energy on the energy of the excited electron, and changes in the ground-state correlations due to the presence of the excited electron. It is pointed out that the general theory also contains dynamic relaxation effects.

I. INTRODUCTION

A proper treatment of electron correlations in semiconductors is a challenging problem. This holds true for ground-state as well as excited-state calculations. For the ground state it was demonstrated recently that correlation-energy calculations can be done with an accuracy as is customary in quantum chemistry calculations of small molecules.[1] This was shown by treating diamond as an example.[2] Thereby a local approach to the correlation problem was applied. It had been successfully tested before for small molecules[3] and avoids certain shortcomings of configuration-interaction (CI) methods, which prevent the latter from being applied to, e.g., electrons in excited, delocalized states. It is therefore tempting to also apply the same local approach to excited-state calculations of semiconductors. It is worth recalling briefly some of the earlier developments with respect to that problem. For example, it has been known for a long time that electron correlations have a pronounced effect on the energy gap of a semiconductor. This is easily seen by considering a system in which an extra electron has been added to the ground state. This extra electron will polarize its surroundings. The change in field energy due to the induced dipoles is beyond a self-consistent-field treatment of the energy of the extra electron and therefore a correlation effect. The same holds true when a hole is added to the ground state. Mott and Littleton[4] were among the first to treat this effect assuming that the extra electron (or hole) remains fixed to a bond or site (see also Ref. 5). The additional motion of the extra electron (or hole) was taken into account in the electronic polaron model of Toyozawa[6] and further developed by, e.g., Fowler,[7] Inone *et al.*,[8] and Kunz.[9] An alternate description of electron correlations was given by Hermanson[10] in terms of a plasmon model. The screened exchange plus Coulomb-hole approximation by Hedin[11] has been applied to insulators by Brener[12] using a momentum-dependent but static dielectric function.

These treatments also strongly suggest that a proper treatment of *short-range* correlations is of importance for an accurate determination of the excitation energy. To these belong local-field effects[13–15] but also orbital relaxation effects, which occur when an electron is added to a bond. The former have been treated most extensively by Hanke and co-workers using Green's-function techniques[16] but only within a minimal basis set. Relaxation effects require a larger basis set and have been discussed, e.g., by Pantelides *et al.*,[17] by means of perturbational methods in the spirit of CI. In particular, the short-range part of the electron correlation hole suggests a treatment by means of a method that can be applied not only to solids but to small molecules as well. This should allow for reliable checks concerning the accuracy of any approximations made, since in small molecules short-range correlations are well understood.

In applying the above-mentioned local approach we shall consider the case of an extra electron (or hole) added to the ground state. This implies that we do not consider excitonic effects that result from an interaction of the excited electron with its hole. This is planned to be the subject of a separate investigation. Instead we assume here that the exciton is in its "ionized" state with the electron and hole well separated. The present paper contains the general formalism for calculating the energy and wave function of semiconductors with an extra electron in the conduction band. The paper is organized as follows. In the next section a formulation of the Hamiltonian and various quantities such as the ground-state wave function and energy is given in terms of a basis set that usually consists of Gaussian-type orbitals. Section III describes the wave function and energy when an extra electron is added to the conduction band. The correlation energy is expressed in terms of certain expectation values. The rules for their evaluation are given in Sec. IV. Section V contains the application of the formalism to a simple model. It allows for a physical interpretation of the various contributions to the correlation energy, which is useful when the theory is applied to diamond. In particular, it is seen that the polarization effects mentioned above are contained in the formalism, as well as effects resulting from the motion of the extra electron and changes in the types of correlations that are present in the ground state. Relaxation effects are contained in the general formalism but not in the simple model. Finally, Sec. VI contains the discussions and conclusions.

II. GROUND-STATE WAVE FUNCTION AND ENERGY

We start out by defining a basis set $f_i(\vec{r})$ in terms of which all calculations will be done. We assume that the $f_i(\vec{r})$ represent $\bar{N}$ groups of Gaussian-type orbitals centered at different atoms. When the single-electron field operators $\Psi_\sigma(\vec{r})$ are expanded in terms of this basis set new operators $a_{i\sigma}$ defined by

$$\Psi_\sigma(\vec{r}) = \sum_i a_{i\sigma} f_i(\vec{r}) \ . \tag{1}$$

Here σ denotes the spin of the electron. Similarly, an expansion of $\Psi^\dagger_\sigma(\vec{r})$ defines operators $a^\dagger_{i\sigma}$. The $a_{i\sigma}, a^\dagger_{i\sigma}$ fulfill the following anticommutation relations:

$$[a_{i\sigma}, a^\dagger_{j\sigma'}]_+ = S^{-1}_{ij}\delta_{\sigma\sigma'} \ , \tag{2}$$

where S_{ij} is the overlap matrix

$$\langle f_i \,|\, f_j \rangle = S_{ij} \ . \tag{3}$$

The Hamiltonian is then written within the Hilbert space spanned by the $f_i(\vec{r})$ and takes the form

$$H = \sum_{i,j,\sigma} \epsilon_{ij} a^\dagger_{i\sigma} a_{j\sigma} + \frac{1}{2} \sum_{i,j,k,l,\sigma,\sigma'} V_{ijkl} a^\dagger_{i\sigma} a^\dagger_{k\sigma'} a_{l\sigma'} a_{j\sigma} \ . \tag{4}$$

Here the ϵ_{ij} and V_{ijkl} are defined through

$$\begin{aligned} \epsilon_{ij} &= \int d^3r\, f^*_i(\vec{r})[-\tfrac{1}{2}\Delta + V(\vec{r})] f_j(\vec{r}) \ , \\ V_{ijkl} &= \int d^3r\, d^3r'\, f^*_i(\vec{r}) f_j(\vec{r}) \frac{1}{|\vec{r}-\vec{r}\,'|} \\ &\quad \times f^*_k(\vec{r}\,') f_l(\vec{r}\,') \ . \end{aligned} \tag{5}$$

Atomic units have been used for convenience, i.e., $m=e=\hbar=1$. $V(\vec{r})$ is the single-electron potential due to the nuclei. Since we are considering crystals, we assume that the index i involves both a cell index $\vec{i}$ and an index α for different functions within the unit cell, i.e., $i=(\vec{i},\alpha)$. The same applies for the indices j,k,l.

A prerequisite for the correlation-energy calculations is a knowledge of the self-consistent-field (SCF) ground-state wave function $|\Phi_{\text{SCF}}\rangle$ and energy. For that reason we divide H into a SCF part H_0 and a residual interaction part H_{res}, i.e.,

$$H = H_0 + H_{\text{res}} \ , \tag{6}$$

with

$$H_0 = \sum_{i,j,\sigma} f_{ij} a^\dagger_{i\sigma} a_{j\sigma} \ , \tag{7}$$

where f_{ij} denotes the Fock matrix

$$f_{ij} = \epsilon_{ij} + \sum_{k,l,\sigma'} (V_{ijkl} - \tfrac{1}{2} V_{ilkj}) \langle a^\dagger_{k\sigma'} a_{l\sigma'} \rangle \ , \tag{8}$$

and

$$\begin{aligned} H_{\text{res}} = \frac{1}{2} &\sum_{i,j,k,l,\sigma,\sigma'} V_{ijkl} a^\dagger_{i\sigma} a^\dagger_{k\sigma'} a_{l\sigma'} a_{j\sigma} \\ &- \sum_{i,j,k,l,\sigma,\sigma'} (V_{ijkl} - \delta_{\sigma\sigma'} V_{ilkj}) \langle a^\dagger_{k\sigma'} a_{l\sigma'} \rangle a^\dagger_{i\sigma} a_{j\sigma} \ . \end{aligned} \tag{9}$$

The matrix $\langle a^\dagger_{k\sigma'} a_{l\sigma'} \rangle$ is the one-particle density matrix. Hereby the notation $\langle \ \rangle$ is an abbreviation for $\langle \Phi_{\text{SCF}} | (\ ) | \Phi_{\text{SCF}} \rangle$, which will be used frequently. The second term on the right-hand side (rhs) of Eq. (9) has the effect that it excludes contractions within H_{res} when expectation values are calculated that involve H_{res}.

The SCF ground-state energy per unit cell, E_{SCF}, is given by

$$E_{\text{SCF}} = \frac{1}{2} \sum_{[i],j,\sigma} (\epsilon_{ij} + f_{ij}) \langle a^\dagger_{i\sigma} a_{j\sigma} \rangle + E_{NN} \ . \tag{10}$$

The notation $[i]$ indicates that the summation is over α only, i.e., $\vec{i}$ is kept fixed. The interaction energy E_{NN} per unit cell between nuclei has been added in order to obtain finite results for the energy when the system becomes infinitely large.

For treatment of electron correlations we introduce another set of local functions $g_m(\vec{r})$ that are defined through

$$g_m(\vec{r}) = \sum_{j=1}^{\bar{N}} \gamma_{mj} f_j(\vec{r}) \ . \tag{11}$$

Again, m stands for $(\vec{m},\mu)$ where $\vec{m}$ denotes different unit cells and μ labels different functions within a given cell.

We want to define creation and annihilation operators for electrons in state $g_m(\vec{r})$ and denote them by $b^\dagger_{m\sigma}$ and $b_{m\sigma}$, respectively. For that purpose we introduce creation and annihilation operators $\hat{a}^\dagger_{i\sigma}, \hat{a}_{i\sigma}$ for electrons in states $f_i(\vec{r})$. The $\hat{a}_{i\sigma}$ are the adjoint operators of the $a_{i\sigma}$ and obey the following anticommutation relations[3,18]:

$$[\hat{a}_{i\sigma}, a^\dagger_{j\sigma'}]_+ = \delta_{ij}\delta_{\sigma\sigma'} \ . \tag{12}$$

The $b^\dagger_{m\sigma}$ are related to the $\hat{a}^\dagger_{j\sigma}$ according to Eq. (11) through

$$b^\dagger_{m\sigma} = \sum_{j=1}^{\bar{N}} \gamma_{mj} \hat{a}^\dagger_{j\sigma} \ . \tag{13}$$

With $b^\dagger_{m\sigma}$ and $b_{m\sigma}$ one can construct density operators $n_{m\sigma}$ and spin operators $\vec{s}_m$,

$$\begin{aligned} n_{m\sigma} &= b^\dagger_{m\sigma} b_{m\sigma} \ , \\ (\vec{s}_m)_{\sigma\sigma'} &= b^\dagger_{m\sigma} \vec{s}_{\sigma\sigma'} b_{m\sigma} \ , \end{aligned} \tag{14}$$

which will be used later. The matrices $\vec{s}_{\sigma\sigma'}$ equal $\frac{1}{2}$ times the Pauli matrices. In a series of papers[2,3] it has been shown how the ground-state wave function $|\Psi_0\rangle$ of a correlated electron system can be constructed in terms of these density and spin-density operators. We set

$$|\Psi_0\rangle = \exp\left[-\sum_{m,n} \eta_{mn}^{(0)} O_{mn}\right] |\Phi_{\text{SCF}}\rangle$$

$$= \exp(S_0)\,|\Phi_{\text{SCF}}\rangle \;. \tag{15}$$

The operators O_{mn} are written as

$$O_{mn} = O'_{mn} - \langle O'_{mn} \rangle \;, \tag{16}$$

where the O'_{mn} are of the following three forms:

$$O'_{mn} = \begin{cases} n_{m\uparrow} n_{m\downarrow} \delta_{mn} & \text{(17a)} \\ n_m n_n = \sum\limits_{\sigma} n_{m\sigma} \sum\limits_{\sigma'} n_{n\sigma'} & \text{(17b)} \\ \vec{s}_m \cdot \vec{s}_n \;. & \text{(17c)} \end{cases}$$

The operator O_{mn} [Eq. (16)] when applied on $|\Phi_{\text{SCF}}\rangle$ creates one- and two-particle excitations on top of the SCF ground state. For simplicity we neglect single-particle excitations in the following by excluding contractions within O_{mn} when expectation values of matrix elements are formed. The justification is that single-particle excitations do not couple to the SCF ground state directly according to Brillouin's theorem but only indirectly via the two-particle excitations, i.e., correlation effects. The readjustment of the single-particle eigenstates due to correlations is expected to be reasonably small in covalent semiconductors, however. The inclusion of the one-particle excitations is straightforward and would lead only to minor modifications.

When applied on $|\Phi_{\text{SCF}}\rangle$ the operator O_{mn} selects those states in which electrons are simultaneously present in the local states $g_{m\sigma}(\vec{r})$ and $g_{n\sigma'}(\vec{r})$, respectively. By means of the prefactor

$$\exp\left[-\sum_{m,n} \eta_{mn}^{(0)} O_{mn}\right]$$

these states obtain a different weight than they have in $|\Phi_{\text{SCF}}\rangle$. In this way a correlation hole is generated around each electron. The proper choice of the functions $g_{m\sigma}(\vec{r})$ is essential for the present method. It has been described in detail, e.g., in Ref. 2, with particular reference to diamond.

We point out that in Refs. 2 and 3 instead of Eq. (15) the following ansatz for $|\Psi_0\rangle$ has been used:

$$|\Psi_0\rangle = \prod_{m,n} (1 - \eta_{mn}^{(0)} O_{mn})\, |\Phi_{\text{SCF}}\rangle \;. \tag{18}$$

Within the approximations described later when calculating the energy E from $|\Psi_0\rangle$, both forms, i.e., (15) and (18), lead to the same results. We shall use the form (15) in the following since it has a number of advantages, as we will see.

The $\eta_{mn}^{(0)}$ parameters are determined by minimizing the energy

$$E^0 = \langle \Psi_0 | H | \Psi_0 \rangle \langle \Psi_0 | \Psi_0 \rangle^{-1} \;.$$

According to a linked-cluster theorem (see Ref. 18) one can also write $E^0 = \langle e^{S_0} H e^{S_0} \rangle_c$, where the subscript c implies taking into account only connected contractions (see Appendix A). This expression is evaluated by approximating $\exp(S_0) = 1 + S_0$ and expanding E^0 to second order in $\eta_{mn}^{(0)}$. This results in

$$E^0 = \langle H \rangle - 2 \sum_{m,n} \eta_{mn}^{(0)} \langle O_{mn} H \rangle_c$$

$$+ \sum_{m,n} \sum_{m',n'} \eta_{mn}^{(0)} \eta_{m'n'}^{(0)} \langle O_{mn} H O_{m'n'} \rangle_c \;. \tag{19}$$

Owing to this expansion, one no longer obtains an upper bound for the energy when minimizing Eq. (19). The expansion corresponds in quantum chemistry to a perturbation calculation within a coupled-cluster ansatz and is called CEPA-0 (see Ref. 19). The approximation (19) limits us to electronic systems that are not too strongly correlated.

III. EXCITED-STATE WAVE FUNCTION AND ENERGY

We start out from a semiconductor in its SCF ground state $|\Phi_{\text{SCF}}\rangle$. When an electron is moved from a valence-band to a conduction-band state the SCF excited state is

$$|\Phi_{\text{ex}}(\vec{k},b;\vec{k}',b')\rangle = c^{\dagger}_{\vec{k}b\sigma} c_{\vec{k}'b'\sigma} |\Phi_{\text{SCF}}\rangle \;. \tag{20}$$

Here $c_{\vec{k}'b'\sigma}$ annihilates an electron in the valence-band Bloch state $\phi_{\vec{k}'b'\sigma}(\vec{r})$ of momentum $\vec{k}'$, band index b', and spin σ, while $c^{\dagger}_{\vec{k}b\sigma}$ creates an electron in a conduction-band Bloch state. For a zinc-blende-type lattice with two atoms per unit cell we shall label the four conduction bands by $b = 1, \ldots, 4$ and the four valence bands by $b = 5, \ldots, 8$.

When one neglects the interaction of the electron in the conduction band with its hole in the valence band, i.e., excitonic effects, then one can consider separately the case of an added electron and an added hole, respectively. One writes then

$$|\Phi_{\sigma}^{(e)}(\vec{k},b)\rangle = c^{\dagger}_{\vec{k}b\sigma} |\Phi_{\text{SCF}}\rangle, \quad b = 1, \ldots, 4 \tag{21a}$$

and

$$|\Phi_{0}^{(h)}(\vec{k},b)\rangle = c_{\vec{k}b\sigma} |\Phi_{\text{SCF}}\rangle, \quad b = 5, \ldots, 8 \;. \tag{21b}$$

We shall leave a discussion of excitonic effects to a future investigation and consider in the following the case of an added electron or hole only. By starting from the SCF state [Eq. (21a) or (21b)], we want to construct the correlated or many-body wave function and calculate the corresponding energy. This will enable us to determine the excitation energy and in particular the energy gap of a semiconductor. In the following it will turn out to be advantageous to work with localized Wannier functions instead of delocalized Bloch functions. Therefore we express the latter in terms of the former. For that purpose we divide the lattice into N_c unit cells where each cell $\vec{t}$ is characterized by a lattice vector $\vec{R}_{\vec{t}}$. For each unit cell one can construct a number of localized Wannier functions $\phi_\tau(\vec{r}-\vec{R}_{\vec{t}})$. For example, for a zinc-blende or a diamond structure there are eight Wannier functions $(\tau=1,\ldots,8)$ corresponding to the eight conduction and valence bands. There are different ways in which one can choose the Wannier functions. One way is to have them centered in a bond. In that case the eight functions are bonding and antibonding wave functions belonging to the four bonds of a unit cell. The bonding functions can be ascribed to the four valence bands, while the antibonding functions can be ascribed to the four conduction bands. Another possibility is to choose the Wannier functions so that they reflect the point symmetry of the lattice sites. Then they cannot be separated into two groups belonging to the conduction and the valence bands, respectively. In the following we will assume that we are dealing with Wannier functions that are centered in a bond. Let $w_{t\sigma}^\dagger$ denote the creation operator for an electron in the Wannier state $\phi_\tau(\vec{r}-\vec{R}_{\vec{t}})$ where $t=(\vec{t},\tau)$ includes the cell index $\vec{t}$ as well as the index τ within a cell. Then the following relation holds:

$$c_{\vec{k}b\sigma}^\dagger=N_c^{-1/2}\sum_t e_\tau(\vec{k},b)w_{t\sigma}^\dagger\exp(i\vec{k}\cdot\vec{R}_{\vec{t}}) \ . \tag{22}$$

The matrix $e_\tau(\vec{k},b)$ provides the connection between Bloch and Wannier states and depends on the particular choice of the Wannier functions. It is unitary and fulfills the relations

$$\begin{aligned}&\sum_\tau e_\tau^*(\vec{k},b)e_\tau(\vec{k},b')=\delta_{bb'} \ ,\\ &\sum_b e_\tau^*(\vec{k},b)e_{\tau'}(\vec{k},b)=\delta_{\tau\tau'} \ .\end{aligned} \tag{23}$$

Within the SCF approximation the energy of the extra electron in conduction-band state $\phi_{\vec{k}b\sigma}(\vec{r})$ $(b=1,\ldots,4)$ is given by

$$\epsilon_{\mathrm{SCF}}(\vec{k},b)=N_c^{-1}\sum_{t,t'}G_{tt'}(\vec{k},b)F_{tt'} \ . \tag{24}$$

The function

$$G_{tt'}(\vec{k},b)=e_\tau^*(\vec{k},b)e_{\tau'}(\vec{k},b)\exp[i\vec{k}\cdot(\vec{R}_{\vec{t}'}-\vec{R}_{\vec{t}})] \tag{25}$$

results from the transformation (22), while

$$F_{tt'}=\langle 0\,|\,w_{t\sigma}H_0w_{t'\sigma}^\dagger\,|\,0\rangle \tag{26}$$

is the Fock matrix in the Wannier representation. $|\,0\rangle$ denotes the vacuum state. Owing to the exponential falloff of the Wannier functions, only functions in the close neighborhood of each other contribute to the Fock matrix. For that reason a relatively small number of independent Fock matrix elements is usually sufficient in order to describe the energy bands of a semiconductor within the SCF approximation. For example, in the case of diamond the inclusion of bonds up to the third-nearest neighbor turns out to be sufficient. We are now in the position to state the ansatz for the correlated wave function $|\,\Psi_\sigma(\vec{k},b)\rangle\rangle$ when an electron $(b=1,\ldots,4)$ or hole $(b=5,\ldots,8)$ is added to the ground state. For simplicity we consider the first case only. We write

$$|\,\Psi_\sigma(\vec{k},b)\rangle\rangle=e^S c_{\vec{k}b\sigma}^\dagger\,|\,\Phi_{\mathrm{SCF}}\rangle \ . \tag{27}$$

The operator S is of the form

$$S=-\sum_{m,n}[\eta_{mn}^{(0)}O_{mn}P_{mn}(\vec{k},b)+\eta_{mn}^{(e)}O_{mn}Q_{mn}(\vec{k},b)] \ , \tag{28}$$

with

$$P_{mn}(\vec{k},b)+Q_{mn}(\vec{k},b)=1 \ . \tag{29}$$

The operators O_{mn} are the same as those used for the ground state in Eq. (15). The projection operators $P_{mn}(\vec{k},b)$ and $Q_{mn}(\vec{k},b)$ are defined according to

$$\begin{aligned}&[O_{mn}P_{mn}(\vec{k},b),c_{\vec{k}b\sigma}^\dagger]=0 \ ,\\ &O_{mn}Q_{mn}(\vec{k},b)\,|\,\Phi_{\mathrm{SCF}}\rangle=0 \ .\end{aligned} \tag{30}$$

Here the operator $O_{mn}P_{mn}(\vec{k},b)$ denotes the part of the operator O_{mn} that generates the correlated ground state. This operator commutes with $c_{\vec{k}b\sigma}^\dagger$:

$$O_{mn}P_{mn}(\vec{k},b)c_{\vec{k}b\sigma}^\dagger\,|\,\Phi_{\mathrm{SCF}}\rangle=c_{\vec{k}b\sigma}^\dagger O_{mn}\,|\,\Phi_{\mathrm{SCF}}\rangle \ , \tag{31}$$

which follows from Eqs. (29) and (30). The parameters $\eta_{mn}^{(0)}$ associated with $O_{mn}P_{mn}(\vec{k},b)$ agree with those determined for the correlated ground state according to Eq. (19). The second operator $O_{mn}Q_{mn}(\vec{k},b)$, which does not commute with $c_{\vec{k}b\sigma}^\dagger$, describes the scattering of the added particle. Physically its role is to create a polarization and relaxation cloud around the extra electron characterized by the second set of variational parameters $\eta_{mn}^{(e)}$. In the following we need not write down explicit expressions for the operators $P_{mn}(\vec{k},b)$ and $Q_{mn}(\vec{k},b)$. Instead, when evaluating matrix elements containing $O_{mn}P_{mn}(\vec{k},b)$ we apply the rule that there is no contraction formed between the operators O_{mn} and $c_{\vec{k}b\sigma}^\dagger$, whereas in the case of $O_{mn}Q_{mn}(\vec{k},b)$ there is always such a contraction formed. This rule is equivalent to the conditions (29) and (30).

The total energy of the $(N+1)$-particle system is given by

$$E_{N+1}=\frac{\langle\Psi_\sigma(\vec{k},b)\,|\,H\,|\,\Psi_\sigma(\vec{k},b)\rangle}{\langle\Psi_\sigma(\vec{k},b)\,|\,\Psi_\sigma(\vec{k},b)\rangle} \ . \tag{32}$$

This expression can be split into two terms by making use of the linked-cluster expansion derived in Appendix A,

$$E_{N+1}=\epsilon(\vec{k},b)+E_N^0 \ , \tag{33}$$

where

$$\epsilon(\vec{\mathrm{k}},b)=\frac{\langle c_{\vec{\mathrm{k}}b\sigma}e^{S^\dagger}He^{S}c^\dagger_{\vec{\mathrm{k}}b\sigma}\rangle_c}{\langle c_{\vec{\mathrm{k}}b\sigma}e^{S^\dagger}e^{S}c^\dagger_{\vec{\mathrm{k}}b\sigma}\rangle_c}\,, \tag{34}$$

$$E_N^0=\langle e^{S^\dagger}He^{S}\rangle_c\,. \tag{35}$$

The form of Eq. (33) shows that $\epsilon(\vec{\mathrm{k}},b)$ plays the role of a quasiparticle energy. When we set $\exp(S)=1+S$, Eq. (35) becomes identical to Eq. (19). This follows from the fact that $O_{mn}Q_{mn}\mid\Phi_{\mathrm{SCF}}\rangle=0$. The $\epsilon(\vec{\mathrm{k}},b)$ in Eq. (33) results from processes that involve the extra electron $c^\dagger_{\vec{\mathrm{k}}b\sigma}$ and depends on both parameter sets $\eta^{(0)}_{mn}$ and $\eta^{(e)}_{mn}$. The parameters η^{κ}_{mn} with $\kappa=0,e$ must be chosen in such a way that $\partial E_{N+1}/\partial\eta^{\kappa}_{mn}=0$. This implies

$$\frac{\partial\epsilon(\vec{\mathrm{k}},b)}{\partial\eta^{\kappa}_{mn}}+\delta_{\kappa,0}\frac{\partial E_N^0}{\partial\eta^{(0)}_{mn}}=0\,. \tag{36}$$

From this equation it is seen that it is well justified to choose in Eq. (28) the same $\eta^{(0)}_{mn}$, as they follow from Eq. (19). The energy E_N^0 is proportional to the total electron number N, while $\epsilon(\vec{\mathrm{k}},b)$ corresponds to a single electron. Therefore the $\eta^{(0)}_{mn}$ are determined from $\partial E_N^0/\partial\eta^{(0)}_{mn}=0$ as in a ground-state calculation.

The contributions of the correlations to the quasiparticle energy are given by

$$\epsilon_{\mathrm{corr}}(\vec{\mathrm{k}},b)=\epsilon(\vec{\mathrm{k}},b)-\epsilon_{\mathrm{SCF}}(\vec{\mathrm{k}},b)\,, \tag{37}$$

where

$$\epsilon_{\mathrm{SCF}}(\vec{\mathrm{k}},b)=\langle c_{\vec{\mathrm{k}}b\sigma}Hc^\dagger_{\vec{\mathrm{k}}b\sigma}\rangle-\langle H\rangle\,.$$

Replacing e^S by $1+S$ in Eq. (34) we can write for the correlation energy

$$\begin{aligned}\epsilon_{\mathrm{corr}}(\vec{\mathrm{k}},b)=[&\langle c_{\vec{\mathrm{k}}b\sigma}(S^\dagger H+HS+S^\dagger HS)c^\dagger_{\vec{\mathrm{k}}b\sigma}\rangle_c\\&-\epsilon_{\mathrm{SCF}}(\vec{\mathrm{k}},b)\langle c_{\vec{\mathrm{k}}b\sigma}S^\dagger Sc^\dagger_{\vec{\mathrm{k}}b\sigma}\rangle_c]\\&\times(1+\langle c_{\vec{\mathrm{k}}b\sigma}S^\dagger Sc^\dagger_{\vec{\mathrm{k}}b\sigma}\rangle_c)^{-1}\,.\end{aligned} \tag{38}$$

In the next step we express the Bloch operators $c^\dagger_{\vec{\mathrm{k}}b\sigma}$ in terms of Wannier operators $w^\dagger_{t\sigma}$ [see Eqs. (22) and (25)]. This enables us to express all quantities in terms of matrix elements of local operators. For convenience we introduce $O^{(\kappa)}_{mn}$ ($\kappa=0,e$) where $O^{(0)}_{mn}=O_{mn}P_{mn}$ and $O^{(e)}_{mn}=O_{mn}Q_{mn}$. Furthermore, we show in the following explicitly the $\vec{\mathrm{k}}$ and b dependence of the parameters η^{κ}_{mn}. Thus

$$\begin{aligned}\epsilon_{\mathrm{corr}}(\vec{\mathrm{k}},b)=\Bigg[N_c^{-1}\sum_{t,t'}G_{tt'}(\vec{\mathrm{k}},b)\Bigg[&-2\sum_{m,n,\kappa}\eta^{\kappa}_{mn}(\vec{\mathrm{k}},b)\langle w_{t'\sigma}HO^{(\kappa)}_{mn}w^\dagger_{t\sigma}\rangle_c\\&+\sum_{m,n,\kappa}\sum_{m',n',\kappa'}\eta^{\kappa}_{mn}(\vec{\mathrm{k}},b)\eta^{\kappa'}_{m'n'}(\vec{\mathrm{k}},b)[\langle w_{t'\sigma}O^{(\kappa')\dagger}_{m'n'}HO^{(\kappa)}_{mn}w^\dagger_{t\sigma}\rangle_c\\&-\epsilon_{\mathrm{SCF}}(\vec{\mathrm{k}},b)\langle w_{t'\sigma}O^{(\kappa')\dagger}_{m'n'}O^{(\kappa)}_{mn}w^\dagger_{t\sigma}\rangle_c]\Bigg]\Bigg]\\\times\Bigg[N_c^{-1}\sum_{tt'}G_{tt'}(\vec{\mathrm{k}},b)\Bigg[1+\sum_{m,n,\kappa}\sum_{m',n',\kappa'}&\eta^{\kappa}_{mn}(\vec{\mathrm{k}},b)\eta^{\kappa'}_{m'n'}(\vec{\mathrm{k}},b)\langle w_{t'\sigma}O^{(\kappa')\dagger}_{m'n'}O^{(\kappa)}_{mn}w^\dagger_{t\sigma}\rangle_c\Bigg]\Bigg]^{-1}\,.\end{aligned} \tag{39}$$

It is worth pointing out that this expression can be written as

$$\epsilon_{\mathrm{corr}}(\vec{\mathrm{k}},b)=N_c^{-1}\sum_{t,t'}G_{tt'}(\vec{\mathrm{k}},b)\delta F_{tt'}(\vec{\mathrm{k}},b)\,, \tag{40}$$

indicating that the correlations can be considered as giving rise to a supplement to the Fock matrix [see Eq. (24)].

The evaluation of the matrix elements appearing in Eq. (39) is discussed in detail in Sec. IV. They depend neither on $\vec{\mathrm{k}}$ nor on b and need to be evaluated only once.

In order to compute $\epsilon_{\mathrm{corr}}(\vec{\mathrm{k}},b)$ for a given $\vec{\mathrm{k}}$ point we transform the local matrix elements of Eq. (39) into a Bloch basis, i.e.,

$$(HO^{(\kappa)}_{mn})_{\vec{\mathrm{k}}b}=N_c^{-1}\sum_{t,t'}G_{tt'}(\vec{\mathrm{k}},b)\langle w_{t'\sigma}HO^{(\kappa)}_{mn}w^\dagger_{t\sigma}\rangle_c\,, \tag{41a}$$

$$(O^{(\kappa')\dagger}_{m'n'}[H-\epsilon_{\mathrm{SCF}}(\vec{\mathrm{k}},b)]O^{(\kappa)}_{mn})_{\vec{\mathrm{k}}b}=N_c^{-1}\sum_{t,t'}G_{tt'}(\vec{\mathrm{k}},b)\langle w_{t'\sigma}O^{(\kappa')\dagger}_{m'n'}[H-\epsilon_{\mathrm{SCF}}(\vec{\mathrm{k}},b)]O^{(\kappa)}_{mn}w^\dagger_{t\sigma}\rangle_c\,, \tag{41b}$$

$$(O^{(\kappa')\dagger}_{m'n'}O^{(\kappa)}_{mn})_{\vec{\mathrm{k}}b}=N_c^{-1}\sum_{t,t'}G_{tt'}(\vec{\mathrm{k}},b)\langle w_{t'\sigma}O^{(\kappa')\dagger}_{m'n'}O^{(\kappa)}_{mn}w^\dagger_{t\sigma}\rangle_c\,. \tag{41c}$$

Equation (39) is then rewritten as

$$\epsilon_{\mathrm{corr}}(\vec{\mathrm{k}},b)=D^{-1}\Bigg[-2\sum_{m,n,\kappa}\eta^{\kappa}_{mn}(\vec{\mathrm{k}},b)(HO^{(\kappa)}_{mn})_{\vec{\mathrm{k}}b}+\sum_{m,n,\kappa}\sum_{m',n',\kappa'}\eta^{\kappa}_{mn}(\vec{\mathrm{k}},b)\eta^{\kappa'}_{m'n'}(\vec{\mathrm{k}},b)(O^{(\kappa')\dagger}_{m'n'}[H-\epsilon_{\mathrm{SCF}}(\vec{\mathrm{k}},b)]O^{(\kappa)}_{mn})_{\vec{\mathrm{k}}b}\Bigg]\,, \tag{42}$$

where

$$D=1+\sum_{m,n,\kappa}\sum_{m',n',\kappa'}\eta^{\kappa}_{mn}(\vec{k},b)\eta^{\kappa'}_{m'n'}(\vec{k},b)(O^{(\kappa')\dagger}_{m'n'}O^{(\kappa)}_{mn})_{\vec{k}b}\ . \tag{43}$$

By making use of the condition (36), one can rewrite $\epsilon_{\text{corr}}(\vec{k},b)$ in a more condensed form as

$$\epsilon_{\text{corr}}(\vec{k},b)=\epsilon^{(0)}_{\text{corr}}(\vec{k},b)+\epsilon^{(e)}_{\text{corr}}(\vec{k},b)\ , \tag{44}$$

where

$$\epsilon^{(0)}_{\text{corr}}(\vec{k},b)=-\sum_{m,n}\eta^{(0)}_{mn}(HO^{(0)}_{mn})_{\vec{k}b}+\frac{D}{2}\sum_{m,n}\frac{\partial\epsilon_{\text{corr}}(\vec{k},b)}{\partial\eta^{(0)}_{mn}}\eta^{(0)}_{mn}\ , \tag{45a}$$

$$\epsilon^{(e)}_{\text{corr}}(\vec{k},b)=-\sum_{m,n}\eta^{(e)}_{mn}(HO^{(e)}_{mn})_{\vec{k}b}\ . \tag{45b}$$

The term $\epsilon^{(0)}_{\text{corr}}(\vec{k},b)$ describes the contributions to the correlation energy from changes in the ground-state correlations when the additional quasiparticle is present. The second term $\epsilon^{(e)}_{\text{corr}}(\vec{k},b)$ contains the energy changes due to polarization, relaxation, etc., caused by that quasiparticle. As pointed out before, the parameter set $\eta^{(e)}_{mn}$ must be calculated from Eq. (36) while the $\eta^{(0)}_{mn}$ are known from the ground-state calculations. With the form (42) for $\epsilon_{\text{corr}}(\vec{k},b)$ one obtains from Eq. (36)

$$-(HO^{(e)}_{mn})_{\vec{k}b}+\sum_{m',n',\kappa'}\eta^{\kappa'}_{m'n'}\{(O^{(\kappa')\dagger}_{m'n'}[H-\epsilon_{\text{SCF}}(\vec{k},b)]O^{(e)}_{mn})_{\vec{k}b}-\epsilon_{\text{corr}}(\vec{k},b)(O^{(\kappa')\dagger}_{m'n'}O^{(e)}_{mn})_{\vec{k}b}]=0\ . \tag{46}$$

Here the expression containing $\epsilon_{\text{corr}}(\vec{k},b)$ is due to the presence of the denominator D in (42). Hence the above equation depends on

$$\epsilon(\vec{k},b)=\epsilon_{\text{SCF}}(\vec{k},b)+\epsilon_{\text{corr}}(\vec{k},b)\ , \tag{47}$$

that is, the self-consistently determined quasiparticle energy, and not merely on the SCF energy. Thus Eq. (46) can be rewritten as

$$-(HO^{(e)}_{mn})_{\vec{k}b}+\sum_{m',n',\kappa'}\eta^{\kappa'}_{m'n'}(O^{(\kappa')\dagger}_{m'n'}[H-\epsilon(\vec{k},b)]O^{(e)}_{mn})_{\vec{k}b}=0\ . \tag{48}$$

Since the ground-state parameters $\eta^{(0)}_{m'n'}$ are known, one obtains by inversion

$$\eta^{(e)}_{mn}(\vec{k},b)=\sum_{m',n'}\left[(HO^{(e)}_{m'n'})_{\vec{k}b}-\sum_{m'',n''}\eta^{(0)}_{m''n''}(O^{(0)\dagger}_{m''n''}[H-\epsilon(\vec{k},b)]O^{(e)}_{m'n'})_{\vec{k}b}\right]\{(O^{(e)\dagger}_{i'j'}[H-\epsilon(\vec{k},b)]O^{(e)}_{ij})_{\vec{k}b}\}^{-1}{}_{m'n';mn}\ . \tag{49}$$

The first term on the rhs is due to the polarization cloud as well as the relaxation around the electron in the conduction band, while the second term takes into account the influence of the ground-state correlations on the former.

In Eq. (49) the pairs of variables m,n and m',n' characterize the spatial regions in the operators O_{mn} and $O_{m'n'}$. In order to perform the inversion one must take into account translational invariance, which implies that $\eta^{(e)}_{mn}(\vec{k},b)$ with $m=(\vec{m},\mu)$ and $n=(\vec{n},\nu)$ does depend on $\vec{m}-\vec{n}$, μ, and ν only. The number of independent $\eta^{(e)}_{mn}$ is further reduced by point-symmetry considerations.

After having formally developed the theory we want to draw attention to the following point. Since one is dealing here with a variational method [see Eq. (36)] it must be ensured that each state is properly orthogonal to all lower-lying states of the same symmetry. As far as the lowest-lying conduction band is concerned, this does not pose any problem for any value of $\vec{k}$ since it is the ground state of the $(N+1)$-electron system with a given momentum. The same holds true for higher conduction bands having different symmetries. When that is not the case, the states of higher bands must be kept orthogonal to those of lower bands. An analysis reveals, however, that the energy corrections due to the orthogonalization procedure are of order η^3_{mn} and therefore are neglected within the present theory.

This completes the description of the calculations of the correlated wave function $|\Psi_\sigma(\vec{k},b)\rangle$ and the correlation energy $\epsilon_{\text{corr}}(\vec{k},b)$. They require the computation of expectation values of local operators, which are the subject of the next section.

IV. COMPUTATION OF EXPECTATION VALUES

In the last section we have shown that the computation of the correlation energy $\epsilon_{\text{corr}}(\vec{k},b)$ can be reduced to the computation of particluar expectation values. They are of the forms

$$\langle w_{t'\sigma}O^{(\kappa)\dagger}_{mn}H_{\text{res}}w^{\dagger}_{t\sigma}\rangle_c\ , \tag{50a}$$

$$\langle w_{t'\sigma}O^{(\kappa')\dagger}_{m'n'}HO^{(\kappa)}_{mn}w^{\dagger}_{t\sigma}\rangle_c\ , \tag{50b}$$

$$\langle w_{t'\sigma}O^{(\kappa')\dagger}_{m'n'}O^{(\kappa)}_{mn}w^{\dagger}_{t\sigma}\rangle_c\ . \tag{50c}$$

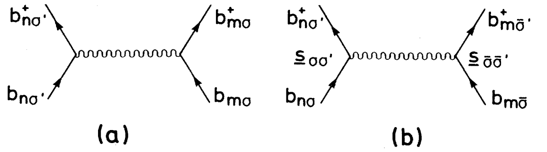

FIG. 1. Diagrammatic element associated with the operator O_{mn} (a) when O_{mn} is of the form $n_m n_n$ or (b) when O_{mn} is of the form $\vec{s}_m \vec{s}_n$.

Note that $\langle w_{t'\sigma} O^{(\kappa)\dagger}_{mn} H_0 w^\dagger_{t\sigma}\rangle_c = 0$ since contractions within the O_{mn} operators are excluded. Here we want to discuss the evaluation of the expectation values (50), which involve an additional electron in the Wannier state $\phi_\tau(\vec{r} - \vec{R}_{\vec{t}})$. They are calculated by contracting pairwise the fermion operators. There are many different ways of contracting the Fermi operators, and each way yields a contribution to (50). This holds true despite the fact that only connected diagrams are considered. In order to keep track of them we associate with each type of a contraction a particular diagram. In the following we list the rules for finding all relevant different diagrams that are associated with an expectation value of the form of Eq. (50) and obtain their contribution to the latter.

We start out by discussing the elements that form a diagram. We associate with each operator $O^{(\kappa)}_{mn}$ (or $O^{(\kappa)\dagger}_{mn}$) a wavy line with vertices as shown in Fig. 1. Thereby a distinction is made between the forms $n_m n_n$ and $\vec{s}_m \cdot \vec{s}_n$ for $O^{(\kappa)}_{mn}$ [see Eqs. (17b) and (17c)], but it is not necessary to treat separately the form $n_{m\uparrow} n_{m\downarrow}$. With H_0 we associate a cross with incoming and outgoing lines as indicated in Fig. 2(a). The residual interaction $H_{\rm res}$ is represented by a dashed line with vertices as shown in Fig. 2(b). Finally, $w^\dagger_{t\sigma}$ is the starting point and $w_{t\sigma}$ is the point of termination of a solid line (see Fig. 3). In order to obtain all possible connected contractions for a given expectation value of the form of Eq. (50), draw the diagrammatic symbols for each of the operators as given by Figs. 1—3. Maintain the correct sequence of operators by starting with the symbol for $w^\dagger_{t\sigma}$ at the bottom and continuing with the symbols for the following operators on top of the preceding operator. As an example we show in Fig. 4(a) the sequence for

$$\langle w_{t'\sigma} O^{(\kappa')\dagger}_{m'n'} H_{\rm res} O^{(\kappa)}_{mn} w^\dagger_{t\sigma}\rangle_c \ .$$

Connect the directed solid lines so that they form a continuous path starting from $w^\dagger_{t\sigma}$ and ending at $w_{t'\sigma}$. Make sure that the spin indices match. All wavy and dashed lines must be linked in this connected path in order to ensure that all contractions are "connected." The remaining

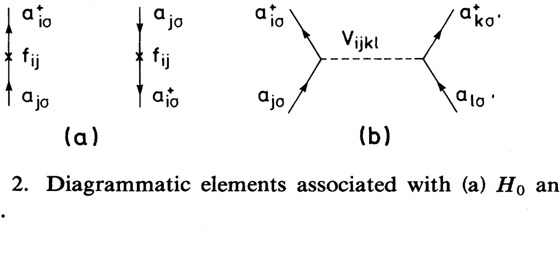

FIG. 2. Diagrammatic elements associated with (a) H_0 and (b) $H_{\rm res}$.

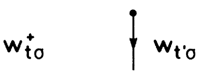

FIG. 3. Symbols for $w^\dagger_{t\sigma}$ and $w_{t'\sigma}$.

solid lines that do not take part in the continuous path are connected to form closed loops. The sum of all possible connected diagrams is obtained by doing the path connections in all possible topologically different ways that are in agreement with the above descriptions. We consider two diagrams to be topologically different when they cannot be transformed into each other by twisting while keeping the ends fixed. As an example we show in Fig. 4(b) a particular diagram that appears in the evaluation of (50b).

After having described the construction of the diagrams we want to find their contributions to the expectation values (50a)—(50c). The contribution of a given diagram is found as follows. Each solid line consists of different sections, each having a creation and annihilation operator associated with it. Associate with each section an expectation value. The following expectation values can appear:

$$\begin{aligned}
\langle a^\dagger_{i\sigma} b_{m\sigma}\rangle &= \langle b^\dagger_{m\sigma} a_{i\sigma}\rangle = R_{im} \ , \\
\langle a_{i\sigma} b^\dagger_{m\sigma}\rangle &= \langle b_{m\sigma} a^\dagger_{i\sigma}\rangle = D_{im} \ , \\
\langle b^\dagger_{m\sigma} b_{n\sigma}\rangle &= \langle b^\dagger_{n\sigma} b_{m\sigma}\rangle = \bar{P}_{mn} \ , \\
\langle b_{m\sigma} b^\dagger_{n\sigma}\rangle &= \langle b_{n\sigma} b^\dagger_{m\sigma}\rangle = \bar{D}_{mn} \ , \\
\langle a_{i\sigma} w^\dagger_{t\sigma}\rangle &= \langle w_{t\sigma} a^\dagger_{i\sigma}\rangle = C_{it} \ , \\
\langle b_{m\sigma} w^\dagger_{t\sigma}\rangle &= \langle w_{t\sigma} b^\dagger_{m\sigma}\rangle = \bar{C}_{mt} \ .
\end{aligned} \tag{51}$$

In order to find the appropriate expectation value for a section of a solid line one must use the operator to the right that comes first from below when considering that particular section. For an upward (downward) running line this will be a creation (annihilation) operator).

The distinction between the operators $O^{(0)}_{mn}$ and $O^{(e)}_{mn}$ is made by contraction. When in the matrix elements (50) $O^{(\kappa)}_{mn}$ is connected with $w^\dagger_{t\sigma}$, the operator is identified with $O^{(e)}_{mn}$, and the corresponding variational parameter is $\eta^{(e)}_{mn}$.

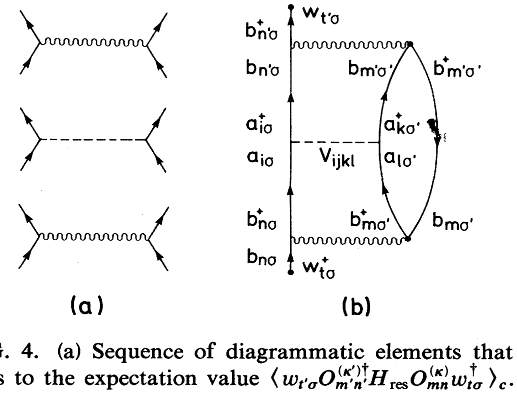

FIG. 4. (a) Sequence of diagrammatic elements that corresponds to the expectation value $\langle w_{t'\sigma} O^{(\kappa')\dagger}_{m'n'} H_{\rm res} O^{(\kappa)}_{mn} w^\dagger_{t\sigma}\rangle_c$. (b) A particular diagram that appears in the evaluation of the expectation value.

Otherwise, that is, when $O^{(\kappa)}_{mn}$ is not connected with $w^{\dagger}_{t\sigma}$, one is dealing with $O^{(0)}_{mn}$ and $\eta^{(0)}_{mn}$, respectively. The same holds true for the operators on the left-hand side of the expressions (50), i.e., for $O^{(\kappa')\dagger}_{m'n'}$ and $w_{t'\sigma}$. A factor of 2 must be associated with each $O^{(\kappa)}_{mn}$ in order to account for equivalent diagrams.

Furthermore, a dashed line gives a factor V_{ijkl} and a cross gives a factor f_{ij}; both require a sum over i,j,k,l and i,j, respectively. A sum must be taken over all spin variables in closed loops, resulting in a factor of 2 for each loop. In addition, a factor of -1 must be associated with each closed loop and also with each electron line which is directed downwards.

When we apply these rules to the evaluation of the diagram shown in Fig. 4 we find the following corresponding contribution to the expectation value:

$$2\sum_{i,j,k,l} V_{ijkl}\bar{C}_{nl}D_{jn}D_{in'}\bar{C}_{n'l'}D_{lm}D_{km'}\bar{P}_{mm'} \ . \tag{52}$$

This concludes the procedure for computing the expectation values (50a)—(50c). More details about the different types of diagrams are found in Appendix B. It also contains explicit expressions for the different expectation values (50a)—(50c).

V. PHYSICAL INTERPRETATIONS: DISCUSSION OF A SIMPLE MODEL

In order to explain and visualize the physical context of the formalism presented in the last section, we consider here a simple model that reveals the most important electron correlations that contribute to the reduction of the energy gap in a semiconductor. The simplifications are the following. First of all, the adopted model is one-dimensional. Furthermore, a minimal basis set is employed that consists of two basis functions $a^{\dagger}_{1\sigma}(i)$ and $a^{\dagger}_{2\sigma}(i)$ for each bond i. Finally, the bond orbital approximation (BOA) is made, which is explained below. The assumption of a minimal basis set excludes electron relaxation effects, while the BOA implies that there are no electron transitions between different bonds. Although these assumptions are restrictive they allow nevertheless for a study of most of the processes that influence the reduction of the energy gap in a semiconductor. The simple model greatly facilitates the understanding of the physics contained in the general formulation given before.

We start out by considering a chain of atoms. We form *sp* hybrids for each atom and assume that they have been orthogonalized with respect to each other. Let $a^{\dagger}_{1\sigma}(i)$ and $a^{\dagger}_{2\sigma}(i)$ denote the creation operators for electrons with spin σ in the two orthogonalized hybrids forming the bond i. Then we can form the bonding and antibonding combinations

$$\begin{aligned} B^{\dagger}_{i\sigma} &= 2^{-1/2}[a^{\dagger}_{1\sigma}(i)+a^{\dagger}_{2\sigma}(i)] \ , \\ A^{\dagger}_{i\sigma} &= 2^{-1/2}[a^{\dagger}_{1\sigma}(i)-a^{\dagger}_{2\sigma}(i)] \ . \end{aligned} \tag{53}$$

The BOA assumes that

$$\langle 0 | A_{t\sigma} H B^{\dagger}_{t'\sigma} | 0 \rangle = 0 \ ,$$

which implies that the Wannier states labeled before by $w^{\dagger}_{t\sigma}$ with $t=(\vec{t},\tau)$ can be identified with $A^{\dagger}_{t\sigma'}$ $(\tau=1)$ and $B^{\dagger}_{t\sigma'}$ $(\tau=2)$.

The SCF Hamiltonian H_0 is then of the form

$$\begin{aligned} H_0 = \sum_{t,\sigma} [& -T_0 B^{\dagger}_{t\sigma}B_{t\sigma} + T_B(B^{\dagger}_{t\sigma}B_{t+1\sigma}+\text{H.c.}) \\ & + T_0 A^{\dagger}_{t\sigma}A_{t\sigma} - T_A(A^{\dagger}_{t\sigma}A_{t+1\sigma}+\text{H.c.})] \ . \end{aligned} \tag{54}$$

The centers of the valence and conduction bands are at $\pm T_0$, respectively, while the respective bandwidths are determined by $4T_B$ and $4T_A$.

The interaction Hamiltonian for the model is most conveniently expressed in the $a_{\alpha\sigma}(i)$ operators and is chosen to be of the form

$$H_{\text{int}} = \tfrac{1}{2}\sum_{i,j}\sum_{\alpha,\beta,\sigma,\sigma'} V_{\alpha\beta}(i-j)a^{\dagger}_{\beta\sigma}(j)a^{\dagger}_{\alpha\sigma'}(i)a_{\alpha\sigma'}(i)a_{\beta\sigma}(j) \ . \tag{55}$$

The matrix elements $V_{\alpha\beta}(i-j)$ are defined according to Eq. (5) where the $a^{\dagger}_{\alpha\sigma}(i)$ are the creation operators for the f functions.

By inspection of Fig. 5 one notices that for a given $i-j$ the $V_{\alpha\beta}(i-j)$ depend on $\alpha-\beta$ only. Hence there are three different $V_{\alpha-\beta}(i-j)$ for each value of $i-j$.

Next we consider the operator $\exp(S_0)$ [see Eq. (15)], which transforms the SCF ground state into the correlated ground state. We shall assume that S_0 contains only density correlations, and therefore we will neglect spin correlations. They result in a Hund's-rule coupling and are comparatively small in semiconductors (see Ref. 2). Furthermore, we identify the regions $g_m(\vec{r})$ with different hybrids, which implies that the $b^{\dagger}_{m\sigma}$ operators [see Eq. (13)] are the same as the operators $a^{\dagger}_{\alpha\sigma}$. Therefore S_0 is written as

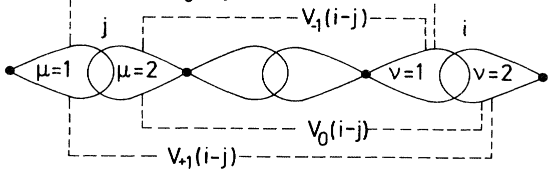

FIG. 5. Sketch of the *sp*-hybrid functions of the one-dimensional model. There exist three different Coulomb matrix elements connecting the hybrids in cell i with those in cell j, namely, $V_{-1}(i-j)$, $V_0(i-j)$, and $V_{+1}(i-j)$.

$$S_0 = -\sum_{i,j,\alpha,\beta} \eta^{(0)}_{\alpha-\beta}(i-j)\, n_\alpha(i) n_\beta(j) \tag{56}$$

with

$$n_\alpha(i) = \sum_\sigma a^\dagger_{\alpha\sigma}(i) a_{\alpha\sigma}(i) \; .$$

As with $V_{\alpha\beta}(i-j)$ the $\eta_{\alpha\beta}(i-j)$ only depend on the difference $\alpha-\beta$. Before we evaluated the correlation energy according to the rules described in Secs. III and IV, it is instructive to consider the effect of S when applied on the SCF ground state with an extra electron (or hole) added [see Eqs. (21a) and (28)]. We set

$$|\Phi^{(e)}_{\bar\sigma}(k)\rangle = \sum_m e^{ikm} A^\dagger_{m\bar\sigma} |\Phi_{\rm SCF}\rangle \; . \tag{57}$$

Here the atomic distance has been set equal to 1. When S is applied on $|\Phi^{(e)}_{\bar\sigma}(k)\rangle$ and when the $n_\alpha(i)$ are expressed in terms of the $A_{i\sigma}$ and $B_{i\sigma}$ operators [see Eq. (53)], one finds

$$\begin{aligned} S|\Phi^{(e)}_{\bar\sigma}(k)\rangle = -\sum_{i,j}\sum_{\sigma,\sigma'} [&\kappa(i-j) A^\dagger_{i\sigma} B_{i\sigma} A^\dagger_{j\sigma'} B_{j\sigma'} \\ &+ 2\pi(i-j) A^\dagger_{i\sigma} B_{i\sigma} n^A_{j\sigma'}] \\ &\times |\Phi^{(e)}_{\bar\sigma}(k)\rangle \; . \end{aligned} \tag{58}$$

Here $n^A_{j\sigma'} = A^\dagger_{j\sigma'} A_{j\sigma'}$ and the following notation has been introduced:

$$\begin{aligned} \kappa(i-j) &= \eta^{(0)}_{-1}(i-j) - 2\eta^{(0)}_0(i-j) + \eta^{(0)}_1(i-j) \; , \\ 2\pi(i-j) &= \eta^{(e)}_{-1}(i-j) - \eta^{(e)}_1(i-j) \; . \end{aligned} \tag{59}$$

The $\eta^{(0)}_\nu(i-j)$ and therefore the $\kappa(i-j)$ are determined by a ground-state calculation while the $\pi(i-j)$ are not. The role of the operator $A^\dagger_{i\sigma} B_{i\sigma} \eta^A_{j\bar\sigma}$ is to generate a polarization of the bond i when the extra electron with spin $\bar\sigma$ is sitting in bond j. This is easily checked by decomposing the occupation number operators $n_{1\sigma}(i)$ and $n_{2\sigma}(i)$ of the two hybrids 1 and 2 of bond i in terms of the $A_{i\sigma}, B_{i\sigma}$ operators. The function $\pi(i-j)$ is then a measure of the induced dipole strength.

We proceed by computing $\epsilon_{\rm corr}(k)$ as given by Eq. (39) or (42). Before considering the expectation values which appear in that equation we state the particular forms of the matrices (51) within the present model. By identifying the $b^\dagger$ operators with the $a^\dagger$ operators, one finds within the BOA that the matrices are diagonal with respect to the bond coordinates, i.e.,

$$\begin{aligned} R_{\alpha\beta}(i-j) &= \langle a^\dagger_{\alpha\sigma}(i) a_{\beta\sigma}(j)\rangle = \tfrac{1}{2}\delta_{ij} \; , \\ D_{\alpha\beta}(i-j) &= \langle a_{\alpha\sigma}(i) a^\dagger_{\beta\sigma}(j)\rangle \\ &= -\tfrac{1}{2}\delta_{ij}(1-2\delta_{\alpha\beta}) \; , \\ C_\alpha(i-t) &= \langle a_{\alpha\sigma}(i) A^\dagger_{t\sigma}\rangle \\ &= 2^{-1/2}\delta_{it}(\delta_{\alpha,1}-\delta_{\alpha,2}) \; . \end{aligned} \tag{60}$$

Furthermore,

$$\bar P_{\alpha\beta}(i-j) = R_{\alpha\beta}(i-j), \;\; \bar D_{\alpha\beta}(i-j) = D_{\alpha\beta}(i-j)$$

and

$$\bar C_\alpha(i-l) = C_\alpha(i-l) \; .$$

First we evaluate the term

$$I_1 = -2 \sum_{m,n,\kappa} \eta^\kappa_{mn} \langle w_{t'\sigma} H O^{(\kappa)}_{mn} w^\dagger_{t\sigma}\rangle_c \; .$$

From what has been discussed below Eqs. (50) it follows that H can be replaced by $H_{\rm res}$. The diagrams that correspond to the different contractions within the expression (50a) are shown in Fig. 6. They are labeled $\mathscr{D}$(6.1a)—$\mathscr{D}$(6.1d). By using Eq. (B2) we can compute I_1.

For the purpose of demonstration we calculate first only the contributions from $\mathscr{D}$(6.1a) and $\mathscr{D}$(6.1c) to I_1. One finds

$$\begin{aligned} \mathscr{D}(6.1\text{a}) &\Longrightarrow -4\delta_{tt'} \sum_{n,\nu,\mu} \eta^{(e)}_{\mu-\nu}(t-n) \sum_{\alpha,\beta} V_{\alpha-\beta}(t-n) C_\alpha(0) R_{\beta\nu}(0) D_{\beta\nu}(0) D_{\alpha\mu}(0) \bar C_\mu(0) \; , \\ \mathscr{D}(6.1\text{c}) &\Longrightarrow 4\delta_{tt'} \sum_{n,\mu,\nu} \eta^{(0)}_{\mu-\nu}(t-n) \sum_{\alpha,\beta} V_{\alpha-\beta}(t-n) C_\mu(0) R_{\beta\nu}(0) D_{\beta\nu}(0) R_{\alpha\mu}(0) \bar C_\alpha(0) \; . \end{aligned} \tag{61}$$

After performing the sums this goes over into

$$\begin{aligned} \mathscr{D}(6.1\text{a}) &\Longrightarrow -\tfrac{1}{4}\delta_{tt'} \sum_j [V_{-1}(j) - V_1(j)] 2\pi(j) \; , \\ \mathscr{D}(6.1\text{c}) &\Longrightarrow \tfrac{1}{4}\delta_{tt'} \sum_j [V_{-1}(j) - 2V_0(j) + V_1(j)] \kappa(j) \; . \end{aligned} \tag{62}$$

The exchange diagrams $\mathscr{D}$(6.1b) and $\mathscr{D}$(6.1d) contribute only for $j=0$ in which case they lead to a reduction of the same terms in $\mathscr{D}$(6.1a) and $\mathscr{D}$(6.1c) by a factor of $\frac{1}{2}$. In order to shorten the notation we introduce

$$\begin{aligned} V'(j) &= V_{-1}(j) - V_1(j) \; , \\ V''(j) &= V_{-1}(j) - 2V_0(j) + V_1(j) \; . \end{aligned} \tag{63}$$

$V'(j)$ and $V''(j)$ can be considered as the first- and second-order difference quotients of the interaction potential. When the contributions of all four diagrams are taken into account one finds

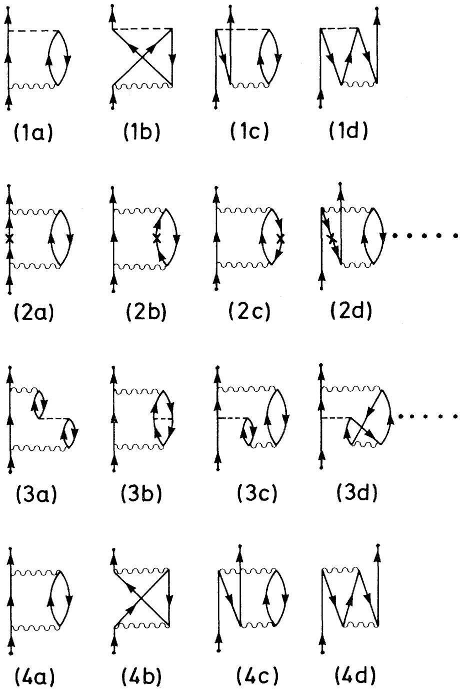

FIG. 6. Typical diagrams $\mathscr{D}(\nu)$ contributing to the quasiparticle energy (42). One can distinguish four classes of matrix elements, i.e., first-order matrix elements containing (1) the interaction H_{res}, (2) second-order matrix elements arising from the kinetic energy H_0, (3) the interaction energy H_{res}, and (4) the denominator.

$$I_1=\delta_{tt'}\left[-\sum_{j\neq 0}V'(j)\pi(j)+\tfrac{1}{2}\sum_j V''(j)\kappa(j)-\tfrac{1}{4}V''(0)\kappa(0)\right]. \tag{64}$$

Here use has been made of $\pi(0)=0$, which follows from symmetry arguments. The first term on the rhs comes from $\mathscr{D}$(6.1a), and can be interpreted as the electrostatic energy that an induced dipole $\pi(j)$ experiences in the electric field $V'(j)$ caused by the additional electron in the conduction band. The second and third terms result from changes in the ground-state correlations due to the presence of the extra electron. These changes are easily visualized within the BOA. The extra electron blocks the two-particle excitations in the bond in which it is sitting, and therefore the ground-state correlations are lost within that bond. This is clearly a strong overemphasis of what will happen in a realistic system, and it is due to the fact that we are working within the BOA with a minimal basis set.

We proceed by discussing the term

$$I_2=\sum_{m,n,\kappa}\sum_{m',n',\kappa}\eta^{\kappa}_{mn}\eta^{\kappa'}_{m'n'}\langle w_{t'\sigma}O^{(\kappa')\dagger}_{m'n'}H_0O^{(\kappa)}_{mn}w^{\dagger}_{t\sigma}\rangle_c$$

in Eq. (39). The corresponding diagrams $\mathscr{D}$(6.2) are shown in parts in Fig. 6. We evaluate their contributions to I_2 by making use of Eq. (B4) and the relations (60). The result is

$$\begin{aligned}I_2=&\delta_{tt'}6T_0\sum_j\pi^2(j)\\&+(\delta_{t,t'+1}+\delta_{t,t'-1})2T_A\sum_j\pi(j)\pi(j+1)\\&-\delta_{t,t'}\tfrac{3}{2}T_0\sum_j\kappa^2(j)(1-\tfrac{1}{2}\delta_{j0})\ .\end{aligned} \tag{65}$$

The first term on the rhs is related to the excitation energy across the gap, which is required in order to generate induced dipoles of strength $\pi(j)$ in bonds j. It results from $\mathscr{D}$(6.2a–6.2c). The second term comes from $\mathscr{D}$(6.2a) and is due to electron hopping between bonds. It leads to a momentum dependence of the correlation energy, i.e., a narrowing of the valence and conduction bands. The third term results from diagrams such as $\mathscr{D}$(6.2d) and describes again a correction to the ground-state correlations.

According to Eq. (41b) I_2 must be considered together with $-\epsilon_{\text{SCF}}(k)I_4$, where I_4 is due to the denominator

$$\begin{aligned}I_4=&\sum_{m,n,\kappa}\sum_{m',n',\kappa'}\eta^{\kappa}_{mn}\eta^{\kappa'}_{m'n'}\langle w_{t'\sigma}O^{(\kappa')}_{m'n'}O^{(\kappa)}_{mn}w^{\dagger}_{t\sigma}\rangle_c\\=&\left[2\sum_j\pi^2(j)+\tfrac{1}{2}\sum_j\kappa^2(j)(1-\tfrac{1}{2}\delta_{j0})\right]\delta_{tt'}\ .\end{aligned} \tag{66}$$

In Fig. 6 diagrams $\mathscr{D}$(6.4a) and $\mathscr{D}$(6.4b) contribute to $\pi^2(j)$ while $\mathscr{D}$(6.4c) and $\mathscr{D}$(6.4d) lead to the $\kappa^2(j)$ and $\kappa^2(0)$ terms, respectively.

Making use of $\epsilon_{\text{SCF}}(k)=T_0+2T_A\cos k$, one obtains

$$I_2-\epsilon_{\text{SCF}}(k)I_4=\delta_{tt'}4T_0\sum_j\pi^2(j)+(\delta_{t,t'+1}+\delta_{t,t'-1})2T_A\sum_j[\pi(j)\pi(j+1)-\pi^2(j)]-\delta_{tt'}2T_0\sum_j\kappa^2(j)(1-\tfrac{1}{2}\delta_{j0})\ . \tag{67}$$

Next we evaluate

$$I_3=\sum_{m,n,\kappa}\sum_{m',n',\kappa'}\eta^{\kappa}_{mn}\eta^{\kappa'}_{m'n'}\langle w_{t'\sigma}O^{(\kappa')\dagger}_{m'n'}H_{\text{res}}O^{(\kappa)}_{mn}w^{\dagger}_{t\sigma}\rangle_c\ .$$

A selection of diagrams $\mathscr{D}$(6.3a—6.3d) is shown in Fig. 6. By applying Eqs. (B7)—(B9) together with the relations (60) one finds

$$\begin{aligned}I_3=\delta_{tt'}\Bigg[&-\sum_{i,j}V''(i-j)\pi(i)\pi(j)(1-\tfrac{1}{2}\delta_{ij})-\sum_{i,j}V'(i-j)\kappa(i)\pi(j)(1-\tfrac{1}{2}\delta_{i0})\\&-\tfrac{1}{2}\sum_{i,j}V''(i-j)\kappa(i)\kappa(j)(1-\tfrac{1}{2}\delta_{ij}-\tfrac{1}{4}\delta_{i0}-\tfrac{1}{4}\delta_{j0})\Bigg]\ .\end{aligned} \tag{68}$$

The first term on the rhs represents the dipole-dipole interaction energy between dipoles in bonds $t+i$ and $t+j$. It is obtained from diagrams $\mathcal{D}$(6.3a) and $\mathcal{D}$(6.3b). Thereby the latter compensates the self-interaction of the dipoles when $i=j$. This is a local-field correction. The second term is due to diagrams $\mathcal{D}$(6.3c) amd $\mathcal{D}$(6.3d). It describes the interplay between the ground-state correlations $\kappa(i)$ and the polarizations $\pi(j)$. The last term describes a loss in ground-state correlation energy and vanishes when only $\kappa(0)$ is taken into account

The correlation energy $\epsilon_{\text{corr}}(k)$ [see Eq. (42)] can now be written. The functions $G_{tt'}(\vec{k},b)$ in Eqs. (41a)–(41c) are of the simple form $\exp[ik(t'-t)]$ for the present model. We write

$$\begin{aligned}\epsilon_{\text{corr}}(k,e)=D^{-1}\Bigg[&-\sum_j V'(j)\pi(j)+4T_0\sum_j \pi^2(j)+4T_A\cos k\sum_j[\pi(j)\pi(j+1)-\pi^2(j)]\\&-\sum_{i,j}V''(j-i)\pi(j)\pi(i)(1-\tfrac{1}{2}\delta_{ij})-\tfrac{1}{2}\sum_j V'(j)\pi(j)\kappa(0)+\tfrac{1}{4}V''(0)\kappa(0)-T_0\kappa^2(0)\Bigg]\,, \qquad (69)\end{aligned}$$

with

$$D=1+\tfrac{1}{4}\kappa^2(0)+2\sum_j \pi^2(j)\,. \qquad (70)$$

All contributions containing $\kappa(j)$ with $j\neq 0$ have been omitted for simplicity. Note that the ground-state correlations fall off much faster than the polarization terms, the $\kappa(i)$ decay like the second derivative of the interactions $V''(i)$, while $\pi(j)$ is proportional to $V'(j)$. The last two terms on the rhs almost compensate for the ground-state correlation energy for one bond, which is $E_0=-\frac{1}{4}V''(0)\kappa(0)+T_0\kappa^2(0)$. That the compensation is not complete is due to the denominator in Eq. (69). From our definition (63) $V''(0)$ is negative since the interaction potential is convex for short distances. Hence $\kappa(0)$ is also negative. With the same argument one finds a positive contribution from the dipole-dipole interaction if $i=j$. This is the interaction between two dipoles within the same bond formed by the spin-up and spin-down electrons, respectively. On the other hand, when the distance $i-j$ is larger, $V''(i-j)$ becomes positive for a Coulomb interaction. Therefore when i and j are on the same side with respect to the added electron, the dipole-dipole interaction energy is negative resulting in an enhancement of the polarization. This is a special feature of the one-dimensional model and does not persist in three dimensions. There the dipolar interactions *reduce* the polarization, i.e., they lead to a screening of the added electron.

After applying the condition (36) one finds for the correlation energy due to the polarization of the medium [see Eq. (45b)]

$$\epsilon^{(e)}_{\text{corr}}(k)=-\tfrac{1}{2}\sum_j V'(j)\pi(j)\,. \qquad (71)$$

This energy can be understood as the discretized version of the field energy

$$W=-\tfrac{1}{2}\int d^3r\,\vec{E}(\vec{r})\vec{P}(\vec{r}) \qquad (72)$$

of a dielectric in an electric field $\vec{E}(\vec{r})$. From the minimal condition $\partial\epsilon_{\text{corr}}(k)/\partial\pi(l)=0$ one obtains the equation

$$\Bigg[-V'(l)+8T_0\pi(l)+4T_A\cos k[\pi(l+1)-2\pi(l)+\pi(l-1)]-4\pi(l)\epsilon_{\text{corr}}(k)-2\sum_i V''(l-i)\pi(i)(1-\tfrac{1}{2}\delta_{il})-\tfrac{1}{2}V'(l)\kappa(0)\Bigg]=0\,, \qquad (73)$$

which determines $\pi(l)$. Inspection of (73) shows that $\pi(l)$ decays as $V'(l)$, i.e., as l^{-2} for the Coulomb interaction.

Equation (73) can be solved by Fourier transformation. By setting $\pi(l)=N^{-1/2}\sum_q \pi_q\exp(iql)$ one finds

$$\pi_q=\frac{1}{4}\,\frac{V'_q(1+\kappa(0)/2)}{2T_0-2T_A\cos k[1-\cos(q)]-\epsilon_{\text{corr}}(k)-\frac{1}{2}[V''_q-\frac{1}{2}V''(0)]}\,. \qquad (74)$$

Here the term $2T_0$ in the denominator is the average energy of a particle-hole excitation. The second term is related to the the dispersion of the SCF energy

$$\epsilon_{\text{SCF}}(k)=T_0+2T_A\cos k$$

of the quasiparticle. If $2T_A\cos k$ is positive (negative) the polarization and the correlation correction becomes larger (smaller). This results in a reduction of the conduction- and valence-band widths. The last term in the denominator is due to dipolar interactions, while $V''(0)$ represents the local-field corrections, namely, it cancels the self-interaction of the dipoles, which is included in V''_q. Note that the only k dependence, at least in this simple model, enters via the quasiparticle energy.

Equation (74) for π_q must be solved self-consistently together with Eq. (71) for $\epsilon^{(e)}_{\text{corr}}(k)$. The occurrence of the correlation energy $\epsilon_{\text{corr}}(k)$ in the denominator of (74) leads to a reduction of the polarization parameters π_q. A further reduction is due to the term $\kappa(0)/2$ in the numerator, since $\kappa(0)$ is negative. This term has its origin in the coupling of polarization and ground-state correlations.

The simplicity of the results of the above-mentioned model is due to the use of the BOA and the minimal basis set. In particular, a large number of exchange diagrams containing $\pi(0)$ can be omitted since $\pi(0)=0$. However, when dealing with a larger basis set, in principle, all diagrams as listed in Appendix B will give a contribution.

Not contained in the simple model considered above are possible charge transfers between different bonds. Their absence is due to the use of the BOA. They can be obtained by using instead the extended bond orbital approximation (EBOA; see Ref. 20). In distinction to the BOA the Wannier orbital $\phi_\tau(\vec{r}-\vec{R}_t)$ of a bond contains also admixtures of antibonding functions from neighboring bonds. The conduction and valence bands are decoupled in the EBOA. For the one-dimensional model considered in the last section this implies that the Wannier operator for the valence band is of the form

$$w^\dagger_{t\sigma}(v)=B^\dagger_{t\sigma}+\sum_{t'\neq t}\lambda_{tt'}A^\dagger_{t'\sigma}\ , \tag{75}$$

instead of $w^\dagger_{t\sigma}(v)=B^\dagger_{t\sigma}$ as in the discussion following Eq. (53). Assuming $\lambda_{tt'}=\lambda\delta_{t,t+1}$ one finds an additional contribution to Eq. (58),

$$\begin{aligned}\Delta S\,|\Phi^{(e)}_{\bar{\sigma}}(k)\rangle=2\lambda\sum_{j,\sigma,\sigma'}&[\sigma(i-j)-\sigma(i-j+1)]\\ &\times(A^\dagger_{i\sigma}B_{i-1\sigma}+A^\dagger_{i-1\sigma}B_{i\sigma})\\ &\times n^A_{j\sigma'}\,|\Phi^{(e)}_{\bar{\sigma}}(k)\rangle\ .\end{aligned} \tag{76}$$

Here the notation

$$\sigma(i-j)=\eta^{(e)}_{-1}(i-j)+2\eta^{(e)}_{0}(i-j)+\eta^{(e)}_{+1}(i-j) \tag{77}$$

has been introduced. The spatial dependence of $\sigma(l)-\sigma(l+1)$ is the same as that of $\pi(l)$; hence the charge transfer provides an additional contribution to the polarization. This effect is expected to be small in semiconductors with a large gap where the Wannier functions are well localized and λ is small. But charge transfer will become important in narrow-gap semiconductors where the localization of the Wannier functions is less pronounced. The simple model calculations of this section have had the purpose of illustrating the general formalism developed in Sec. III. In particular, we have seen that the correlation energy contains contributions that result from the polarization of the surroundings of an electron in the conduction band. The induced dipole-dipole interactions (local-field effects) are properly included. This is within the spirit of the work by Mott and Littleton, but here we have also included the dynamics of the extra electron in a simple and transparent way. As mentioned above there is also the influence of the ground-state correlations taken into account when the polarization is calculated.

VI. SUMMARY AND CONCLUSIONS

The aim of this investigation has been to set up a theoretical framework for reliable and accurate calculations of the correlation energy in the excited states of semiconductors. The motivation behind this effort has been to obtain a simple and clear understanding of which processes are responsible for the changes in the energy gap and the conduction- and valence-band widths as compared with the results from an independent electron calculation, i.e., a SCF [or Hartree-Fock (HF)] type of treatment. The theory has been developed by extending to excited states a previously developed local approach to the correlation problem of the ground state of a semiconductor. An important approximation that has been made thereby is the neglect of excitonic effects, i.e., the electron and its hole have been assumed to be separated. This enabled us to consider a $(N+1)$- [or $(N-1)$-] electron problem. The wave function of the correlated $(N+1)$-particle system is described by Eq. (27). We want to point out that this form of wave function excludes any possible lifetime effects that are not taken into consideration. The new feature as compared with ground-state calculations is the appearance of a second set of operators $O_{mn}Q_{mn}$ constructed out of the local operators O_{mn}. This set leads to vanishing contributions in the ground-state energy expansion (19) but contributes when there is an extra electron in a conduction band. The correlation energy of the extra electron can be calculated from Eqs. (44), (45), and (49). There are a number of different physical processes contributing to it that we want to summarize. Thereby it is advantageous to distinguish between processes that can be described within the basis set of the bonding and antibonding orbitals (minimal basis set) and those processes for a description of which we need larger basis sets. Let us start out with those of the first kind and list them as follows.

(a) Bond polarizations. The electron in the conduction band generates around itself a polarization cloud by polarizing the different bonds. The process is extracted out of theory when the model in Sec. V is studied. It is the most important process for the reduction of the energy gap. The bond polarization has two contributions: one due to a shift of charge within a bond, while the second results from a transfer of charge between different bonds. The BOA allows only for the first contribution while the EBOA allows also for the second contribution.

(b) Momentum dependence of polarizations. The polarization cloud around the electron in the conduction band depends not only on the particular band, but also on its energy and its momentum. This represents itself in a $\vec{k}$ dependence of the corresponding $\eta^{(e)}_{mn}(k,b)$ and results in a narrowing of the bands.

(c) Local-field effects. The discussion of the model in Sec. IV has shown that local-field effects are properly included in the theory. The advantage of the present approach is that within the approximation (38) *all* diagrams are taken into account. This enables us to study their relative importance with respect of contributing to ϵ_{corr}.

(d) Changes in the ground-state correlations. When the extra electron is in an antibonding Wannier orbital, the correlation energy of the electrons in the bonding Wannier orbitals of its neighborhood is reduced. In particular in the BOA there is no possibility for correlations in the bond in which the extra electron is sitting. Hence the use

of a minimal basis set together with the BOA necessarily leads to an overestimation of the reduction of the ground-state correlation energy.

Next we summarize the processes that require a larger basis set for their description.

(i) Relaxation. In the close neighborhood of the extra electron the orbitals of the other electrons will relax. The inclusion of relaxation, which is known to be very significant in atoms and molecules, requires an extended basis set. Within the present theory the operator $\eta_{mn}^{(e)} O_{mn} Q_{mn}$ locates again the electron in the conduction band and gives particular weight to the occupation of those regions $g_n(\vec{r})$ into which the wave functions of the bonding electrons relax.

(ii) Modified changes in the ground-state correlations. As pointed out above, the reduction in the ground-state correlations in the neighborhood of the extra electron is expected to be considerably reduced when the basis set is enlarged.

This completes the summary of the different processes that contribute to the correlation energy of the quasiparticle in the conduction band. A particular feature of the method formulated above is that it allows the computation of short- and long-range effects within the same framework.

As far as the evaluation of the various contributions to the correlation energy is concerned, it was demonstrated that the theory can be reduced to the computation of a number of expectation values [see Eqs. (50a)—(50c)]. Practical rules for their evaluation were derived and explicit expressions are presented in Appendix B. Here all contributions up to second order in η are evaluated, i.e., no uncontrolled restriction to a certain subset of diagrams is required. The expectation values must be calculated only once for a semiconductor and not for every $\vec{k}$ point. They constitute the largest amount of work in an actual calculation. The $\vec{k}$ dependence enters into the calculations in a simple and straightforward way [see Eqs. (41a)—(41c)]. It was also pointed out that the correlation-energy contribution can be written in terms of a supplement to the Fock matrix [see Eq. (40)].

Finally, we want to remark on possible improvements of the theory. The present formulation of the theory has been done with primarily covalent semiconductors in mind. For that reason we have left out single-particle excitations when describing the ground-state correlations. In polar semiconductors they are of importance, though, and must be included. Their inclusion is simple and straightforward but lengthens the various expressions. Furthermore, we do not foresee any problems in extending the theory so that it includes excitonic effects. In particular, our approach seems to be interesting for cases where one is dealing with excitons which are neither in the Frenkel nor Wannier limit. The theory that has been developed here is planned to be applied to diamond in order to demonstrate that it can be applied to real systems. It is hoped that it can provide a link between calculations for small systems as done by quantum chemists and band-structure calculations as performed by solid-state physicists.

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APPENDIX A: LINKED-CLUSTER EXPANSION

We want to provide a derivation of Eqs. (33)—(35). For that purpose we consider

$$\langle c_\Gamma e^{S^\dagger} H e^{S} c_\Gamma^\dagger \rangle = \sum_{m,n} \frac{1}{m!} \frac{1}{n!} \langle c_\Gamma (S^\dagger)^m H S^n c_\Gamma^\dagger \rangle \ . \quad \text{(A1)}$$

Here Γ stands for $\vec{k}, b, \sigma$ and as in the preceding sections $\langle \ \rangle$ implies an expectation value with respect to $|\Phi_{\text{SCF}}\rangle$. When calculating the expectation value $\langle c_\Gamma (S^\dagger)^m H S^n c_\Gamma^\dagger \rangle$ one must contract the creation and annihilation operators pairwise, thereby taking all combinatorial possibilities into account. In doing this the expectation value will generally factorize into a product of expectation values. We consider separately the expectation value that contains H and cannot further be factorized. In this way we write

$$\langle c_\Gamma (S^\dagger)^m H S^n c_\Gamma^\dagger \rangle = \sum_{k,l} \begin{bmatrix} n \\ l \end{bmatrix} \begin{bmatrix} m \\ k-l \end{bmatrix} [\langle c_\Gamma (S^\dagger)^l H S^{k-l} c_\Gamma^\dagger \rangle_c \langle (S^\dagger)^{n-l} S^{m-k+l} \rangle + \langle (S^\dagger)^l H S^{k-l} \rangle_c \langle c_\Gamma (S^\dagger)^{n-l} S^{m-k+l} c_\Gamma^\dagger \rangle] \ . \quad \text{(A2)}$$

Here the notation $\langle \ \rangle_c$ implies that the contractions are taken in such a way that the expectation value does not factorize. This implies that all operators c_Γ, $c_\Gamma^\dagger$, S^l, or H that appear in square brackets are connected (directly or indirectly) with each other through the contractions. The contracted operator products can be expressed in terms of diagrams as was done in Sec. IV.

The expectation values in Eq. (A2) without the index c contain connected as well as disconnected structures. The prefactors $\binom{n}{l}$ and $\binom{m}{k-l}$ in that equation give the number of possibilities to choose l operators out of n and $k-l$ out of m. Furthermore, there are two terms over which the sums are taken since the operators c_Γ and $c_\Gamma^\dagger$ can belong to a connected diagram which may include H or not.

When we substitute Eq. (A2) into (A1) we can rewrite the different terms. For example, it becomes

$$\sum_{m,n}\frac{1}{m!n!}\sum_{k,l}\begin{bmatrix}n\\ l\end{bmatrix}\begin{bmatrix}m\\ k-l\end{bmatrix}\langle c_\Gamma (S^\dagger)^l H S^{k-l} c_\Gamma^\dagger\rangle_c \langle (S^\dagger)^{n-l} S^{m-k+l}\rangle$$

$$=\sum_{l,k}\frac{1}{l!}\frac{1}{(k-l)!}\langle c_\Gamma (S^\dagger)^l H S^{k-l} c_\Gamma^\dagger\rangle_c \sum_{m,n}\frac{1}{(n-l)!}\frac{1}{(m-k+l)!}\langle (S^\dagger)^{n-l} S^{m-k+l}\rangle$$

$$=\langle c_\Gamma e^{S^\dagger} H e^{S} c_\Gamma^\dagger\rangle_c \langle e^{S^\dagger} e^{S}\rangle \; . \tag{A3}$$

The last equality follows by introducing new variables for $n-l$ and $m-k+l$. In a similar way we can rewrite the second term in Eq. (A1) so that we finally obtain

$$\langle c_\Gamma e^{S^\dagger} H e^{S} c_\Gamma^\dagger\rangle = \langle c_\Gamma e^{S^\dagger} H e^{S} c_\Gamma^\dagger\rangle_c \langle e^{S^\dagger} e^{S}\rangle + \langle e^{S^\dagger} H e^{S}\rangle_c \langle c_\Gamma e^{S^\dagger} e^{S} c_\Gamma^\dagger\rangle \; . \tag{A4}$$

The same procedure can be repeated for $\langle c_\Gamma e^{S^\dagger} e^{S} c_\Gamma^\dagger\rangle$ which appears in the denominator of Eq. (32). One obtains

$$\langle c_\Gamma e^{S^\dagger} e^{S} c_\Gamma^\dagger\rangle = \langle c_\Gamma e^{S^\dagger} e^{S} c_\Gamma^\dagger\rangle_c \langle e^{S^\dagger} e^{S}\rangle \; . \tag{A5}$$

Combining Eqs. (A4) and (A5) results in

$$\frac{\langle c_\Gamma e^{S^\dagger} H e^{S} c_\Gamma^\dagger\rangle}{\langle c_\Gamma e^{S^\dagger} e^{S} c_\Gamma^\dagger\rangle} = \frac{\langle c_\Gamma e^{S^\dagger} H e^{S} c_\Gamma^\dagger\rangle_c}{\langle c_\Gamma e^{S^\dagger} e^{S} c_\Gamma^\dagger\rangle_c} + \langle e^{S^\dagger} H e^{S}\rangle_c \; .$$

This proves that Eqs. (33)—(35) follow from Eq. (32).

APPENDIX B: FURTHER EVALUATION OF THE EXPECTATION VALUES (50a)—(50c)

In the following detailed information is provided with respect to the evaluation of the expectation values (50a)—(50c). Thereby we limit ourselves to O_{mn} operators that describe density-density correlations, i.e., we do not consider spin correlations. A generalization that includes the latter is straightforward.

We begin by considering $\langle w_{t'\sigma} H_{\text{res}} O_{mn}^{(\kappa)} w_{t\sigma}^\dagger\rangle_c$. The four possible diagrams are shown in Figs. 6(1a)—6(1d). From the computational point of view it is useful to introduce the following abbreviations:

$$\begin{aligned} B_{mt'n'n} &= \sum_{i,j,k,l} V_{ijkl} C_{it'} D_{jm} R_{kn'} D_{ln} \; , \\ \bar{B}_{tm'n'n} &= \sum_{i,j,k,l} V_{ijkl} R_{im'} C_{jt} R_{kn'} D_{ln} \; . \end{aligned} \tag{B1}$$

By applying the rules of Sec. IV one finds

$$\begin{aligned} \langle w_{t'\sigma} H_{\text{res}} O_{mn}^{(\kappa)} w_{t\sigma}^\dagger\rangle_c = 2[&\bar{C}_{mt}(2B_{mt'nn} - B_{nt'nm})\delta_{\kappa,e} \\ &- \bar{C}_{mt'}(2\bar{B}_{tmnn} - \bar{B}_{tnmn})\delta_{\kappa,0}] \; . \end{aligned} \tag{B2}$$

The first term corresponds to the diagrams $\mathscr{D}$(6.1a) and $\mathscr{D}$(6.1b) while the second term corresponds to $\mathscr{D}$(6.1c) and $\mathscr{D}$(6.1d). The latter describes changes in the ground-state correlations due to the extra electron.

Next we evaluate $\langle w_{t'\sigma} O_{m'n'}^{(\kappa')\dagger} H_0 O_{mn}^{(\kappa)} w_{t\sigma}^\dagger\rangle_c$. There are twelve possible diagrams associated with the different contractions out of which we show four in Figs. 6(2a)—6(2d). Their structure is obvious from the rules set up in Sec. IV. Let us introduce the notation

$$\begin{aligned} G_{nm} &= \sum_{i,j} f_{ij} D_{in} D_{jm} \; , \\ H_{nm} &= \sum_{i,j} f_{ij} R_{jn} R_{im} \; . \end{aligned} \tag{B3}$$

By applying the rules of Sec. IV it is found that

$$\begin{aligned} \langle w_{t'\sigma} O_{m'n'}^{(\kappa')\dagger} H_0 O_{mn}^{(\kappa)} w_{t\sigma}^\dagger\rangle_c = 4[&2\bar{C}_{m't'}\bar{C}_{mt}(\bar{D}_{n'n}\bar{P}_{n'n}G_{m'm} + \bar{D}_{m'm}\bar{P}_{n'n}G_{n'n} - \bar{D}_{m'm}\bar{D}_{n'n}H_{n'n}) \\ &- \bar{C}_{n't'}\bar{C}_{mt}(\bar{D}_{n'n}\bar{P}_{m'n}G_{m'm} + \bar{D}_{m'm}\bar{P}_{m'n}G_{n'n} - \bar{D}_{m'm}\bar{D}_{n'n}H_{m'n})]\delta_{\kappa,e}\delta_{\kappa',e} \\ +4[&2\bar{C}_{mt'}\bar{C}_{m't}(\bar{D}_{n'n}\bar{P}_{n'n}H_{m'm} + \bar{D}_{n'n}\bar{P}_{m'm}H_{n'n} - \bar{P}_{m'm}\bar{P}_{n'n}G_{n'n}) \\ &- \bar{C}_{nt'}\bar{C}_{m't}(\bar{D}_{n'm}\bar{P}_{n'n}H_{m'm} + \bar{D}_{n'm}\bar{P}_{m'm}H_{n'n} - \bar{P}_{m'm}\bar{P}_{n'n}G_{n'm})]\delta_{\kappa,0}\delta_{\kappa',0} \; . \end{aligned} \tag{B4}$$

The evaluation of the expectation value $\langle w_{t'\sigma} O_{m'n'}^{(\kappa')\dagger} H_{\text{res}} O_{mn}^{(\kappa')} w_{t\sigma}^\dagger\rangle_c$ is as straightforward but more complex. The number of associated diagrams is 10. Only a small number of them are shown in Figs. 6(3a)—3(d). We introduce the abbreviations

$$\begin{aligned} U_{mm'nn'} &= \sum_{i,j,k,l} V_{ijkl} D_{im'} R_{jm} R_{kn} D_{ln'} \; , \quad W_{mm'nn'} = \sum_{i,j,k,l} V_{ijkl} D_{im'} D_{jm} R_{kn} R_{ln'} \; , \\ S_{mm'nn'} &= \sum_{i,j,k,l} V_{ijkl} D_{im'} D_{jm} D_{kn} D_{ln'} \; , \quad P_{mm'nn'} = \sum_{i,j,k,l} V_{ijkl} R_{im'} R_{jm} R_{kn} R_{ln'} \; . \end{aligned} \tag{B5}$$

Furthermore, we introduce

$$\tilde{U}_{t'm'nn'} = \sum_{i,j,k,l} V_{ijkl} D_{im'} C_{jt'} R_{kn} D_{ln'} \; , \quad \tilde{W}_{mm'nt'} = \sum_{i,j,k,l} V_{ijkl} D_{im'} D_{jm} R_{kn} C_{lt'}, \quad \tilde{P}_{t'm'nn'} = \sum_{i,j,k,l} V_{ijkl} R_{im'} C_{jt'} R_{kn} R_{ln'} \; . \tag{B6}$$

In terms of these quantities one finds

$$\begin{aligned}\langle w_{t'\sigma}O_{m'n'}^{(e)\dagger}H_{\text{res}}O_{mn}^{(e)}w_{t\sigma}^{\dagger}\rangle_c = {} & 4\bar{C}_{m't'}\bar{C}_{mt}[2\bar{D}_{m'm}(2U_{n'n'nn}-W_{nn'nn'})+\bar{D}_{n'n}(U_{mnm'n'}-2W_{mm'nn'})+\bar{P}_{n'n}(2S_{mm'nn'}-S_{mn'm'n}) \\ & -\bar{D}_{n'm}(2U_{n'm'nm}-W_{nm'nn'})-\bar{D}_{m'n}(2U_{n'n'nm}-W_{mn'nn'})]\ ,\end{aligned} \tag{B7}$$

$$\begin{aligned}\langle w_{t'\sigma}O_{m'n'}^{(0)\dagger}H_{\text{res}}O_{mn}^{(0)}w_{t\sigma}^{\dagger}\rangle_c = {} & 4\bar{C}_{mt'}\bar{C}_{m't}[2\bar{P}_{mm'}(2U_{nnn'n'}-W_{n'nn'n})+\bar{P}_{nn'}(U_{mnm'n'}-2W_{n'nm'm})-\bar{P}_{nm'}(2U_{mnn'n'}-W_{n'nn'm}) \\ & -\bar{P}_{mn'}(2U_{nnm'n'}-W_{m'nn'n})+\bar{D}_{nn'}(2P_{mm'n'n}-P_{mn'm'n})]\ ,\end{aligned} \tag{B8}$$

and finally for the coupling terms between ground-state parameters $\eta_{mn}^{(0)}$ and excitation parameters $\eta_{mn}^{(e)}$,

$$\begin{aligned}\langle w_{t'\sigma}O_{m'n'}^{(e)\dagger}H_{\text{res}}O_{mn}^{(0)}w_{t\sigma}^{\dagger}\rangle_c = {} & 4\bar{C}_{mt'}[2\bar{D}_{nn'}\bar{P}_{nn'}(2\tilde{U}_{tmm'm'}-\tilde{W}_{m'mm't}) \\ & +\bar{D}_{mm'}\bar{P}_{nn'}(\tilde{U}_{tnm'n'}-2\tilde{W}_{n'nm't})-\bar{D}_{mm'}\bar{P}_{nm'}(2\tilde{U}_{tnn'n'}-\tilde{W}_{n'nn't}) \\ & -\bar{D}_{nn'}\bar{P}_{nm'}(2\tilde{U}_{tmn'm'}-\tilde{W}_{n'mm't})+\bar{D}_{nn'}\bar{D}_{mm'}(2\tilde{P}_{tm'n'n}-\tilde{P}_{tn'm'n})]\ .\end{aligned} \tag{B9}$$

What remains is the evaluation of $\langle w_{t'\sigma}O_{m'n'}^{(\kappa')\dagger}O_{mn}^{(\kappa)}w_{t\sigma}^{\dagger}\rangle_c$. This matrix element is again diagonal with respect to the indices κ,κ':

$$\langle w_{t'\sigma}O_{m'n'}^{(\kappa')\dagger}O_{mn}^{(\kappa)}w_{t\sigma}^{\dagger}\rangle = 4\bar{C}_{m't'}\bar{C}_{mt}[(2\bar{D}_{m'm}\bar{D}_{n'n}\bar{P}_{n'n}-\bar{D}_{n'm}\bar{D}_{m'n}\bar{P}_{n'n})\delta_{k,e}\delta_{k',e}-(2\bar{P}_{mm'}\bar{D}_{nn'}\bar{P}_{nn'}-\bar{P}_{mn'}\bar{D}_{nn'}\bar{P}_{nm'})\delta_{k,0}\delta_{k',0}]\ . \tag{B10}$$

This completes the summary of the matrix elements needed to compute the correlation energy of a quasiparticle in the conduction band. When considering a hole in the valence band still the same formulas apply. In that case in all diagrams the orientation of the solid lines must be inverted, this implies simply a redefinition of the expectation values of Eq. (51). The definitions of R_{im} and D_{im} as well as $\bar{P}_{mn}$ and $\bar{D}_{mn}$ must be interchanged, while the quantities C_{it} and $\bar{C}_{mt}$ are now defined as $C_{it}=\langle a_{i\sigma}^{\dagger}w_{t\sigma}\rangle$ and $\bar{C}_{mt}=\langle b_{m\sigma}^{\dagger}w_{t\sigma}\rangle$.

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[1] For a survey see, e.g., *Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum, New York, 1977).

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