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Electronic excitations in semiconductors: Variational Green's-function approach

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We develop a Green's-function method for calculating electronic excitations in semiconductors. It is variational in character and takes full account of the local part of the correlation hole as well as the long-ranged polarization cloud. Both contribute significantly to the quasiparticles and their energies. The method is based on the Sauermann functional, the stationary point of which is the one-particle Green's function. For the case of a simple model, a connection is established to an earlier method which required the computation of correlated wave functions in order to obtain the excitation energies. Furthermore, we relate the present approach to the single-mode approximation of Overhauser and others which was devised for describing electron correlations in nearly homogeneous systems.

I. INTRODUCTION

The effects of electron correlations are known to be important in semiconductors. For example, they lead to a drastic reduction of the energy gap from its Hartree-Fock value (in diamond from 15 to 7.3 eV) and to a narrowing of the valence and conduction bands.

Recently a method for calculating the ground state[1] and excited states[2,3] (referred to hereafter as I and II, respectively) of a semiconductor was demonstrated for the case of diamond. The method takes full account of the local nature of the correlation hole and the long-ranged polarization cloud. It is variational in nature and can be applied both to molecules[4] and solids. With this method it is now possible to describe correctly the influence of many-body effects on static correlation functions as well as on the energy bands.

In this paper a new method is introduced which allows for calculating the one-particle Green's function variationally. The method is based on the Sauermann functional,[5,6] which has the property that at its stationary point it coincides with the Green's function. This approach has the advantage of a variational procedure but does not suffer from the problems usually encountered with perturbation expansions. At the same time it keeps the conceptional advantage of a Green's-function description.

Calculating the Green's function involves computation of various expectation values with respect to the correlated ground-state wave function. Therefore, we shall describe briefly in Sec. II the construction of the latter. All expressions are thereby written in terms of a finite size basis set which in practice will consist of Gaussian-type orbitals.

In Sec. III we describe how the retarded Green's function can be computed from the Sauermann functional and derive the equation for the variational parameters determining the self-energy and renormalization function. This equation is an improved version of the corresponding equation in I, since correlations in the ground state and in the excited states are treated here more symmetrically. In Sec. IV the connection to and the improvement on the previous method are demonstrated by considering a simple model. Finally, we establish in Sec. V a relation between the present approach and the one-pole approximation of Toyozawa,[7] Overhauser,[8] and Hermanson.[9] A brief summary is given in Sec. VI.

II. BASIS SET AND GROUND-STATE WAVE FUNCTION

We denote by $f_i(\vec{r})$ a set of $\bar{N}$ functions centered at different atoms. In practice these functions are usually groups of Gaussian-type orbitals. They define a set of annihilation and creation operators $a_{i\sigma}$, $a_{i\sigma}^\dagger$. The latter are obtained by expanding the single-electron field operators $\psi_\sigma(\vec{r})$ in terms of the $f_i(\vec{r})$, i.e.,

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

A similar expansion holds for $\psi_\sigma^\dagger(\vec{r})$. The functions $f_i(\vec{r})$ are generally not orthogonal and fulfill the relation,

$$\langle f_i \,|\, f_j\rangle = S_{ij} \ . \tag{2}$$

This implies

$$[a_{i\sigma},a_{j\sigma'}^\dagger]_+ = S_{ij}^{-1}\delta_{\sigma,\sigma'} \ . \tag{3}$$

The Hamiltonian H takes the following form in the Hilbert space spanned by the functions $f_i(\vec{r})$:

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

The matrices ϵ_{ij} and V_{ijkl} are defined by

$$\begin{aligned}\epsilon_{ij}&=\int d^3r\, f_i^*(\vec{r})\left[-\frac{1}{2m}\Delta+V(\vec{r})\right]f_j(\vec{r}) \ ,\\ V_{ijkl}&=\int d^3r\, d^3r' f_i^*(\vec{r})f_j(\vec{r})\frac{e^2}{|\vec{r}-\vec{r}\,'|}f_k^*(\vec{r}\,')f_l(\vec{r}\,') \ ,\end{aligned} \tag{5}$$

where $V(\vec{r})$ is the single-electron potential due to the nuclei.

In the following we want to assume that the index i in $a_{i\sigma}$ involves a cell index $\vec{\mathrm{i}}$ as well as an index α for different functions within a unit cell, i.e., $i=(\vec{\mathrm{i}},\alpha)$. It is advantageous to divide H into a self-consistent field (SCF) part H_0 and a residual interaction part H_{res},

$$H=H_0+H_{\mathrm{res}} \; . \tag{6}$$

Then it can be seen that

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

where f_{ij} is the Fock matrix

$$f_{ij}=\epsilon_{ij}+\sum_{kl\sigma'}(V_{ijkl}-\delta_{\sigma,\sigma'}V_{ilkj})\langle a_{k\sigma'}^{\dagger}a_{l\sigma'}\rangle \; , \tag{8}$$

and

$$H_{\mathrm{res}}=\frac{1}{2}\sum_{\substack{ijkl\\ \sigma,\sigma'}}[V_{ijkl}a_{i\sigma}^{\dagger}a_{k\sigma'}^{\dagger}a_{l\sigma'}a_{j\sigma}-(V_{ijkl}-\delta_{\sigma,\sigma'}V_{ijkl}) \times\langle a_{k\sigma'}^{\dagger}a_{l\sigma'}\rangle a_{i\sigma}^{\dagger}a_{j\sigma}] \; . \tag{9}$$

The notation $\langle\;\rangle$ stands for $\langle\phi_{\mathrm{SCF}}|\quad|\phi_{\mathrm{SCF}}\rangle$ where $|\phi_{\mathrm{SCF}}\rangle$ is the SCF ground state.

For the *correlated* ground state an ansatz is made of the form (see I),

$$\begin{aligned}|\psi_0\rangle&=\exp\left[-\sum_{mn}\eta_{mn}^{(0)}O_{mn}^{(0)}\right]|\phi_{\mathrm{SCF}}\rangle\\ &=\exp(S_0)|\phi_{\mathrm{SCF}}\rangle \; .\end{aligned} \tag{10}$$

The operators $O_{mn}^{(0)}$ refer to local regions m and n. Such a local region can consist of, e.g., part of a bond or part of an atomic volume. It is defined by a local function,

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

and different $g_m(\vec{\mathrm{r}})$'s are generally not orthogonal to each other. Their proper choice has been discussed at great length elsewhere.[4] Related to the $g_m(\vec{\mathrm{r}})$ are operators $b_{m\sigma}^{\dagger}$, $b_{m\sigma}$ which create or annihilate electrons with spin σ in the state $g_m(\vec{\mathrm{r}})$. From them one can construct density and spin-density operators,

$$n_{m\sigma}=b_{m\sigma}^{\dagger}b_{m\sigma} \; , \tag{12}$$

$$\vec{\mathrm{s}}_m=\sum_{\sigma\sigma'}b_{m\sigma}^{\dagger}\vec{\mathrm{s}}_{\sigma\sigma'}b_{m\sigma'} \; . \tag{13}$$

The matrices $\vec{\mathrm{s}}_{\sigma\sigma'}$ equal $\frac{1}{2}$ the Pauli matrices.

The operators $O_{mn}^{(0)}$ are defined by

$$O_{mn}^{(0)}=O_{mn}-O_{mn}^{\mathrm{SCF}} \; , \tag{14}$$

where

$$O_{mn}=\begin{cases}n_{m\uparrow}n_{m\downarrow}\delta_{m,n}\\ n_m n_n=\sum_{\sigma\sigma'}n_{m\sigma}n_{n\sigma'}\\ \vec{\mathrm{s}}_m\vec{\mathrm{s}}_n \; .\end{cases} \tag{15}$$

We subtract the SCF or single-particle part O_{mn}^{SCF} from the operator O_{mn} to ensure that the one-particle density matrix remains unchanged to first order in $\eta_{mn}^{(0)}$.

The $\eta_{mn}^{(0)}$ in Eq. (10) are variational parameters. They are determined by minimizing the ground-state energy after the latter has been expanded up to second order in the $\eta_{mn}^{(0)}$. As has been discussed in detail in I, such a minimization requirement does not fix all of the $\eta_{mn}^{(0)}$ but only certain combinations of them. The ground-state energy is independent of the remaining, and therefore undetermined, linear combinations of the $\eta_{mn}^{(0)}$. This concludes the summary of the construction of the correlated ground-state wave function.

III. ELECTRON PROPAGATOR

The retarded Green's function for the electron system is defined by

$$G_{b\sigma}(\vec{\mathrm{k}},t)=-i\Theta(t)\langle\psi_0|[c_{\vec{\mathrm{k}}b\sigma}(t),c_{\vec{\mathrm{k}}b\sigma}^{\dagger}(0)]_+|\psi_0\rangle \times\langle\psi_0|\psi_0\rangle^{-1} \; . \tag{16}$$

The operators $c_{\vec{\mathrm{k}}b\sigma}^{\dagger}$ create electrons in single-electron eigenstates of H_0 labeled by the band index b. $\Theta(t)$ is the Heaviside step function. The Fourier transform of the Green's function is given by

$$G_{b\sigma}(\vec{\mathrm{k}},\omega)=\left(c_{\vec{\mathrm{k}}b\sigma}^{\dagger}\;\middle|\;\frac{1}{\omega-L+i\delta}\;\middle|\;c_{\vec{\mathrm{k}}b\sigma}^{\dagger}\right) \; . \tag{17}$$

Here we have introduced the Liouville operator. It is a superoperator which acts on other operators A through the relation

$$LA=[H,A]_- \; . \tag{18}$$

Furthermore the scalar product $(A\,|\,B)$ of any two operators is defined by

$$(A\,|\,B)=\frac{\langle\psi_0|[A^+,B]_+|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle} \; . \tag{19}$$

The Liouville operator can be divided into a SCF part L_0 and a residual part L_{res},

$$L=L_0+L_{\mathrm{res}} \; , \tag{20}$$

where

$$\begin{aligned}L_0A&=[H_0,A]_- \; ,\\ L_{\mathrm{res}}A&=[H_{\mathrm{res}},A]_- \; .\end{aligned} \tag{21}$$

If one neglects L_{res}, Eq. (17) becomes

$$G_{b\sigma}^{\mathrm{SCF}}(\vec{\mathrm{k}},\omega)=\frac{1}{\omega-\epsilon_{\mathrm{SCF}}(\vec{\mathrm{k}},b)} \; , \tag{22}$$

where $\epsilon_{\mathrm{SCF}}(\vec{\mathrm{k}},b)$ denotes the excitation energy in the SCF approximation.

In order to compute $G_{b\sigma}(\vec{k},\omega)$ we introduce a functional which is due to Sauermann[5] and has the property that it yields the Green's function as a stationary point. It has the form

$$F_{\vec{k}b\sigma}(\phi,\phi')=(\phi'\,|\,c^{\dagger}_{\vec{k}b\sigma})+(c^{\dagger}_{\vec{k}b\sigma}\,|\,\phi) -(\phi'\,|\,(\omega-L+i\delta)\,|\,\phi)\ . \tag{23}$$

Here ϕ and ϕ' are operators which contain variational parameters and we must search for the stationary point $F_{\vec{k}b\sigma}(\phi_{\mathrm{st}},\phi'_{\mathrm{st}})$. For ϕ and ϕ' we make the following ansatz:

$$\begin{aligned}&|\,\phi)=\alpha\{\,|\,c^{\dagger}_{\vec{k}b\sigma})+Q\,|\,\hat{S}c^{\dagger}_{\vec{k}b\sigma})\}\ ,\\ &(\phi'\,|=\alpha'\{(c^{\dagger}_{\vec{k}b\sigma}\,|+(\hat{S}c^{\dagger}_{\vec{k}b\sigma}\,|\,Q\}\ ,\end{aligned} \tag{24}$$

where $\hat{S}$ is a superoperator (like L). We define it through

$$\hat{S}A=[S,A]_{-}\ , \tag{25}$$

where S is assumed to be of the form

$$S=-\sum_{nm}\eta_{nm}O_{mn}\ . \tag{26}$$

The operators O_{mn} are those defined by Eq. (15). Furthermore, the operator Q is a projection operator. It is defined by

$$\begin{aligned}&Q=1-P\ ,\\ &P=|\,c^{\dagger}_{\vec{k}b\sigma})(c^{\dagger}_{\vec{k}b\sigma}\,|\ .\end{aligned} \tag{27}$$

The operator $|\,\phi)$ can be thought of describing a quasiparticle consisting of the "bare" particle $|\,c^{\dagger}_{\vec{k}b\sigma})$ and the polarization and relaxation cloud $Q\,|\,\hat{S}c^{\dagger}_{\vec{k}b\sigma})$ around it.

The parameters α, α', and η_{mn} are determined by requiring that $F_{\vec{k}b\sigma}(\phi,\phi')$ is stationary. Keeping the η_{mn} fixed and varying with respect to α and α' leads to

$$G_{b\sigma}(\vec{k},\omega)=\frac{Z(\vec{k},b,\eta)}{\omega-\epsilon_{\mathrm{SCF}}(\vec{k},b)-\Sigma(\vec{k},b,\eta)}\ . \tag{28}$$

Here

$$Z(\vec{k},b,\eta)=((1+Q\hat{S})c^{\dagger}_{\vec{k}b\sigma}\,|\,(1+Q\hat{S})c^{\dagger}_{\vec{k}b\sigma})^{-1} \tag{29}$$

is the so-called renormalization function and

$$\Sigma(\vec{k},b,\eta)=\frac{((1+Q\hat{S})c^{\dagger}_{\vec{k}b\sigma}\,|\,[L-\epsilon_{\mathrm{SCF}}(\vec{k},b)]\,|\,(1+Q\hat{S})c^{\dagger}_{\vec{k}b\sigma})}{((1+Q\hat{S})c^{\dagger}_{\vec{k}b\sigma}\,|\,(1+Q\hat{S})c^{\dagger}_{\vec{k}b\sigma})} \tag{30}$$

is the self-energy. The latter can be identified with the correlation energy $\epsilon_{\mathrm{corr}}(\vec{k},b,\eta)$. Both functions do not depend directly on ω, but only indirectly through the matrix η, as will be seen below. Indeed, by considering the η_{mn}'s as variables and requiring that $F_{\vec{k}b\sigma}(\phi,\phi')$ is stationary, one finds that they must obey the equations

$$\frac{\partial G_{b\sigma}(\vec{k},\omega,\eta)}{\partial\eta_{mn}}=0\ . \tag{31}$$

This implies,

$$\frac{\partial\Sigma(\vec{k},b,\eta)}{\partial\eta_{mn}}=-\frac{\partial\ln Z(\vec{k},b,\eta)}{\partial\eta_{mn}}\times[\omega-\epsilon_{\mathrm{SCF}}(\vec{k},b)-\Sigma(\vec{k},b,\eta)]\ , \tag{32}$$

and shows that the η_{mn} are generally ω dependent. For ω values on the energy shell, i.e., for

$$\omega=\epsilon_{\mathrm{SCF}}(\vec{k},b)+\Sigma(\vec{k},b,\eta)\ ,$$

Eq. (32) simplifies to

$$\frac{\partial\Sigma(\vec{k},b,\eta)}{\partial\eta_{mn}}=0\ . \tag{33}$$

By making use of Eq. (30) one can derive the following expression for η_{mn}:

$$\eta_{mn}=-\sum_{ij}\{(\hat{O}c^{\dagger}_{\vec{k}b\sigma}\,|\,Q[\omega(\vec{k},b)-L]Q\,|\,\hat{O}c^{\dagger}_{\vec{k}b\sigma})^{-1}\}_{mn;ij}\times(\hat{O}_{ij}c^{\dagger}_{\vec{k}b\sigma}\,|\,QL_{\mathrm{res}}c^{\dagger}_{\vec{k}b\sigma})\ . \tag{34}$$

The $\hat{O}_{ij}$ are defined through

$$\hat{O}_{ij}A=[O_{ij},A]_{-}\ . \tag{35}$$

When Eq. (34) is used to eliminate the quadratic term in the η_{mn}'s one can write

$$\Sigma(\vec{k},b)=\Sigma_0(\vec{k},b)+\Sigma_1(\vec{k},b) \tag{36}$$

with

$$\Sigma_0(\vec{k},b)=(c^{\dagger}_{\vec{k}b\sigma}\,|\,L_{\mathrm{res}}\,|\,c^{\dagger}_{\vec{k}b\sigma})\ , \tag{37a}$$

$$\Sigma_1(\vec{k},b)=-\sum_{mn}\eta_{mn}(\hat{O}_{mn}c^{\dagger}_{\vec{k}b\sigma}\,|\,QL_{\mathrm{res}}c^{\dagger}_{\vec{k}b\sigma})\ . \tag{37b}$$

$\Sigma_0(\vec{k},b)$ is positive and nonzero, even for $\eta_{mn}=0$. It describes part of the changes in the ground-state correlations due to the presence of the extra electron in state $\vec{k},b,\sigma$.

What remains is a discussion of the evaluation of the scalar products which appear in Eqs. (37a) and (37b). We indicate in the following how this is done. It turns out to be advantageous to express the Bloch function operators in terms of Wannier operators $w^{\dagger}_{t\sigma}$, where again the index t includes a cell index $\vec{t}$ as well as an index τ within a unit cell, i.e., $t=(\vec{t},\tau)$. It is

$$c^{\dagger}_{\vec{k}b\sigma}=\frac{1}{(N_c)^{1/2}}\sum_{t}e_{\tau}(\vec{k},b)w^{\dagger}_{t\sigma}\exp(i\vec{k}\vec{R}_{\vec{t}})\ . \tag{38}$$

N_c is the number of unit cells and the matrix $e_{\tau}(\vec{k},b)$ provides the link between both types of operators. Instead of, e.g., $(\hat{O}_{mn}c^{\dagger}_{\vec{k}b\sigma}\,|\,L_{\mathrm{res}}c^{\dagger}_{\vec{k}b\sigma})$ one then evaluates

$(\hat{O}_{mn} w^{\dagger}_{t'\sigma} \mid L_{\text{res}} w_{t\sigma})$. It is

$$L_{\text{res}} w^{\dagger}_{t\sigma} = \sum_{ijkl\sigma'} V_{ijkl} a^{\dagger}_{i\sigma} a^{\dagger}_{k\sigma'} a_{l\sigma'} [a_{j\sigma}, w^{\dagger}_{t\sigma}]_{+} - \sum_{ijkl\sigma'} (V_{ijkl} - \delta_{\sigma,\sigma'} V_{ilkj}) \times \langle a^{\dagger}_{k\sigma'} a_{l\sigma'} \rangle a^{\dagger}_{i\sigma} [a_{j\sigma}, w^{\dagger}_{t\sigma}]_{+} , \tag{39}$$

and one can now make use of the fact that $[a_{j\sigma}, w^{\dagger}_{t\sigma}]_{+}$ is a c number. We set

$$[a_{j\sigma}, w^{\dagger}_{t\sigma}]_{+} = K_{jt} , \tag{40}$$

and the matrix can be evaluated when the Wannier states are known. In complete analogy one can evaluate $\hat{O}_{mn} w^{\dagger}_{t'\sigma}$ and denote the c number $[b_{n\sigma}, w^{\dagger}_{t'\sigma}]_{+} = \bar{K}_{nt'}$. Then one ends up with the following expression:

$$(\hat{O}_{mn} w^{\dagger}_{t'\sigma} \mid L_{\text{res}} w^{\dagger}_{t\sigma}) = 2\bar{K}_{mn} \sum_{ijkl\sigma'\sigma''} [(b^{\dagger}_{m\sigma} n_{n\sigma'} \mid a^{\dagger}_{i\sigma} a^{\dagger}_{k\sigma''} a_{l\sigma''}) - (b^{\dagger}_{m\sigma} n_{n\sigma'} \mid a^{\dagger}_{i\sigma})(V_{ijkl} - \delta_{\sigma,\sigma'} V_{ilkj}) \langle a^{\dagger}_{k\sigma''} a_{l\sigma''} \rangle K_{jt'}] . \tag{41}$$

The scalar products can be reduced to sums of expectation values of the form, e.g., $\langle \psi_0 \mid n_{m\sigma'} a^{\dagger}_{k\sigma''} a_{l\sigma''} \mid \psi_0 \rangle$. With the help of the linked cluster theorem (see I) we can write

$$\langle \psi_0 \mid \psi_0 \rangle^{-1} \langle \psi_0 \mid n_{m\sigma'} a^{\dagger}_{k\sigma''} a_{l\sigma''} \mid \psi_0 \rangle = \langle e^{s} n_{m\sigma'} a^{\dagger}_{k\sigma''} a_{l\sigma''} e^{s} \rangle_{c} , \tag{42}$$

where c indicates that only connected diagrams must be taken when the expectation value is evaluated. This value is calculated up to terms linear in the η's. The evaluation of Eqs. (37a) and (37b) is then reduced to the same procedure which was discussed extensively in I.

IV. APPLICATION TO A SIMPLE MODEL

In the following we want to apply the above formalism to a simple one-dimensional chain model which was also used in I. This will not only provide some insight into how the above method works in practice, but also enable us to discuss the differences to the approach used previously, i.e., in I and II. We discuss the model relatively briefly and refer for more details to that reference. Consider a chain of atoms forming *sp* bonds. 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 bond i. Then the bonding and antibonding creation operators are given by

$$\begin{aligned} B^{\dagger}_{i\sigma} &= \frac{1}{\sqrt{2}} [a^{\dagger}_{1\sigma}(i) + a^{\dagger}_{2\sigma}(i)] , \\ A^{\dagger}_{i\sigma} &= \frac{1}{\sqrt{2}} [a^{\dagger}_{1\sigma}(i) - a^{\dagger}_{2\sigma}(i)] . \end{aligned} \tag{43}$$

In the following we shall make the bond orbital approximation (BOA) (see Ref. 10). The SCF Hamiltonian H_0 is of the form

$$H_0 = \sum_{i\sigma} [-T_0 B^{\dagger}_{i\sigma} B_{i\sigma} + T_B (B^{\dagger}_{i\sigma} B_{i+1\sigma} + \text{H.c.}) + T_0 A^{\dagger}_{i\sigma} A_{i\sigma} - T_A (A^{\dagger}_{i\sigma} A_{i+1\sigma} + \text{H.c.})] . \tag{44}$$

The centers of the valence and conduction band are therefore given by $\pm T_0$ and the respective band widths are $4T_B$ and $4T_A$. H_0 is supposed to contain the mean-field part of the interaction Hamiltonian

$$H_{\text{int}} = \frac{1}{2} \sum_{i\nu\alpha\beta} V_{\alpha-\beta}(\nu) n_{\alpha}(i) n_{\beta}(i+\nu) , \tag{45}$$

where

$$n_{\alpha}(i) = \sum_{\sigma} a^{\dagger}_{\alpha\sigma}(i) a_{\alpha\sigma}(i) \tag{46}$$

is the number operator for electrons in hybrid α of bond i. It is useful to rewrite H_{int} by introducing the quantities

$$\begin{aligned} n(i) &= \tfrac{1}{2}[n_2(i) + n_1(i)] , \\ p(i) &= \tfrac{1}{2}[n_2(i) - n_1(i)] , \\ \tilde{V}(i) &= V_{-1}(i) + V_{+1}(i) + 2V_0(i) , \\ V'(i) &= V_{-1}(i) - V_{+1}(i) , \\ V''(i) &= V_{-1}(i) + V_{+1}(i) - 2V_0(i) . \end{aligned} \tag{47}$$

Here $2n(i)$ and $2p(i)$ are the electron number and the polarization operator of bond i. Furthermore, $V'(i)$ and $V''(i)$ are the first- and second-order difference quotient of the interaction potential. $\tilde{V}(i)$ is the average interaction potential for electrons which are i bonds apart. In terms of those quantities H_{int} takes the form

$$H_{\text{int}} = \frac{1}{2} \sum_{i\nu} \tilde{V}(\nu) n(i) n(i+\nu) + \sum_{i\nu} V'(\nu) n(i) p(i+\nu) - \frac{1}{2} \sum_{i\nu} V''(\nu) p(i) p(i+\nu) . \tag{48}$$

In the BOA the state $|\phi_{\text{SCF}}\rangle$ is an eigenstate to the operator $n(i)$ with eigenvalue 1. The same holds true for the correlated ground state $|\psi_0\rangle$ [see Eq. (10)] provided that S_0 contains only density-density correlations between hybrids, i.e., $n(i)|\psi_0\rangle = |\psi_0\rangle$. The correlated ground-state wave function contains polarization fluctuations within a bond, but no charge fluctuations between bonds. This implies that the correlation energy depends only on $V''(\nu)$.

In order to calculate the self-energy we write

$$\begin{aligned} S &= -\sum_{ij\alpha\beta} \eta_{\alpha-\beta}(i-j) n_{\alpha}(i) n_{\beta}(j) \\ &= -\sum_{i\nu} \sigma(\nu) n(i) n(i+\nu) - 2\sum_{i\nu} \pi(\nu) n(i) p(i+\nu) \\ &\quad + \sum_{i\nu} \kappa(\nu) p(i) p(i+\nu) . \end{aligned} \tag{49}$$

The $\pi(\nu)$, $\kappa(\nu)$, and $\sigma(\nu)$ are the following independent combinations of the $\eta_{\alpha-\beta}(\nu)$ parameters

$$\pi(\nu)=\eta_{-1}(\nu)-\eta_{+1}(\nu)\ ,$$

$$\kappa(\nu)=\eta_{-1}(\nu)+\eta_{+1}(\nu)-2\eta_0(\nu)\ . \tag{50}$$

$$\sigma(\nu)=\eta_{-1}(\nu)+\eta_{+1}(\nu)+2\eta_0(\nu)\ ,$$

They are closely related to the corresponding quantities in I and describe bond polarizations, van der Waals correlations (these are the only correlations which appear in the ground state), and charge transfer, respectively.

We are interested in calculating the Green's function for the antibonding band. For that purpose we apply $\hat{S}$ on the Fourier transform $A_{k\sigma}^{\dagger}$ of $A_{i\sigma}^{\dagger}$. It takes here the place of the $c_{\vec{k}b\sigma}^{\dagger}$. One finds

$$|\hat{S}A_{k\sigma}^{\dagger})=-\frac{1}{\sqrt{N}}\sum_{j\nu}\exp(ikj)[\,|A_{j\sigma}^{\dagger}p(j+\nu))\pi(\nu)+|B_{j\sigma}^{\dagger}p(j+\nu))\kappa(\nu)+|A_{j\sigma}^{\dagger}n(j+\nu))\sigma(\nu)-|B_{j\sigma}^{\dagger}n(j+\nu))\pi(\nu)]\ . \tag{51}$$

The atomic distance has been set equal to unity.

Owing to the absence of charge fluctuations between bonds in the BOA, we expect that the correlation energy depends on $\pi(\nu)$ and $\kappa(\nu)$ only. The self-energy can be calculated according to Eq. (30). Within the BOA the scalar products can be easily evaluated. They reduce to expressions of the form

$$\langle\psi_0|B_{i\sigma}^{\dagger}B_{j\sigma}|\psi_0\rangle=\delta_{ij}+O((\eta^{(0)})^2)\ ,$$
$$\langle\psi_0|A_{i\sigma}^{\dagger}A_{j\sigma}|\psi_0\rangle=O((\eta^{(0)})^2)\ , \tag{52}$$

and

$$P(\mu-\nu)=\langle\psi_0|p(\mu)p(\nu)|\psi_0\rangle=\tfrac{1}{2}\delta_{\mu\nu}+O(\eta^{(0)})\ . \tag{53}$$

The final answer for $\Sigma(\vec{k},\pi,\kappa)$ is conveniently expressed in terms of the Fourier transforms $\pi(q)$, $\kappa(q)$, V_q', and V_q''. It is $\pi(q)=\sum_l\pi(l)\exp(-iql)$ and similarly for the other quantities. Furthermore,

$$P_q=\frac{1}{N}\sum_{lj}\langle\psi_0|p(j)p(j+l)|\psi_0\rangle\exp(iql)\ . \tag{54}$$

The following result is found:

$$\Sigma(k,\pi,\kappa)=D^{-1}\left[-\sum_q\pi_qV_q'P_q+\sum_q\pi_q^2\{P_q[2T_A\cos q\cos k+T_0-\epsilon_{\text{SCF}}(k)]+T_0\}\right.$$
$$\left.-\sum_q\kappa_qV_q''P_q+\tfrac{1}{4}\kappa(0)V''(0)-\sum_q\kappa_q^2\{P_q[2T_B\cos q\cos k+T_0+\epsilon_{\text{SCF}}(k)]+T_0\}+\kappa^2(0)T_0\right]\ , \tag{55}$$

where small exchange contributions $\sim\kappa_q^2$ have been left out. The denominator D is given by

$$D=1+\sum_q\pi_q^2P_q+\sum_q\kappa_q^2P_q-\tfrac{1}{4}\kappa^2(0)\ . \tag{56}$$

The parameter π_q is determined by requiring that $\partial\Sigma/\partial\pi_q=0$. This results in

$$\pi_q(k)=-\frac{1}{2}\frac{V_q'}{\omega(k)-2T_A\cos q\cos k-T_0-T_0P_q^{-1}}\ . \tag{57}$$

Here $\omega(k)=\epsilon_{\text{SCF}}(k,a)+\Sigma(k,\pi,\kappa)$ and the index a indicates that the SCF solution for the antibonding band is considered.

Similarly one deduces from $\partial\Sigma/\partial\kappa_q=0$ that

$$\kappa_q(k)=\frac{-1}{2}\frac{V_q''}{\omega(k)+2T_B\cos q\cos k+T_0+T_0P_q^{-1}-\Sigma(k,\pi,\kappa)\kappa(0)(4P_q)^{-1}}\ . \tag{58}$$

Equations (57) and (58) can be used to rewrite $\Sigma(\vec{k},\pi,\kappa)$ in the form

$$\Sigma(k,\pi,\kappa)=-\tfrac{1}{2}\sum_qV_q'\pi_qP_q$$
$$-\tfrac{1}{2}\sum_qV_q''\kappa_qP_q+\tfrac{1}{8}\kappa(0)V''(0)\ . \tag{59}$$

A comparison with I reveals that π_qP_q and κ_qP_q correspond to π_q and $\kappa_q^{(0)}$ of that reference. But in distinction to the present approach the $\kappa_q^{(0)}$, or better their Fourier transforms $\kappa^{(0)}(\nu)$, were obtained there from a separate ground-state calculation. Here they follow directly from Eq. (58). One can show that κ_q and $\kappa_q^{(0)}$ are related through

$$\kappa_q(k,T_A=T_B=0)=-\kappa_q^{(0)}+O((V_q'')^2)\ . \tag{60}$$

A closer inspection reveals that the $\kappa_q^{(0)}$ are an average over all occupied k states of the $-\kappa_q(k)$. The present formulation is therefore definitely an improvement over the earlier one given in I and II. It allows for constructing a correlation hole around an electron in the ground state of the system which depends explicitly on its momentum. While the differences are unimportant as far as energy calculations are concerned they lead to considerable improvements for quantitites like the momentum distribution in the ground state $n(k)$.

In order to compare the present form for π_q as given by Eq. (57) with the one obtained in I [see Eq. (74) of that reference] we state without proof that P_q can be written as

$$P_q=\tfrac{1}{2}[1+2\kappa_q^{(0)}-\kappa^0(0)]\ , \tag{61}$$

and

$$T_0P_q^{-1}=2T_0-\tfrac{1}{2}V_q''+\tfrac{1}{2}V''(0)\ . \tag{62}$$

When this expression is put into the denominator of Eq. (57) it agrees with that of Eq. (74) in I [note that $\omega(k)=\epsilon_{\rm SCF}(k)+\epsilon_{\rm corr}(k)$]. However, the numerator of $\pi_q P_q$ does not quite agree with that of Eq. (74) of I and differences occur in the κ-dependent terms. This is due to a somewhat different treatment of the ground-state correlations in the two cases. For details we refer to the Appendix.

Next we want to discuss the simple result obtained by Eq. (59). The first term on the right-hand side (rhs) describes the contribution from the polarization cloud around the electron propagating in state A_k^+. The ground-state properties enter thereby only through the correlation function P_q which describes the polarization fluctuations in the ground state. This is a desirable feature since one can make a phenomenological ansatz for P_q if one does not want or is not able to calculate the correlated ground state as is the case in strongly correlated systems. The second and third term on the rhs of Eq. (59) describe the loss in ground-state correlations due to the presence of the additional electron $A_{k\sigma}^\dagger$.

In conclusion it is seen that the Green's-function method has the advantage of yielding not only the parameters π_q and κ_q at the same time, but also providing for improved ground-state calculations, through the k dependence of κ.

V. SINGLE-MODE APPROXIMATION

In 1970 it was suggested by Overhauser[8] that the treatment of electronic correlations in metals can be simplified by making a single-mode approximation (SMA). Related ideas were expressed before by Toyozawa.[7] The SMA is made for electron-hole excitations which appear when the interaction of a particular electron with the remaining electrons is considered. In the homogeneous electron gas or metals the properties of the single mode $\omega_{\vec{q}}$ are strongly related to density fluctuations $\rho_{\vec{q}}$. More specifically it is

$$\omega_{\vec{q}}=\frac{1}{2}\frac{\langle\psi_0|[\rho_{-\vec{q}},[H,\rho_{\vec{q}}]_-]_-|\psi_0\rangle}{\langle\psi_0|\rho_{-\vec{q}}\rho_{\vec{q}}|\psi_0\rangle}\;. \tag{63}$$

In the limit $q\rightarrow 0$ this expression can be shown to reduce to the plasma frequency while in the limit $q\rightarrow\infty$ it becomes equal to the single-particle excitation $q^2/2m$. A relation of the form (63) was used first by Feynman[11] and Feynman and Cohen[12] for the determination of the excitation spectrum in ^{4}He.

It is interesting to notice that the present variational Green's-function approach can be also considered as a SMA. However, in semiconductors with a large energy gap the role of the density-density correlations is taken by the polarization-polarization correlations as will be seen below.

In order to bring out the SMA character of the present theory it is best to consider the simple model discussed in Sec. IV. Within that model the self-energy $\Sigma(k,\pi,\kappa)$ takes the form (55) with π_q and κ_q given by Eqs. (57) and (58). In order to compare it with the perturbational approach of Overhauser we neglect terms in π_q and κ_q which depend on $\Sigma(k,\pi,\kappa)$. Then one can write

$$\Sigma(k,\pi,\kappa)=\frac{1}{4N}\sum_q\frac{(V_q')^2P_q}{\epsilon_{\rm SCF}(k,a)-\epsilon_{\rm SCF}(k+q,a)-\omega_q}+\frac{1}{4N}\sum_q\frac{(V_q'')^2P_q-\frac{1}{4}V''(0)V_q''}{\epsilon_{\rm SCF}(k,a)-\epsilon_{\rm SCF}(k+q,b)+\omega_q}\;. \tag{64}$$

This equation can be directly compared with Eq. (40) of Ref. 8.

The dispersion of the single mode ω_q is determined by

$$\omega_q=\frac{1}{2}\frac{\langle\psi_0|[p_{-q},[H,p_q]_-]_-|\psi_0\rangle}{\langle\psi_0|p_{-q}p_q|\psi_0\rangle}\approx\frac{T_0}{P_q}\;, \tag{65}$$

which replaces Eq. (63). The p_q are the Fourier transforms of the $p(i)$ [see Eq. (47)] and describe polarization fluctuations. The product $2V_q'P_q$ in the numerator of the first term in Eq. (64) plays the role of a screened interaction between the extra electron and the induced dipoles. The screening is accounted for by the polarization-polarization correlation function $2P_q$. Similarly $2V_q''P_q$ is the screened dipole-dipole interaction. The term $V''(0)V_q''/4$ is the only contribution to the exchange. There is no additional term when the extra electron and the dipole are in the same bond, i.e., $V'(0)=0$. The indices b,a in the denominator of Eq. (64) denote the bonding and antibonding band, respectively. The self-energy (64) which depends on $\epsilon_{\rm SCF}(k,b)$ and $\epsilon_{\rm SCF}(k,a)$ can be used to define a SCF energy-dependent potential for a single-particle Schrödinger equation in the same way as proposed in Refs. 3, 13, and 14.

VI. SUMMARY

It has been shown that the electron Green's function of semiconductors can be calculated variationally by making use of the Sauermann functional. This method is particularly convenient for calculating excitation energies which fully include electron correlations. It is closely related to an approach applied previously to diamond (see I and II) and this relation was discussed in detail. A comparison between the present method and the single-mode approximation of Overhauser and others was presented.

In both cases the dynamical properties of the system are related to static expectation values evaluated with respect to the correlated ground state. Whereas in nearly homogeneous systems, like the metallic ones considered by Overhauser, the density-density correlations are the most important ones it was demonstrated that in large-gap semiconductors this role is taken by the polarization-polarization correlations. We believe that the present approach can be extended without problems to the computation of response functions.

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APPENDIX

The variational form of the Green's function given above was shown to result in almost the same equations for the variational parameters as were derived in I. In the following we want to indicate the changes which have to be made in order to end up with identical equations in both cases. Instead of the retarded Green's function (17) we start out from the propagator $G^{\dagger}_{b\sigma}(\vec{k},\omega)$ which describes the time evaluation of an electron added in subband b to the system. It is

$$G^{\dagger}_{b\sigma}(\vec{k},\omega)=\left(c^{\dagger}_{\vec{k}b\sigma}\left|\frac{1}{\omega-H+E_0}\right|c^{\dagger}_{\vec{k}b\sigma}\right), \tag{A1}$$

but here the scalar product of any two operators is of the form

$$(A\,|\,B)=\frac{\langle\psi_0\,|\,A^{\dagger}B\,|\,\psi_0\rangle}{\langle\psi_0\,|\,\psi_0\rangle}, \tag{A2}$$

and replaces Eq. (19). The E_0 in Eq. (A1) is the ground-state energy. $G^{\dagger}_{b\sigma}(\vec{k},\omega)$ is again a stationary point of the Sauermann functional (23) but now with the definition (A2) for the scalar product and L replaced by $(H-E_0)$. For $|\,\phi)$ and $(\phi'\,|$ an ansatz is made of the form

$$\begin{aligned}|\,\phi)&=\alpha\,|\exp(\hat{S})c^{\dagger}_{\vec{k}b\sigma})\,,\\(\phi'\,|&=\alpha'(\exp(\hat{S})c_{\vec{k}b\sigma}\,|\;.\end{aligned} \tag{A3}$$

S is again defined by Eqs. (25) and (26) but now with O_{mn} replaced by $O^{(0)}_{mn}$ [see Eq. (14)]. Furthermore, those η_{mn} parameters which follow from a ground-state calculation are considered as already determined and therefore are kept fixed. They are identified with the $\eta^{(0)}_{mn}$ of Eq. (10). When $G^{\dagger}_{b\sigma}(\vec{k},\omega)$ is calculated by varying the Sauermann functional with respect to α and α' it is found that the energy,

$$\epsilon(\vec{k},b)=\epsilon_{\mathrm{SCF}}(\vec{k},b)+\Sigma(\vec{k},b\,;\eta,\eta^{(0)}) \tag{A4}$$

is identical to Eq. (34) of I. Here we have indicated explicitly that the self-energy depends on the $\eta^{(0)}$ parameter matrix which follows already from a ground-state calculation and remaining η's. The further procedure is the same as in I and is not repeated here. In particular the determining equations for the remaining η_{mn} are the same as in that reference.

In summary it is seen that the difference between the Green's-function treatment of excited states in this paper and the earlier treatment in I is a subtle one. Here we work with the retarded Green's function while I corresponds to working with $G^{\dagger}_{b\sigma}(\vec{k},\omega)$ [or $G^{-}_{b\sigma}(\vec{k},\omega)$ for a hole]. Working with the retarded Green's function is clearly preferable since, for the correlated ground state $|\,\psi_0\rangle$, it is not only $c^{\dagger}_{\vec{k}b\sigma}\,|\,\psi_0\rangle\neq 0$ but also $c_{\vec{k}b\sigma}\,|\,\psi_0\rangle\neq 0$ when b refers to a conduction band. This implies that electrons and holes should be treated simultaneously as is done when the retarded Green's function is used.

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