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Method of increments for excitations in correlated electron systems

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Abstract The method of increments has been invaluable for electronic structure calculations of solids based in wavefunctions, i.e., quantum chemical techniques. While it is well documented for ground-state calculations we want to give here a coherent description when it is applied to the computation of excitations of weakly and strongly correlated electron systems. Previous applications can be viewed as special cases of the general scheme.

Keywords electron correlations · energy bands · projection method

them we find it mandatory to use an incremental computational scheme of the form suggested and tested by Stoll [1, 2]. It resembles the Bethe–Goldstone method in nuclear physics [3]. Without using the method of increments it is extremely hard to compute energy bands of semiconductors and insulators with reasonable accuracy. The computational effort is simply too large. The aim of this communication is primarily not to present new results but rather to consider various approaches to energy band structures from a unifying point of view with a focus on Stoll’s method of increments.

1 Introduction

Electronic structure calculations is an important branch of condensed matter physics. This holds particularly true for the determination of energy bands of periodic solids. Presently they are usually calculated by various approximations to density functional theory. Although that theory is strictly speaking one for the ground state of a system it has been also successfully applied to excitations. But one should be well aware of the fact that as regards energy bands the approximations are uncontrolled and therefore can fail badly, e.g., when electron correlations are strong. In the latter case one would also like to be able to calculate satellite structures. From that point of view it is desirable to find alternative ways of computing energy bands of solids. In the following we want to discuss some of them. They are based on a quasiparticle description when electron correlations are weak and on a Green’s function or projection operator approach when they are strong. In both cases intersite correlation contributions to the energy bands require special attention. In order to deal with

2 Special representation

We start from a Hamiltonian of the form

$$H = \sum_{ij\sigma} t_{ij} a_{i\sigma}^+ a_{j\sigma} + \frac{1}{2} \sum_{\substack{ijkl \\ \sigma\sigma'}} V_{ijkl} a_{i\sigma}^+ a_{k\sigma'}^+ a_{l\sigma'} a_{j\sigma}. \quad (1)$$

The index i of the creation and annihilation operators $a_{i\sigma}^+$, $a_{i\sigma}$ is a compact one consisting of a cell index I and an intracell index n , i.e., $i = \{I, n\}$. The a operators fulfill the anticommutation relations

$$[a_{i\sigma}^+, a_{j\sigma'}]_+ = S_{ij}^{-1} \delta_{\sigma\sigma'} \quad (2)$$

where S_{ij} is the overlap matrix of the basis functions $f_i(\mathbf{r})$ and $f_j(\mathbf{r})$. We shall use the Fourier transform

$$a_{n\sigma}^+(\mathbf{k}) = \frac{1}{\sqrt{N_0}} \sum_I a_{n\sigma}^+(I) e^{-i\mathbf{k}\mathbf{R}_I} \quad (3)$$

where \mathbf{R}_I is the lattice vector of cell I and N_0 is the number of unit cells. When we divide H into $H = H_{\text{SCF}} + H_{\text{res}}$, where H_{SCF} is the self-consistent field part of H , the eigenstates of H_{SCF} are Bloch waves which can be expressed in terms of the $a_{n\sigma}^+(I)$ as

$$c_{v\sigma}^+(\mathbf{k}) = \frac{1}{\sqrt{N_0}} \sum_{nl} \alpha_{vn}(\mathbf{k}) a_{n\sigma}^+(I) e^{-i\mathbf{k}\mathbf{R}_I}. \quad (4)$$

The matrix elements $\alpha_{vn}(\mathbf{k})$ define a structure matrix.

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Next we consider a set of operators $\{A_\nu(\mathbf{k})\}$ which refer to microscopic processes describing correlations and which will be specified later. One of them will be $c_{v\sigma}^+(\mathbf{k})$. Associated with the $A_\nu(\mathbf{k})$ via a Fourier transformation (3) are operators A_i where again $i = \{I, n\}$. We define a retarded Green's function through

$$G_{\mu\nu}(\mathbf{k}, z) = \left(A_\mu(\mathbf{k}) \left| \frac{1}{z - L} A_\nu(\mathbf{k}) \right. \right); \quad (5)$$

where z has a positive infinitesimal imaginary part, i.e., $z = \omega + i\delta$. The bilinear form $(A|B)$ is defined by

$$(A|B) = \left\langle \psi_0 \left| [A^+, B]_+ \right| \psi_0 \right\rangle \quad (6)$$

with $|\psi_0\rangle$ denoting the exact ground state of the electronic system under investigation. The quantity L in Eq. (5) is the Liouvillean, a superoperator which acts on operators A , according to

$$LA = [H, A]_- . \quad (7)$$

The imaginary part of $G_{\mu\nu}(\mathbf{k}, z)$ is directly related to the corresponding spectral function $S_{\mu\nu}(\mathbf{k}, \omega)$ by the relation

$$S_{\mu\nu}(\mathbf{k}, \omega) = -\frac{1}{\pi} \lim_{\delta \rightarrow 0^+} \text{Im} G_{\mu\nu}(\mathbf{k}, \omega + i\delta). \quad (8)$$

The computation of spectral densities is a major goal of solid-state theory. There are two different ways of achieving it, which depend on the importance of electron correlations. When the correlations are relatively weak like in conventional semiconductors one identifies with the set $\{A_\nu(\mathbf{k})\}$ simply the $c_{v\sigma}^+(\mathbf{k})$. From Eqs. (6) and (7) it follows that in this case Eq. (5) is a diagonal matrix with

$$G_\nu(\mathbf{k}, z) = \left\langle \psi_0 \left| c_{v\sigma}(\mathbf{k}) \frac{1}{z - H + E_0^N} c_{v\sigma}^+(\mathbf{k}) \right. \right. \\ \left. \left. + c_{v\sigma}^+(\mathbf{k}) \frac{1}{z + H - E_0^N} c_{v\sigma}(\mathbf{k}) \right| \psi_0 \right\rangle. \quad (9)$$

In the quasiparticle approximation only the second term is taken where ν is referring to a valence band, while only the first term is used when it is a conduction band index. When the electronic correlations are strong one has to proceed differently. In that case the most important microscopic processes must be identified which form the correlation hole around an electron. The corresponding operators define the set $\{A_\nu(\mathbf{k})\}$. By limiting oneself to the operator space spanned by the $A_\nu(\mathbf{k})$ one can diagonalize the matrix $G_{\mu\nu}(\mathbf{k}, z)$ for each \mathbf{k} point and compute the spectral densities accordingly. In both cases, i.e., for small and large correlation energy contributions the method of increments reduces the amount of computations decisively.

3 Quasiparticle approximation

In the quasiparticle approximation the life time of the excitations is neglected. This gives rise to well-defined

energy bands. Satellite structures do not appear. Consider the valence bands of a conventional semiconductor such as silicon. In evaluating

$$R_\nu(\mathbf{k}, z) = \left\langle \psi_0 \left| c_{v\sigma}^+(\mathbf{k}) \frac{1}{z + H - E_0^N} c_{v\sigma}(\mathbf{k}) \right| \psi_0 \right\rangle \quad (10)$$

one may insert a complete set of intermediate states of which only the states $|\psi_{v\sigma}^{N-1}(\mathbf{k})\rangle$ are kept, which develop out of the SCF $(N-1)$ electron states $|\Phi_{v\sigma}^{N-1}(\mathbf{k})\rangle = c_{v\sigma}(\mathbf{k})|\Phi_{\text{SCF}}\rangle$. States corresponding to one particle–two holes, two particle–three holes etc. SCF states are neglected. This results in

$$R_\nu(\mathbf{k}, z) = \frac{\langle \psi_{v\sigma}^{N-1}(\mathbf{k}) | c_{v\sigma}(\mathbf{k}) | \psi_0 \rangle^2}{z + E_\nu^{N-1}(\mathbf{k}) - E_0^N} \quad (11)$$

where $E_\nu^{N-1}(\mathbf{k})$ is the energy of $|\psi_{v\sigma}^{N-1}(\mathbf{k})\rangle$.

Thus the excitation energy is given by

$$\epsilon_\nu(\mathbf{k}) = \langle \psi_{v\sigma}^{N-1}(\mathbf{k}) | H | \psi_{v\sigma}^{N-1}(\mathbf{k}) \rangle - E_0^N \\ = \epsilon_\nu^{\text{SCF}}(\mathbf{k}) + \epsilon_\nu^{\text{corr}}(\mathbf{k}). \quad (12)$$

We have decomposed it into an SCF and a correlation contribution. In the same way as we have related $c_{v\sigma}^+(\mathbf{k})$ to the $a_{n\sigma}^+(I)$ through Eq. (4) we can relate $|\psi_{v\sigma}^{N-1}(\mathbf{k})\rangle$ to $|\tilde{\psi}_{n\sigma}^{N-1}(I)\rangle$ by the complex conjugate of the same equation where $|\tilde{\psi}_{n\sigma}^{N-1}(I)\rangle = \tilde{\Omega} a_n(I) |\Psi_{\text{SCF}}^N\rangle$ and $\tilde{\Omega}$ is a wave operator. It transforms the uncorrelated SCF state with one missing electron in orbital $f_{nI}(\mathbf{r})$, i.e., $a_n(I) |\Psi_{\text{SCF}}^N\rangle$ into $|\tilde{\psi}_{n\sigma}^{N-1}(I)\rangle$. Thus we obtain

$$\epsilon_\nu(\mathbf{k}) = \sum_{nm} \sum_I \alpha_{\nu n}(\mathbf{k}) \alpha_{\nu m}^* \\ \times e^{i\mathbf{k}\mathbf{R}_I} \left\langle \tilde{\psi}_{m\sigma}^{N-1}(0) | H | \tilde{\psi}_{n\sigma}^{N-1}(I) \right\rangle - E_0^N. \quad (13)$$

Since the SCF part $\epsilon_\nu^{\text{SCF}}(\mathbf{k})$ of $\epsilon_\nu(\mathbf{k})$ can be calculated, e.g., by using the CRYSTAL [4] or Wannier [5, 6] program package, we concentrate here on $\epsilon_\nu^{\text{corr}}(\mathbf{k})$. In [7] it was shown that the correlation energy contribution can be written in the form

$$\epsilon_\nu^{\text{corr}}(\mathbf{k}) = \sum_{nm} \sum_I \alpha_{\nu n}(\mathbf{k}) \alpha_{\nu m}^*(\mathbf{k}) e^{i\mathbf{k}\mathbf{R}_I} \\ \times \langle \Psi_{\text{SCF}}^N | a_{m\sigma}^+(0) H_{\text{res}} S a_{n\sigma}(I) | \Psi_{\text{SCF}}^N \rangle_c; \\ \nu = 1, \dots, 4 \quad (14)$$

where $S = \tilde{\Omega} - 1$ is the scattering operator and the subscript c indicates that the cumulant of that expectation value must be taken. Strictly speaking S relates to $\Omega - 1$ where in distinction to $\tilde{\Omega}$ the operator Ω is defined only in connection with cumulants (for more details see [7]). For a closely related description in terms of an effective Hamiltonian by Albrecht et al. see [8, 9, 10].

The cumulant scattering operator S does two things. It generates a relaxation- and polarization cloud around the hole created by $a_{n\sigma}(I)$ and it accounts for the loss of ground-state correlations. These are correlations which are present in the N electron ground state but absent in the $N - 1$ particle system due to the missing electron.

There are two ways by which one may evaluate $\epsilon_v^{\text{corr}}(\mathbf{k})$ given by Eq. (14) and similarly when $\nu = 5, \dots, 8$, i.e., for the conduction bands. One is a simplified computational scheme which has been discussed in [11]. The relaxation- and polarization cloud is thereby determined by a new SCF calculation with the hole generated by $a_{n\sigma}(I)$ kept fixed at the center of a cluster. By calculating the matrix elements of H with respect to nonorthogonal SCF states one obtains one part of $\epsilon_v^{\text{corr}}(\mathbf{k})$, i.e., the one from relaxation- and the polarization cloud. The loss of ground-state correlations due to the hole is computed by identifying all those correlation contributions to $|\psi_0\rangle$ which involve the annihilated electron.

The second way is based on the method of increments and has been applied, e.g., in [12]. We formulate here the main idea in a form which is also applicable to strongly correlated electrons. For that purpose we decompose the residual interactions into

$$H_{\text{res}} = \sum_I H_I + \sum_{\langle IJ \rangle} H_{IJ} + \sum_{\langle IJK \rangle} H_{IJK} + \sum_{\langle IJKL \rangle} H_{IJKL}. \quad (15)$$

The different parts refer to the unit cells I, J, \dots to which the $a_{n\sigma}^+(I), a_{m\sigma'}(J)$ etc. operators in H_{res} belong. For example, in H_I the two creation and two annihilation operators in H_{res} refer all to unit cell I , while in H_{IJ} they involve cells I and J etc. In fact, in order to calculate the effect of H_{res} with the help of standard quantum chemical program packages one has to reformulate H_{res} slightly so that the annihilation operators refer to orthogonal states. But this has been discussed, e.g., in [13] and need not to concern us here. The scattering operator S can then be decomposed into increments according to

$$S = \sum_I S_I + \sum_{\langle IJ \rangle} (S_{IJ} - S_I - S_J) + \dots \quad (16)$$

where $\langle IJ \rangle$ denotes pairs and the next terms include triples, quadruples etc. S_I is the scattering operator of a Hamiltonian $H_{\text{SCF}} + H_I$ and S_{IJ} is the one of a Hamiltonian $H_{\text{SCF}} + H_I + H_J + H_{IJ}$. This way the N electron scattering problem is broken up into scattering problems of a few electrons which can be handled without problems. The method turns out to be rapidly convergent, i.e., three-site scattering processes S_{IJK} play little role in weakly correlated semiconductors like the elemental ones. Details are found, e.g., in [13].

4 Strongly correlated electrons

When electron correlations are not weak, satellite structures may have a strong influence on the spectral density. Therefore the microscopic processes which lead to satellites have to be treated sufficiently accurate [14]. This is done by including them in the set $\{A_\nu(\mathbf{k})\}$ or their Fourier transform $\{A_\nu(I)\}$, respectively. We transform

$$G_{\mu\nu}(\mathbf{k}, z) = \frac{1}{N_0} \sum_I e^{-i\mathbf{k}\mathbf{R}_I} \left(A_\mu(0) \left| \frac{1}{z-L} A_\nu(I) \right. \right) \quad (17)$$

and determine the matrix element as follows. We decompose $L = L_{\text{SCF}} + L_{\text{res}}$ where L_{SCF} and L_{res} refer to H_{SCF} and H_{res} , respectively (see (7)). Then

$$\frac{1}{z-L} = G_0 + G_0 T G_0 \quad (18)$$

with $G_0 = (z - L_{\text{SCF}})^{-1}$ and a T matrix given by

$$T = L_{\text{res}} \frac{1}{1 - G_0 L_{\text{res}}}. \quad (19)$$

Note that T is a superoperator, i.e., it acts on operators and not on states. Next we decompose L_{res} into

$$L_{\text{res}} = \sum_I L_I + \sum_{\langle IJ \rangle} L_{IJ} + \dots = \sum_\alpha L_\alpha, \quad \text{where } \alpha = I, IJ, \dots \quad (20)$$

where L_I, \dots, L_{IJKL} are the Liouvilleans associated with H_I, \dots, H_{IJKL} , respectively. In close analogy to Eq. (16) we find

$$T = \sum_I T_I + \sum_{\langle IJ \rangle} (T_{IJ} - T_I - T_J) + \dots = \sum_I T_I + \sum_{\langle IJ \rangle} \delta T_{IJ} + \dots \quad (21)$$

where T_I is the T matrix superoperator to a Hamiltonian $H_{\text{eff}}(I) = H_{\text{SCF}} + H_I$ and T_{IJ} is the one to $H_{\text{eff}}(I, J) = H_{\text{SCF}} + H_I + H_J + H_{IJ}$ etc.

The cluster T matrices T_I, T_{IJ} etc. are expressed in terms of the cluster Liouvilleans L_α as

$$T_I = L_I \frac{1}{1 - G_0 L_I}, \quad T_{IJ} = L_{IJ} \frac{1}{1 - G_0 (L_I + L_J + L_{IJ})} \quad (22)$$

etc. This enables us to write

$$G_{\mu\nu}(I, z) = \left(A_\mu(0) \left| \frac{1}{z-L} A_\nu(I) \right. \right) = \left(A_\mu(0) \left| G_0 \left(1 + \sum_L T_L + \sum_{\langle LJ \rangle} \delta T_{LJ} + \dots \right) G_0 A_\nu(I) \right. \right) \quad (23)$$

and to compute the $G_{\mu\nu}(I, z)$ in an incremental way. At each step one must diagonalize the matrix $G_{\mu\nu}(I, z)$ and by inserting the result into Eq. (17) one obtains the functions $G_n(\mathbf{k}, z)$ from which the spectral density can be computed (see (9)). Each n gives rise to a dispersion $\omega(\mathbf{k})$.

The same procedure can be applied when the memory matrix $M_{\mu\nu}(\mathbf{k}, z)$ is considered instead of Green's function. In that case one starts out from

$$G_v(\mathbf{k}, z) = \left(c_{v\sigma}^+(\mathbf{k}) \left| \frac{1}{z-L} c_{v\sigma}^+(\mathbf{k}) \right. \right) \quad (24)$$

and rewrites it in the form [15, 16]

$$G_v(\mathbf{k}, z) = \frac{1}{z - \Omega_v(\mathbf{k}) - M_v(\mathbf{k}, \omega)}. \quad (25)$$

Here the frequency matrix is $\Omega_v(\mathbf{k}) = (c_{v\sigma}^+(\mathbf{k}) | L c_{v\sigma}^+(\mathbf{k}))$ and the memory function $M_v = (\mathbf{k}, z)$ is given by

$$M_v(\mathbf{k}, z) = \left(c_{v\sigma}^+(\mathbf{k}) \left| L Q \frac{1}{z - QLQ} L c_{v\sigma}^+(\mathbf{k}) \right. \right). \quad (26)$$

The latter has again the form of Eq. (24) but with $c_{v\sigma}^+(\mathbf{k})$ replaced by $L c_{v\sigma}^+(\mathbf{k})$ and L replaced by QLQ where the projector Q projects onto a space perpendicular to $c_{v\sigma}^+(\mathbf{k})$, i.e., $Q c_{v\sigma}^+(\mathbf{k}) = 0$ and $Q^2 = Q$. Since $QL c_{v\sigma}^+(\mathbf{k})$ may generate a number of operators A_v we are back to the problem of determining Eq. (5). Based on Eq. (25) the incremental method has been applied in order to study the Hubbard model on a square lattice near half filling [17]. This calculation was combined with the coherent potential approximation (CPA) by embedding the cluster memory functions into a medium. The latter is self-consistently determined from a CPA condition. As a result a marginal Fermi liquid like behavior was

found for a range of hole doping and size of the Hubbard parameter U . Without the method of increments a calculation of that type would not be feasible.

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