Calculating excitation energies with the help of cumulants

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Abstract

Recently, it has been shown that the ground-state energy of a quantum many-body system can be written in terms of cumulants. In this paper we show that the energies of excited states can be expressed similarly. These representations are suitable for various approximation schemes, e.g., projection techniques. The explicit use of cumulants ensures size consistency in all approximations.

The theory is then applied to the computation of the energy bands of a semiconductor with diamond structure. As we focus especially on the effects of electron correlations, we consider a simplified model and re-derive results obtained previously by the variational Local Ansatz method.
I. INTRODUCTION

Energy is a size-extensive quantity, i.e., the energy of two well-separated, but otherwise identical systems equals twice the value of a single system. Approximations which are applied when energies of a system are calculated must preserve this property. In the standard diagrammatic approach size consistency is ensured in any approximation by considering linked diagrams only [1]. However, the diagrammatic description makes essential use of Wick’s theorem, which is applicable only if the dominant part of the Hamiltonian is a one-particle operator. Therefore this approach is restricted to weakly correlated systems in which the electron-electron interaction is weak and may be treated perturbatively.

It is known from classical statistical mechanics that size consistency is attained by expressing size-extensive quantities in terms of cumulants [2]. Kubo defined the cumulant of a quantum mechanical expectation value [3]. It is denoted by a superscript $^c$ and, with respect to the vector $|\phi\rangle$, it is given by

$$
\langle \phi| A_1 \ldots A_n |\phi\rangle^c = \left. \frac{\partial}{\partial \lambda_1} \ldots \frac{\partial}{\partial \lambda_n} \log \langle \phi| e^{\lambda_1 A_1} \ldots e^{\lambda_n A_n} |\phi\rangle \right|_{\lambda_1 = \ldots = \lambda_n = 0}
$$

(1.1)

One immediately finds, e.g.,

$$
\langle \phi| A_1 |\phi\rangle^c = \langle \phi| A_1 |\phi\rangle
$$

(1.2)

$$
\langle \phi| A_1 A_2 |\phi\rangle^c = \langle \phi| A_1 A_2 |\phi\rangle - \langle \phi| A_1 |\phi\rangle \langle \phi| A_2 |\phi\rangle.
$$

Based on the Horn-Weinstein theorem [4], an infinite series termed “connected moment expansion” (CMX) has been derived for the ground-state energy [5–7]. Involving cumulants only (rather than ordinary expectation values), any truncation of the series leads to size-consistent estimates for the ground-state energy.

Here we would like to proceed as in Ref. [8], where a different representation of the ground-state energy in terms of cumulants has been derived and which we refer to for details. The interacting many-body system is described by a Hamiltonian $H$. We assume that the ground state $|\Phi_0\rangle$ of a part $H_0$ of the Hamiltonian $H$ is known.
\[ H_0 |\Phi_0\rangle = \epsilon_0 |\Phi_0\rangle. \] (1.3)

Provided that \( |\Phi_0\rangle \) has a finite overlap with the ground state of \( H \), the ground-state energy \( E_0 \) of \( H \) is given by

\[ E_0 = (H |\Omega\rangle). \] (1.4)

Here we introduced the abbreviation

\[ (A|B) = \langle \Phi_0 |A^\dagger B|\Phi_0 \rangle^c. \] (1.5)

It serves as a form on the vector space (the Liouville space) spanned by the operators which are defined on the usual Hilbert space. \( \Omega \) is a superoperator which acts on the Liouville space. It is defined by

\[ \Omega = 1 + \lim_{z \to 0} \frac{1}{z - (L_0 + H_1)} H_1. \] (1.6)

\( L_0 \) is the Liouville operator with respect to \( H_0 \). It acts on any operator \( A \) according to \( L_0 A = [H_0, A]_\pm \). \( \Omega \) characterizes the transformation of the unperturbed ground state \( |\Phi_0\rangle \) into the ground state of \( H \), \( |\Psi_0\rangle \). Thus it bears similarities to the wave operator of quantum mechanics and we will refer to it as “wave operator” in the following. Note, however, that \( \Omega \) appears only in an expectation value, Eq. (1.5), and does not yield the wave function \( |\Psi_0\rangle \).

The explicit use of cumulants in Eq. (1.4) ensures size consistency in any subsequent approximation and can be considered as replacing the afore-mentioned “linked diagrams”. However, it is important to notice that the cumulant representation of the ground-state energy, Eq. (1.4), does not have the limitations which the diagrammatic approaches often have since it holds for an arbitrary decomposition of \( H \) into \( H_0 \) and \( H_1 \). In particular, \( H_0 \) need not be an one-particle Hamiltonian (e.g., Hartree-Fock) as in the standard diagrammatic approach. Hence, the present description is applicable to strongly correlated systems as well, e.g., to spin systems described by the Heisenberg Hamiltonian.
Another advantage of using Eq. (1.4) is that quite different types of approximations can be applied than in diagrammatic approaches. One example is a partitioning of the Liouville space, which was pioneered by Löwdin and by the Uppsala and Gainsville Quantum Chemistry Groups [9–11]. Consider a set of operators $A_\nu$, which span a subspace of the Liouville space. Taking into account this “relevant” subspace only and, thereby, neglecting the remaining part the following ansatz for the wave operator $\Omega$ (1.6) is made

$$\Omega = 1 + \sum_\nu \eta_\nu A_\nu . \tag{1.7}$$

The coefficients $\eta_\nu$ are determined by

$$\langle A_\nu | H \Omega \rangle = 0 . \tag{1.8}$$

This equation holds generally for all operators $A$ and is easily proven by inserting the definition (1.6) of $\Omega$ [12]. Making the linear ansatz (1.7) for $\Omega$ is equivalent to applying projection technique to Eq. (1.4) [8]. In particular, if we choose the powers of the Hamiltonian as relevant operator set, i.e., $A_\nu = H^\nu (\nu = 1 \ldots N)$ we recover the improved CMX as in Refs. [6,7]. For a more general ansatz than Eq. (1.7) and other approximation schemes, see Ref. [12].

For these reasons it would be desirable to express not only the ground-state energy, but also the excitation energies in terms of cumulants. The way this has to be done can be conjectured by considering the Rayleigh-Schrödinger perturbation theory. By expanding $\Omega$ in terms of $H_1$ and taking the limit $z \to 0$ one arrives at the perturbation expansion of the ground-state energy:

$$E_0 = \epsilon_0 + \sum_{n=0}^{\infty} \left( H_1 \left( -\frac{1}{L_0} H_1 \right)^n \right). \tag{1.9}$$

The generalization to excited states, which suggests itself, is to take the expectation values with respect to an excited state $|\Phi_i\rangle$ of $H_0$ instead of $|\Phi_0\rangle$

$$H_0 |\Phi_i\rangle = \epsilon_i |\Phi_i\rangle \tag{1.10}$$
so that the expansion of the energy of an excited state of $H$ becomes

$$E_i = \epsilon_i + \sum_{n=0}^{\infty} \left( H_1 \left\langle \left( -\frac{1}{L_0} H_1 \right)^n \right\rangle_i \right). \quad (1.11)$$

The subscript $i$ indicates that the expectation values are now taken with respect to the excited state $|\Phi_i\rangle$

$$(A|B)_i = \langle \Phi_i | A^\dagger B | \Phi_i \rangle^c \quad (1.12)$$

[cf. Eq. (1.5)]. Summing the geometric series in Eq. (1.11), we arrive at the conjecture

$$E_i = \left( H \left| 1 + \lim_{z \to 0} \frac{1}{z - (L_0 + H_1)} H_1 \right\rangle_i \right) = \left( H|\Omega\right)_i \quad (1.13)$$

where $\Omega$ is defined as in Eq. (1.6). Note the interchange of the limits $z \to 0$ and $n \to \infty$.

In the next section, we show that the conjecture (1.13) is indeed true under certain circumstances. In Sec. II we present a specific application of the formalism by calculating the quasiparticle energy bands of a semiconductor in the Bond-Orbital Approximation (BOA). In Sec. IV we compare the results with previous work. Finally, we give a brief summary and conclude in Sec. V.

II. EXPRESSING EXCITATION ENERGIES IN TERMS OF CUMULANTS

In this section we prove that Eq. (1.13) holds indeed provided $|\langle \Phi_i | \Psi_i \rangle|^2 > 1/2$. Here, $|\Psi_i\rangle$ denotes an eigenstate of $H$ with eigenvalue $E_i$. Further, let $\beta^{(i)}_\mu = |\langle \Phi_i | \Psi_\mu \rangle|^2$. We consider the following function

$$f_i(t) = \log \langle \Phi_i | e^{-itH} | \Phi_i \rangle = \log \sum_{\mu} \beta^{(i)}_\mu e^{-itE_\mu} \quad (2.1)$$

for $t \geq 0$. Note that the derivative of $f_i(-i\lambda)$ with respect to $\lambda$ is the function introduced by Horn and Weinstein in Ref. [4], which tends to the ground-state
energy at the limit $\lambda \to \infty$ (provided that $\beta_0^{(i)} \neq 0$). However, the function defined here need not tend to the ground-state energy as $t \to \infty$ since the arguments of the exponentials are imaginary. This is shown next.

The argument of the logarithm is a complex number and, therefore, we have to specify the branch of the logarithm. This is done by requiring that $f_i(t)$ is analytic in a neighborhood of the positive real $t$-axis. As we assume that $\beta_i^{(i)} > 1/2$, it is $\langle \Phi_i | \exp(-iHt) | \Phi_i \rangle \neq 0$ for all $t \geq 0$ and this requirement can be fulfilled. We continue straightforwardly

$$f_i(t) = \log \sum_{\mu} \beta_{\mu}^{(i)} e^{-itE_{\mu}}$$

$$= \log \left[ \beta_i^{(i)} e^{-itE_i} \left( 1 + \sum_{\mu \neq i} \frac{\beta_{\mu}^{(i)}}{\beta_i^{(i)}} e^{-it(E_{\mu} - E_i)} \right) \right] \quad (2.2)$$

$$= -itE_i + \log \beta_i^{(i)} + \log \left( 1 + \sum_{\mu \neq i} \frac{\beta_{\mu}^{(i)}}{\beta_i^{(i)}} e^{-it(E_{\mu} - E_i)} \right) + 2\pi in(t) .$$

The integer function $n(t)$ guarantees that we remain on the correct branch of the logarithm. $n(t)$ is fixed by the previous requirement, namely that $f_i(t)$ is analytic for $t \geq 0$. The first two terms of the last line in Eq. (2.2) are analytic. The third term is analytic, too, because

$$\left| \sum_{\mu \neq i} \frac{\beta_{\mu}^{(i)}}{\beta_i^{(i)}} e^{-it(E_{\mu} - E_i)} \right| \leq \sum_{\mu \neq i} \frac{\beta_{\mu}^{(i)}}{\beta_i^{(i)}} = \frac{1}{\beta_i^{(i)}} - 1 < 1 \quad (2.3)$$

(remember that $\beta_i^{(i)} > 1/2$). Therefore $n(t)$ is a constant, which vanishes because $n(0) = 0$. As the argument of the logarithm in Eq. (2.2) is bounded the asymptotic behavior of $f_i(t)$ is

$$\frac{f_i(t)}{t} \to -iE_i \quad (t \to \infty) , \quad (2.4)$$

i.e., the energy of the excited state is given by the behavior of $f_i(t)$ for large $t$.

In order to calculate $E_i$ with the help of Eq. (2.4), we consider the half-sided Fourier transform of $f_i$

$$\hat{f}_i(z) = -i \int_0^{\infty} dt \ e^{itz} f_i(t) . \quad (2.5)$$
Since $f_i(t)/t$ approaches a constant for $t \to \infty$, the integral is well-defined for $\text{Im } z > 0$. From the asymptotic behavior (2.4) we readily obtain the energy of the excited state in terms of $\hat{f}_i(z)$:

$$E_i = \lim_{z \to i0^+} z^2 \hat{f}_i(z).$$  \hfill (2.6)

We finally introduce cumulants by making use of Eq. (1.1)

$$f_i(t) = \log\langle \Phi_i | e^{-iHt} | \Phi_i \rangle = \langle \Phi_i | e^{-iHt} - 1 | \Phi_i \rangle^c. \hfill (2.7)$$

This enables us to take the Fourier transform (2.5) explicitly and after some algebra (cf. Ref. [8]) we obtain

$$\hat{f}_i(z) = \frac{\epsilon_i}{z^2} + \frac{1}{z^2} \left\langle \Phi_i \left| H_1 \left(1 + \frac{1}{z - (L_0 + H_1)}\right) \right| \Phi_i \right\rangle^c. \hfill (2.8)$$

Hence the energy of the exited state is given by

$$E_i = \lim_{z \to i0^+} z^2 \hat{f}_i(z) = (H | \Omega)_i, \hfill (2.9)$$

where we again used the definition (1.6) of $\Omega$ and the abbreviation (1.12).

### III. APPLICATION TO SEMICONDUCTORS

The formalism presented in the previous section will now be used to calculate the electronic excitation energies of a semiconductor. These quasiparticle (quasi-hole) energies are defined as the energy difference between an excited state with momentum $\mathbf{k}$ of the $N + 1$- ($N - 1$-) particle system and the ground state of the $N$-particle system, where $N$ denotes the number of electrons in the charge neutral system.

To be specific, we treat a semiconductor of diamond-type structure. It is described by orthogonalized atomic-like $sp^3$ hybrids and the resulting functions are denoted by $g_i(r)$. The corresponding electron creation (annihilation) operators $a_{i\sigma}^\dagger$ ($a_{i\sigma}$) fulfill the usual anticommutation relations.
In this basis the Hamiltonian reads as follows:

\[
H = H_0 + H_{\text{int}}
\]

\[
H_0 = \sum_{i,j,\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma}
\]

\[
H_{\text{int}} = \frac{1}{2} \sum_{i,j,k,l,\sigma,\sigma'} V_{ijkl} a_{i\sigma}^\dagger a_{k\sigma'}^\dagger a_{l\sigma'} a_{j\sigma}.
\] (3.1)

Here

\[
t_{ij} = \int d^3r \, g_i^*(r) \left( -\frac{1}{2m} \Delta + V_{\text{ext}}(r) \right) g_j(r)
\] (3.2)

is the bare hopping matrix element between the hybrid orbitals \(i\) and \(j\), and \(V_{\text{ext}}(r)\) is the electrostatic potential set up by the nuclei and the core electrons.

\[
V_{ijkl} = \int d^3r \, g_i^*(r) g_j(r) g_k(r) g_l(r) \frac{e^2}{|r - r'|} g_i^*(r') g_j(r')
\] (3.3)

are the interaction matrix elements.

In the Hartree-Fock (HF) approximation, the effective one-particle Hamiltonian is given by

\[
H_{\text{HF}} = \sum_{i,j,\sigma} f_{ij} a_{i\sigma}^\dagger a_{j\sigma}
\] (3.4)

where \(f_{ij}\) denotes the Fock matrix:

\[
f_{ij} = t_{ij} + \sum_{k,l,\sigma'} \left( V_{ijkl} - \frac{1}{2} V_{lki} \right) \langle \Phi_{\text{HF}} | a_{k\sigma'}^\dagger a_{l\sigma'} | \Phi_{\text{HF}} \rangle.
\] (3.5)

\(|\Phi_{\text{HF}}\rangle\) is the HF ground state which has to be determined self-consistently from Eqs. (3.4) and (3.5). The HF ground-state energy is given by

\[
E_{\text{HF}}^0 = \langle \Phi_{\text{HF}} | H_0 + H_{\text{int}} | \Phi_{\text{HF}} \rangle + E_{\text{NN}}
\] (3.6)

where \(E_{\text{NN}}\) denotes the interaction energy of the nuclei and the core electrons.

To proceed further, we introduce bonding and antibonding functions for each bond \(I\) with corresponding creation operators
\begin{equation}
B_{I\sigma}^\dagger = \frac{1}{\sqrt{2}}(a_{I1\sigma}^\dagger + a_{I2\sigma}^\dagger) \\
A_{I\sigma}^\dagger = \frac{1}{\sqrt{2}}(a_{I1\sigma}^\dagger - a_{I2\sigma}^\dagger)
\end{equation}

The operators $a_{I1\sigma}^\dagger$ and $a_{I2\sigma}^\dagger$ refer to the $sp^3$ hybrids $I1$ and $I2$ which form bond $I$. In the bond-orbital approximation (BOA) \cite{13} the $N$-particle HF ground state is approximated by occupying all bonding states

\begin{equation}
|\Phi^{\text{HF}}\rangle = \prod_{I,\sigma} B_{I\sigma}^\dagger |0\rangle.
\end{equation}

In a more refined calculation the bonding orbitals are constructed from the HF orbitals by applying the localization method of Foster and Boys \cite{14} or with the help of a localization potential, which acts within the space of the occupied HF orbitals only.

When an electron with momentum $\mathbf{k}$ is added to the system the $N + 1$-particle HF wave function is given within the BOA by

\begin{equation}
|\Phi^{\text{HF}}_{\mathbf{k}m\sigma}\rangle = A_{\mathbf{k}m\sigma}^\dagger |\Phi^{\text{HF}}\rangle
\end{equation}

where $A_{\mathbf{k}m\sigma}^\dagger$ creates an electron with momentum $\mathbf{k}$ in the conduction band $m$. The operator $A_{\mathbf{k}m\sigma}^\dagger$ is decomposed into

\begin{equation}
A_{\mathbf{k}m\sigma}^\dagger = \sum_{I} \alpha_{\mathbf{k}m\sigma}(I)A_{I\sigma}^\dagger
\end{equation}

and the $\alpha_{\mathbf{k}m\sigma}(I)$ are found from the solution of the HF eigenvalue problem.

The wave function (3.9) yields an energy eigenvalue $E^{\text{HF}}_{\mathbf{k}m\sigma}$. From this we find the energy of a quasiparticle in the conduction band

\begin{equation}
\epsilon_{\mathbf{k}m\sigma}^{\text{HF}} = E^{\text{HF}}_{\mathbf{k}m\sigma} - E_0^{\text{HF}},
\end{equation}

which, according to Koopmans’ theorem \cite{15}, coincides with an eigenvalue of the one-electron Hamiltonian $H_{\text{HF}}$. Similarly, the valence bands are calculated.

We now want to determine the correlation contributions to these quasiparticle energies. They reflect the influence of the residual Hamiltonian.
\[ H_{\text{res}} = H - H_{\text{HF}} \]
\[ = H_{\text{int}} - \frac{1}{2} \sum_{i,j,k,l,\sigma,\sigma'} (V_{ijkl} - \delta_{\sigma,\sigma'} V_{ilkj}) \langle \Phi^{\text{HF}} | a_{k\sigma}' a_{l\sigma} | \Phi^{\text{HF}} \rangle a_{i\sigma} a_{j\sigma}. \tag{3.12} \]

We have to include the effect of correlations on both, the \( N \)-particle ground-state energy, \( E_0 \), and the (excited) \( N + 1 \)-particle energy \( E_{2m\sigma} \).

The first problem has already been treated in Ref. [16]. The authors made a variational ansatz for the ground-state wave function in order to include correlation effects. We want to re-derive their results by directly making use of the cumulant representation of the ground-state energy, Eq. (1.4),
\[ E_0 = (H | \Omega). \tag{3.13} \]

It is impossible to determine the wave operator \( \Omega \) exactly. Instead, we make an ansatz for \( \Omega \) in the Liouville space taking into account only the most important processes which are induced by \( H_{\text{res}} \). Within the Local Ansatz method they are described by the following operator [16]
\[ S_{\eta}^{i,j} = \frac{1}{4} \sum_{\sigma,\sigma'} A_{j\sigma}' B_{j\sigma} A_{i\sigma} B_{i\sigma}. \tag{3.14} \]

\( S_{\eta}^{i,j} \) excites electrons in bonds \( I \) and \( J \) from a bonding into an antibonding state, thus changing the charge distribution in these bonds. This reflects the van-der-Waals interaction between the bonds \( I \) and \( J \), as well as the interaction within one bond (\( I = J \)). Our ansatz for the wave operator \( \Omega \) in Eq. (3.13) reads [see Eqs. (1.7) and (1.8)]:
\[ \Omega = 1 + \sum_{i,j} \eta_{i,j}^{(0)} S_{i,j}^{\eta}. \tag{3.15} \]

The coefficients \( \eta_{i,j}^{(0)} \) are determined from
\[ 0 = (S_{i,j}^{\eta} | H \Omega). \tag{3.16} \]

Thus we are lead to the same result for the ground-state energy as in Ref. [16], which we refer to for the further evaluation of the expectation values.
This procedure to calculate the ground-state energy is advantageous because it applies for excited states, too, as is shown below.

The energies \( E_{k m \sigma} \) which we consider next are, in fact, excited energies of the \( N+1 \)-particle system. According to Sec. [14], they are given by

\[
E_{k m \sigma} = (H|\Omega)_{k m \sigma} ,
\]

where the expectation values are taken with respect to an excited \( N+1 \)-particle state \( |\Phi_{k m \sigma}^{\text{HF}}\rangle \). Again, we make an ansatz for the wave operator \( \Omega \). In this case, however, there are two different correlation effects which we have to take into account. They have already been discussed in detail in Ref. [15]. The first process is the induced dipole-dipole interaction as it was present in the \( N \)-particle ground state above. It is described by the operators \( S_{I J}^\eta \), Eq. (3.14). The second process is the formation of a polarization cloud around the added particle. It is described by

\[
S_{I J}^\pi = \frac{1}{4} \sum_{\sigma, \sigma'} A_{I \sigma}^\dagger B_{J \sigma'} A_{I \sigma'}^\dagger A_{I \sigma} .
\]

This is seen from

\[
S_{I J}^\pi |\Phi_{k m \sigma}^{\text{HF}}\rangle = \frac{\alpha_{k m \sigma} (I)}{4} \sum_{\sigma'} A_{I \sigma}^\dagger B_{J \sigma'} A_{I \sigma'}^\dagger |\Phi_{k m \sigma}^{\text{HF}}\rangle
\]

where the extra electron in bond \( I \) induces a transition of an electron in bond \( J \) from a bonding to an antibonding state resulting in a polarization of bond \( J \).

For the wave operator \( \Omega \) in Eq. (3.17) we make the following ansatz

\[
\Omega = 1 + \sum_{I J} \eta_{I J}(k m \sigma) S_{I J}^\eta + \sum_{I J} \pi_{I J}(k m \sigma) S_{I J}^\pi .
\]

Note that the coefficients describing the dipole-dipole interaction, \( \eta_{I J} \), do not necessarily equal \( \eta_{I J}^{(0)} \). Furthermore, the coefficients \( \eta_{I J}(k m \sigma) \) and \( \pi_{I J}(k m \sigma) \) may depend on the quantum numbers \( k, m, \) and \( \sigma \). They are determined from

\[
0 = (S_{K L}^\eta |H \Omega)_{k m \sigma}
\]

\[
0 = (S_{K L}^\pi |H \Omega)_{k m \sigma} .
\]
This linear system of equations for $\eta_{IJ}(k m \sigma)$ and $\pi_{IJ}(k m \sigma)$ leads via Eqs. (3.20) and (3.17) to improved energies of the $N + 1$-particle system. Subtracting the ground-state energy $E_0$ of the $N$-particle system, Eq. (3.13) with Eq. (3.15), we arrive at quasiparticle energies $\epsilon_{k m \sigma}$, which include the main effect of electron correlations.

Obviously, the case of one added hole can be treated in close analogy. This will yield the valence bands.

IV. DISCUSSION

In this section we want to compare the results with previous work done in Ref. [16]. There the same model is treated as here. Starting from a HF calculation, the authors make a variational ansatz for both, ground and excited states. The correlation operators are the same as in Eqs. (3.14) and (3.19). The authors consider the quasiparticle energy directly and, by making use of a linked-cluster theorem, they introduce cumulants ensuring size-consistency. Finally, they derive equations for the variational parameters $\eta_{IJ}$ and $\pi_{IJ}$ by minimizing the energy. The final equations look similar to the Eqs. (3.21) and (3.22) derived here, the main difference being that $A_{k m \sigma}^\dagger$ is subjected to cumulant ordering there, while it is included in the wave function here and, thus, not subjected to cumulant ordering. This difference is not surprising: When the quasiparticle energy is calculated directly, only processes which are connected to the extra particle contribute, e.g., the blocking of ground-state correlations in the neighborhood of the extra particle. This is ensured by subjecting $A_{k m \sigma}^\dagger$ to cumulant ordering. In this work, however, we calculate the energy of the $N$- and $N \pm 1$-particle system separately. Therefore, we must also include processes which are not connected to the extra particle, e.g., ground-state correlations far apart from the extra particle.

By exploiting the properties of cumulants we may rewrite the expectation values in Eqs. (3.21) and (3.22) such that they are taken with respect to $|\Phi_0\rangle$ only, thus
subjecting $A^\dagger_{\kappa m\sigma}$ to cumulant ordering. Taking the energy difference between $E_{k m \sigma}$ and $E_0$, we arrive at essentially the same quasiparticle energies as in Ref. [16] as will be shown next.

We begin with the expectation values which involve $S^\eta_{\sigma}^{\sigma}$:

\[
(S^\eta_{I J}|H)_{\kappa m\sigma} = \langle \Phi_{HF}|A^\dagger_{\kappa m\sigma}S^\eta_{I J} |H|A^\dagger_{\kappa m\sigma}\rangle_{\Phi_{HF}}
\]

\[
= \langle \Phi_{HF}|A^\dagger_{\kappa m\sigma}S^\eta_{I J} |H|A^\dagger_{\kappa m\sigma}\rangle_{\Phi_{HF}} + \langle \Phi_{HF}|S^\eta_{I J} |H|A^\dagger_{\kappa m\sigma}\rangle_{\Phi_{HF}}
\]

\[
= (S^\eta_{I J}A^\dagger_{\kappa m\sigma} |H|A^\dagger_{\kappa m\sigma}) + (S^\eta_{I J}|H).
\]

Similarly,

\[
(S^\eta_{I J}|H S^\eta_{KL})_{\kappa m\sigma} = (S^\eta_{I J}A^\dagger_{\kappa m\sigma} |H - \epsilon_{\kappa m\sigma}^{|S^\eta_{KL}|A^\dagger_{\kappa m\sigma}}) + (S^\eta_{I J}|H S^\eta_{KL})
\]

since $(A^\dagger_{\kappa m\sigma} |H|A^\dagger_{\kappa m\sigma}) = \epsilon_{\kappa m\sigma}^{|S^\eta_{KL}|A^\dagger_{\kappa m\sigma}}$. The operators $S^\eta_{I J}$ are connected to $A^\dagger_{\kappa m\sigma}$. Hence,

\[
(S^\eta_{I J}|H)_{\kappa m\sigma} = (S^\eta_{I J}A^\dagger_{\kappa m\sigma} |H|A^\dagger_{\kappa m\sigma})
\]

\[
(S^\eta_{I J}|H S^\eta_{KL})_{\kappa m\sigma} = (S^\eta_{I J}A^\dagger_{\kappa m\sigma} |H S^\eta_{KL}|A^\dagger_{\kappa m\sigma})
\]

\[
(S^\eta_{I J}|H S^\eta_{KL})_{\kappa m\sigma} = (S^\eta_{I J}A^\dagger_{\kappa m\sigma} |H - \epsilon_{\kappa m\sigma}^{|S^\eta_{KL}|A^\dagger_{\kappa m\sigma}})
\]

When we insert Eqs. (4.1)-(4.3) into Eq. (3.21) we find

\[
0 = (S^\eta_{I J}A^\dagger_{\kappa m\sigma} |H|A^\dagger_{\kappa m\sigma}) + (S^\eta_{I J}|H)
\]

\[
+ \sum_{KL} \eta_{KL}(\kappa m\sigma) \left\{ \left\langle S^\eta_{I J}A^\dagger_{\kappa m\sigma} |H - \epsilon_{\kappa m\sigma}^{|S^\eta_{KL}|A^\dagger_{\kappa m\sigma}} \right\rangle + \left\langle S^\eta_{I J} |H S^\eta_{KL} \right\rangle \right\}
\]

\[
+ \sum_{KL} \pi_{KL}(\kappa m\sigma) \left\langle S^\eta_{I J}A^\dagger_{\kappa m\sigma} |H S^\eta_{KL} A^\dagger_{\kappa m\sigma} \right\rangle
\]

The individual expectation values differ in their behavior as $N \to \infty$. While the cumulants involving $A^\dagger_{\kappa m\sigma}$ turn out to be of order $N^{-1}$, the others are $O(N^0)$. To leading order in $N$

\[
0 = (S^\eta_{I J}|H) + \sum_{KL} \eta_{KL}(\kappa m\sigma)(S^\eta_{I J}|H S^\eta_{KL})
\]

Comparing with Eqs. (3.15) and (3.16) we find that $\eta_{KL}(\kappa m\sigma)$ is the same as for the $N$-particle system (in leading order in $N$):

\[
\eta_{IJ}(\kappa m\sigma) = \eta_{IJ}^{(0)} + O(N^{-1}).
\]
This result was obtained in Ref. [16], too.

Next we consider Eq. (3.22), which determines the coefficients $\pi_{IJ}$. They describe the formation of the polarization cloud around the added particle. Inserting again Eqs. (4.1)–(4.3) we find

$$0 = \left( S_{\pi}^\dagger A_{k}^\dagger \mid H A_{k}^\dagger \right) + \sum_{KL} \eta_{KL}(k m \sigma) \left( S_{\pi}^\dagger A_{k}^\dagger \mid H S_{KL}^\pi A_{k}^\dagger \right)$$

\[ + \sum_{KL} \pi_{KL}(k m \sigma) \left( S_{\pi}^\dagger A_{k}^\dagger \mid H - \epsilon_{HF}^{k} S_{KL}^\pi A_{k}^\dagger \right). \]  

(4.7)

The only difference to Ref. [16] is that instead of the exact quasiparticle energy $\epsilon_{k m \sigma}$ the Hartree-Fock energy $\epsilon_{HF}^{k}$ enters Eq. (4.7). This is due to a different introduction of cumulants and different approximations thereafter: As already mentioned above, the energies of the $N$- and the $N \pm 1$-particle system are calculated separately here, whereas the quasiparticle energy is calculated directly in Ref. [16].

Finally, the quasiparticle energies are given by

$$\epsilon_{k m \sigma} = E_{k m \sigma} - E_0 = (H|\Omega)_{k m \sigma} - (H|\Omega)$$

\[ = \left( H \mid 1 + \sum_{IJ} \eta_{IJ}(k m \sigma) S_{IJ}^{\eta} + \sum_{IJ} \pi_{IJ}(k m \sigma) S_{IJ}^{\pi} \right)_{k m \sigma} - \left( H \mid 1 + \sum_{IJ} \eta_{IJ}^{(0)} S_{IJ}^{\eta} \right). \]  

(4.8)

Applying Eq. (4.6) this can be rewritten in the form

$$\epsilon_{k m \sigma} = \epsilon_{HF}^{k} + \sum_{IJ} \eta_{IJ}^{(0)} \left( A_{k m \sigma}^\dagger \mid H S_{IJ}^{\eta} A_{k m \sigma}^\dagger \right) + \sum_{IJ} \pi_{IJ}(k m \sigma) \left( A_{k m \sigma}^\dagger \mid H S_{IJ}^{\pi} A_{k m \sigma}^\dagger \right)$$

(4.9)

The same expression for the quasiparticle energy was derived in Ref. [16]. By using $\eta_{IJ}^{(0)}$ from a ground-state calculation and determining $\pi_{IJ}(k m \sigma)$ from Eq. (4.7) the energy bands for diamond are obtained. The energy gap is found to be only 50% of the HF energy gap and the widths of the valence and conduction bands are considerably reduced from their HF values [16].

**V. SUMMARY AND CONCLUSIONS**

In this paper, we showed how excitation energies are expressed in terms of cumulants. This work generalizes the cumulant representation of the ground-state energy.
which has been derived recently \cite{8}. Introducing cumulants explicitly implies that all subsequent approximations are \textit{a priori} size consistent. We would like to emphasize that these representations of ground-state and excitation energies hold irrespectively of the particular splitting of the Hamiltonian $H$ into a solvable part $H_0$ and the remaining part $(H - H_0)$, which has to be treated approximately. This contrasts the standard diagrammatic approaches, in which $H_0$ has to be a one-particle operator. Therefore, forming the cumulant can be viewed as considering “linked diagrams” only in the case of weakly correlated systems and as their generalization in the case of strongly correlated systems for which one-particle wave functions would be a poor starting point.

To give an application of the theory, we calculated the quasiparticle energy bands of a semiconductor. We made two separate calculations, one for the ground-state energy of the charge-neutral system and one for the (excited) system where one electron (hole) with momentum $k$ is added. With the help of the new representation of excitation energies it was possible to perform both calculations within the same formalism, i.e., to apply the same approximations in both cases. Taking the difference of the two energies, we obtained the quasiparticle energy. Finally we discussed the connection of the present calculations with a variational treatment of this problem \cite{16} and essentially reproduced the results obtained there.

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