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The Properties of the Iterative Solution of the Inverse Dyson Equation for the Calculation of Correlation Corrected Band Structures of Polymers

WOLFGANG FÖRNER

Theoretical Chemistry and Laboratory of the National Foundation for Cancer Research, Friedrich-Alexander University, Egerlandstrasse 3, D-91058 Erlangen, Germany

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In this paper we discuss the convergence properties of the iterative solution of the inverse Dyson equation for quasiparticle corrections to HF energy eigenvalues. Especially we show that this iteration converges only if a principal solution exists. In this case it converges exactly to that solution. We show that a solution to which the iteration converges must have a pole strength larger than $\frac{1}{2}$ and that this solution must be the one with the largest pole strength, because the pole strength has to have values between 0 and 1, and the sum over all the pole strengths has to equal 1. As an example a tight binding model is discussed. © 1996 Academic Press, Inc.

I. INTRODUCTION

The ab initio Hartree–Fock crystal orbital (HF-CO) formalism using a linear combination of atomic orbitals (LCAO) was developed by Del Re, Ladik, and Biczo [1a] and by Andre, Gouverneur, and Leroy [1b], independently, after earlier attempts by Löwdin [2] and a tight binding version by Peacock and McWeeny [3]. Important contributions are due to Harris and Monkhorst [4]. We do not want to discuss here in detail the numerous applications of the method reported up to now. General purpose programs have been developed by the groups of Ladik (see [5] as a review and references therein), Andre [2, 6] and Pisani [7]. A more recent version utilizing Gaussian lobe functions which includes also correlation effects was developed by Otto [8]. Attempts to increase the efficiency of correlation programs are currently in progress [9–11].

For ab initio calculations on polymers, a solution of the correlation problem is of utmost importance and there, especially, the calculation of correlation corrected band structures. The development of these concepts on the basis of Møller–Plesset perturbation theory [12] goes back to Suhai and Ladik [13–15]. For details we refer the reader to the book written by Ladik [5]. An improvement of the theory, based on Green's function approaches and the inverse Dyson equation, is known for a long time (see, e.g., [16–21]). Reviews were given, e.g., by Öhrn [22], Cederbaum and Domcke [19], and Simons [23]. Books which cover the theory were written, e.g., by Fetter and Walecka [24], Linderberg and Öhrn [25], Mattuck [26], and Szabo and Ostlund [27]. For polymers up to third-order perturbation theory the approach was worked out and applied by Liegener and Ladik [28, 29]. This approach was already extensively studied by other groups for the case of molecules (see, e.g., [16–21]). A more complete list of references to work done on the correlation problem for polymers can be found in [30], where also concepts of other research groups are mentioned, which do not attempt to correct the band structure, but only the total energy. Most recently we also attempted to apply the coupled cluster theory of correlation effects [31] to polymers (see [30, 32] and references therein). In this paper we discuss the behaviour of an iterative procedure for the solution of the inverse Dyson equation for the correction of the band structure for correlation. This method has the advantage over grid search (also called the "graphical method") that it is numerically much simpler to perform. However, there are doubts about the convergence criteria of the method, and if it converges, whether it yields the principal quasiparticle pole, if it exists, or another one.

Of course, for molecules, i.e., for discrete spectra, the Green's function methods, combined with the inverse Dyson equation for the calculation of correlation corrected ionization potentials and electron affinities, were worked out very well and were numerically applied to a large number of molecules in the past, especially by the group of Cederbaum (see, e.g., [19, 33]). However, methods like that developed in [33]—namely to rewrite the Dyson equation into a matrix eigenvalue problem—cannot be used for polymers. The reason is simply that this matrix contains the poles of the self-energy explicitly and in the case of polymers it has an infinite number of poles which, in addition, form infinitely dense sets. Therefore, in the case of continuous spectra one has to rely on more direct methods to solve the inverse Dyson equation by a grid search or the above-mentioned iteration method.

Since the evaluation of the self-energy involves summa-

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tions (and integrations) over the excitations, it is computationally very tedious. The grid search, on one hand, requires the calculation of this self-energy for a rather large set of points on the energy scale while, on the other hand, in the iterative procedure this step has to be performed only once in each iteration. Therefore a detailed study of the convergence properties of this iteration in the case of polymers is rather important.

For this purpose, we start in Section II with some rather well-known definitions to fix notations. In Section III we study the iterative procedure for discrete spectra, mainly because from these results one can easily deduce those for polymers, which is done in Section IV. We concentrate on the region of the energy scale which lies outside the poles of the self-energy. We discuss that this makes sense for our purpose, because the HF-energy bands, as well as the correlation corrected quasiparticle bands in all cases studied so far fall into this region. In case they would not, the method as it is breaks down completely, because the self-energy itself and, thus, also the Green's function are not defined in the region of the poles of the self-energy. Finally, in Section V we discuss for didactic reasons a very simplified model self-energy based on the tight binding approach. In the last section VI we give a short summary of the results.

II. THE INVERSE DYSON EQUATION

In this section we just want to give the necessary definitions and the basic, well-known equations (see, e.g., the review papers [19, 22, 23], books [24–27], or also research papers like [33]) of the Green's function approach to the correlation problem. The correlation corrected quasiparticle bands corresponding to a HF-band I, where capital indices represent a combination of band index i and quasimomentum k_i are calculated by the solution of the inverse Dyson equation in diagonal approximation [29], which is nothing else than the quasiparticle model, because only in this case the poles of the Green's function can be assigned uniquely to Hartree–Fock one-particle states (note, that the approximation is only justified if there exists a principal pole for each state which has a much larger pole strength than all its satellites),

$$\omega_I = \varepsilon_I + M_{II}(\omega_I), \tag{1}$$

where ω_1 is the quasiparticle energy of state I, ε_I is the corresponding HF eigenvalue, and $M_{II}(\omega_I)$ is the diagonal irreducible self-energy part, which in Møller–Plesset [12] perturbation theory up to second order (MP2) is given by

$$\begin{aligned} M_{II}(\boldsymbol{\omega}_I) &= \lim_{\eta\to 0^+}\left[\sum_{JRS}\frac{V_{IJ}^{RS}(2\,V_{IJ}^{RS}-V_{JI}^{RS})^*}{\omega_I+\varepsilon_J-\varepsilon_R-\varepsilon_S+i\eta}\right. \\ &\qquad \left.+\sum_{RJK}\frac{V_{IR}^{JK}(2\,V_{IR}^{JK}-V_{RI}^{JK})^*}{\omega_I+\varepsilon_R-\varepsilon_J-\varepsilon_K-i\eta}\right] \\ M_{RR}(\omega_R) &= \lim_{\eta\to 0^+}\left[\sum_{JST}\frac{V_{RJ}^{ST}(2\,V_{RJ}^{ST}-V_{JR}^{ST})^*}{\omega_R+\varepsilon_J-\varepsilon_S-\varepsilon_T+i\eta}\right. \\ &\qquad \left.+\sum_{SJK}\frac{V_{RS}^{JK}(2\,V_{RS}^{JK}-V_{SR}^{JK}{}^*)}{\omega_R+\varepsilon_S-\varepsilon_J-\varepsilon_K-i\eta}\right], \end{aligned} \tag{2}$$

where I, J, K represent doubly occupied and R, S, T virtual states, while η is a positive infinitesimal real number which tends to zero (in the distributional sense). Note, that for our discussion, the introduction of this limit is only necessary in the case of continuous poles, not for molecules or large but finite systems which have only discrete ones. In this case the limit can be trivially performed and yields just a real function (with the exception of its poles, where it is complex). Formally we can use as an example for the discrete case (see below) the function $f(\omega, \pm\eta)$ to see this:

$$\begin{aligned} f(\omega,\pm\eta) &= \sum_{j=1}^{M}\frac{a_j}{\omega+b_j\pm i\eta} = \sum_{j=1}^{M} a_j\left[\frac{(\omega+b_j)\mp i\eta}{(\omega+b_j)^2+\eta^2}\right] \\ \lim_{\eta\to 0^+} f(\omega,\pm\eta) &= \sum_{j=1}^{M}\frac{a_j}{\omega+b_j} \mp i\pi\sum_{j=1}^{M} a_j\delta(\omega+b_j) \\ f(\omega) &\equiv \mathrm{Re}\,[\lim_{\eta\to 0^+} f(\omega,\pm\eta)] = \sum_{j=1}^{M}\frac{a_j}{\omega+b_j}, \end{aligned} \tag{3}$$

where a_j and b_j are arbitrary real numbers and $f(\omega)$ contains poles at $\omega = -b_j$. Thus the limit can be performed at the beginning for a discrete and finite set of poles, since for our discussion we only need the values of ω apart from the poles.

Further, the arbitrary phase factors at the HF-crystal orbitals cancel out, because in the products of integrals each phase factor is multiplied by its complex conjugate. A summation over a capital index means summation over the corresponding band index and integration over k in $-\pi \leq k \leq \pi$ with a factor of $1/(2\pi)$. Dyson's equation connects within a suitable basis space the unperturbed Green matrix $\mathbf{G}_0(\omega)$ for the HF case with the correlated one $\mathbf{G}(\omega)$ via the irreducible self energy part $\mathbf{M}(\omega)$, which in our case is computed using MP2 perturbation theory:

$$\mathbf{G}(\omega) = \mathbf{G}_0(\omega) + \mathbf{G}_0(\omega)\,\mathbf{M}(\omega)\,\mathbf{G}(\omega); \quad \mathbf{G}_0(\omega) = (\omega\mathbf{1} - \boldsymbol{\varepsilon})^{-1}, \tag{4}$$

where $\boldsymbol{\varepsilon}$ is a diagonal matrix with the HF eigenvalues as elements. This equation can be rearranged to yield the solutions, or quasi-particle poles, as the roots of the determinant

$$\det[\omega\mathbf{1} - \boldsymbol{\varepsilon} - \mathbf{M}(\omega)] = 0. \tag{5}$$

In the diagonal approximation for the self-energies $M_{IJ}(\omega) = M_{II}(\omega)\delta_{IJ}$ we ge the scalar equation given above. The non-vanishing two-electron integrals are

$$V_{IJ}^{KL} = \langle\phi_i^{k_i}(1)\phi_j^{k_j}(2)\left|\frac{1}{r_{12}}\right|\phi_k^{k_k}(1)\phi_l^{k_l}(2)\rangle\cdot\delta(k_i + k_j - k_k - k_l), \tag{6}$$

where $\phi_i^k(l)$ is the HF-CO in band i at k-point k for electron l. The quasiparticle approximation is applicable if there exists one principal root of the inverse Dyson equation which has a considerably larger pole strength than the other ones, where the pole strength of a satellite j is given by

$$P_{jU} = \left[1 - \frac{\partial M_{UU}(\omega)}{\partial\omega}\Big|_{\omega=\omega_{jU}}\right]^{-1}, \tag{7}$$

where U stands for an arbitrary occupied or virtual state. In the original work by Liegener *et al.* [28, 29] the solutions of the inverse Dyson equation were found by a grid search method which is quite time consuming in practical applications, while Palmer *et al.* apply an iterative technique [9] which uses the HF eigenvalue of the state which should be corrected, as a starting value of the iteration. This is then substituted for ω in the self-energy part to obtain a better approximation to the root, which is then again inserted in $M(\omega)$ and so on until convergence is achieved. As Palmer and Ladik [9] observed, numerically for the systems they studied the iteration either converges to that quasiparticle energy which has the largest pole strength of all satellites, or it diverges if such a principal root does not exist. It is now interesting to find an answer to the question whether this behaviour is general, or if the iteration could converge also to roots which are not the principal ones.

III. DISCRETE SPECTRA

For our purpose it is useful to simplify the inverse Dyson equation. First of all we assume that there is no quasimomentum, but just a summation over states. Then the equation has the general form

$$\omega = \varepsilon + f(\omega); \quad f(\omega) = \sum_{j=1}^{M}\frac{a_j}{\omega + b_j}, \tag{8}$$

where for the moment the a's and b's are arbitrary real numbers and the self-energy $M_{UU}(\omega)$ is renamed to $f(\omega)$ to indicate that it is a model function (without loss of generality). M is an arbitrary integer. The two terms in the self-energies are thus condensed to one via the different possible values of b_j. Then it is obvious that the equation corresponds just to that for the roots of a polynomial of degree $M + 1$:

$$(\omega - \varepsilon)\prod_{k=1}^{M}(\omega + b_k) - \sum_{j=1}^{M}a_j\prod_{\substack{k=1\\k\neq j}}^{M}(\omega + b_k) = 0 \tag{9}$$

with $M + 1$ roots which, by construction of the inverse Dyson equation, are all real and in general not degenerate. The iterative scheme is

$$\omega_0 = \varepsilon; \quad \omega_1 = \varepsilon + f(\varepsilon); \quad \omega_2 = \varepsilon + f[\varepsilon + f(\varepsilon)]; \ldots; \\ \omega_i = \varepsilon + f(\omega_{i-1}) \tag{10}$$

which in the case $M = 1$ is simply a continued fraction

$$\omega_1 = \varepsilon + \frac{a}{\varepsilon + b}; \quad \omega = \varepsilon + \cfrac{a}{\varepsilon + b + \cfrac{a}{\varepsilon + b + \cfrac{a}{\cdots}}} \tag{11}$$

which always converges with the exception of the point $\varepsilon = -b$. The reason is that at this point ω_1 is infinite. For $a > 0$, which is always the case, because a is in principle the squared absolute value of an integral over spin orbitals, and $\varepsilon < 0$ (without loss of generality we can put b equal to 0 in this example) the iteration must converge to the negative one of the two solutions, since in this case all $f(\omega_i)$ values are negative. This is also the solution with the larger pole strength of the two. Graphically, in a (y, ω)-plane, the desired solutions of Eq. (8) for our example with $M = 1$ ($b = 0$, $a = 1$) are the intersection points of the straight line $y = (\omega - \varepsilon)$ through ε on the ω-axis having slope 1 with the hyperbola $y = 1/\omega$ with its pole at $\omega = 0$. If $\varepsilon < 0$ then the negative intersection point is always farther away from the pole on the left-hand branch of the hyperbola than the positive one on the right-hand branch. Since the hyperbola is a monotonically decreasing function, its slope is always negative and, the larger in absolute value, the closer a given point is to the pole. Therefore, if $\varepsilon < 0$, the negative solution is always found by the iteration and it is the one with the larger pole strength, since the positive one is closer to the pole. For $\varepsilon > 0$ the opposite holds.

Analytically, for our example we have the solutions

$$\omega - \varepsilon = \frac{a}{\omega} \Rightarrow \omega_{1,2} = \frac{1}{2}(\varepsilon \pm \sqrt{\varepsilon^2 + 4a}) \tag{12}$$

with the pole strengths

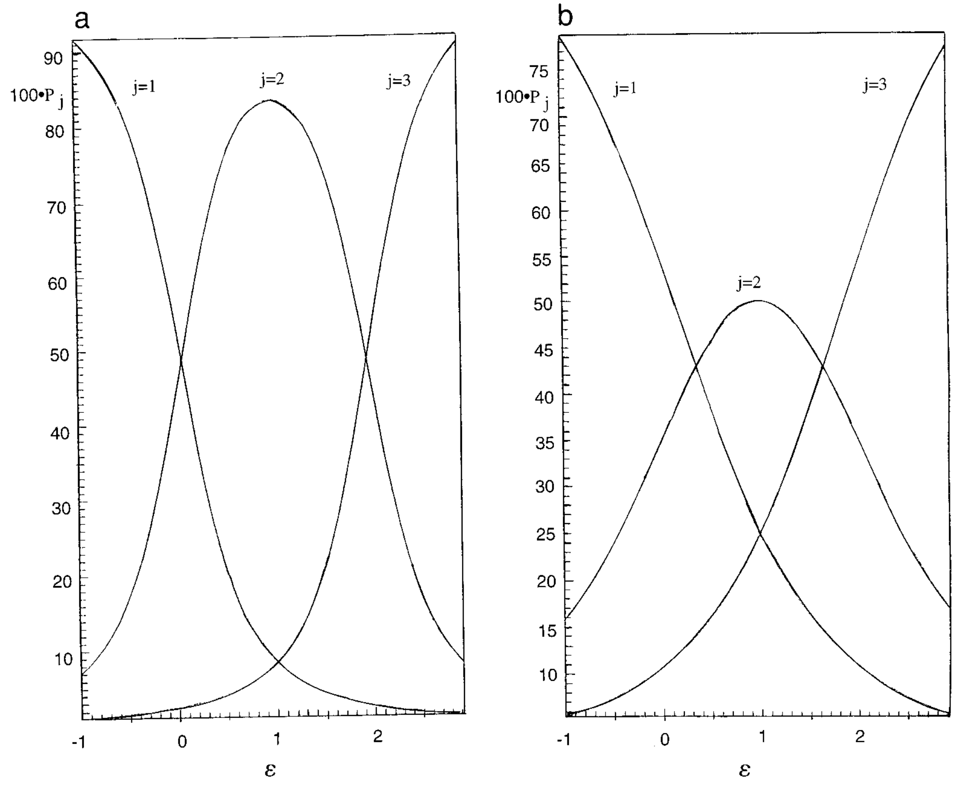

FIG. 1. The pole strengths $P_i(\varepsilon)$ ($i = 1, 2, 3$) multiplied by 100 for the three solutions $\omega_1(\varepsilon)$, $\omega_2(\varepsilon)$, and $\omega_3(\varepsilon)$ of our example for the inverse Dyson equation containing two poles $\omega = \varepsilon + a[1/\omega + 1/(\omega + c)]$ for $c = -2$ as functions of ε. The solutions were found by a grid search: (a) $a = 0.1$; (b) $a = 0.5$.

$$P^{-1}_{1,2} = \frac{dF(\omega)}{d\omega}\Big|_{\omega=\omega_{1,2}}, \quad F(\omega) = \omega - \varepsilon - \frac{a}{\omega}$$
$$P_{1,2} = \frac{\varepsilon^2 + 2a \pm \varepsilon\sqrt{\varepsilon^2 + 4a}}{\varepsilon^2 + 4a \pm \varepsilon\sqrt{\varepsilon^2 + 4a}}. \tag{13}$$

Some trivial manipulations lead to the result that the two pole strengths add up to 1, a fact which is rather important and will be shown to hold also for the general case later on.

Let us now consider the case of two poles. Then $f(\omega)$ is a superposition of two hyperbolas, one with its pole at $-b_1$ and the other one at $-b_2$ where we assume that $-b_1 < -b_2$. For $\varepsilon < -b_1$ and $\varepsilon > -b_2$ the same reasonings and conclusions hold as for the case of one hyperbola if $a_1 = a_2$. In general this is true as long as the hyperbolas do not overlap that much, that one of them distorts considerably the shape of the other one on the opposite side of its pole. To visualize these facts, we have studied numerically the simple example

$$\omega = \varepsilon + f(\omega); \quad f(\omega) = a\left(\frac{1}{\omega} + \frac{1}{\omega + c}\right) \tag{14}$$

for $c = -2$. We solved the equation with a grid search, as well as with the iterative method for different values of ε between -1 and 3. Figure 1 shows the pole strengths of the three solutions as functions of ε. Note that in any case the three pole strengths again add up to 1.

In Fig. 1a the case of non-overlapping hyperbolas is shown, i.e., for $a = 0.1$. It is obvious that—except for a small region of ε around the two poles—we have always one pronounced quasi-particle pole. Interestingly, the iteration converges (close to the poles very slowly) for all values of ε, where the pole-strength of one of the possible solutions exceeds the value of $\frac{1}{2}$. This is also the solution to which the iteration converges. In the two small regions around the poles where two curves intersect and all the pole-strengths are smaller (although slightly) than $\frac{1}{2}$, the iteration diverges. In Fig. 1b we show a case where the two hyperbolas overlap considerably, i.e., $a = 0.5$. Here, obviously, in the whole region of ε between the two poles no pronounced principal pole exists. In this case the numerical result is, again, that the iteration converges only for values of ε, where a solution with pole strength larger than $\frac{1}{2}$ exists; i.e., it diverges nearly in the complete region between the two poles. An interesting fact is that in cases where the iteration diverges sometimes quasi-convergent behaviour shows up. This means that the iteration remains sometimes for large numbers of iteration cycles around some value of ω. This could lead to the conclusion that the iteration has converged and a solution is found. However, the actual values of ω to which the iteration seems to converge in such cases cannot be identified with the solutions from the grid search and, in addition, if more and more cycles are performed, the iteration jumps quite suddenly away from these pseudo-converged values. Since in real ab initio calculations this might lead to misinterpretations of seemingly converged results, one has to ask for the general behaviour of the iterative method.

The numerical examples suggest the following theorem: The iterative method can only be convergent, if there exists a solution with a pole strength larger than $\frac{1}{2}$ and it will converge to this solution. Since the pole strengths of all solutions add up to 1 and are all positive, this must be also the solution with the largest pole strength. In cases where the iteration diverges, no principal quasi-particle pole exists, and the model breaks down anyway.

Our model equation in its general form is given by

$$\begin{gathered} F(\omega) = \omega - \varepsilon - f(\omega); \quad F(\omega_j) = 0; \quad j = 1, \dots, M+1, \\ f(\omega) = \sum_{j'=1}^{M} \frac{a_{j'}}{\omega + b_{j'}}. \end{gathered} \tag{15}$$

Note, that here indices j denote the solutions of $F(\omega) = 0$ ($\omega = \omega_j$), while indices j' denote the poles of the self-energy: $f(\omega_{j'}) = 0$ ($\omega_{j'} = -b_{j'}$). The pole strengths of the $M + 1$ solutions ω_j, P_j are given by

$$P_j = \frac{1}{1 - f'(\omega_j)} = \frac{1}{1 + \sum_{j'=1}^{M} \frac{a_{j'}}{(\omega_j + b_{j'})^2}}. \tag{16}$$

Since $a_j > 0$ (the $a_{j'}$, represent the squared absolute values of integrals over spin orbitals) we can deduce immediately from the above equation that $0 < P_j < 1$. From this it follows that the derivative of $f(\omega)$ with respect to ω is everywhere negative and, thus, the equation $\omega - \varepsilon - f(\omega) = 0$ can have non-degenerate roots only. Since

$$\begin{gathered} G(\omega) = \frac{1}{\omega - \varepsilon - f(\omega)} \equiv \frac{g(\omega)}{F(\omega)}; \\ g(\omega) = 1; \quad F(\omega) = \omega - \varepsilon - f(\omega), \end{gathered} \tag{17}$$

where in $\omega = \omega_j$ $g(\omega)$ and $F(\omega)$ are holomorphic and, further, $F(\omega_j) = 0$ and $F'(\omega_j) \neq 0$ we can calculate the residua of $G(\omega)$ at the poles ω_j as

$$\mathrm{Res}_{\omega_j}\, G(\omega) = \frac{g(\omega_j)}{F'(\omega_j)} = P_j. \tag{18}$$

$G(\omega)$ can be cast into the form

$$\begin{aligned} G(\omega) &= \frac{\prod_{j'=1}^{M} (\omega + b_{j'})}{(\omega - \varepsilon) \prod_{j'=1}^{M} (\omega + b_{j'}) - \sum_{j'=1}^{M} a_{j'} \prod_{\substack{j''=1 \\ j'' \neq j'}}^{M} (\omega + b_{j''})} \\ &= \frac{\prod_{j'=1}^{M} (\omega + b_{j'})}{\prod_{j=1}^{M+1} (\omega - \omega_j)}. \end{aligned} \tag{19}$$

Further, we can write $G(\omega)$ as a Laurent series. Since in a Laurent series

$$G(\omega) = \sum_{j=1}^{M+1} \left[\sum_{n=-\infty}^{\infty} a_{nj} (\omega - \omega_j)^n \right] \tag{20}$$

the coefficients are as usual (see textbooks) given by

$$a_{nj} = \frac{1}{2\pi i} \oint_{K_j} \frac{G(\omega)}{(\omega - \omega_j)^{n+1}}\, d\omega \tag{21}$$

we have $a_{-1j} = P_j$ and $a_{nj} = 0$, if $n \neq -1$. Therefore our function can be written as

$$G(\omega) = \frac{1}{\omega - \varepsilon - f(\omega)} = \sum_{j=1}^{M+1} \frac{P_j}{\omega - \omega_j}; \quad \omega_j - \varepsilon - f(\omega_j) = 0. \tag{22}$$

Now we can equate the two different representations of the Green's function of Eq. (19) and Eq. (22) and multiply the result with the complete denominator for $\omega \neq \omega_j$ to obtain

$$\prod_{j'=1}^{M} (\omega + b_{j'}) = \sum_{j=1}^{M+1} P_j \prod_{\substack{k=1 \\ k \neq j}}^{M+1} (\omega - \omega_k). \tag{23}$$

Since the factors at the different powers of ω must be the same on both sides of the equation, we can deduce our desired sum rule from the Mth power of ω:

$$\omega^M = \sum_{j=1}^{M+1} P_j \omega^M \Rightarrow \sum_{j=1}^{M+1} P_j = 1. \tag{24}$$

This result is also consistent with a sum-rule from the theory of Green's functions (see, e.g., [34]). Green's function is derived from the Lehmann representation which has its poles at the ionization potentials and electron affinities of the system (neglecting again the k-dependence)

$$\begin{aligned} G_{ij}(\omega) &= \sum_n \left[\frac{a_{n,ij}^{(N+1)}}{\omega - E_n} + \frac{a_{n,ij}^{(N-1)}}{\omega + E'_n} \right] \\ E_n &= E_n^{(N+1)} - E_0^{(N)}; \quad E'_n = E_0^{(N)} - E_n^{(N-1)} \\ a_{n,ij}^{(N-1)} &= \langle \Phi_0^{(N)} | \hat{c}_i^{+} | \Phi_n^{(N-1)} \rangle \langle \Phi_n^{(N-1)} | \hat{c}_j | \Phi_0^{(N)} \rangle \\ a_{n,ij}^{(N+1)} &= \langle \Phi_0^{(N)} | \hat{c}_i | \Phi_n^{(N+1)} \rangle \langle \Phi_n^{(N+1)} | \hat{c}_j^{+} | \Phi_0^{(N)} \rangle, \end{aligned} \tag{25}$$

where (N), $(N \pm 1)$ refer to the (N), $(N \pm 1)$-particle systems, the $\hat{c}$'s are electron creation and annihilation operators, E_n is an ionization potential, E'_n is an electron affinity, $E_p^{(M)}$ is the energy of the pth state of the M-particle system, and the $\Phi_p^{(M)}$ are the corresponding state vectors. The a's correspond directly to our P_j's. In our example we have condensed the two terms in Eq. (25) to a single one, where in the summation over j the different ω_j's represent both the ionization potentials and the electron affinities. $G_{ij}(\omega)$ can then be written also in terms of the spectral density functions $A_{ij}(\varepsilon)$ and $B_{ij}(\varepsilon)$:

$$\begin{aligned} G_{ij}(\omega) &= \int_{-\infty}^{\infty} \left[\frac{A_{ij}(\varepsilon)}{\omega - \varepsilon} + \frac{B_{ij}(\varepsilon)}{\omega + \varepsilon} \right] d\varepsilon \\ A_{ij}(\varepsilon) &= \sum_n a_{n,ij}^{(N+1)}\, \delta(\varepsilon - E_n) \\ B_{ij}(\varepsilon) &= \sum_n a_{n,ij}^{(N-1)}\, \delta(\varepsilon - E'_n) \end{aligned} \tag{26}$$

for which the sum rule

$$\int_{-\infty}^{\infty} [A_{ij}(\varepsilon) + B_{ij}(\varepsilon)]\, d\varepsilon = 1 \tag{27}$$

holds. In our case (diagonal approximation and suppression of indices) we have

$$\begin{aligned} A(\varepsilon) + B(\varepsilon) &= \sum_{j=1}^{M+1} P_j \delta(\varepsilon - \omega_j) \\ \Rightarrow \int_{-\infty}^{\infty} [A(\varepsilon) + B(\varepsilon)]\, d\varepsilon &= \sum_{j=1}^{M+1} P_j \int_{-\infty}^{\infty} \delta(\varepsilon - \omega_j)\, d\varepsilon \\ &= \sum_{j=1}^{M+1} P_j = 1 \end{aligned} \tag{28}$$

which proves again that the pole strengths of all solutions for one HF-eigenstate add up to 1.

Consider now the ith cycle of our iteration:

$$\omega^{(i)} = \varepsilon + f(\omega^{(i-1)}); \quad \omega^{(0)} = \varepsilon \tag{29}$$

If we assume that we are already close to a converged solution—in the case that the iteration converges at all, we can expand $f(\omega^{(i-1)})$ around the exact solution ω_0 and truncate the expansion after the first-order term:

$$\begin{aligned} f(\omega^{(i-1)}) &= f(\omega_o) + \frac{df(\omega)}{d\omega}\Big|_{\omega=\omega_o} (\omega^{(i-1)} - \omega_o) \\ \Rightarrow \omega^{(i)} &= \varepsilon + f(\omega_o) + \frac{df(\omega)}{d\omega}\Big|_{\omega=\omega_o} \Delta\omega^{(i-1)} \\ \Delta\omega^{(i)} &\equiv \omega^{(i)} - \omega_o; \quad \varepsilon + f(\omega_o) = \omega_0. \end{aligned} \tag{30}$$

This yields

$$\Delta\omega^{(i)} = -\left[1 - \frac{df(\omega)}{d\omega}\Big|_{\omega=\omega_o} \right] \Delta\omega^{(i-1)} + \Delta\omega^{(i-1)} \tag{31}$$

$$\Rightarrow \Delta\omega^{(i)} = \left(1 - \frac{1}{P_o} \right) \Delta\omega^{(i-1)}. \tag{32}$$

From this we obtain for the sequence $\Delta\omega^{(i)}$ to converge to 0, i.e., for convergence of the iteration, the criterion

$$\left| \frac{\Delta\omega^{(i)}}{\Delta\omega^{(i-1)}} \right| = \left| 1 - \frac{1}{P_0} \right| < 1. \tag{33}$$

From this it follows directly that the iteration can only converge to solutions with pole strengths $\frac{1}{2} < P_j < \infty$, or since $0 < P_j < 1$, it will converge only if $\frac{1}{2} < P_j < 1$. This corresponds also to the fact that such an iteration converges for the general case $x = \psi(x)$ only if $|\psi'(x)| < 1$. In fact, it is trivial to show that for $\Delta x^{(i)} = x^{(i-1)} - x^{(i)}$ in the ith iteration cycle where $x^{(i)} = \psi[x^{(i-1)}]$ we have

$$\begin{aligned} \frac{\Delta x^{(i+1)}}{\Delta x^{(i)}} &= \frac{\psi(x^{(i)} + \Delta x^{(i)}) - \psi(x^{(i)})}{\Delta x^{(i)}} \\ &= \psi'(x^{(i)} + \vartheta\, \Delta x^{(i)}); \quad 0 < \vartheta < 1. \end{aligned} \tag{33b}$$

With $\psi(x) = \varepsilon + f(x)$ and $P(x) = [1 - f'(x)]^{-1}$ the criterion $|\psi'(x)| < 1$ implies directly $|1 - 1/P(x)| < 1$. Since the sum over all P_j's equals 1, such a solution is the one with the largest possible pole strength.

IV. CONTINUOUS SPECTRA (POLYMERS)

In the case of polymers we have in principle a similar situation, but with a very dense set of an infinite number of poles in the self-energy $f(\omega)$:

$$\begin{aligned} f(k, \omega) &= \frac{1}{4\pi^2} \lim_{\eta \to 0^+} \sum_{j'} \int_{-\pi}^{\pi} dk' \int_{-\pi}^{\pi} dk'' \frac{a_{j'}(k, k', k'')}{\omega + b_{j'}(k, k', k'', \eta)} \\ \omega - \varepsilon(k) &= f(k, \omega) \end{aligned} \tag{34}$$

The dependence of f on k will be suppressed later on, because the equations for different k-values are independent of each other. Thus, instead of $f(k, \omega)$, $a_{j'}(k, k', k'')$ and $b_{j'}(k, k', k'', \eta)$ we will write from now on $f(\omega)$, $a_{j'}(k', k'')$ and $b_{j'}(k', k'', \eta)$, respectively, where k' and k'' remain to denote the integration variables. The actual form of the k', k''-dependence of the a's and b's depends on the system under consideration. If ω falls into the region of the "excitation band" $-b_{j'}(k', k'')$, the integral is usually not defined. The Green's function is as usual given by

$$G(\omega) = [\omega - \varepsilon - f(\omega)]^{-1}. \tag{35}$$

Since an integration over k' or k'' and a derivative with respect to ω can be interchanged, we obtain for the derivative of $f(\omega)$ with respect to ω,

$$\frac{df(\omega)}{d\omega} = -\frac{1}{4\pi^2} \lim_{\eta\to 0^+} \sum_{j'} \int_{-\pi}^{\pi} dk' \int_{-\pi}^{\pi} dk'' \frac{a_{j'}(k', k'')}{[\omega + b_{j'}(k', k'', \eta)]^2}, \tag{36}$$

and thus at points $\omega = \omega_j$ with $\omega_j - \varepsilon - f(\omega_j) = 0$ (again the ω_j are non-degenerate because $df(\omega)/d\omega$ is everywhere negative); i.e., at the poles of the Green's function the pole strengths are

$$P_j = \frac{1}{4\pi^2}\left\{1 + \lim_{\eta\to 0^+} \sum_{j'} \int_{-\pi}^{\pi} dk' \int_{-\pi}^{\pi} dk'' \frac{a_{j'}(k', k'')}{[\omega_j + b_{j'}(k', k'', \eta)]^2}\right\}^{-1}. \tag{37}$$

Since, as in the discrete case, we have $a_{j'}(k', k'') > 0$, for the pole strengths obviously $0 < P_j < 1$ holds again. For the case that ω falls into an "excitation band" $[\omega = -b_{j'}(k', k'')]$ and the integral is indefinite, the Green's function will not have poles in this region.

In polymers we have to realize that the above representation of $f(\omega)$ as a superposition, in form of an integral, of an infinitely dense set of first order poles is a valid one, although the final analytical form of $f(\omega)$ after the integration might differ from it. It will lead to a discrete set of poles which usually are not of first order. In general, the function $f(\omega)$ will approach infinity at the edges of the excitation bands $-b_{j'}(k', k'')$ and will be indefinite inside these bands. However, in practical calculations it is improbable that $f(\omega)$ has to be calculated for values of ω inside these bands, and if it occurs, the whole model breaks down (see below). However, the proof that the iteration can only converge to solutions ω_j with a pole strength $P_j > \frac{1}{2}$ does not depend at all on the explicit form of the self-energy. Further, since the sum rule for the pole strengths holds for any arbitrarily dense set of poles in $f(\omega)$, independent of the number or density of the poles, it holds also for an infinitely dense set and, thus, also for polymers. The poles of the perturbed Green's function $G(\omega)$, w_j, are still first-order ones. Thus we can derive a similar Laurent series for $G(\omega)$ as in the discrete case and use the argument involving the spectral density functions as above to show that for the P_j's the same sum rule holds. The basic difference lies in the order of the poles of $f(\omega)$ and not in $G(\omega)$ itself. In any case we can use the representation of the self-energy as a superposition of an infinite set of first-order poles to argue in the same way as in the discrete case.

As Eq. (37) shows we can write $G(\omega)$ for polymers again in the form

$$G(\omega) = \frac{g(\omega)}{F(\omega)}; \quad F(\omega) = \omega - \varepsilon - f(\omega); \quad g(\omega) = 1, \tag{38}$$

where in $\omega = \omega_j$ the functions $F(\omega)$ and $g(\omega)$ are holomorphic and $F(\omega_j) = 0$, $F'(\omega_j) \neq 0$. Thus the pole strengths P_j again equal the residua of $G(\omega)$:

$$P_j = \mathrm{Res}_{\omega_j} G(\omega) = \frac{1}{F'(\omega)} = \frac{1}{1 - f'(\omega)}. \tag{39}$$

In actual calculations the values of ω occurring during the iterations are close to HF eigenvalues, while the excitation bands occurring in the denominators of the self-energies are at least of the size of the gap between the bands under consideration. In the first iteration with $\omega^{(1)} = \varepsilon + f(\varepsilon)$, the self-energy contains simply HF double excitation energies of the (N)- and the $(N \pm 1)$-electron systems. Then, if the poles would occur in the k', k''-integration in a practical evaluation of the self-energy during the iteration, it would imply that we deal with a system with a ground state nearly degenerate with an excited state. However, in pathological cases like that neither an MP2 ansatz with a one-determinantal reference nor the quasiparticle model are applicable from the beginning. Thus one does not expect poles in the self-energy in regions of ω which occur in practice. From the above discussion, we expect that in the region of the excitation band $-b_{j'}(k', k'')$ the self-energy will be indefinite and will approach infinity at the edges of these bands, as also the example discussed below shows.

We can view the integration over k' and k'' as an integration over a two-dimensional Brillouin zone. Separating the dependence of the b's on η, taking only one term of the summation, and only the $\pm i\eta$-term in the self-energy (Eq. (2)), we have to calculate for the limit $\eta \to 0^+$,

$$f_{j'}^{+}(\omega) = \frac{1}{4\pi^2} \lim_{\eta\to 0^+} \int_{-\pi}^{\pi} dk_x \int_{-\pi}^{\pi} dk_y \frac{a_{j'}(\mathbf{k})}{\omega + b_{j'}(\mathbf{k}) + i\eta}. \tag{40}$$

Then one can perform a transformation of variables to $\omega' = -b_{j'}(\mathbf{k})$

$$f^{+}_{j'}(\omega) = -\frac{1}{4\pi^2}\lim_{\eta\to 0^+}\int_{\omega'_{\min}}^{\omega'_{\max}}\frac{K_{j'}(\omega')}{\omega-\omega'+i\eta}\,d\omega'$$

$$K_{j'}(\omega') = \int_{S(\omega')}\frac{a_{j'}(\mathbf{k})}{|\nabla_{\mathbf{k}} b_{j'}(\mathbf{k})|}\,dS(\omega') \tag{41}$$

$$\omega'_{\min} \equiv \min[-b_{j'}(\mathbf{k})];\quad \omega'_{\max} \equiv \max[-b_{j'}(\mathbf{k})],$$

where the line integrals $\mathbf{K}_{j'}(\omega')$ have to be taken along lines of constant $\omega' = -b_{j'}(\mathbf{k})$ in the integration region. Then we can use Cauchy's principal value denoted by P with

$$\lim_{\eta\to 0^+}\int_{-\infty}^{\infty}\frac{f(x)}{x+i\eta}\,dx = P\int_{-\infty}^{\infty}\frac{f(x)}{x}\,dx - i\pi\int_{-\infty}^{\infty}f(x)\,\delta(x)\,dx$$

$$P\int_{-\infty}^{\infty}\frac{f(x)}{x}\,dx = \lim_{\tau\to 0^+}\left[\int_{-\infty}^{-\tau}\frac{f(x)}{x}\,dx + \int_{+\tau}^{\infty}\frac{f(x)}{x}\,dx\right] \tag{42}$$

to obtain, finally,

$$f^{+}_{j'}(\omega) = -\frac{1}{8\pi^3}\left[P\int_{\omega'_{\min}}^{\omega'_{\max}}\frac{K(\omega')}{\omega-\omega'}\,d\omega' - i\pi K(\omega)\right] \tag{43}$$

which implies that the line integral is essentially the imaginary part of $f^{+}_{j'}(\omega)$. With this the real part is obtained by a Hilbert transformation. If ω is not within the excitation band, the two limits coincide and are real, while in the other case $f^{+}_{j'}(\omega)$ is the complex conjugate of $f^{-}_{j'}(\omega)$. Since the two limits exist, but do not coincide if a pole occurs in the integrand the self-energy is indefinite in this case. However, since—as discussed above—this situation does not occur in practical applications, we do not want to discuss this case further.

V. THE TIGHT BINDING MODEL

To get a qualitative feeling how such a self-energy would look like, let us consider a simple tight binding model for a chain of two equivalent sites per unit cell. In this case we have two bands, an occupied one (the unit of energy is negative here) $\varepsilon_1(k) = 2\cdot(\cos(k/2)$ and a virtual one with $\varepsilon_2(k) = -2\cdot\cos(k/2)$, which are degenerate at $k = \pi$. Since there is no electron–electron interaction in this case, we assume the two-electron integrals to be all equal to 1 and without any k-dependence. Then we obtain for the two bands ($i = 1, 2$), together with Eq. (2) the inverse Dyson equations

$$\omega - \varepsilon_i(k) = \frac{1}{4\pi^2}\lim_{\eta\to 0^+}\int_{-\pi}^{\pi}dk'\int_{-\pi}^{\pi}dk''\left[\frac{1}{\omega+h(k,k',k'',\eta)} + \frac{1}{\omega-h(k,k',k'',\eta)}\right]. \tag{44}$$

For $i = 1$ we obtain the occupied quasiparticle band and for $i = 2$ the virtual one. Further, we have

$$h(k,k',k'',\eta) = 2\left[\cos\frac{k'+k''-k}{2} + \cos\frac{k'}{2} + \cos\frac{k''}{2}\right] + i\eta. \tag{45}$$

The necessary double integration in Eq. (44) is quite tedious and would lead to complicated results, which would allow no clear insight. Thus we assume a further simplified model for the function h

$$h(k,k',k'',\eta) = \left[2\cdot\cos\frac{k'}{2} + i\eta\right]\delta(k'-k'')\,\delta(k), \tag{46}$$

where we neglect the k- and k'-dependence of the integrand. Since in this case the bands are degenerate at $k = \pi$, we introduce an artificial gap of $2a$, $a > 0$, by setting $\varepsilon_{1,2} = \pm[a + 2\cdot\cos(k/2)]$ which leads by substitution into Eq. (2) to our final model self-energy, where we have kept the simple factor of 2 in the dispersion term:

$$\Omega(\omega) = \frac{1}{4\pi^2}\lim_{\eta\to 0^+}\int_{-\pi}^{\pi}dk\left[\frac{1}{\omega+3a+i\eta+2\cdot\cos(k/2)} + \frac{1}{\omega-3a-i\eta-2\cos(k/2)}\right]. \tag{47}$$

The integration is trivial, using the substitutions $k' = k/2$ and $z = \tan(k'/2)$ with $dk' = 2\,dz/(1+z^2)$ and $\cos(k') = (1-z^2)/(1+z^2)$ which yields, together with the abbreviations $\alpha = \omega + 3a + i\eta$ and $\beta = \omega - 3a - i\eta$ in the regions $|\alpha| > 2$ and $|\beta| > 2$ after performing the limit $\eta \to 0^+$:

$$\Omega(\omega) = \frac{8}{\pi^2}[H_1(\omega) + H_2(\omega)]$$

$$H_1(\omega) = \frac{\operatorname{sgn}(\omega+3a+2)}{\sqrt{(\omega+3a)^2-4}}\arctan\sqrt{\frac{\omega+3a-2}{\omega+3a+2}} \tag{48}$$

$$H_2 = \frac{\operatorname{sgn}(\omega-3a-2)}{\sqrt{(\omega-3a)^2-4}}\arctan\sqrt{\frac{\omega-3a+2}{\omega-3a-2}}$$

where $\operatorname{sgn}(x) = 1$ for $x \geq 0$ and $\operatorname{sgn}(x) = -1$ for $x < 0$.

Let us first discuss $H_1(\omega)$. For this purpose we define $x = \omega + 3a$ to obtain

$$H_1(x) = \frac{\operatorname{sgn}(x+2)}{\sqrt{x^2-4}} \operatorname{arc\,tan} \sqrt{\frac{x-2}{x+2}}. \tag{49}$$

Obviously $H_1(x)$ has a pole at $x = -2$, where $H_1(x)$ approaches $-\infty$ if x approaches -2 from the negative side. If x approaches $+2$ from the positive side, we have the case "0/0" in the sense of L'Hopital's rule which yields a limit of $\frac{1}{4}$ at $x = +2$. For $x \to \pm\infty$ we have $H_1(x) \to \pm 0$. The derivative of $\mathrm{H}_1(x)$ for $|x| > 2$ is given by

$$\frac{dH_1(x)}{dx} = -\frac{|x|}{(\sqrt{x^2-4})^3} \operatorname{arc\,tan} \sqrt{\frac{x-2}{x+2}} + \frac{1}{x(x^2-4)}. \tag{50}$$

For $x < -2$ the derivative is negative as required. For $x > 2$ the situation is less clear. Since $H_1(x)$ approaches 0 from above if x approaches infinity, the derivative must be negative in this case. If it should be positive somewhere, $H_1(x)$ must have at least one maximum x_0 in this region. This requires $H_1'(x_0) = 0$ and thus

$$\operatorname{arc\,tan} \sqrt{\frac{x_0-2}{x_0+2}} = \frac{1}{x_0^2}\sqrt{x_0^2-4}. \tag{51}$$

The left-hand side of this equation is a monotonously increasing function in x_0, with the value 0 for $x_0 = 2$ and $\pi/4$ for x_0 approaching infinity. The right-hand side also starts at the value 0 for $x_0 = 2$, is always positive and vanishes for $x_0 \to \infty$. Its extremum, which can be easily calculated by setting its derivative to 0 is at $x_0^2 = 8$, where the maximum value of the right-hand side is thus $\frac{1}{4}$. For Eq. (51) to be fulfilled, the left-hand side must have a smaller value at $x_0 = \sqrt{8}$ than the maximum value of the right-hand side, since the latter one increases up to $x_0 = \sqrt{8}$ and then decreases, while the former increases in the complete region. However, at $x_0 = \sqrt{8}$ the left-hand side has a value of approximately 0.39, considerably larger than $\frac{1}{4}$. Therefore, the derivative of $H_1(x)$ is negative in the complete region $|x| > 2$, as required.

In the region $|x| < 2$ the integration yields

$$\begin{aligned} H_1(x) &= \frac{1}{\sqrt{4-x^2}} \operatorname{ar\,tanh} \sqrt{\frac{2-x}{2+x}} \\ \frac{dH_1(x)}{dx} &= \frac{x}{(\sqrt{4-x^2})^3} \operatorname{ar\,tanh} \sqrt{\frac{2-x}{2+x}} - \frac{1}{x(4-x^2)} \end{aligned} \tag{52}$$

which is not defined for $-2 < x < 0$, because in this interval the argument of area tangents hyperbolicus is larger than 1. The function has a pole at $x = 0$ with $H_1(x)$ approaching $+\infty$ and the limit (case "0/0") for x approaching $+2$ from the left is again $\frac{1}{4}$. The function is everywhere positive in the interval $0 < x < 2$. Thus it must have at least one minimum in order to be not monotonously decreasing. This would require again $H_1'(x_0) = 0$ and thus the equation

$$\operatorname{ar\,tanh} \sqrt{\frac{2-x_0}{2+x_0}} = \frac{1}{x_0^2}\sqrt{4-x_0^2} \tag{53}$$

would have to be fulfilled. First of all, we notice that both sides of the equation are monotonously decreasing functions of x_0, both from $+\infty$ to 0 for x_0 increasing from 0 to $+2$. Thus the above equation has no solution if the slope of one side is smaller than that of the other one in the whole interval $0 < x_0 < 2$. The derivatives of the two sides can be written as

$$\begin{aligned} &\text{left-hand side derivative: } \frac{-x_0^2}{x_0^3\sqrt{4-x_0^2}} \\ &\text{right-hand side derivative: } \frac{-8+x_0^2}{x_0^3\sqrt{4-x_0^2}}. \end{aligned} \tag{54}$$

The denominators are positive for $0 < x_0 < 2$ and the nominator of the left hand side derivative $(-x_0^2)$ is always larger than that of the right hand side $(-8 + x_0^2)$ in the whole interval. Thus our above equation has no solution and the derivative of $H_1(x)$ is negative everywhere where it is defined.

Let us now turn to $H_2(\omega)$. For this purpose we define $x = \omega - 3a$ to obtain

$$H_2(x) = \frac{\operatorname{sgn}(x-2)}{\sqrt{x^2-4}} \operatorname{arc\,tan} \sqrt{\frac{x+2}{x-2}}. \tag{55}$$

$H_2(x)$ has a pole at $x = 2$, where $H_2(x)$ approaches $+\infty$ if x approaches 2 from the positive side. If x approaches -2 from the negative side we have again the case "0/0" which yields a limit of $-\frac{1}{4}$ at $x = -2$. For $x \to \pm\infty$ we have again $H_2(x) \to \pm 0$. The derivative of $H_2(x)$ is given by

$$\frac{dH_2(x)}{dx} = -\frac{|x|}{(\sqrt{x^2-4})^3} \operatorname{arc\,tan} \sqrt{\frac{x+2}{x-2}} - \frac{1}{x(x^2-4)}. \tag{56}$$

For $x > 2$ the derivative is negative as required. For $x < -2$ the situation is again less clear. Since $H_2(x)$ approaches 0 from below if x approaches $-\infty$, the derivative must be negative in this case. If it should be positive somewhere $H_2(x)$ must have at least one extremum x_0 in this region. This requires $H_2'(x_0) = 0$ and thus

$$\operatorname{arc\,tan} \sqrt{\frac{x_0+2}{x_0-2}} = \frac{1}{x_0^2}\sqrt{x_0^2-4}. \tag{57}$$

A similar argumentation as in the case of $H_1(x)$ shows again that this equation cannot be fulfilled.

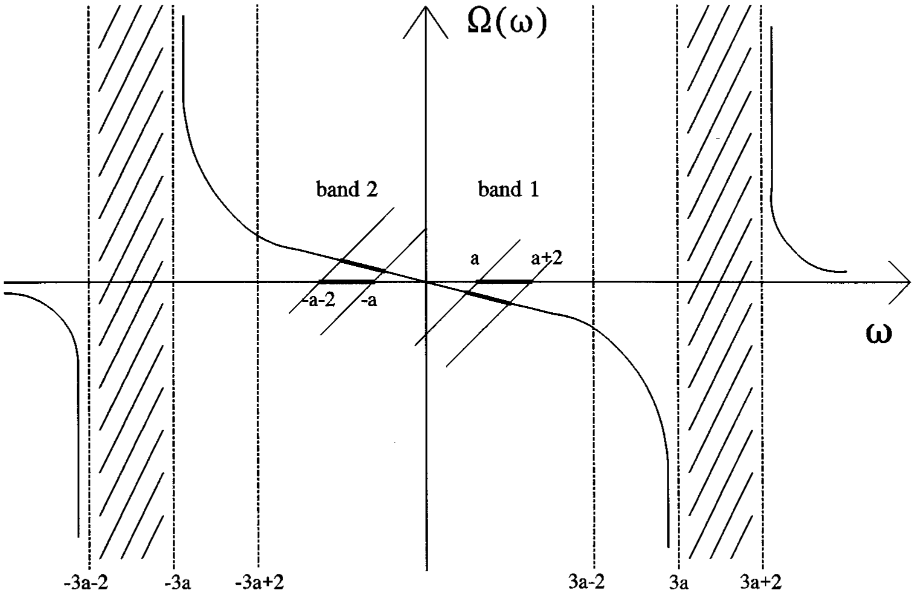

FIG. 2. Sketch of the model of self-energy discussed in the text as function of ω and the graphical solution of the inverse Dyson equations for the two bands under consideration.

In the region $-2 < x < 0$ the integral and its derivative is

$$\begin{aligned} H_2(x) &= -\frac{1}{\sqrt{4-x^2}} \operatorname{ar\,tanh} \sqrt{\frac{2+x}{2-x}} \\ \frac{dH_2(x)}{dx} &= -\frac{x}{(\sqrt{4-x^2})^3} \operatorname{ar\,tanh} \sqrt{\frac{2+x}{2-x}} + \frac{1}{x(4-x^2)}. \end{aligned} \tag{58}$$

Note that in $0 < x < 2$ the function is not defined. The function has a pole at $x = 0$ with $H_2(x)$ approaching $-\infty$ and the limit (case "0/0") for x approaching -2 from the right is again $-\frac{1}{4}$. The function is everywhere negative in the interval $-2 < x < 0$. With the same argumentation as above one can show that also the derivative of this part of $H_2(x)$ is negative everywhere where it is defined. Thus all possible solutions of $\omega_j - \varepsilon - \Omega(\omega_j) = 0$ have a pole strength P_j between 0 and 1 as required.

As discussed above for the general case, we have two regions in our model self-energy, where it is not defined. These are the regions where ω lies within the excitation bands. The pole structure of the self-energy is similar to that of the discrete case, only the poles are no longer of first order and they surround the regions where the self-energy is not defined and not a single point as in the discrete case. Thus all arguments used in the discrete case can be applied here also.

Figure 2 shows a sketch of the self-energy as function of ω and of the graphical solution of the inverse Dyson equations for the two bands. It is obvious that the valence band (positive) is shifted downward, i.e. upward in energy (due to the negative unit of energy), while the conduction band (negative) is shifted upward, i.e., downward in energy and the gap is decreased, as it is observed in most practical ab initio calculations on polymers, too. Further, the widths of the two bands are decreased, again as in most ab initio calculations.

VI. SUMMARY

We have shown, starting from the well studied case of discrete spectra, that in the case of polymers the iterative procedure for the solution of the inverse Dyson equation in its diagonal approximation for the MP2 case converges only if a principal quasi-particle pole exists with a pole strength larger than $\frac{1}{2}$. Since the summation over the pole strengths of all satellites for a given state could be shown to equal 1, this principal quasi-particle pole to which the iteration can converge is also that one with the largest pole-strength (all pole-strengths are positive). From this we could conclude that for polymers the iterative method can be used safely, instead of the computationally very tedious grid search procedure. Further, the iteration provides—if it converges—the principal quasi-particle pole and—in case of divergence—indicates that the quasi-particle concept breaks down. Since the HF-energy bands as well as the quasi-particle poles of the Green's function fall in all known cases (for polymers) into the region where the self-energy contains no poles, it is sufficient to discuss only that region of energy. This follows also qualitatively from the structure of the self-energy in the MP2 approximation.

We have shown for didactic purposes that even a self-energy obtained from a quite simplified tight-binding approach to a simple polymer already yields the effects which in most cases are also obtained in ab initio calculations, namely the HF-bands become usually narrower and the valence band is shifted upward, while the conduction band is shifted downward in energy upon the introduction of correlation corrections. Consequently, correlation reduces the fundamental gap in polymers, which is generally too large on the HF-level.

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