Perturbation of the quasicontinuous spectrum of a system by locally attached fragments

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General expressions are derived for the shifts of individual energy levels of a quasicontinuous spectrum and for the perturbations of the wave functions of a large system for the case in which arbitrary fragments are attached locally. A method of quantum Green's functions is used. Relations between the additive effective parameters and the Green's functions of the end groups are derived for long-chain polymethine dyes.

1. INTRODUCTION

Problems in the theory of crystal defects are basically classified as either descriptions of vibrational and electronic states of intrinsic defects (local and resonant states), along with their contributions to the macroscopic properties of the crystal, or analyses of how the defects influence individual energy levels of the crystal.[1] Problems of the first type have been developed most extensively for macroscopically large systems (containing $N_A \sim 10^{23}$ atoms) with a quasicontinuous spectrum.[2-4] For systems in which the number N of atoms is large but smaller than N_A $(1 \ll N \ll N_A)$, and in which the energy levels are not spaced too closely together, it is useful to solve problems of the second type.[5] Important entities of this type are macromolecules in which electronic transitions observable in the optical range are sensitive to structural modifications induced by attaching fragments locally.[6]

The standard methods for describing crystal defects are based on I. M. Lifshits' ideas of degenerate regular perturbations,[7] which incorporate the changes induced by a defect in the matrix elements of the original unperturbed Hamiltonian, written in the basis of the numbers of the atoms. A difference between a crystal defect and an attached fragment is that the latter introduces a topological change in the original system which is characterized by an eigenenergy spectrum and which cannot be classified as a degenerate regular perturbation. Nevertheless, the results derived in the present study show that the perturbation of this spectrum caused by locally attached fragments in certain parts of the quasicontinuous spectrum can be analyzed at a general level in terms of Green's functions of the defects. The simplification is achieved by focusing on the rapidly varying (cotangent) contribution of the Green's functions of a large subsystem (as in Refs. 7, 8) and of comparatively small fragments. The shifts of the perturbed energy levels and the corresponding wave functions are expressed in terms of the well-determined Green's functions of the fragments and the retarded Green's function of a subsystem with the quasicontinuous spectrum.

To illustrate the approach, we discuss the derivation of optical and chemical properties of a class of macromolecules of practical importance: polymethine dyes. The exact expression for the Green's function of a one-dimensional polymethine chain contains a cotangent contribution, as do the approximate expressions for the Green's functions of systems with a quasicontinuous spectrum. This circumstance substantially expands the range of applicability of this approach in the direction of short polymethine chains, which are the ones most common in practical chemistry.

2. GENERAL DESCRIPTION OF THE SPECTRUM OF LOCALLY COUPLED SUBSYSTEMS

It is often necessary to work from information on the spectra of individual subsystems to estimate the properties of an overall system. In other words, if we are given, say, the spectra of the Hamiltonians of the subsystems A and Γ, which are interacting with each other through a perturbation operator $\hat V$, then we need to determine the eigenvalues and eigenfunctions of the Hamiltonian $\hat H$ of the overall system:

$$\hat H=\hat H_0+\hat V, \qquad \hat H_0=\hat H_A+\hat H_\Gamma, \qquad \hat H\Psi_z(l)=z\Psi_z(l). \tag{1}$$

A general solution of problems of this type can be written most simply in the formalism of Green's functions. Using the Dyson equation

$$\hat G(z)=\hat g(z)+\hat g(z)\hat V\hat G(z), \tag{2}$$

which relates the Green's operators of the system A + Γ when it is perturbed, $\hat G(z)=(z\hat 1-\hat H)^{-1}$, to the corresponding operator for the unperturbed system, $\hat g(z)=(z\hat 1-\hat H_0)^{-1}$, we easily find the equations

$$\begin{gathered}\hat G_{AA}(z)=\hat g_A(z)+\hat g_A(z)\hat V_{A\Gamma}\hat g_\Gamma(z)\hat V_{\Gamma A}\hat G_{AA}(z),\\ \hat G_{\Gamma A}(z)=\hat g_\Gamma(z)\hat V_{\Gamma A}\hat G_{AA}(z),\end{gathered} \tag{3}$$

and corresponding equations for $\hat G_{\Gamma\Gamma}(z)$ and $\hat G_{A\Gamma}(z)$. The operators $\hat G_{AA}(z)$ and $\hat G_{\Gamma\Gamma}(z)$ here correspond to blocks of the matrix of the operator $\hat G(z)$ in the basis of the variables of subsystems A and Γ; the operators $\hat G_{A\Gamma}(z)$ and $\hat G_{\Gamma A}(z)$ correspond to the nondiagonal blocks of the same matrix. The operators $\hat V_{A\Gamma}$ and $\hat V_{\Gamma A}$ correspond to nondiagonal blocks of the matrix of the operator $\hat V$ ($\hat V_{AA}=\hat V_{\Gamma\Gamma}=0$ by virtue of the definition of $\hat V$).

Equation (3) determines the energy spectrum z and the wave functions $\Psi_z(l)$:

$$\det\hat D(z)=\det\hat D_A(z)=\det\hat D_\Gamma(z)=0, \tag{4}$$

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$$\hat{D}_{\mathrm{A}}(z)=\hat{1}-\hat{g}_{\mathrm{A}}(z)\hat{V}_{\mathrm{A}\Gamma}\hat{g}_{\Gamma}(z)\hat{V}_{\Gamma\mathrm{A}},$$

$$\hat{D}_{\Gamma}(z)=\hat{1}-\hat{g}_{\Gamma}(z)\hat{V}_{\Gamma\mathrm{A}}\hat{g}_{\mathrm{A}}(z)\hat{V}_{\mathrm{A}\Gamma},$$

$$\hat{D}_{\mathrm{A}}(z)\Psi_z(\alpha)=0, \quad \hat{D}_{\Gamma}(z)\Psi_z(\gamma)=0, \quad l=\alpha,\ \gamma, \tag{5}$$

(where $l=\alpha\in\mathrm{A}$, $l=\gamma\in\Gamma$). Equations (4) and (5) are in a form more convenient than that of (1) for cases of locally attached subsystems, because $\det\hat{D}_{\mathrm{A}}(z)=\det\hat{D}_{\Gamma}(z)$ reduces to the determinant of a matrix $\hat{D}$ of low dimensionality (the same as the rank of the matrix of the operator $\hat{V}_{\mathrm{A}\Gamma}$).

The Green's-function formalism makes it simple to follow the changes in the density of states

$$\rho(z)=-\pi^{-1}\,\mathrm{Im}\,\mathrm{Sp}\,\hat{G}(z+i0) \tag{6}$$

as the subsystems interact with each other. Specifically, we have

$$\rho(z)=-\pi^{-1}\,\mathrm{Im}[\mathrm{Sp}\,\hat{G}_{\mathrm{AA}}(z+i0)+\mathrm{Sp}\,\hat{G}_{\Gamma\Gamma}(z+i0)], \tag{7}$$

where, according to (3)

$$\mathrm{Sp}\,\hat{G}_{\mathrm{AA}}(z)=\mathrm{Sp}\,\hat{D}_{\mathrm{A}}^{-1}(z)\hat{g}_{\mathrm{A}}(z)=\mathrm{Sp}\,\hat{g}_{\mathrm{A}}(z)$$
$$+\mathrm{Sp}\,\hat{g}_{\mathrm{A}}^{2}(z)\hat{V}_{\mathrm{A}\Gamma}\hat{g}_{\Gamma}(z)\hat{V}_{\Gamma\mathrm{A}}\hat{D}_{\mathrm{A}}^{-1}(z). \tag{8}$$

Using the identities $\hat{g}_{\mathrm{A}}^{2}(z)=-\hat{g}'(z)$ and $\mathrm{Sp}\ln\hat{M}=\ln\det\hat{M}$ (the prime means the derivative with respect to z, and $\hat{M}$ is an arbitrary operator), and writing the corresponding expressions for $\mathrm{Sp}\hat{G}_{\Gamma\Gamma}(z)$, we find the expression which we need for the density of states of the overall system:

$$\rho(z)=\rho_{\mathrm{A}}(z)+\rho_{\Gamma}(z)+\frac{d}{dz}T(z), \tag{9}$$

$$T(z)=-\pi^{-1}\,\mathrm{Im}\ln\det\hat{D}(z+i0). \tag{10}$$

The last term in (9) describes the change caused in the density of states by the interaction between the subsystems. The integer quantity $T(z)$ changes abruptly with increasing z when levels of either the perturbed or unperturbed system are crossed. In the former case, the abrupt change is an increase, and in the latter case a decrease, by an amount equal to the degree of degeneracy of the level.

We turn now from the general formulation of the method to an analysis of the perturbation of the spectrum of system A by fragments Γ_j which are attached locally and which do not interact with each other. We assume that subsystem Γ is a set of such fragments ($\Gamma=\Sigma_j\Gamma_j$). The Green's operator $\hat{g}_{\Gamma}(z)$ is then equal to the direct sum of the $\hat{g}_{\Gamma_j}(z)$. If we also ignore the interaction between fragments via subsystem A (because of the "large distances" between attachment points), we find that the effects of the individual fragments on the spectrum of subsystem A are additive:

$$T(z)=\sum_j T_j(z). \tag{11}$$

From this point on the analysis can be restricted to the case in which only one fragment Γ is attached locally (we will now omit the index j).

We will use the words "local attachment" of subsystems A and Γ to mean the very simplest connection of the two: between and atom $\alpha_1\in\mathrm{A}$ and an atom $\gamma_1\in\Gamma$. The matrix elements $\hat{V}_{\mathrm{A}\Gamma}$ in the basis of the numbers of the atoms $\alpha\in\mathrm{A}$ and $\gamma\in\Gamma$ are thus

$$V_{\alpha\gamma}=\beta\delta_{\alpha\alpha_1}\delta_{\gamma\gamma_1} \tag{12}$$

(β is a coupling constant). In the same basis, the matrix elements of the Green's operator become

$$g_{ll'}(z)=\langle l|\hat{g}(z)|l'\rangle=\sum_q\frac{\psi_q(l)\psi_q^*(l')}{z-\lambda_q}, \tag{13}$$

where λ_q and $\psi_q(l)$ are the eigenvalues and eigenfunctions of the unperturbed Hamiltonian H_{A} ($l=\alpha$) or H_{Γ} ($l=\gamma$). Equation (4), an eigenvalue equation for the Hamiltonian H, defined in (1), is transformed as follows:

$$\det\hat{D}=1-\beta^2 g_{\alpha_1\alpha_1}(z)g_{\gamma_1\gamma_1}(z)=0. \tag{14}$$

If we express the Green's function in terms of the ratios of the corresponding cofactors and the determinants of the matrices $z\hat{1}-\hat{H}_{\mathrm{A}}$ and $z\hat{1}-\hat{H}_{\Gamma}$, relation (14) reduces to the Heilbronner formula.[9] Figure 1 shows a graphical solution of Eq. (14) for the case of nondegenerate unperturbed levels. Far from points with $g_{\gamma_1\gamma_1}(z)=0$, the perturbed levels alternate with the unperturbed levels of the subsystem A. Treating degenerate levels as the limit of closely spaced levels, we easily see that the position of an n-fold-degenerate unperturbed level ($n\geqslant 2$) is the same as that of an ($n-1$)-fold-degenerate perturbed level.[7]

The wave functions of the two subsystems are related by

$$\Psi_z(\alpha)=\beta g_{\alpha\alpha_1}(z)\Psi_z(\gamma_1), \quad \Psi_z(\gamma)=\beta g_{\gamma\gamma_1}(z)\Psi_z(\alpha_1). \tag{15}$$

Using these relations, the normalization condition

$$\sum_\alpha|\Psi_z(\alpha)|^2+\sum_\gamma|\Psi_z(\gamma)|^2=1 \tag{16}$$

and the identity used above for derivatives of a Green's operator (or function), we find an explicit expression for $\Psi_z(\alpha_1)$:

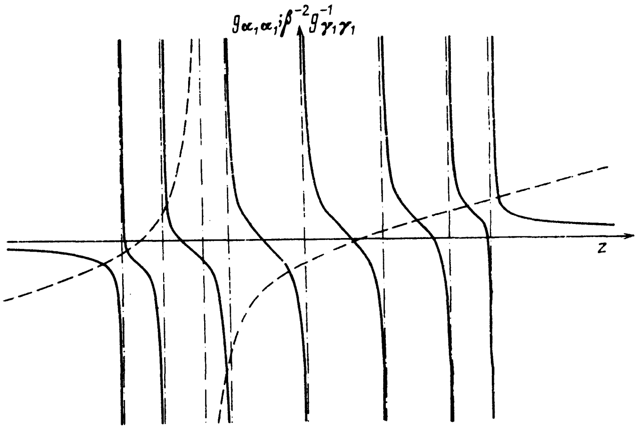

FIG. 1. Graphical determination of the energy levels of a system perturbed by the local attachment of a fragment. Solid lines—$g_{\alpha_1\alpha_1}(z)$; dashed lines—$\beta^{-2}g^{-1}_{\gamma_1\gamma_1}(z)$; dot-dashed lines—asymptotes at the points of poles of $g_{\alpha_1\alpha_1}(z)$ and zeros of $g_{\gamma_1\gamma_1}(z)$.

$$\Psi_z(\alpha_1)=|\beta|^{-1}[-g_{\gamma_1\gamma_1}(z)-\beta^2 g'_{\alpha_1\alpha_1}(z)g^{2}_{\gamma_1\gamma_1}(z)]^{-1/2}. \tag{17}$$

Using (15), we can reconstruct the wave function of the system.

3. QUASICONTINUOUS SPECTRUM OF ONE SUBSYSTEM

Analytic expressions for the solutions of Eq. (14) and the explicit expressions for the wave function in (15) and (17) are pertinent to the case (of practical importance) in which one of the subsystems has a large number of atoms and a quasicontinuous spectrum. Following Ref. 7, we introduce the concept of a quasicontinuous spectrum in the following way. We number the energy levels of the subsystem A which correspond to states q with wave functions $\psi_q(\alpha)$ by means of the index m, in such a way that we have $\lambda_{m+1}>\lambda_m$. We denote the degree of degeneracy of level λ_m by ϑ_m. We introduce the small parameter $\varepsilon=N^{-1}$ (N is the number of atoms in the subsystem A), which determines the structure of the energy spectrum. We say that the spectrum λ_m is, for sufficiently small ε, "quasicontinuous with respect to ε" if there exist ε-independent, piecewise-continuous functions $\lambda(u)$ and $\vartheta_{\alpha\alpha'}(u)$ which have piecewise-continuous derivatives at the points of discontinuity and which are such that for $u_m=m\varepsilon$ the following relations hold:

$$\lambda_m=\lambda(u_m)+O(\varepsilon),\qquad \Delta\lambda_m=\lambda_{m+1}-\lambda_m=\varepsilon\left[\left(\frac{d\lambda}{du}\right)_{u_m}+O(\varepsilon)\right], \tag{18}$$

$$\sum_{q\in m}\psi_q(\alpha)\psi_q^*(\alpha')=\varepsilon[\vartheta_{\alpha\alpha'}(u_m)+O(\varepsilon)]. \tag{19}$$

An additional summation over $\alpha=\alpha'$ in (19) gives us the degree of degeneracy of ϑ_m.

The Green's function (13) for subsystem A can be written

$$g_{\alpha\alpha'}(z)=\varepsilon\left[\sum_m\frac{\vartheta_{\alpha\alpha'}(u_m)}{z-\lambda(u_m)}+O(\varepsilon)\right]$$
$$=\fint\frac{\vartheta_{\alpha\alpha'}(u)du}{\lambda(u_p)-\lambda(u)}+\frac{\pi\vartheta_{\alpha\alpha'}(u_p)}{(d\lambda/du)u_p}\operatorname{ctg}\pi\zeta(u_p)+O(\varepsilon), \tag{20}$$

where the limit $\varepsilon\to0$ has been taken in the last equation, as in Ref. 7, and where $z\in[\lambda_p,\lambda_{p+1}]$:

$$z_p=\lambda(u_p)+\varepsilon\left[\left(\frac{d\lambda}{du}\right)_{u_p}\zeta(u_p)+O(\varepsilon)\right]\approx\lambda_p+\zeta_p\Delta\lambda_p,\quad 0\leqslant\zeta_p<1. \tag{21}$$

The Green's function written in this manner varies substantially (with ζ_p) over energy intervals on the order of $\Delta\lambda_p$. However, it is convenient to work with a Green's function which varies smoothly over intervals on the order of the width of the zone of quasicontinuous spectrum. We accordingly introduce a retarded Green's function $\tilde g_{\alpha\alpha'}(z)$ which is smoothed over intervals $\Delta\lambda_p$:

$$\tilde g_{\alpha\alpha'}(\lambda_p)\equiv\int\frac{\vartheta_{\alpha\alpha'}(u)du}{\lambda_p-\lambda(u)+i0}=\fint\frac{\vartheta_{\alpha\alpha'}(u)du}{\lambda_p-\lambda(u)}-i\frac{\pi\vartheta_{\alpha\alpha'}(u_p)}{(d\lambda/du)_{u_p}}. \tag{22}$$

In the last equation we have used Sokhotskiĭ's formula, and u_p is the root of the equation $\lambda(u_p)=\lambda_p$. Comparing (20) with (22), we conclude that

$$g_{\alpha\alpha'}(z_p)=\frac{1}{2}[\tilde g_{\alpha\alpha'}(\lambda_p)+\tilde g^{*}_{\alpha'\alpha}(\lambda_p)]$$
$$+\frac{i}{2}[\tilde g_{\alpha\alpha'}(\lambda_p)-\tilde g^{*}_{\alpha'\alpha}(\lambda_p)]\cdot\operatorname{ctg}\pi\zeta_p,$$

$$g_{\alpha\alpha}(z_p)=\operatorname{Re}\tilde g_{\alpha\alpha}(\lambda_p)-\operatorname{Im}\tilde g_{\alpha\alpha}(\lambda_p)\cdot\operatorname{ctg}\pi\zeta_p. \tag{23}$$

While the microscopically exact density of states $\rho(z)$ of the subsystem A with the Green's function (23), which is determined by a relation like (6), gives us the peaks described by a δ-function at the levels λ_p, the coarse density of states $\tilde\rho(z)$ is equal to the average number of levels in a unit energy interval:

$$\tilde\rho_A(\lambda_p)=-\pi^{-1}\operatorname{Im}\sum_\alpha\tilde g_{\alpha\alpha}(\lambda_p)\approx\frac{\vartheta_p}{\Delta\lambda_p}. \tag{24}$$

Let us find the change in the coarse density of states associated with the local attachment of a small fragment Γ to the subsystem A. For this purpose we make use of (10) and (14), with retarded Green's functions, for which we set $\tilde g_{\gamma_1\gamma_1}(\lambda_p)\simeq g_{\gamma_1\gamma_1}(\lambda_p)$, because the subsystem Γ is small in comparison with A:

$$\tilde T(\lambda_p)=-\pi^{-1}\operatorname{Im}\ln[1-\beta^2\tilde g_{\alpha_1\alpha_1}(\lambda_p)g_{\gamma_1\gamma_1}(\lambda_p)]=-\zeta_p, \tag{25}$$

where the quantity ζ_p, introduced in (21) is found from Eq. (14) with (23):

$$\operatorname{ctg}\pi\zeta_p=\frac{\beta^2 g_{\gamma_1\gamma_1}(\lambda_p)\operatorname{Re}\tilde g_{\alpha_1\alpha_1}(\lambda_p)-1}{\beta^2 g_{\gamma_1\gamma_1}(\lambda_p)\operatorname{Im}\tilde g_{\alpha_1\alpha_1}(\lambda_p)}. \tag{26}$$

It determines the position of the perturbed energy level with respect to the closest unperturbed levels. The change in the density of states which we are seeking can then be written

$$\Delta\tilde\rho(\lambda_p)=-\frac{d\zeta_p}{d\lambda_p}=-\frac{1}{\pi}\beta^2\operatorname{Im}\tilde g_{\alpha_1\alpha_1}(\lambda_p)$$
$$\times\{\beta^4 g^{2}_{\gamma_1\gamma_1}(\lambda_p)(\operatorname{Im}\tilde g_{\alpha_1\alpha_1}(\lambda_p))^2$$
$$+[\beta^2 g_{\gamma_1\gamma_1}(\lambda_p)\operatorname{Re}\tilde g_{\alpha_1\alpha_1}(\lambda_p)-1]^2\}^{-1}$$
$$\times\{g'_{\gamma_1\gamma_1}(\lambda_p)+\beta^2 g^{2}_{\gamma_1\gamma_1}(\lambda_p)\operatorname{Re}\tilde g'_{\alpha_1\alpha_1}(\lambda_p)$$
$$-g_{\gamma_1\gamma_1}(\lambda_p)[\beta^2 g_{\gamma_1\gamma_1}(\lambda_p)\operatorname{Re}\tilde g_{\alpha_1\alpha_1}(\lambda_p)-1]\frac{d}{d\lambda_p}\ln\operatorname{Im}\tilde g_{\alpha_1\alpha_1}(\lambda_p)\Big\}. \tag{27}$$

The maximum value of $\Delta\tilde\rho(\lambda_p)$ is reached under the conditions

$$\beta^2 g_{\gamma_1\gamma_1}(\lambda_p)\operatorname{Re}\tilde g_{\alpha_1\alpha_1}(\lambda_p)=1,\qquad \zeta_p={}^1/_2, \tag{28}$$

which determine the resonant states. In the general case of arbitrary λ_p, relations (26) and (27) solve the problem of approximately calculating the perturbed spectrum z_p [see also (21)] and the energy gaps between neighboring perturbed levels:

$$\Delta z_p = z_{p+1} - z_p \approx (\Delta\lambda_p{}^{-1} - d\zeta_p/d\lambda_p)^{-1}. \tag{29}$$

To find the perturbed wave functions, we should express the derivative $g'_{\alpha_1\alpha_1}(z)$ in (17) in terms of the characteristics of the quasicontinuous spectrum:

$$g'_{\alpha_1\alpha_1}(z_p) = \frac{d}{dz_p} g_{\alpha_1\alpha_1}(\lambda_p, \zeta_p) = \frac{\partial g_{\alpha_1\alpha_1}}{\partial\lambda_p} + \frac{1}{\Delta\lambda_p}\frac{\partial g_{\alpha_1\alpha_1}}{\partial\zeta_p}. \tag{30}$$

The partial derivative $\partial g_{\alpha_1\alpha_1}/\partial\lambda_p$ is determined by the following system of equations, which incorporates (14):

$$\begin{aligned} &\frac{d}{d\zeta_p} g_{\alpha_1\alpha_1}(\lambda_p, \zeta_p) = \frac{\partial g_{\alpha_1\alpha_1}}{\partial\zeta_p} + \frac{\partial g_{\alpha_1\alpha_1}}{\partial\lambda_p}\frac{d\lambda_p}{d\zeta_p}, \\ &\frac{d}{d\zeta_p} g_{\alpha_1\alpha_1}(\lambda_p, \zeta_p) = \frac{d}{d\lambda_p}\left(\frac{1}{\beta^2 g_{\gamma_1\gamma_1}(\lambda_p)}\right)\frac{d\lambda_p}{d\zeta_p}. \end{aligned} \tag{31}$$

We thus find

$$\frac{\partial g_{\alpha_1\alpha_1}}{\partial\lambda_p} = -\frac{g'_{\gamma_1\gamma_1}(\lambda_p)}{\beta^2 g^2_{\gamma_1\gamma_1}(\lambda_p)} - \frac{\partial g_{\alpha_1\alpha_1}}{\partial\zeta_p}\frac{d\zeta_p}{d\lambda_p}. \tag{32}$$

Substituting (32) into (30), we find

$$g'_{\alpha_1\alpha_1}(z_p) = -\frac{g'_{\gamma_1\gamma_1}(\lambda_p)}{\beta^2 g^2_{\gamma_1\gamma_1}(\lambda_p)} + \frac{1}{\Delta z_p}\frac{\partial g_{\alpha_1\alpha_1}}{\partial\zeta_p}. \tag{33}$$

Calculating $\partial g_{\alpha_1\alpha_1}/\partial\zeta_p$ from (23), using (26), and substituting the result for $g'_{\alpha_1\alpha_1}(z_p)$ into (17), we find the perturbed wave function at atom α_1:

$$\Psi_z(\alpha_1) = \left[-\frac{\Delta z_p}{\pi\,\mathrm{Im}\,\tilde{g}_{\alpha_1\alpha_1}(\lambda_p)}\right]^{1/2}\frac{\sin\pi\zeta_p}{\beta^2 g_{\gamma_1\gamma_1}(\lambda_p)}. \tag{34}$$

According to (15), the perturbed wave function at subsystem Γ is then found by multiplying (34) by $\beta g_{\gamma\gamma_1}(\lambda_\rho)$, while that at subsystem A becomes

$$\begin{aligned} \Psi_{z_p}(\alpha) = \frac{1}{2i}\left[\frac{\Delta z_p}{\pi\,\mathrm{Im}\,\tilde{g}_{\alpha_1\alpha_1}(\lambda_p)}\right]^{1/2} |\tilde{g}_{\alpha\alpha_1}(\lambda_p)|\cdot \\ \times\{\exp[i(\pi\zeta_p - \arg\tilde{g}_{\alpha_1\alpha}(\lambda_p))] - \exp[-i(\pi\zeta_p - \arg\tilde{g}_{\alpha\alpha_1}(\lambda_p))]\}. \end{aligned} \tag{35}$$

Relations (26), (27), (29), and (35) give an exhaustive description of the characteristics of a system consisting of a large subsystem with a quasicontinuous spectrum and a locally attached fragment, in terms of the Green's functions of the subsystems.

4. APPLICATION OF THE THEORY TO THE OPTICAL SPECTRA OF POLYMETHINE DYES

Some entities of practical importance whose observable spectral properties might be affected substantially by attached fragments are the so-called polymethine dyes $\Gamma_2(\mathrm{CH})_N$, in which various molecular fragments Γ can be attached to the ends of the polymethine chains $(\mathrm{CH})_N$ (Refs. 6, 10, and 11). An equation for the unperturbed Green's functions of the three subsystems (the two end fragments, which are attached by bonds β_1 and β_2 to the polymethine chain of N atoms) which determines the energy spectrum z of the system can be found from Eq. (4) if the Green's operator $\hat{g}_\Gamma(z)$ is understood as the direct sum of the unperturbed Green's operators of the fragments, and if the perturbation operator $\hat{V}$ links these fragments to the polymethine chain:

$$\begin{aligned} &1 - [\beta_1{}^2 g_1(z) + \beta_2{}^2 g_2(z)]\,g_{11}(z) \\ &\quad + \beta_1{}^2\beta_2{}^2 g_1(z) g_2(z)\,[g_{11}{}^2(z) - g_{N1}{}^2(z)] = 0. \end{aligned} \tag{36}$$

Here $g_1(z)$ and $g_2(z)$ are the Green's functions of the end fragments $g_{\gamma_1\gamma_1}(z)$ with indices γ_1 corresponding to the atoms of the fragments which are attached to atoms 1 and N of the polymethine chain. The energy spectrum and wave functions of the unperturbed polymethine chain are given by

$$\begin{aligned} &\lambda_q = -2\cos\frac{\pi q}{N+1}, \\ &\psi_q(\alpha) = \left(\frac{2}{N+1}\right)^{1/2}\sin\frac{\pi q\alpha}{N+1}; \quad q, \alpha = 1, \ldots, N, \end{aligned} \tag{37}$$

where the energy is reckoned from the midpoint of the quasiband and is expressed in units of the magnitude of the coupling constant ($\beta = -1$). An explicit expression for the Green's function of the unperturbed polymethine chain can be found directly from the definition $g_{\alpha\alpha'}(z) = \langle\alpha|(z\hat{1} - \hat{H}_\mathrm{A})^{-1}|\alpha'\rangle$ or by summing over q in (13) and using (37):

$$g_{\alpha\alpha'}(z) = g_{\alpha'\alpha}(z) = \frac{\sin\alpha'\theta}{\sin\theta}[-\cos\alpha\theta + \sin\alpha\theta\,\mathrm{ctg}(N+1)\theta],$$

$$\alpha \geqslant \alpha', \tag{38}$$

$$\theta = \arccos(-z/2). \tag{39}$$

In (36) we made use of the symmetry properties of $g_{\alpha\alpha'}(z)$, in particular, the equality $g_{11}(z) = g_{NN}(z)$.

A distinctive feature of a one-dimensional chain is that the exact expression for the Green's function in (38) contains a rapidly oscillating function $\cot(N+1)\theta$, just as the approximate relation (23) does. The additivity of the parameters in (11) and (25) for the attached fragments—this additivity holds at large N—can be utilized to derive exact equations for arbitrary N:

$$\pi\zeta \equiv (N+1)\theta - \pi q = \pi\zeta_1 + \pi\zeta_2, \tag{40}$$

where the functions $\zeta_j(z)$, $j = 1, 2$ are determined by (26), with λ_q replaced by z:

$$\begin{aligned} \zeta_j = F_j(z) &= \frac{1}{\pi}\,\mathrm{arcctg}\,\frac{\beta_j{}^2 g_j(z)\,\mathrm{Re}\,\tilde{g}_{11}(z) - 1}{\beta_j{}^2 g_j(z)\,\mathrm{Im}\,\tilde{g}_{11}(z)} \\ &= \frac{1}{\pi}\,\mathrm{arcctg}\,\frac{1 + \beta_j{}^2 g_j(z)\cos\theta}{\beta_j{}^2 g_j(z)\sin\theta}. \end{aligned} \tag{41}$$

In the last equation we have made use of the explicit expression for the retarded Green's function $\tilde{g}_{\alpha\alpha'}(z)$, which follows from (38) when we use (23):

$$\tilde{g}_{\alpha\alpha'}(z)=-\frac{\sin\alpha'\theta}{\sin\theta}e^{i\alpha\theta},\qquad \alpha\geqslant\alpha'. \tag{42}$$

We can now use (35) (replacing λ_q by z), in which, according to (29), we have

$$\Delta z_p\approx\left[\frac{N+1}{2\pi\sin\theta}-\frac{d}{dz}(\zeta_1+\zeta_2)\right]^{-1}=\frac{2\pi\sin\theta}{N+1+l(z)}, \tag{43}$$

to find the perturbed wave function of the polymethine chain:

$$\Psi_z(\alpha)=\left(\frac{2}{N+1+l(z)}\right)^{1/2}\sin[\pi F_1(z)-\alpha\theta(z)], \tag{44}$$

where

$$l(z)=\sum_{j=1}^{2}l_j(z),\qquad l_j(z)=-2\pi\sin\theta(z)F_j'(z)\;=-\frac{\beta_j^2[2g_j'(z)+\beta_j^2g_j^2(z)]\sin^2\theta+\beta_j^2g_j(z)\cos\theta(1+\beta_j^2g_j(z)\cos\theta)}{1+\beta_j^4g_j^2(z)+2\beta_j^2g_j(z)\cos\theta} \tag{45}$$

might be called the "effective length of the end fragments," determining that effective elongation of the polymethine chain would generate the same energy gaps as the system under consideration.

We wish to stress that relations (36)–(41), (44), and (45) are valid for arbitrary N. This point can be verified by a direct check based on the correspondence between (38)–(41) and Eq. (36) and that between (44), (45) and the eigenfunction equation of the type in (5) or explicit expressions of the type in (15)–(17), with allowance for the additional fragment. The additive representation of the contributions of the end fragments to the energy spectrum in (40) and to the wave function in (44) of this system was worked out in Ref. 12 by a method of secular-polynomial matrices, without the use of the Green's-function formalism. The latter makes it possible to relate the particular results for a specific system to the general properties of perturbations of a quasicontinuous spectrum caused by locally attached fragments. The transition to the quasicontinuous spectrum for this as given corresponds to fairly large values of N. Compounds with odd values of N and a half-filled π-electron band, so the Fermi level passes through the unperturbed level $\lambda_q=0$ with $q=(N+1)/2$, are usually classified as polymethine dyes. The first electronic transition occurs between the levels closest to the Fermi level on its two sides. The positions of these levels can be found by expanding (40) in the small parameter $\varepsilon=[N+1]^{-1}$:

$$\zeta=F(z)=F(0)-l(0)\varepsilon\zeta-\pi l'(0)\varepsilon^2\zeta^2+O(\varepsilon^3). \tag{46}$$

This approach is equivalent to an expansion in the renormalized small parameter $\tilde{\varepsilon}=[N+1+l(0)]^{-1}$:

$$\zeta=\frac{\tilde{\varepsilon}}{\varepsilon}F(0)[1-\pi l'(0)F(0)\tilde{\varepsilon}^2+O(\tilde{\varepsilon}^3)], \tag{47}$$

$$z=2\sin\pi\varepsilon\zeta=2\pi\tilde{\varepsilon}F(0)\left[1-\pi\left(l'(0)+\frac{\pi}{6}F(0)\right)\right.$$
$$\left.\times F(0)\tilde{\varepsilon}^2+O(\tilde{\varepsilon}^3)\right]. \tag{48}$$

If we understand $F(0)$ as the fractional part of the sum

$$F(0)=\{F_1(0)+F_2(0)\} \tag{49}$$

[here we have $0\leqslant F(0)<1$, in agreement with (41), which determines $F_j(z)$ in this interval, by virtue of the range of arctan$x$], then we can find the value of the positive level (i.e., that above the Fermi level) from (46)–(48). The position of the negative level can then be found from (48) by replacing $F(0)$ by $F(0)^{-1}$ [as follows from (41), if the values of $F_j(0)$ for the neighboring levels are determined by the multivalued function arcot x]. The energy of the first electronic transition is then

$$\Delta z=2\pi\tilde{\varepsilon}\left\{1-\pi\left[l'(0)(2F(0)-1)\right.\right.$$
$$\left.\left.+\frac{\pi}{6}(3F^2(0)-3F(0)+1)\right]\tilde{\varepsilon}^2+O(\tilde{\varepsilon}^3)\right\}. \tag{50}$$

We can write an explicit expression for the quantities $F_j(0)$, $l_j(0)$ and $l_j'(0)$ $(j=1,2)$, which are, according to (45) and (49), additive contributions to $F(0)$, $l(0)$, and $l'(0)$, respectively:

$$F_j(0)=\pi^{-1}\operatorname{arcctg}[\beta_j^2g_j(0)]^{-1}, \tag{51}$$

$$l_j(0)=-\frac{\beta_j^2[2g_j'(0)+\beta_j^2g_j^2(0)]}{1+\beta_j^4g_j^2(0)}, \tag{52}$$

$$l_j'(0)=-\frac{2\beta_j^2g_j''(0)}{1+\beta_j^4g_j^2(0)}$$
$$-\beta_j^2g_j(0)\frac{8\beta_j^2g_j'(0)[1-\beta_j^2g_j'(0)]+\beta_j^4g_j^2(0)-1}{2[1+\beta_j^4g_j^2(0)]^2}. \tag{53}$$

The approximate expression for the wave function is found by substituting expansions of $l(z)$ and (47) into (44), to within terms on the order of $\tilde{\varepsilon}$:

$$\Psi_0(\alpha)\approx(2\tilde{\varepsilon})^{1/2}\sin\left\{\frac{\pi}{2}\alpha+\pi\tilde{\varepsilon}[F_2(0)\alpha-F_1(0)(N+1-\alpha)]\right\}. \tag{54}$$

The asymptotic $(z\to 0)$ molecular orbital in (54) undergoes the largest perturbations with respect to the unperturbed state $\psi(\alpha)=(2\varepsilon)^{1/2}\sin(\pi\alpha/2)$ near the ends of the chain, with $\alpha\sim 1$ and $\alpha\sim N$ under the influence of the fragments with $F_1(0)$ and $F_2(0)$, respectively (this is as it should be).

The system of relations (47), (48), (50)–(54), written to within terms on the order of $\tilde{\varepsilon}$, has been called the "long-chain approximation" of polymethine dyes.[13] A surprising property of this approximation is that it is valid for short chains with $N = 3$ and even $N = 1$, which are the most typical chains for real polymethine dyes.[13] This property of the approximation follows from estimates of the corrections of order $\tilde{\varepsilon}^2$ in (47) and (50): For small fragments, the coefficient of $\tilde{\varepsilon}^2$ turns out to be numerically small, while for large fragments of n atoms this correction corresponds in order of magnitude to

$$\beta_j^2 g(0) n / [(1+\beta_j^2 g(0)(N+n)^2] \ll 1$$

even at small values of N (this result is actually due to the switch from the parameter ε to the even smaller $\tilde{\varepsilon}$). On the other hand, the range in which this approximation is valid—as is true of any approach which ignores the interelectron repulsion—is limited to values of N which are not too large, so that one may ignore the energy gap which arises in the spectrum of infinite one-dimensional systems. It follows from the results of Ref. 10, for example, that as the limit $N \to \infty$ is approached an antiferromagnetic state with a gap becomes preferable from the energy standpoint to the gapless solutions only for $N \gtrsim 10$. The construction of a Green's function from the wave functions of antiferromagnetic states in Ref. 10 would make it possible to extend the method developed here to chains of arbitrarily great length.

In summary, compact equations relating the additive parameters of the end fragments[12] to their Green's functions have been found in this section of the paper. These equations can be used to analyze various perturbations of the states of a polymethine chain. They simplify the search for end fragments which would impart particular optical and chemical properties to polymethine dyes. In particular, the parameter $F(0)$ characterizes the ability of a molecule to acquire or give up electrons: The molecule will act as an electron acceptor if $0 < F(0) < 1/2$ and as a donor if $1/2 < F(0) < 1$. It remains in a form stable with respect to oxidation-reduction reactions at $F(0) = 1/2$. A search for stable molecules of this sort was carried out in Refs. 14 and 15 in the long-chain approximation. On the other hand, the same condition corresponds to a resonant state, according to (28). Resonant states near the Fermi level thus acquire a nontrivial chemical interpretation.

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