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Many-Electron Effects in the X-Ray Absorption Spectra and the One-Particle Green's Function

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Some aspects of influence of many-electron processes on X-ray absorption spectra by the Green's function formalism are investigated. The discrete and continuous near edge and extended fine structures are analyzed in detail, each taken separately. A connection is established between the photoelectron and X-ray absorption spectroscopy data.

Key words: X-ray absorption spectra – Many-electron effects – Green's function.

1. Introduction

In recent years much progress has been made in our understanding the role of many-electron effects in the formation of electron [1–7] and X-ray emission [8–12] molecular (and, naturally, atomic) spectra. To a considerable extent it is due to the introduction of various many-particle theories to molecular physics. The purpose of this paper is to investigate some of the many-electron effects in X-ray absorption (XA) spectra of molecules with completely closed orbitals by using the Green's function formalism [1, 13, 14].

The one-electron transitions from occupied orbitals k to vacant bound orbitals $\nu(k \to \nu)$ or continuous states $e(k \to e)$ are known to usually make the largest contribution to the XA cross section. Such transitions are well described within the framework of the so-called one-electron ionic model [15–17] which takes into account the influence on the excited electron of both the hole on the orbital k and the rearrangement of electron orbitals under the action of the hole, i.e. the electron relaxation effect, by the self-consistent field method. In this model the Hartree–Fock orbitals of the ground 0 and of the ionized k^{-1} (with the hole on the orbital k) self-consistent field states are used as the originating k and terminating ν or e orbitals, respectively. And the one-electron XA cross section is given by the formula [17] (the atomic units $\hbar = m = e = 1$ are used throughout this paper):

$$\sigma_k^0(w) = 4\pi^2\alpha^2 \sum_\nu w_{\nu k} |\langle \nu | \boldsymbol{re} | k\rangle|^2 \frac{\gamma_k/2\pi}{(w - w_{\nu k})^2 + \gamma_k^2/4}, \tag{1a}$$

$$\sigma_k^0(w) = 4\pi^2\alpha^2 w \int_0^\infty |\langle e | \boldsymbol{re} | k\rangle|^2 \frac{\gamma_k/2\pi}{(w - w_{ek})^2 + \gamma_k^2/4} d\varepsilon_e, \tag{1b}$$

where w and $\boldsymbol{e}$ are the energy and the polarization vector of the exciting X-ray photon, respectively. The first formula (1a) corresponds to the discrete transitions and the second (1b), to the direct photoionization; the transition energies are calculated as follows

$$w_{\nu k} = E_{k^{-1}} + \varepsilon_\nu - E_0;\ w_{ek} = E_k + \varepsilon_e - E_0,$$

where E_0 and $E_{k^{-1}}$ are the Hartree–Fock energies of the ground 0 and the ionized k^{-1} molecular states, γ_k is the radiative half-width of the core hole state k^{-1}. Eqs. (1a) and (1b) are the basis of practically all modern methods for interpreting XA spectra and extracting from them the data on the electronic and atomic structure of matter [18–22].

It is evident that the concept of pure one-electron transitions is an idealization. Many-electron relaxation and correlation processes do affect one-electron transitions over a certain range and, besides, cause many-electron ones. Therefore, it is rather expedient to establish the correctness frames of the one-electron ionic model for describing the XA spectra.

2. XA Spectra and the One-Particle Green's Function

Let us now consider the process of X-ray absorption by the N-electron system taking into account the many-electron effects. In the well-known dipole approximation the XA cross section is given by the formula [18]:

$$\sigma(w) = 4\pi^2\alpha^2 w \sum_m |\langle m | W | 0\rangle|^2 \frac{\gamma/2\pi}{(w - w_{m0})^2 + \gamma^2/4}, \tag{2}$$

where the summing up is carried out over all the states m of the molecule with the energies $w_{m0} = E_m - E_0$. Further we shall use the formalism of the second quantization where the electromagnetic interaction operator W is written as follows

$$W = \sum_{i=1}^{N} \boldsymbol{er}_i = \sum_{kl} W_{kl} a_k^+ a_l \equiv \sum_{kl} \langle k | \boldsymbol{er} | l\rangle a_k^+ a_l,$$

where a_k^+ and a_l are the creation and annihilation operators for an electron in the one-particle states k and l of the one-electron ionic model which uses the appropriate ion for self-consistent field calculating vacant bound and continuous states. Let us now introduce the main approximation [1, 23] in the present work for all the high excited states of the molecule involved in Eq. (2)

$$|m\rangle \cong A|e\rangle|s\rangle; \quad E_m = E_s + \varepsilon_e, \tag{3}$$

where s is the exact state of the positive N-1-electron molecular ion, e is the bound or continuous one-particle state of the excited electron and A is the antisymmetrization operator, which we shall further omit for brevity. It is evident that this approximation is valid in the high energy limits i.e. in case the photoelectron energy ε_e is rather high. In the opposite case near the ionization threshold we may hope that this approximation describes rather well such collective processes as many-electron excitation shake-up or shake-off. In what follows we shall be mainly interested in this type of many-electron phenomena in this energy region. Using Eqs. (3) and the known relation

$$(\gamma/2)/(\beta^2+\gamma^2/4) = \mathrm{Im}\,(1/(\beta - i\gamma/2)), \tag{4}$$

it is easy to obtain the following relationship between the XA cross section and the known one-particle Green's function G_{ln}:

$$\begin{aligned}
\sigma(w) &\cong 4\pi\alpha^2 w \sum_{es} \langle 0| \sum_{mn} W^*_{mn} a^+_n a_m |e\rangle|s\rangle \\
&\quad \cdot \langle e|\langle s| \sum_{kl} W_{kl} a^+_k a_l |0\rangle \frac{\gamma/2}{(w - E_s - \varepsilon_e + E_0)^2 + \gamma^2/4} \\
&\cong 4\pi\alpha^2 w \sum_{eln} W^*_{en} W_{el}\, \mathrm{Im} \sum\!\!\!\!\!\!\int_s \frac{\langle 0|a^+_n|s\rangle\langle s|a_l|0\rangle}{\varepsilon_e - w + I_s - i\gamma/2} \\
&\equiv 4\pi\alpha^2 w \sum_{eln} W^*_{en} W_{el}\, \mathrm{Im}\, G^A_{ln}(\varepsilon_e - w) \\
&= 4\pi\alpha^2 w \sum_{eln} W^*_{en} W_{el}\, \mathrm{Im}\, G_{ln}(\varepsilon_e - w),
\end{aligned} \tag{5}$$

where G^A_{ln} is the advanced Green's function [1, 13, 14], I_s is the ionization potential of the state $s: I_s = E_s - E_0$, the symbol $\sum\!\!\!\!\!\!\int_s$ stands for the summing up over discrete, and the integration over continuous, ionic states s. It may be shown [1, 13] that

$$\begin{aligned}
G_{ln}(\varepsilon_e - w) &= G^A_{ln}(\varepsilon_e - w) + G^R_{ln}(\varepsilon_e - w) \\
&\equiv \sum\!\!\!\!\!\!\int_s \frac{\langle 0|a^+_n|s\rangle\langle s|a_l|0\rangle}{\varepsilon_e - w + I_s - i\gamma/2} + \sum\!\!\!\!\!\!\int_r \frac{\langle 0|a_l|r\rangle\langle r|a^+_n|0\rangle}{\varepsilon_e - w + A_r + i\gamma/2},
\end{aligned} \tag{6}$$

where G^R_{ln} is the retarded Green's function, r is the exact state of the negative N+1-electron molecular ion and A_r is the electron affinity of this state: $A_r = E_0 - E_r$. Thus we have shown that the main features of the XA spectra are connected with the poles of Green's functions G_{ln} or G^A_{ln}. The fundamental equations of the Green's function formalism are presented below in the Appendix.

But it is more convenient to deal with the eigenvalues D_k of the Green's function matrix $\boldsymbol{G}$ with the elements G_{ln}. Therefore, following [1] define the matrices

$\boldsymbol{W}_e$ with the real elements W_{el} and $\boldsymbol{W}_e(z)=\boldsymbol{W}_e\boldsymbol{S}(z)$, where $\boldsymbol{S}$ is the unitary eigenvector matrix of the Green's function matrix $\boldsymbol{G}$, and relate the XA cross section with these matrices

$$\begin{aligned}\sigma(w)&=4\pi\alpha^2 w\sum_{enl} W^*_{en}W_{el}\,\mathrm{Im}\,G_{ln}(\varepsilon_e-w)\\&=4\pi\alpha^2 w\sum_{e}\mathrm{Im}\,\boldsymbol{W}_e\boldsymbol{SDS}^{-1}\boldsymbol{W}^+_e\\&=4\pi\alpha^2 w\sum_{ek}|W_{ek}(\varepsilon_e-w)|^2\,\mathrm{Im}\,D_k(\varepsilon_e-w)\\&=4\pi\alpha^2 w\sum_{ek}|W_{ek}(\varepsilon_e-w)|^2\\&\quad\times\frac{b\gamma/2+\mathrm{Im}\,\Sigma_k(\varepsilon_e-w)}{((w-\varepsilon_e)-(-\varepsilon_k-\mathrm{Re}\,\Sigma_k(\varepsilon_e-w)))^2+(b\gamma/2+\mathrm{Im}\,\Sigma_k(\varepsilon_e-w))^2}.\end{aligned}\tag{7}$$

Let us now make the following assumption. Let the intervals between the discrete poles z_s of the functions $D_k(z)$ be greater than the quantities $b\gamma/2+\mathrm{Im}\,\Sigma_k(z)$. Then, with the help of Eq. (A7), one obtains the following expression near these poles:

$$\begin{aligned}\sigma(w)&=4\pi\alpha^2 w\sum_{ek}|W_{ek}(\varepsilon_e-w)|^2\\&\quad\cdot\sum_{s}P_k(s)\frac{1/2\cdot(b\gamma+\Gamma_k(s))}{(w-(\varepsilon_e+I_k(s)))^2+1/4\cdot(b\gamma+\Gamma_k(s))^2},\end{aligned}\tag{8}$$

where by definition

$$\Gamma_k(s)/2\equiv\mathrm{Im}\,\Sigma_k(z_s);\ I_k(s)\equiv-\varepsilon_k-\mathrm{Re}\,\Sigma_k(\varepsilon_s-w).$$

It is interesting that if the one-particle continuous states e are not taken into account in calculating Green's function, in other words, if in Eq. (5) one restricts himself to the summing up only over the approximate bound ionic states s, then as follows from Eq. (6),

$$\mathrm{Re}\,z_s=-I_s;\qquad \mathrm{Im}\,z_s=\gamma/2.$$

Hence,

$$I_K(s)=I_s;\qquad \Gamma_k(s)=0.$$

Thus, one obtains the possibility of interpreting $\Gamma_k(s)$ as an additional contribution to the full width of the approximate bound ionic state s due to its interaction with the continuous states, i.e. due to the many-electron Auger effect, and considering $I_k(s)$ as an approximate ionization potential of the exact state s.

As was shown in [1, 2] by direct calculation of molecules consisting of atoms of elements contained in the second and third Periods one can use rather often the diagonal approximation for the Green's function matrix $\boldsymbol{G}$

$$G_{ln}=G_{ll}\delta_{ln}=D_l\delta_{ln}$$

It follows that the self-energy part Σ is also diagonal. In this approximation the matrix S is equal to the unity one, therefore the matrix elements W_{ek} in Eqs. (7) and (8) are independent of energy. It is convenient to analyse in detail every XA energy region, each taken separately.

3. Discrete Region

The discrete region of the XA spectrum is defined as the region (5–10 eV) below the ionization threshold of the core orbital k. Within the framework of the one-electron ionic model this region is mainly due to the one-electron transitions from the originating occupied orbital k to the terminating vacant bound or discrete orbitals ν. On these grounds we can employ here the approximate formula instead of Eq. (8)

$$\sigma(w) \cong \sigma_k(w) \cong 4\pi\alpha^2 w \sum_{\nu} |W_{\nu k}|^2 P_k(k^{-1}) \cdot \frac{1/2 \cdot (\gamma + \Gamma_k(k^{-1}))}{(w - (\varepsilon_\nu + I_k(k^{-1})))^2 + 1/4 \cdot (\gamma + \Gamma_k(k^{-1}))^2}. \tag{9}$$

Comparing Eqs. (9) and (1a) one gets a clear answer to the question of how the many-electron processes affect the discrete one-electron transitions. Firstly, they make an additional contribution $\Gamma_k(k^{-1})$ to the fullwidth of the lines, and, secondly, they significantly decrease the full intensity of all the transitions $k \to \nu$ since, according to the computation [1, 2] for core orbitals k the pole strengths of the respective core hole states $k^{-1} P_k(k^{-1}) = 0.6$–0.8.

It is of interest that in accordance with Eq. (9) the many-electron relaxation and correlation effects do not influence the relative discrete one-electron XA transition intensities. This conclusion is confirmed, for instance, by the computations of the XA spectra of the atom Ne [27] and molecules HCl, H_2S, PH_3 and SiH_4 [28] which were carried out taking into account the relaxation effect only. As will be shown in what follows, the "lost" $(1 - P_k(k^{-1})) \cdot 100\%$ of full intensity is transferred to the continuous region near the ionization threshold due to the many-electron excitations.

It is also interesting that, if, in calculating Green's function in the diagonal approximation, one ignores the one-electron continuous states, then one obtains the following relationship between our, and the sudden perturbation [24–26] theories:

$$P_k(s) = |\langle 0|a_k^+|s\rangle^2 = |\langle k_0^{-1}|s\rangle|^2 \geq 0, \tag{10}$$

where k_0^{-1} is the frozen core hole state k^{-1}: $|k_0^{-1}\rangle = a_k|0\rangle$.

4. X-Ray Absorption Near Edge Fine Structure (XANEFS)

Let us now study the XA continuous region near the ionization threshold of the core orbital k where the photoelectron energy ε_e equals 0–30 eV. In molecules and solids here one often observes the XANEFS due both to one-electron shape resonances which are described by the one-electron ionic model and to many-electron excitations [18, 29–31]. For the XA cross section we may evidently use the approximate formula

$$\sigma(w) \cong \sigma_k(w) \cong 4\pi\alpha^2 w \sum_e |W_{ek}|^2 \cdot \sum_s P_k(s) \frac{1/2 \cdot (\gamma+\Gamma_k(s))}{(w-(\varepsilon_e+I_k(s)))^2+1/4 \cdot (\gamma+\Gamma_k(s))^2}, \tag{11}$$

where the term with $s = k^{-1}$ corresponds to the one-electron and the others to many-electron transitions. It is easy to see that the following sum rule takes place in the diagonal approximation without taking into account the one-electron continuous states

$$\sum_s P_k(s) = \sum_s |\langle s|a_k|0\rangle|^2 \cong 1.$$

Therefore, one can interpret the role of the many-electron processes in forming XA spectra near the ionization threshold as follows. Electron relaxation and correlation decrease the intensities of the one-electron transitions which gives rise to many-electron excitations, part of their intensity being transferred from the discrete one-electron transition region. Owing to this phenomenon in the region under discussion there may occur rather intense spectral bands of many-electron nature which are partners to the one-electron discrete transitions and shape resonances.

It should be noted that Eqs. (3), (7), (8) and (11) are probably not valid very near the ionization threshold where the so-called post collision interaction many-electron effects can be large [6, 32].

5. Extended X-Ray Absorption Fine Structure (EXAFS)

Let us now pass over to the investigation of the continuous region of the XA spectrum where the photoelectron energy ε_e is equal to 30–2000 eV. The EXAFS of this region is traditionally attributed to the oscillations of the one-electron XA cross section $\sigma_k^0(w)$. The EXAFS theory establishes a rather simple relationship of these oscillations with atomic structure parameters which permits one to use XA spectroscopy as a structural method. Indeed, the EXAFS spectrum is defined as the oscillating part of the XA spectrum

$$\chi(q) = (\sigma(q) - \sigma_m(q))/\sigma_m(q),$$

where $\sigma_m(q)$ – some "mean" smooth cross section. Taking into account only the one-electron transitions from the originating core orbital k of the atom α ($k = 1s_\alpha$) one obtains the above relationship [33]:

$$\chi^0(q) \sim \sum_{\beta \neq \alpha} \frac{1}{qR^2_{\beta\alpha}} |f^\beta_q| M_\beta \sin(2qR_{\beta\alpha} + \eta_\beta(q)). \tag{12}$$

Here the photoelectron momentum $q=\sqrt{2(w-I_{k^{-1}})}$, $R_{\beta\alpha}$ is the distance from the absorbing atom α to its co-ordination sphere β with the M_β atoms, f_q^β is the back-scattering amplitude and $\eta_\beta(q)$ is the photoelectron phase shift due to the atom α potential and the amplitude f_q^β:

$$\eta_\beta(q)=2\delta_\alpha^1(q)+\arg(f_q^\beta).$$

Let us show how many-electron processes can distort such a simple relationship of the EXAFS spectrum with structural data on the substance. For the energy region in question assumption (3) works evidently rather well and we consider Eq. (7) to be practically exact. Since we wish to take into account the shake-off processes we do not here restrict ourselves to the discrete summing up as was done in Eqs. (8) and (11). One can get a more simple formula than (7) starting from (5) and using the diagonal approximation for the Green's function

$$\sigma(w)\cong 4\pi^2\alpha^2 w\sum_k\int|W_{ek}^*|^2\sum\!\!\!\!\!\!\!\int_s g_k(s)\delta(w-(I_s+\varepsilon_e))\,d\varepsilon_e, \tag{13}$$

where the radiative linewidth γ_k is ignored ($\gamma_k=0$) and the notations $g_k(s)$ are employed for Feynman–Dyson amplitudes [34]

$$g_k(s)=|\langle s|a_k|0\rangle|^2\geq 0;\qquad \sum\!\!\!\!\!\!\!\int_s g_k(s)=1.$$

For the sake of simplicity we take only one term in the sum over k and transform (13) to the more convenient relationship

$$\begin{aligned}\sigma(w)&\cong\sigma_k(w)=4\pi^2\alpha^2 w\int|\langle\varepsilon_e|\boldsymbol{re}|k\rangle|^2\sum\!\!\!\!\!\!\!\int_s g_k(s)\delta(\varepsilon_e-(-I_s+w))\,d\varepsilon_e\\&=4\pi^2\alpha^2 w\sum\!\!\!\!\!\!\!\int_s g_k(s)|\langle w-I_s|\boldsymbol{re}|k\rangle|^2\\&=g_k(k^{-1})\sigma_k^0(w)+\sum\!\!\!\!\!\!\!\int_s g_k(s)\sigma_k^0(w-\Delta I_s),\end{aligned} \tag{14}$$

where

$$\sigma_k^0(w)=4\pi^2\alpha^2 w|\langle w-I_{k^{-1}}|\boldsymbol{re}|k\rangle|^2\quad\text{(cf. (1b))},$$

$$\Delta I_s=I_s-I_{k^{-1}}.$$

Thus we obtain the following result. The total cross section is the sum of partial ones due to the one-electron and many-electron transitions, all partial cross sections being described by the same function $\sigma_k^0(w-\Delta I_s)$, but with different argument shifts ΔI_s. Eq. (14) is the generalization of the respective formula (6) derived in [35] taking into account only the relaxation effect within the framework of the sudden perturbation theory, where $g_k(s)=|\langle s^{\mathrm{HF}}|k_0^{\mathrm{HF}^{-1}}\rangle|^2$, and s^{HF} and $k_0^{\mathrm{HF}^{-1}}$ are respective Hartree–Fock states.

Following the method [35] one obtains, taking into account the many-electron relaxation and correlation effects, the relationships

$$\chi(q)\sim\sum_{\beta\neq\alpha}|A_\beta(q)|\frac{1}{qR_{\beta\alpha}^2}|f_q^\beta|M_\beta\sin(2qR_{\beta\alpha}+\eta_\beta(q)+\phi_\beta(q)), \tag{15}$$

$$A_\beta(q) \equiv |A_\beta(q)| \exp(i\phi_\beta(q)) = \sum_s g_k(s) \exp(i\phi_s^\beta(q)).$$

$$\phi_s^\beta(q) = 2R_{\beta\alpha}(\sqrt{q^2 - 2\Delta I_s} - q).$$

Eq. (15) shows that the many-electron effects change the phase and reduce the amplitude of the EXAFS spectrum oscillations. By calculation [35] of the K-spectrum of the molecule Br_2 the phase shift $\phi_\beta(q) \cong 9°$ and the amplitude reduction factor $|A_\beta(q)| \cong 0.9$, but at the same time the many-electron effects make a more valuable, 40 per cent, contribution to the total cross section $\sigma(w)$ ($g_{B1s}(B1s^{-1}) \cong 0.6$). Moreover, they do not change such an important quantity as the frequency of the oscillations. It is precisely these facts that provide the possibility of extracting some structural information from EXAFS spectra, making use of the conventional one-electron EXAFS theory. One can look at this matter from another point of view.

Eq. (14) can be interpreted as that for extracting the partial one-electron cross section $\sigma_k^0(w)$ from the experimental XA spectrum, i.e. $\sigma(w)$. For this it is necessary to have a knowledge of the quantities $g_k(s)$ and ΔI_s. On the one hand, they can be computed, on the other they can be obtained by photoelectron spectroscopy. Indeed, in terms of the assumption made by the total cross section of photoionization of the orbital k is described by the formula

$$\sigma_k^p(\varepsilon_e) \cong 4\pi^2\alpha^2 w |W_{ek}^*|^2 \sum_s g_k(s)\delta(\varepsilon_e - w + I_{k^{-1}} + \Delta I_s). \tag{16}$$

We also propose some other methods of obtaining XA continuous spectra due only to the one-electron transitions. Thus, for instance, one can measure the one-electron photoionization cross section (i.e. the intensity of the main photoelectron line of the photoelectron spectrum) versus on the X-ray exciting photon energy w:

$$\begin{aligned}\sigma_k^p(\varepsilon_e) &= \sigma_k^p(w - I_{k^{-1}}) = 4\pi^2\alpha^2 w g_k(k^{-1}) |\langle w - I_{k^{-1}} | \boldsymbol{re} | k \rangle|^2 \\ &= \sigma_k^0(w) g_k(k^{-1}).\end{aligned}$$

Or one can measure the X-ray emission cross section (i.e. the intensity of the main or diagrammatic line $i \to k$ of the X-ray emission spectrum) as a function of w which is transformed into the cross section $\sigma_k^0(w)$ sought for trivially too. If the primary photoelectron lines are on the strong background due to the secondary inelastic scattering electrons, then, in order to eliminate this background, one can register the photoelectrons and X-ray emitted photons in coincidence as was proposed by the present authors earlier [36]. Moreover, using the energy conservation law for the X-ray fluorescence process $k \to e$, $k^{-1} \to s$

$$w + E_0 = w' + \varepsilon_e + E_s,$$

where w' is the energy of the X-ray emitted photon, one can see, that the photoelectron-X-ray emitted photon coincidence technique enables one to obtain the X-ray emission, the X-ray photoelectron and, hence, the EXAFS spectra with the total line width of the final state s of the ion $\Gamma_s^{\text{tot}} \cong \gamma_i + \Gamma_i(s)$, which is usually much smaller than that of the intermediate core hole state k^{-1} of the ion $\Gamma_{k^{-1}}^{\text{tot}} = \gamma_k + \Gamma_k(k^{-1})$. It is necessary for that to apply a flux of the exciting X-ray radiation with the line width $\Delta w \cong \Gamma_s^{\text{tot}} \ll \Gamma_{k^{-1}}^{\text{tot}}$. Thus we obtain the possibility of investigating experimentally the EXAFS (and X-ray photoelectron) spectra of the very deep core shells of the heavy atoms.

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Appendix

Consider some known relationships of the Green's function formalism [1, 13, 14]. The Dyson equation can serve as a definition of the self-energy part $\boldsymbol{\Sigma}$:

$$\boldsymbol{G}(z) = \boldsymbol{G}^0(z) + \boldsymbol{G}^0(z)\boldsymbol{\Sigma}(z)\boldsymbol{G}(z), \tag{A1}$$

where z is a complex variable, $\boldsymbol{G}(z)$, $\boldsymbol{\Sigma}(z)$ and $\boldsymbol{G}^0(z)$ are the matrices with the elements $G_{ln}(z)$, $\Sigma_{ln}(z)$ and

$$G_{ln}^0(z) = \frac{\delta_{ln}}{z - \varepsilon_l - ib\gamma/2}, \qquad b = \begin{cases} 1, & l \in F \\ -l, & 1 \notin F. \end{cases} \tag{A2}$$

Here F is the set of orbitals occupied in the ground state of the molecule. Introduce further the eigen values $D_k(z)$ and vectors $\boldsymbol{S}_k(z)$ of the matrix $\boldsymbol{G}(z)$

$$\boldsymbol{G}(z)\boldsymbol{S}_k(z) = D_k(z)\boldsymbol{S}_k(z).$$

From the column-matrices $\boldsymbol{S}_k(z)$ we construct the matrix $\boldsymbol{S}$ diagonalizing the matrix $\boldsymbol{G}$:

$$\boldsymbol{S}^{-1}\boldsymbol{G}\boldsymbol{S} = \boldsymbol{D}; \qquad D_{ln}(z) = D_l(z)\delta_{ln}.$$

By analogy with Green's function $\boldsymbol{G}$ defines the eigen values $\Sigma_k(z)$ of the self-energy part $\boldsymbol{\Sigma}(z)$. It follows from the Dyson Eq. (A1) that the poles of the function $\boldsymbol{G}(z)$ and hence those of its eigen values $D_k(z)$ are equal to the zeros of the eigen values $\Gamma_k(z)$ of the inverse matrix:

$$\boldsymbol{G}^{-1}(z) = z \cdot \mathbf{1} - \boldsymbol{\varepsilon} - i\gamma\boldsymbol{b}/2 - \boldsymbol{\Sigma}(z),$$

where $\mathbf{1}$ is the unity matrix, $\boldsymbol{\varepsilon}$ is the one-electron energy matrix with the elements $\varepsilon_{kl} = \varepsilon_k\delta_{kl}$ and the matrix $\boldsymbol{b}$ has the elements $b_{kl} = b \cdot \delta_{kl}$. The zeros z_s of the matrix $\boldsymbol{G}^{-1}$ and of its eigen values $\Gamma_k(z) = z - \varepsilon_k - i\gamma b/2 - \Sigma_k(z)$ are determined by the equations

$$z_s - \varepsilon_k = \Sigma_k(z_s) + ib\gamma/2,$$

or

$$\begin{aligned} \operatorname{Re} z_s - \varepsilon_k &= \operatorname{Re} \Sigma_k(z_s), \\ \operatorname{Im} z_s &= \operatorname{Im} \Sigma_k(z_s) + b\gamma/2. \end{aligned} \tag{A3}$$

The so-called pole strengths $P_k(s)$ of the $D_k(z) = 1/\Gamma_k(z)$ are obtained by the formula (in case of the simple discrete pole z_s)

$$P_k(s) = 1/\Gamma'_k(z_s) = [1 - \Sigma'_k(z_s)]^{-1}, \tag{A4}$$

where $\Gamma'_k(z_s) = (d\Gamma_k(z)/dz)_{z=z_s}$; $\Sigma'_k(z_s) = (d\Sigma_k(z)/dz)_{z=z_s}$.

Eqs. (A.3) and (A.4) are basic in calculating the spectra by means of the Green's function formalism. In what follows we may need the expression for the imaginary part of the $D_k(z)$

$$\begin{aligned}\operatorname{Im} D_k(z) &= \operatorname{Im} \frac{1}{z - \varepsilon_k - ib\gamma/2 - \Sigma_k(z)} \\ &= \frac{b\gamma/2 + \operatorname{Im} \Sigma_k(z) - \operatorname{Im} z}{(\operatorname{Re} z - (\varepsilon_k + \operatorname{Re} \Sigma_k(z)))^2 + (b\gamma/2 + \operatorname{Im} \Sigma_k(z) - \operatorname{Im} z)^2}.\end{aligned} \tag{A5}$$

Using the relationships (A3) one can transform this expression near the simple pole z_s in the following manner ($\operatorname{Im} \Sigma_k(z_s) \cong 0$)

$$\begin{aligned}\operatorname{Im} D_k(z) &\cong \operatorname{Im} \frac{1}{z - \varepsilon_k - ib\gamma/2 - \Sigma_k(z_s) - \Sigma'_k(z_s)(z - z_s)} \\ &= P_k(s) \frac{\gamma b/2 + \operatorname{Im} \Sigma_k(z_s) - \operatorname{Im} z}{(\operatorname{Re} z - (\varepsilon_k + \operatorname{Re} \Sigma_k(z_s)))^2 + (b\gamma/2 + \operatorname{Im} \Sigma_k(z_s) - \operatorname{Im} z)^2}.\end{aligned} \tag{A6}$$

In that region where the distances between two neighbouring poles are much less than $b\gamma/2 + \operatorname{Im} \Sigma_k(z_s)$ we can express the function $\operatorname{Im} D_k(z)$ as an approximate sum over the poles z_s

$$\operatorname{Im} D_k(z) \cong \sum_s P_k(s) \frac{b\gamma/2 + \operatorname{Im} \Sigma_k(z_s) - \operatorname{Im} z}{(\operatorname{Re} z - (\varepsilon_k + \operatorname{Re} \Sigma_k(z_s)))^2 + (b\gamma/2 + \operatorname{Im} \Sigma_k(z_s) - \operatorname{Im} z)^2}. \tag{A7}$$

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