

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/229613324>

# The issues of size- and charge-consistency, and the implications of translational symmetry in advanced Green's function theories

ARTICLE *in* INTERNATIONAL JOURNAL OF QUANTUM CHEMISTRY · JUNE 2003

Impact Factor: 1.43 · DOI: 10.1002/qua.10552

---

CITATIONS

31

---

READS

9

## 1 AUTHOR:



[Michael S Deleuze](#)

Hasselt University

132 PUBLICATIONS 2,673 CITATIONS

SEE PROFILE

---

# The Issues of Size and Charge Consistency and the Implications of Translation Symmetry in Advanced Green's Function Theories

---

MICHAEL S. DELEUZE

*Departement SBG, Limburgs Universitair Centrum, Universitaire Campus,  
B3590 Diepenbeek, Belgium*

*Received 15 January 2002; accepted 8 January 2003*

DOI 10.1002/qua.10552

---

**ABSTRACT:** The issues of size consistency and charge consistency in advanced Green's function theories of ionization or electron attachment spectra are thoroughly discussed by adapting the so-called third-order algebraic diagrammatic construction scheme [ADC(3)] to the formalism of crystalline orbitals for an extended periodic system. A comparison is made with a number of lower-order one-particle Green's function (or one-electron propagator) schemes, derived using the general algebraic approach in superoperators and binary products. In the canonical picture, one of the implications of size consistency in the dissociation and thermodynamic limits is that a balance must prevail between the number of satellites and the strength of configuration interactions between the main ( $1h$ ,  $1p$ ) and secondary (shake-up or shake-on) states in the cation or anion. Charge consistency, or the preservation of the exact particle number upon correlation corrections to the Hartree–Fock ground-state one-electron density, is a necessary condition for the correct, i.e., size-intensive, scaling of static self-energies and, thus, ionization energies in large inhomogeneous systems. © 2003 Wiley Periodicals, Inc. *Int J Quantum Chem* 93: 191–211, 2003

**Key words:** Green's function theories; size consistency; charge consistency; ionization; electron attachment; shake-ups; excited states; extended periodic systems

---

## Introduction

The concept of size consistency [1] is one of the cornerstones of molecular quantum mechanics. In this context, size consistency in the calcula-

tion of size-extensive (e.g., total energies, polarizabilities, . . .) or size-intensive (ionization energies, electron affinities, electron excitation energies, . . .) properties implies that for a system consisting of identical noninteracting entities the computed quantities must be proportional to or independent

of the number of elements in the system, respectively. The relationships between the correct scaling properties and the linked-cluster theorem [2, 3] have first been firmly established through tests of diagrammatic perturbation theories on oversimplified models such as the cellular model [4] of nuclear matter, a large homogeneous nucleus with negligible surface effects [5], or an homogeneous electron gas embedded in a positive uniform background [6, 7]. Examples of theories based on a linked-cluster expansion comprise many-body perturbation theory [8–13], coupled cluster theory [9, 12–15], Green's function theory [16], or, equivalently, propagator theory [17–19]. A recent and useful extension of the concept of size consistency is that of scheme consistency [20], implying that in a hierarchy of treatments of single-, double-, triple-, ... particle processes linked by recursive relations (such as, e.g., one-electron and Auger ionization) the global and individual transition energies and moments should be treated at the same level in electron correlation.

The translational invariance [21] in homogeneous systems enables major simplifications, in the form of a straightforward cancellation of divergences arising from the long-range contributions to the Hamiltonian [7]. Couched in molecular terms, such an analysis gave rise to the widespread idea that (quoting Bartlett in [14]) "any large molecule can be viewed, in a first approximation, as a superposition of largely noninteracting electron pair bonds." As a result, the concepts of size consistency and size extensivity have, in practice, become totally (and abusively) interchangeable in modern molecular physics and quantum chemistry. It should be noted that Bartlett chose to associate "size extensivity" to the absence of unlinked diagrams and "size consistency" to the correct mathematical (multiplicative) separability of the reference wave function describing dissociating systems [14] as well as to the correct (additive) separability of observables such as the total energy. These considerations are obviously of relevance when describing molecules breaking into open-shell fragments but misleading with regard to applications of many-body theories on "large" molecules.

The idea of size extensivity is borrowed from thermodynamics and is therefore most commonly understood as the correct scaling of collective properties in the limit of an infinitely large system with finite densities of charges. Therefore, associating too straightforwardly size extensivity to the linked diagrammatic properties of many-body expansion

schemes, based on the Dyson evolution operator, can lead to inexact views on the convergence properties of results obtained by applying such schemes to molecules of increasing size. When dealing with extended periodic systems such as stereoregular polymers or crystalline solids, complications quickly arise, even at the Hartree–Fock (HF) level, in the form of size-related difficulties [22–41] mathematically expressed as conditionally and/or slowly convergent series of terms involving multi-center integrals. It must be reminded that, at the end of the day, polymers or solids are simply "extremely large" molecules. Relatedly, the usual periodic boundary conditions required in band structure calculations on such systems are nothing other than a clever trick enabling a proper discretization of one-electron states.

Divergence problems for perturbative treatments of the static part of the self-energy entering the Dyson expansion of the one-particle Green's function have first been predicted [42] and fully characterized [43] at third order in correlation. At this order, the size intensivity of the static self-energy is warranted by a strict cancellation of logarithmic divergences [43] in one set of self-energy antigraphs [16c]. On the other hand, at odds with the most common expectations for linked-cluster expansions, divergences with system increasing size do arise [43] (i.e., can be numerically followed in tests on model molecular chains, and analytically understood) when using a renormalized treatment of the  $1p$ -GF such as the third-order algebraic diagrammatic construction [ADC(3)] scheme [44–47]. In continuation to the work of Refs. [42] and [43], size-related difficulties have also been identified at third order in many-body perturbation theory [48], as well as in coupled cluster theory [49]. In the latter study [49], it has been shown that an expansion of the total Hamiltonian of an extended periodic system can, by a proper combination of long-range electron–electron repulsion and electron–nuclear attraction terms, be turned into a lattice summation that runs over quadratically decreasing terms in the asymptotic region. Therefore, at odds with the final conclusions of Refs. [42] and [43], it seems again well justified [49] to neglect such long-range contributions in high-order many-body perturbation or coupled cluster theories. Indeed, in straightforward analogy with the analysis of Ref. [43] for the third-order static self-energy, cancellation of singularities in the integration interval over one-electron momenta can in both cases be achieved through proper pairwise combinations of (vacuum amplitude) dia-

grams [48] or cluster amplitudes [49]. Taking the one-electron Green's function (1p-GF) theory of ionization or electron attachment spectra as a main example, the first purpose of the present contribution is to solve the apparent paradox between the conclusions of Refs. [42, 43] and [48, 49]. Such a clarification has become mandatory, as high-order 1p-GF calculations on fairly large molecules are already feasible (see, e.g., Ref. [50]).

Another important aspect of Green's function theory concerns the treatment of multiple-particle processes, such as, for instance, those producing shake-up or shake-on states, which consist of a mixture of excited configurations in the cation or anion. Studies of satellites in molecular ionization spectra are abundant and well documented (see Ref. [16c], and references therein, or Ref. [51]). On the other hand, except for a pioneering but qualitative Green's function study of polyacetylene at second order in correlation [52], nothing is known about the correlation bands in the ionization spectra of extended systems with pronounced metallic properties. However, from advanced [ADC(3)] Green's function studies on series of model oligomers [50, 53–57] the shake-up processes must obviously embezzle a major part of the total ionization intensity of low band-gap polymers or solids. As the one-electron states from which they borrow their intensity, these satellites must organize in bands when approaching the limit of an infinite periodic system, as seems to indicate a first investigation on large but finite model hydrogen chains [53]. For these correlation states, the implications of size consistency and translation symmetry are still unclear and deserve a formal analysis.

The plan of the present review is therefore as follows. To pinpoint the origin of all possible size-related difficulties, a general derivation of advanced 1p-GF schemes is first presented, using standard matrix approaches or diagrammatic perturbation expansions. The most commonly employed approximation schemes for the treatment of ionization or electron attachment spectra are derived in the third section and ranked according to the level of correlation attained for all their components, with attention focused on the most complete of these approaches, namely, the ADC(3) scheme [44–47]. In the fourth and fifth sections, the behavior of one-electron and shake-up (or shake-on) states is analyzed at the ADC(3) level both in the thermodynamic and dissociation limits, using, as common starting (zeroth-order) solutions, the crystalline HF orbitals of an extended stereoregular polymer. At last, analysis of

long-range effects in this model brings to light a usually neglected requirement in quantum mechanics in general, and Green's function theory in particular, namely, that of charge consistency. Besides the size-related difficulties that a breach of this requirement generates, other implications of charge consistency are also briefly reviewed, in the context of scattering and response theories.

### Implications of Charge Inhomogeneities in Green's Function Theory

The equation-of-motion (EOM) formalism derived using the algebra of superoperators [18, 58] provides the most general approach of one-particle Green's function (or equivalently propagator) theory. In the energy domain, it is well known that the one-particle Green's function (1p-GF) of a  $N$ -particle system described by a reference wave function  $|\Psi_0^N\rangle$  and energy  $E_0^N$  has the spectral representation [7, 12, 13, 16–19]

$$G_{ij}(\omega) \equiv \langle\langle a_i, a_j^+ \rangle\rangle_\omega = \sum_p \frac{\langle\Psi_0^N|a_i|\Psi_p^{N+1}\rangle\langle\Psi_p^{N+1}|a_j^+|\Psi_0^N\rangle}{\omega - (E_p^{N+1} - E_0^N) + i0^+} + \sum_h \frac{\langle\Psi_0^N|a_j^+|\Psi_h^{N-1}\rangle\langle\Psi_h^{N-1}|a_i|\Psi_0^N\rangle}{\omega - (E_0^N - E_h^{N-1}) - i0^+}, \quad (1)$$

where  $0^+$  represents infinitesimals. In this expression, the sums over  $p$  and  $h$  run over all possible anion and cation states of the system,  $|\Psi_p^{N+1}\rangle$  and  $|\Psi_h^{N-1}\rangle$ , with energies  $E_p^{N+1}$  and  $E_h^{N-1}$ , respectively. The above expression is cast in matrix form over a basis of spin-orbitals  $\{\phi_i\}$  through the interplay of a set of standard destruction ( $a_i$ ) and creation ( $a_i^+$ ) operators. The importance of the 1p-GF in electronic structure theory is immediately apparent because (vertical) ionization and electron attachment energies can be straightforwardly derived from the location of its poles in the complex  $\omega$ -plane. These energies can also be formally obtained from the following relationships:

$$\begin{aligned} \langle\Psi_0^N|[a_i, H]_-|\Psi_p^{N+1}\rangle &= (E_p^{N+1} - E_0^N)\langle\Psi_0^N|a_i|\Psi_p^{N+1}\rangle \\ \langle\Psi_p^{N+1}|[a_i, H]_-|\Psi_0^N\rangle &= (E_0^N - E_h^{N-1})\langle\Psi_p^{N+1}|a_i|\Psi_0^N\rangle, \end{aligned} \quad (2)$$

## DELEUZE

with  $H$  the exact Hamiltonian of the system ( $[a_i, H]_- = a_i H - H a_i$ ). Because

$$\frac{\omega}{\omega - \omega_0} = 1 + \frac{\omega_0}{\omega - \omega_0}, \quad (3)$$

the EOM [13, 18] of the one-particle Green's function in the energy domain is found immediately:

$$\omega \langle \langle a_i, a_j^+ \rangle \rangle_\omega = \langle \Psi_0^N | [a_i, a_j^+]_+ | \Psi_0^N \rangle + \langle \langle [a_i, H]_-, a_j^+ \rangle \rangle_\omega. \quad (4)$$

Superoperators are introduced at this stage to decouple the system of equations resulting from Eq. (4) using a standard matrix approach based on a linear vector space. For a general operator  $A$ , the unit and Hamiltonian superoperators are defined [18] as

$$\begin{aligned} \hat{1}A &= A \\ \hat{H}A &= [A, H]_-. \end{aligned} \quad (5)$$

In the algebra of superoperators, the equivalent of the scalar product in standard vectorial algebra is the binary product:

$$(X|Y) = \langle \Psi_0^N | [X^+, Y]_+ | \Psi_0^N \rangle, \quad (6)$$

with  $X$  and  $Y$  representing two arbitrary operators. By iterating Eq. (4),

$$\begin{aligned} \langle \langle a_i, a_j^+ \rangle \rangle_\omega &= \left( a_j \left| \frac{\hat{1}}{\omega} a_i \right. \right) + \left( a_j \left| \frac{\hat{H}}{\omega^2} a_i \right. \right) \\ &+ \left( a_j \left| \frac{\hat{H}^2}{\omega^3} a_i \right. \right) + \dots, \end{aligned} \quad (7)$$

the one-particle Green's function can be easily recast as the matrix representation in an operator basis  $\underline{a} = \{a_i\}$  of a superoperator resolvent:

$$\begin{aligned} G_{ij}(\omega) &= \langle \langle a_i, a_j^+ \rangle \rangle_\omega = (a_i | (\omega \hat{1} - \hat{H})^{-1} | a_j); \\ \mathbf{G}(\omega) &= (\underline{a} | (\omega \hat{1} - \hat{H})^{-1} | \underline{a}). \end{aligned} \quad (8)$$

The metrics of this operator basis is defined by the binary product:

$$(a_i | a_j) = \langle \Psi_0^N | [a_i^+, a_j]_+ | \Psi_0^N \rangle = \delta_{ij}. \quad (9)$$

Because  $|\Psi_0^N\rangle$  is an eigenfunction of  $H$ , the Hamiltonian superoperator is Hermitian. Upon inner projection [59] of the superoperator resolvent over a general and complete operator basis  $\underline{h}$ , the Green's function can therefore be recast as

$$\mathbf{G}(\omega) = (\underline{a} | \underline{h}) (\underline{h} | \omega \hat{1} - \hat{H} | \underline{h})^{-1} (\underline{h} | \underline{a}). \quad (10)$$

Considering the nature of the  $(\underline{a} | \underline{h})$  and  $(\underline{h} | \underline{a})$  binary products in Eq. (12), this basis can be restricted to the following sets of operators [60]:

$$\begin{aligned} \underline{h} &= \underline{h}_1 \oplus \underline{h}_3 \oplus \underline{h}_5 \oplus \dots \\ &= \{a_i\} \oplus \{a_i^+ a_j a_k\} \oplus \{a_i^+ a_j^+ a_k a_m\} + \dots \end{aligned} \quad (11)$$

To represent the Hamiltonian superoperator and overlap metrics in this extended operator basis, the following notations are adopted:

$$H_{ij} = (h_i | \hat{H} | h_j) = \langle \Psi_0^N | [h_i^+ [h_j, H]]_+ | \Psi_0^N \rangle \quad (12)$$

$$S_{ij} = (h_i | h_j) = \langle \Psi_0^N | [h_i^+ h_j]_+ | \Psi_0^N \rangle. \quad (13)$$

Partitioning the operator manifold as

$$\underline{h} = \underline{a} + \underline{f} \quad (14)$$

and improving the complementary basis  $\underline{f}$  by Schmidt orthogonalization

$$\underline{f}' = \underline{f} - \underline{a} (\mathbf{S}^{aa})^{-1} \mathbf{S}^{af} \quad (15)$$

so that

$$(\underline{a} | \underline{f}') = (\underline{a} | \underline{f}) - (\underline{a} | \underline{a}) (\mathbf{S}^{aa})^{-1} \mathbf{S}^{af} = \mathbf{S}^{af} - \mathbf{S}^{af} = \mathbf{0}, \quad (16)$$

it is always possible [because  $\mathbf{S}^{aa} = \mathbf{1}$ ; Eq. (9)] to rewrite Eq. (10) as

$$\mathbf{G}(\omega) = \begin{bmatrix} \mathbf{1}^{aa} & \mathbf{0} \end{bmatrix} \begin{bmatrix} \omega \mathbf{1}^{aa} - \mathbf{H}^{aa} & -\mathbf{H}^{af'} \\ -\mathbf{H}^{f'a} & \omega \mathbf{1}^{f'f'} - \mathbf{H}^{f'f'} \end{bmatrix}^{-1} \begin{bmatrix} \mathbf{1}^{aa} \\ \mathbf{0} \end{bmatrix}. \quad (17)$$

Therefore, searching the poles of the  $1p$ -GF is in general equivalent to solving a secular equation of the type [61]

$$\mathbf{H}\mathbf{X} = \mathbf{X}\mathbf{E}; \quad \mathbf{X}^+ \mathbf{X} = \mathbf{1}, \quad (18)$$

with

$$H = \begin{bmatrix} H^{aa} & H^{af'} \\ H^{f'a} & H^{f'f'} \end{bmatrix}. \quad (19)$$

Expressing the  $N$ -electron ground-state wave function as

$$|\Psi_0^N\rangle = |\Phi_0^N\rangle + |\text{corr}\rangle \quad (20)$$

with  $|\text{corr}\rangle$  the correlation corrections to the zeroth-order (e.g., HF) ground-state wave function  $|\Phi_0^N\rangle$ , it is essential to note that Eq. (17) is strictly equivalent to the well-known Dyson equation [7, 12, 13, 16–19]

$$(G(\omega))^{-1} = (G^0(\omega))^{-1} - \Sigma(\omega) \quad (21)$$

together with

$$(G^0(\omega))^{-1} = (a|\omega\hat{1} - \hat{H}_0|a)_{\Phi} \quad (22)$$

$$\Sigma(\omega) = \Sigma(\infty) + M(\omega) \quad (23)$$

$$\Sigma(\infty) = (a|\hat{H}|a)_{\text{corr}} \quad (24)$$

$$M(\omega) = (a|\hat{H}|f')(f'|\omega\hat{1} - \hat{H}|f')^{-1}(f'|\hat{H}|a). \quad (25)$$

The subscripts ( $\Phi$  and  $\text{corr}$ ) in Eqs. (22) and (24) indicate that the binary product is taken with respect to  $|\Phi_0^N\rangle$  and  $|\text{corr}\rangle$ , respectively. By virtue of Eq. (21), the description of ionization or electron attachment events, or more generally scattering processes in many-body systems [62], has been reduced to a tractable one-body problem through the introduction of an effective, energy-dependent and nonlocal, one-particle potential: the self-energy  $\Sigma(\omega)$ . The static (i.e., energy-independent) part of the self-energy,  $\Sigma(\infty)$ , relates to instantaneous scattering processes in the time domain.  $G^0(\omega)$  is a zeroth-order (e.g., HF) approximation of the exact one-electron propagator, whose spectral representation reads

$$G_{ij}^0(\omega) = \delta_{ij}[\bar{n}_i(\omega - \varepsilon_i + i0^+)^{-1} + n_i(\omega - \varepsilon_i - i0^+)^{-1}], \quad (26)$$

where  $n_i = 1$  if  $\phi_i$  is occupied,  $n_i = 0$  if  $\phi_i$  is unoccupied, and  $\bar{n}_i = 1 - n_i$ .

The dynamic (energy-dependent) part of the self-energy,  $M(\omega)$ , relates to long-time scale polarization effects induced by the propagation of an extra electron or hole in a correlated background. On the contrary, the static (i.e., energy-independent) part of the self-energy,  $\Sigma(\infty)$ , relates to instantaneous

scattering processes. More specifically, this self-energy component is the electrostatic potential felt by an ingoing or outgoing particle due to the changes induced by electron correction,  $Q$ , in the zeroth-order (HF) ground-state one-electron density,  $\rho^0$ . Therefore, an exact expression for  $\Sigma(\infty)$  is [46, 63]

$$\Sigma_{ij}(\infty) = \sum_{lm} \langle il | jm \rangle Q_{ml}, \quad (27)$$

with

$$\begin{aligned} Q_{ml} &= \rho_{ml}^{\text{exact}} - \rho_{ml}^0 \\ &= \frac{1}{2\pi i} \oint_C d\omega (G_{ml}(\omega) - G_{ml}^0(\omega)), \end{aligned} \quad (28)$$

where the Coulson contour [13, 64],  $C$ , is introduced to evaluate  $Q$  through integration in the complex  $\omega$ -plane. From Eqs. (1) and (27), and a residue analysis over this contour, it is indeed immediately found that

$$\begin{aligned} \frac{1}{2\pi i} \oint_C d\omega G_{ml}(\omega) &= \sum_h \langle \Psi_0^N | a_l^\dagger | \Psi_h^{N-1} \rangle \langle \Psi_h^{N-1} | a_m | \Psi_0^N \rangle \\ &= \langle \Psi_0^N | a_l^\dagger a_m | \Psi_0^N \rangle, \end{aligned} \quad (29)$$

$$\frac{1}{2\pi i} \oint_C d\omega G_{ml}^0(\omega) = n_l \delta_{lm}, \quad (30)$$

which clearly correspond to the exact and HF expressions for the one-electron density matrix, respectively.

In homogeneous and translationally invariant systems, the exact one-electron density is obviously a constant that is matched at any point by the HF one-electron density. For such systems, therefore, the correlation part of the one-electron density,  $Q$ , as well as the static self-energy, identically vanish. In other words,  $\Sigma(\infty)$  is the direct outcome of inhomogeneities in the electron density of molecular or extended periodic systems.

### Linked-Cluster Expansions of the One-Particle Green's Function

In straightforward analogy with Eq. (1), because there are no possible couplings between anion and

cation states the dynamic self-energy can be partitioned [16b, 65] in two terms

$$M(\omega) = M^+(\omega) + M^-(\omega), \quad (31)$$

which relate to excitations of the  $(N + 1)$ - and  $(N - 1)$ -particle systems, respectively. Specifically, the operator manifold, required to expand  $M^+(\omega)$ , spans all possible  $2p - 1h, 3p - 2h, \dots$ , (two-particle/one-hole, three-particle/two-hole. . .) shake-on excitations of the  $(N + 1)$ -particle system, whereas for the  $M^-(\omega)$  component the required manifold encompasses the  $2h - 1p, 3h - 2p, \dots$ , (two-hole/one-particle, three-hole/two-particle. . .) shake-up excitations of the  $(N - 1)$ -particle system (here, the indices  $p$  and  $h$  mean particle and hole and describe creation of an electron in a virtual level and destruction of an electron in an occupied level, respectively). In close analogy with Eq. (25),  $M(\omega)$  has the exact algebraic form [44, 46]

$$M_{ij}^\pm(\omega) = (\mathbf{U}_i^\pm)^\dagger (\omega - \mathbf{K}^\pm - \mathbf{C}^\pm)^{-1} \mathbf{U}_j^\pm, \quad (32)$$

where the matrices  $\mathbf{K}^\pm + \mathbf{C}^\pm$  describe configuration interactions between the (shake-up or shake-on) excited states of the  $(N \pm 1)$  particle systems

$$\mathbf{K}^\pm + \mathbf{C}^\pm = \langle f' | \hat{H} | f' \rangle, \quad (33)$$

whereas the vectors  $\mathbf{U}_i^\pm$  and their adjoints contain the coupling amplitudes between these states and the  $\{N \pm 1\}$ -particle states arising from a one-electron ionization or attachment process:

$$\begin{aligned} \mathbf{U}_i^\pm &= \langle f' | \hat{H} | a_i \rangle \\ (\mathbf{U}_i^\pm)^\dagger &= \langle a_i | \hat{H} | f' \rangle. \end{aligned} \quad (34)$$

$\mathbf{K}^\pm$  is most conveniently defined as a diagonal matrix containing the zeroth-order, i.e., HF, estimation of the shake-on and shake-up energies, respectively. From a Born expansion [66] of the matrix inverse in Eq. (32), it follows that infinite but partial series of dynamic self-energy terms are implicitly accounted for.

$$\begin{aligned} M_{ij}^\pm(\omega) &= (\mathbf{U}_i^\pm)^\dagger (\omega - \mathbf{K}^\pm)^{-1} \mathbf{U}_j^\pm \\ &+ (\mathbf{U}_i^\pm)^\dagger (\omega - \mathbf{K}^\pm)^{-1} \mathbf{C}^\pm (\omega - \mathbf{K}^\pm)^{-1} \mathbf{U}_j^\pm + \dots \end{aligned} \quad (35)$$

Due to the partitioning of Eq. (31), assuming decouplings of electron excitations in the  $(N + 1)$ - and the  $(N - 1)$ -particle systems (see further) the matrix to

diagonalize to identify the poles of the one-particle Green's function is therefore of the general form

$$\mathbf{H} = \begin{bmatrix} \varepsilon + \Sigma(\infty) & \mathbf{U}^+ & \mathbf{U}^- \\ (\mathbf{U}^+)^\dagger & \mathbf{K}^+ + \mathbf{C}^+ & \mathbf{0} \\ (\mathbf{U}^-)^\dagger & \mathbf{0} & \mathbf{K}^- + \mathbf{C}^- \end{bmatrix}, \quad (36)$$

which is still an exact expression. Clearly, approximations are necessary to turn investigations of ionization and electron attachment spectra into a tractable secular problem. A first one concerns the manifolds of shake-on and shake-up excitation operators in which the above matrix is cast. Another approximation lies in the form of the reference wave function with which the binary products of Eqs. (22) and (24) must be expanded.

In practice, now, the most commonly employed Green's function schemes aim at one-electron binding energies and self-energies that are correct through third order in correlation by virtue of the renormalization embodied in Eq. (35). Such schemes comprise the ADC(3) scheme [44–47] and the closely related EPT(3+) [19] or, equivalently, third-order EOM  $1p$ -GF approaches [67]. The latter approaches have been derived on algebraic grounds only, whereas the ADC(3) scheme originates from a comparison of the exact algebraic expression of Eq. (32) with diagrammatic expansions of the self-energy. Except for the treatment of the static component of the self-energy (see further), these approaches are strictly equivalent.

From Eq. (25), a third-order treatment of  $M(\omega)$  is obviously ensured by an expansion of the vectors of the coupling amplitudes  $\mathbf{U}^\pm$  and the matrices of energy shifts  $\mathbf{C}^\pm$  at second and first orders in electron correlation, respectively. Also, the contributions pertaining to the excitations described by the  $h_5, h_7, \dots$  manifolds of shake-on or shake-up operators can be dropped, as these only contribute to  $M(\omega)$  at fourth order and beyond. Therefore, restricting these manifolds to the sets of single-electron shake-on or shake-up excitations  $h_3$ , expanding  $|\Psi_0^N\rangle$  at second order of Rayleigh–Schrödinger perturbation theory, and working out the binary products of Eq. (34) leads to the following expressions for the vectors of coupling amplitudes  $\mathbf{U}_j^\pm$  [44, 67]:

$$\begin{aligned} U_{ars,j}^{+(2)} &= \langle sr | ja \rangle + \frac{1}{2} \sum_{bc} \frac{\langle sr | bc \rangle \langle bc | ja \rangle}{\varepsilon_b + \varepsilon_c - \varepsilon_r - \varepsilon_s} \\ &- (1 - P_{rs}) \sum_{bt} \frac{\langle st | ab \rangle \langle br | jt \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t} \end{aligned} \quad (37a)$$

$$U_{rab,j}^{(2)} = \langle ba | jr \rangle + \frac{1}{2} \sum_{st} \frac{\langle ba | st \rangle \langle st | jr \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_t} - (1 - P_{ab}) \sum_{sc} \frac{\langle bc | rs \rangle \langle sa | jc \rangle}{\varepsilon_b + \varepsilon_c - \varepsilon_r - \varepsilon_s}, \quad (37b)$$

with  $P_{ij}$  a permutation operator over orbital labels  $i$  and  $j$ . At this stage, we have, from here and henceforth, adopted the convention that labels  $a, b, c, \dots$  and  $r, s, t, \dots$  describe occupied and unoccupied spin orbitals, respectively. Similarly, expanding the binary product of Eq. (33) within a HF reference wave function leads [63, 67] to first-order configuration interactions. In the outlook of practical applications, these matrix elements are most commonly presented [44, 67] for nonredundant manifolds of shake-up or shake-on states, i.e., ( $r < s$ ) or ( $a < b$ ). Using, for simplicity in further analysis, the unrestricted  $h_3$  operator manifold of Eq. (11), these expressions are strictly equivalent to [65]

$$C_{ars,a'r's'}^{+(1)} = \frac{1}{2} \langle sr | s'r' \rangle \delta_{aa'} - \langle sa' | s'a \rangle \delta_{rr'} - \langle ra' | r'a \rangle \delta_{ss'}, \quad (38a)$$

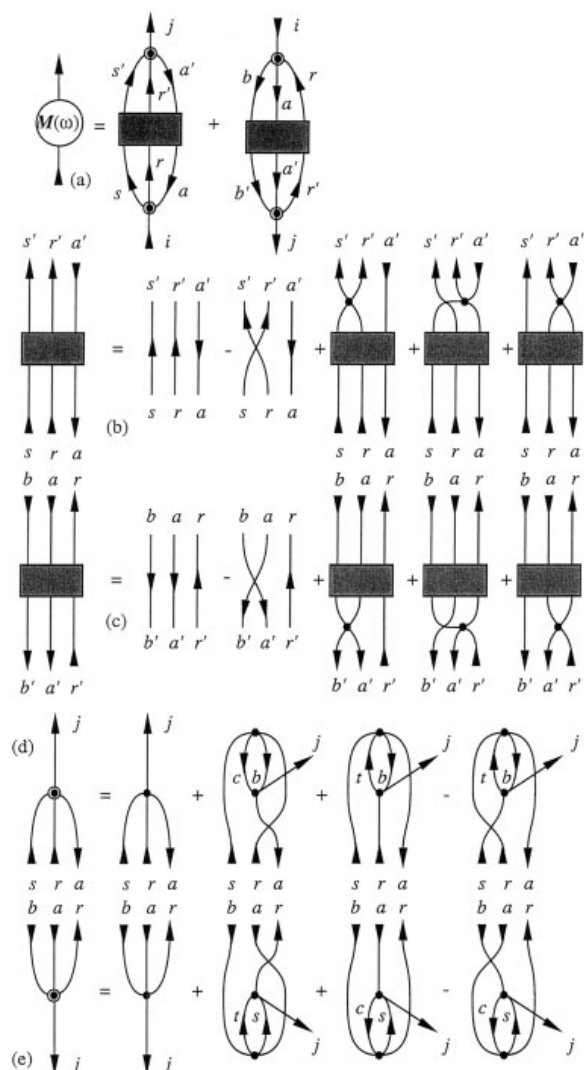
$$C_{rab,r'a'b'}^{-(1)} = -\frac{1}{2} \langle ba | b'a' \rangle \delta_{rr'} + \langle br' | b'r \rangle \delta_{aa'} + \langle ar' | a'r \rangle \delta_{bb'}. \quad (38b)$$

The corresponding zeroth-order shake-on and shake-up excitation energies are

$$K_{ars,a'r's'}^{+(0)} = (\varepsilon_r + \varepsilon_s - \varepsilon_a) \delta_{rr'} \delta_{ss'} \delta_{aa'} \quad (39a)$$

$$K_{rab,r'a'b'}^{-(0)} = (\varepsilon_a + \varepsilon_b - \varepsilon_r) \delta_{aa'} \delta_{bb'} \delta_{rr'}, \quad (39b)$$

respectively. A complete diagrammatic overview of the dynamic self-energy amounting to the  $1p$ -GF/ADC(3) scheme in terms of linked and time-ordered (Hugenholtz) diagrams is provided in Figure 1. Specifically, Figure 1(a) represents the two components,  $M^+(\omega)$  and  $M^-(\omega)$  of the dynamic self-energy of Eq. (31), of which the  $2p - 1h/2p - 1h$  and  $2h - 1p/2h - 1p$  kernels relating to the  $K^{(0)\pm} + C^{(1)\pm}$  matrices of Eqs. (38) and (39) are iteratively expanded [Figs. 1(b) and 1(c); [44]] through first order in correlation. The diagrams of Figures 1(d) and 1(e) directly amount to the vectors of second-order coupling amplitudes,  $U^{(2)\pm}$ . These can be regarded as screened bielectron interactions in a correlated background because the second-order



**FIGURE 1.** Diagrammatic expansion amounting to the ADC(3) dynamic self-energy.

corrections of Eq. (37) tend most generally to limit the impact of electron relaxation on one-electron binding energies.

In the EOM(3) or EPT(3+) schemes, the third-order static self-energy is simply derived from second-order correlation corrections to the one-electron density matrix

$$Q_{ml}^{(2)} = \sum_{i=1}^6 Q_{i;ml}^{(2)}, \quad (40)$$

with



$$Q_{1;ml}^{(2)} = -\frac{1}{2} n_m n_l \sum_{ars} \frac{\langle ma | rs \rangle \langle rs | la \rangle}{(\varepsilon_m + \varepsilon_a - \varepsilon_r - \varepsilon_s)(\varepsilon_l + \varepsilon_a - \varepsilon_r - \varepsilon_s)} \quad (41a)$$

$$Q_{2;ml}^{(2)} = +\frac{1}{2} \bar{n}_m \bar{n}_l \sum_{abr} \frac{\langle mr | ab \rangle \langle ab | lr \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_m - \varepsilon_r)(\varepsilon_a + \varepsilon_b - \varepsilon_l - \varepsilon_r)} \quad (41b)$$

$$Q_{3;ml}^{(2)} = +\frac{1}{2} \bar{n}_m n_l \sum_{ars} \frac{\langle ma | rs \rangle \langle rs | la \rangle}{(\varepsilon_l - \varepsilon_m)(\varepsilon_l + \varepsilon_a - \varepsilon_r - \varepsilon_s)} \quad (41c)$$

$$Q_{4;ml}^{(2)} = +\frac{1}{2} n_m \bar{n}_l \sum_{ars} \frac{\langle ma | rs \rangle \langle rs | la \rangle}{(\varepsilon_m - \varepsilon_l)(\varepsilon_m + \varepsilon_a - \varepsilon_r - \varepsilon_s)} \quad (41d)$$

$$Q_{5;ml}^{(2)} = -\frac{1}{2} n_m \bar{n}_l \sum_{abr} \frac{\langle mr | ab \rangle \langle ab | lr \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_m - \varepsilon_r)(\varepsilon_l - \varepsilon_m)} \quad (41e)$$

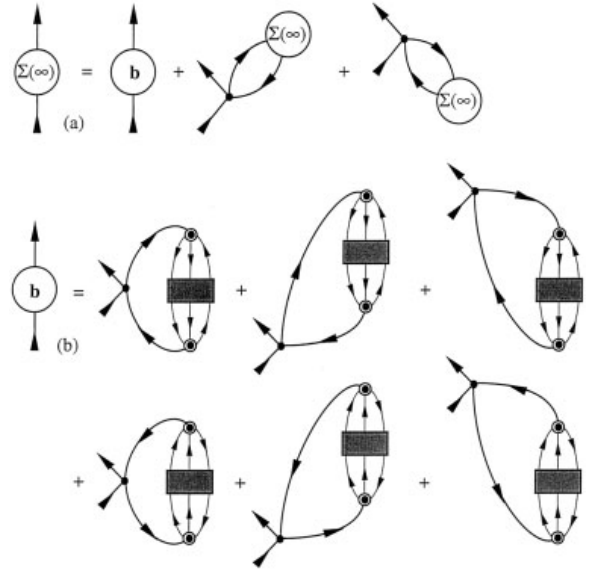
$$Q_{6;ml}^{(2)} = -\frac{1}{2} \bar{n}_m n_l \sum_{abr} \frac{\langle mr | ab \rangle \langle ab | lr \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_l - \varepsilon_r)(\varepsilon_m - \varepsilon_l)}, \quad (41f)$$

whereas in the ADC(3) scheme higher orders are more conveniently attained [46] by inserting in Eq. (28) a truncated Dyson expansion (21) of the Green's function:

$$Q = \frac{1}{2\pi i} \oint_C d\omega (G^{(0)}(\omega) \Sigma(\omega) G^{(0)}(\omega)). \quad (42)$$

Using expression (32) as a starting approximation for  $\Sigma(\omega)$  and iterating over Eqs. (27), (28), (23), and (42), the determination of  $\Sigma(\infty)$  can be recast in a set of linear inhomogeneous equations:

$$\Sigma_{ij}(\infty) = b_{ij} + \sum_{ar} \frac{\langle ia | jr \rangle}{\varepsilon_a - \varepsilon_r} \Sigma_{ra}(\infty) + \sum_{ar} \frac{\langle ir | ja \rangle}{\varepsilon_a - \varepsilon_r} \Sigma_{ar}(\infty), \quad (43)$$



**FIGURE 2.** Diagrammatic expansion amounting to the ADC(3) static self-energy.

which amounts to the RPA-like diagrammatic expansion of Figure 2(a). The inhomogeneities  $b$  involved in these equations are given by [46]

$$b_{ij} = \sum_{lm} \langle il | jm \rangle Q_{ml}^{(\text{ADC})} = \sum_{lm} \langle il | jm \rangle \frac{1}{2\pi i} \int_C d\omega G_{mm}^{(0)}(\omega) M_{ml}^{(\text{ADC})}(\omega) G_{ll}^{(0)}(\omega). \quad (44)$$

In straightforward analogy with the second-order one-electron density,  $Q^{(2)}$  [Eq. (40)], these inhomogeneities can be sorted out into six distinct (time-ordered) contributions [see Fig. 2(b)], according to

$$Q_{ml}^{(\text{ADC})} = \sum_{i=1}^6 Q_{i;ml}^{(\text{ADC})} \quad (45)$$

and

$$Q_{1;ml}^{(\text{ADC})} = -n_m n_l (\mathbf{U}_m^+)^+ (\varepsilon_m - \mathbf{K}^+ - \mathbf{C}^+)^{-1} \times (\varepsilon_l - \mathbf{K}^+ - \mathbf{C}^+)^{-1} \mathbf{U}_l^+ \quad (46a)$$

$$Q_{2;ml}^{(\text{ADC})} = +\bar{n}_m \bar{n}_l (\mathbf{U}_m^-)^+ (\varepsilon_m - \mathbf{K}^- - \mathbf{C}^-)^{-1} \times (\varepsilon_l - \mathbf{K}^- - \mathbf{C}^-)^{-1} \mathbf{U}_l^- \quad (46b)$$

$$Q_{3;ml}^{(\text{ADC})} = +\bar{n}_m n_l (\varepsilon_l - \varepsilon_m)^{-1} (\mathbf{U}_m^+)^+ (\varepsilon_l - \mathbf{K}^+ - \mathbf{C}^+)^{-1} \mathbf{U}_l^+ \quad (46c)$$

TABLE I

Ranking of one-electron Green's function or propagator methods in function of the last complete order attained in correlation for the self-energy and its components.

Method	$K^- + C^-$	$U_j^-$	$K^+ + C^+$	$U_j^-$	$M^-(\omega)$	$M^+(\omega)$	$Q^\pm$	$\Sigma(\infty)$	$\Sigma(\omega)$
EPT(2) <sup>a</sup>	0	1	0	1	2	2	—	—	2
EOM(2) <sup>b</sup>	1	1	1	1	>2	>2	—	—	>2
NR2 <sup>c</sup>	1	"1.5" <sup>+</sup> if $n_j = 1$ 1 if $n_j = 0$	0	1	>2	2	—	—	>2
SH2 <sup>d</sup>	2	"1.5" <sup>+</sup> if $n_j = 1$ 1 if $n_j = 0$	1	1	>2	>2	—	—	>2
ADC(2) or 2ph-TDA	1	1	1	1	>2	>2	>2	>3	>2
EPT(3) <sup>e</sup>	0	2	0	2	3	3	2	3	3
EOM3 or EPT(3+) <sup>f</sup>	1	2	1	2	>3	>3	2	3	>3
ADC(3) or EPT(3+4+)	1	2	1	2	>3	>3	>3	>4	>3

<sup>+</sup>, fractional order, by virtue of a symmetrization ( $\frac{1}{2}(\mathbf{H} + \mathbf{H}^\dagger)$ ) of the originally non-Hermitian NR2 or SH2 schemes; >, infinite but incomplete series are included beyond the indicated order, through renormalization.

<sup>a</sup> Second-order one-electron propagator.

<sup>b</sup> Second-order EOM [63, 67].

<sup>c</sup> Nondiagonal renormalized second-order scheme [69].

<sup>d</sup> (Partial) second-order treatment of shake-ups [70].

<sup>e</sup> Third-order one-electron propagator [19].

<sup>f</sup> Through-third-order one-electron propagator [19], alias third-order EOM scheme [67].

$$Q_{4,ml}^{(\text{ADC})} = +n_m \bar{n}_l (\varepsilon_m - \varepsilon_l)^{-1} (U_m^+)^+ (\varepsilon_m - K^+ - C^+)^{-1} U_l^+ \quad (46d)$$

$$Q_{5,ml}^{(\text{ADC})} = -n_m \bar{n}_l (\varepsilon_l - \varepsilon_m)^{-1} (U_m^-)^+ (\varepsilon_l - K^- - C^-)^{-1} U_l^- \quad (46e)$$

$$Q_{6,ml}^{(\text{ADC})} = -\bar{n}_m n_l (\varepsilon_m - \varepsilon_l)^{-1} (U_m^-)^+ (\varepsilon_m - K^- - C^-)^{-1} U_l^- \quad (46f)$$

By virtue of the matrix inverses in Eq. (46), it follows that at the ADC(3) level the one-electron density is determined, as the dynamic self-energy, through third order in correlation, which in turn implies that the static self-energy is correctly expanded through fourth order. For this reason, this scheme has been occasionally referred to as the EPT(3+4+) approach [68]. In the ADC(2) [44] scheme, or nearly equivalently [44], the two-particle-hole Tamm–Dancoff (2ph-TDA) approximation [65], the second-order corrections to the vectors of coupling amplitudes are dropped and the dynamic and dynamic self-energies are therefore obtained through second and third orders, respectively. Other lower-order one-particle Green's function schemes are compared with the ADC(3) level through the interplay of Table I.

In this comparison of the most currently employed EOM-based or ADC expansion schemes of the 1p-GF, coupling terms between the manifolds of shake-up ( $2h - 1p, 3h - 2p$ ) and shake-on ( $2p - 1h, 3p - 2h, \dots$ ) operators have been dropped [see Eqs. (33) and (34)] for the sake of ease and clarity in the presentation. Due to the partitioning of Eq. (31), these coupling terms are, by construction, set to zero in the ADC schemes, whereas mixed  $H^{2h1p-2p1h}$  matrix elements in the EOM expansion scheme have nonvanishing contributions at second and higher orders in correlation [71, 72]. Such coupling terms only appear in EOM schemes recovering the 1p-GF through fourth or higher orders, which go beyond the scope of the present analysis. Notice that, in the EOM secular equation, excitations in the  $(N + 1)$ - and  $(N - 1)$ -particle systems can always be decoupled through a convenient Gram-Schmidt orthogonalization of precursor excited states [71].

### Implications of Translation Symmetry in Green's Function Theory

One of the most elegant ways to identify and/or assess the various implications of size consistency

with a given many-body approach is to adapt this approach to an extended periodic system and switch off artificially all interactions between the cells of the lattice describing this system. In this work, we consider, without any loss of generality compared with solid-state physics, the model of an extended stereoregular polymer with nonvanishing band gap. This model is most conveniently expressed in terms of a 1-D lattice consisting of a large number,  $N_0$ , of cells of length  $a_0$  lined up in the direction of periodicity,  $\vec{e}_z$ , under the usual Born-Von Karman cyclic boundary constraints. As is well known, the one-electron eigenstates of such a periodic system are Bloch functions, which can be classified according to  $N_0$  discrete values of a reduced wave number  $k$  (or electron momentum) within the first Brillouin zone [BZ] of the corresponding reciprocal lattice, in this case the interval  $(-\pi/a_0 \leq k < \pi/a_0)$ . These series become (quasi)-continuous in the thermodynamic limit,  $N_0 \rightarrow \infty$ , which permits integrations in  $k$ -space. In the present work, assuming for simplicity that the band index recovers the spin label, we expand these Bloch functions in LCAO form

$$\phi_n(k, \vec{r}) = \frac{1}{\sqrt{N_0}} \sum_{p=1}^{M_0} C_{pn}(k) \sum_{\mu=1}^{N_0} e^{ik\mu a_0} \gamma_p^\mu(\vec{r}), \quad (47)$$

with  $M_0$  the number of atomic functions per cell. For the atomic functions, use is made of the following notation:

$$\gamma_p^\mu(\vec{r}) = \gamma_p^0(\vec{r} - \vec{r}_p - \mu a_0 \vec{e}_z), \quad (48)$$

where  $\vec{r}_p$  represents the center of the atomic function  $\gamma_p$  in the reference unit cell. Bloch functions are eigenfunctions of a one-electron translation operator,  $t^\mu$ , of the form

$$t^\mu f(\vec{r}) = f(\vec{r} - \mu a_0 \vec{e}_z) \quad (49)$$

with eigenvalue  $e^{-ik\mu a_0}$

$$t^\mu \phi_n(k, \vec{r}) = e^{-ik\mu a_0} \phi_n(k, \vec{r}). \quad (50)$$

In direct analogy with the above equation, we define the translation operator associated with the direct lattice vector  $\mu a_0 \vec{e}_z$  for the many-electron reference wave function function  $|\Psi_0^N\rangle$  as

$$T^\mu |\Psi_0^N\rangle = e^{-iK\mu a_0} |\Psi_0^N\rangle, \quad (51)$$

where  $K$  represents the total electron momentum of the system [in general,  $K = 0$  because in a doubly filled Slater determinant each occupied spin orbital  $\phi_n(k, \vec{r})$  has an occupied counterpart  $\phi_n(-k, \vec{r})$ ]. From an analysis in Taylor series [21], it can be shown that the creation and annihilation operators, corresponding to Bloch one-electron eigenstates, have, under such a many-electron translation operator, the following transformation properties:

$$T^\mu a_n^+(k) T^{-\mu} = e^{-ik\mu a_0} a_n^+(k) \quad (52)$$

$$T^\mu a_n(k) T^{-\mu} = e^{ik\mu a_0} a_n(k). \quad (53)$$

With regard to the one-to-one correspondence between first and second quantizations, the one-particle Green's function of an extended stereoregular polymer is, at first glance, of the form

$$\begin{aligned} G_{ij}(k', k'', \omega) &= \sum_p \frac{\langle \Psi_0^N | a_i(k') | \Psi_p^{N+1} \rangle \langle \Psi_p^{N+1} | a_j^+(k'') | \Psi_0^N \rangle}{\omega - (E_p^{N+1} - E_0^N) + i0^+} \\ &+ \sum_h \frac{\langle \Psi_0^N | a_j^+(k'') | \Psi_h^{N-1} \rangle \langle \Psi_h^{N-1} | a_i(k') | \Psi_0^N \rangle}{\omega - (E_0^N - E_h^{N-1}) - i0^+}. \end{aligned} \quad (54)$$

Because  $T^\mu T^{-\mu} = 1$ , it follows readily and in general that

$$\begin{aligned} &\langle \Psi_0^N | a_i(k') | \Psi_p^{N+1} \rangle \langle \Psi_p^{N+1} | a_j^+(k'') | \Psi_0^N \rangle \\ &= \langle \Psi_0^N | T^\mu T^{-\mu} a_i(k') T^\mu T^{-\mu} | \Psi_p^{N+1} \rangle \\ &\quad \times \langle \Psi_p^{N+1} | T^\mu T^{-\mu} a_j^+(k'') T^\mu T^{-\mu} | \Psi_0^N \rangle \\ &= e^{i(k' - k'')\mu a_0} \langle \Psi_0^N | a_i(k') | \Psi_p^{N+1} \rangle \langle \Psi_p^{N+1} | a_j^+(k'') | \Psi_0^N \rangle \end{aligned} \quad (55)$$

and similarly for the ionization component of the one-particle Green's function. Therefore,

$$G_{ij}(k', k'', \omega) [1 - e^{-i(k' - k'')\mu a_0}] = 0, \quad (56)$$

which implies that  $G(k', k'', \omega)$  vanishes unless

$$k' - k'' = \frac{2\pi\mu}{a_0}; \quad \mu = 0, \pm 1, \pm 2, \dots, \pm N_0/2. \quad (57)$$

The latter equation shows that wave vectors in periodic systems are conserved only within a vector of the reciprocal lattice due to all possible Bragg

refractions of electron waves through the direct lattice. The most important outcome of this well-known property of extended periodic systems is the diagonalization of  $G(\omega)$  over  $N_0$  discrete values of  $k' - k''$ . In the limit of a stereoregular polymer consisting of  $N_0$  noninteracting unit cells, this diagonalization in turn implies a decoupling of the Green's function for the whole system into  $N_0$  strictly degenerate forms. Because the Hamiltonian and translation operators commute, it is easy, using similar reasoning, to demonstrate the diagonalization in  $k$ -space of the static self-energy,

$$(a_i(k')|\hat{H}|a_j(k''))_{\text{corr}}[1 - e^{-(k'-k'')\mu a_0}] = 0, \quad (58)$$

as well as of all individual components of the dynamic self-energy

$$\begin{aligned} M(k', k'', \omega) \approx & (\underline{a}(k')|\hat{H}|\underline{h}_3(K'_3))(\underline{h}_3(K'_3)|\omega\hat{1} \\ & - \hat{H}|\underline{h}_3(K''_3))^{-1}(\underline{h}_3(K''_3)|\hat{H}|\underline{a}(k'')) + \dots, \end{aligned} \quad (59)$$

with

$$\underline{h}_3(K_3) = \{a_i^+(k_1)a_j(k_2)a_k(k_3)\}; \quad K_3 = k_1 - k_2 - k_3 \quad (60)$$

because

$$\begin{aligned} (\underline{a}(k')|\hat{H}|\underline{h}_3(K'_3))[1 - e^{-i(k'-K'_3)\mu a_0}] &= 0 \\ (\underline{h}_3(K'_3)|\omega\hat{1} - \hat{H}|\underline{h}_3(K''_3))[1 - e^{-i(K'_3-K''_3)\mu a_0}] &= 0 \\ (\underline{h}_3(K''_3)|\hat{H}|\underline{a}(k''))[1 - e^{-i(K''_3-k'')\mu a_0}] &= 0. \end{aligned} \quad (61)$$

As shown by the above equations, the diagonalization in the  $k$ -space of the  $\mathbf{U}^\pm$  and  $\mathbf{K}^\pm + \mathbf{C}^\pm$  matrix elements of Eqs. (32) or (36) complicate slightly because it has to be completed over odd-numbered combinations of wave numbers for each set of shake-up or shake-on excitation operators. Here, also, the total electron momenta characterizing these sets are, by translation symmetry, conserved only within a vector of the reciprocal lattice and should therefore be regarded as quasimomenta. This is only when expanding the bielectron interactions over Bloch functions and summing all possible interferences among electron waves that a rule of conservation over quasimomenta is seemingly fully restored. Indeed, by expanding Bloch functions in LCAO form and taking account of the lattice periodicity, and because

$$\sum_{\mu}^{N_0} [e^{i(k_n+k_o-k_l-k_m)\mu a_0}] = N_0 \delta_{(k_n+k_o-k_l-k_m)}, \quad (62)$$

one finds immediately [42] that

$$\begin{aligned} \langle \phi_l(k_l)\phi_m(k_m) | \phi_n(k_n)\phi_o(k_o) \rangle \\ = (N_0)^{-1} \delta_{(k_n+k_o-k_l-k_m)} \tau \begin{pmatrix} k_l & k_m \\ l & m \end{pmatrix} \begin{vmatrix} k_n & k_o \\ n & o \end{vmatrix} \end{aligned} \quad (63)$$

with

$$\begin{aligned} \tau \begin{pmatrix} k_l & k_m \\ l & m \end{pmatrix} \begin{vmatrix} k_n & k_o \\ n & o \end{vmatrix} \\ = \sum_{pqrs}^{M_0} C_{pl}^*(k_l)C_{qn}(k_n)C_{rm}^*(k_m)C_{so}(k_o) \\ \times \sum_{\mu\mu'\mu''}^{N_0} [e^{i(k_n\mu+k_o\mu''-k_m\mu')a_0} \langle \gamma_p^0 \gamma_r^{\mu'} | \gamma_q^{\mu} \gamma_s^{\mu''} \rangle] \end{aligned} \quad (64)$$

a complex and, regardless of the long-range character of the Coulomb force, bounded function in the thermodynamic limit  $N_0 \rightarrow \infty$ . From the conservation rule on momenta associated with Eq. (63), it follows readily that the dynamic self-energy of Eq. (53), for instance, is strictly diagonal in  $k$ -space because

$$k' = K'_3 = K''_3 = k''. \quad (65)$$

Assuming from now on a single momentum label  $k$  for the one-particle Green's function and the corresponding self-energies, an analysis of all possible momentum transfers in the diagrammatic expansion of Figure 1 shows that, for an adaptation of one of the second- or third-order Green's function schemes of Table I to the formalism of crystalline orbitals (COs), the sets of shake-on or shake-up excitation operators to consider will be of the type

$$\begin{aligned} a_r^+(k_r)a_a(k+q)a_b(k_r-q) \quad \text{or} \\ a_a^+(k_a)a_r(k+q)a_s(k_a-q), \end{aligned} \quad (66)$$

where  $q$  represents the electron momentum transferred at the level of the screened bielectron interactions  $\mathbf{U}^\pm(k)$  or their adjoints. Therefore, besides the principal momentum variable  $k$ , which defines the irreducible representation of the translation symmetry group under which the EOM(3) or ADC(3) secular equations can be block diagonalized, four additional secondary momentum variables are necessary to cast the  $\mathbf{K}^\pm + \mathbf{C}^\pm$  matrices in CO form:

$$\begin{aligned}
 K_{ars,a'r's'}^{+(0)}(k; k_a, q, k'_a, q') &= (\varepsilon_r(k+q) + \varepsilon_s(k_a - q) - \varepsilon_a(k_a)) \delta_{rr'} \delta_{ss'} \delta_{aa'} \delta(q - q') \delta(k_a - k'_a) \\
 K_{rab,r'a'b'}^{-(0)}(k; k_r, q, k'_r, q') &= (\varepsilon_a(k+q) + \varepsilon_b(k_r - q) - \varepsilon_r(k_r)) \delta_{aa'} \delta_{bb'} \delta_{rr'} \delta(q - q') \delta(k_r - k'_r) \quad (67)
 \end{aligned}$$

$$\begin{aligned}
 C_{ars,a'r's'}^{+(1)}(k; k_a, q, k'_a, q') &= (N_0)^{-1} \left\{ \frac{1}{2} \delta_{aa'} \delta(k_a - k'_a) \tau \left( \begin{matrix} k_a - q & k + q \\ s & r \end{matrix} \middle| \begin{matrix} k'_a - q' & k + q' \\ s' & r' \end{matrix} \right) - \delta_{rr'} \delta(q - q') \right. \\
 &\quad \left. \tau \left( \begin{matrix} k_a - q & k'_a \\ s & a' \end{matrix} \middle| \begin{matrix} k'_a - q' & k_a \\ s' & a \end{matrix} \right) - \delta_{ss'} \delta(k_a + q' - k'_a - q) \tau \left( \begin{matrix} k + q & k'_a \\ r & a' \end{matrix} \middle| \begin{matrix} k + q' & k_a \\ r' & a \end{matrix} \right) \right\} \\
 C_{rab,r'a'b'}^{-(1)}(k; k_r, q, k'_r, q') &= (N_0)^{-1} \left\{ -\frac{1}{2} \delta_{rr'} \delta(k_r - k'_r) \tau \left( \begin{matrix} k_r - q & k + q \\ b & a \end{matrix} \middle| \begin{matrix} k'_r - q' & k + q' \\ b' & a' \end{matrix} \right) - \delta_{aa'} \delta(q - q') \right. \\
 &\quad \left. \tau \left( \begin{matrix} k_r - q & k'_r \\ b & r' \end{matrix} \middle| \begin{matrix} k'_r - q' & k_r \\ b' & r \end{matrix} \right) - \delta_{bb'} \delta(k_r + q' - k'_r - q) \tau \left( \begin{matrix} k + q & k'_r \\ a & r' \end{matrix} \middle| \begin{matrix} k + q' & k_r \\ a' & r \end{matrix} \right) \right\}. \quad (68)
 \end{aligned}$$

Similarly, in the formalism of COs, the vectors of coupling amplitudes  $\mathbf{U}^\pm(k)$  will be parametrized

depending on two secondary momentum variables

$$\begin{aligned}
 U_{ars,j}^{+(2)}(k; k_a, q) &= (N_0)^{-1} \tau \left( \begin{matrix} k_a - q & k + q \\ s & r \end{matrix} \middle| \begin{matrix} k & k_a \\ j & a \end{matrix} \right) \\
 &+ \frac{1}{2} (N_0)^{-2} \sum_{bc} \sum_{q'} \frac{\tau \left( \begin{matrix} k_a - q & k + q \\ s & r \end{matrix} \middle| \begin{matrix} k + q' & k_a - q' \\ b & c \end{matrix} \right) \tau \left( \begin{matrix} k + q' & k_a - q' \\ b & c \end{matrix} \middle| \begin{matrix} k & k_a \\ j & a \end{matrix} \right)}{\varepsilon_b(k + q') + \varepsilon_c(k_a - q') - \varepsilon_r(k + q) - \varepsilon_s(k_a - q)} \\
 &- (N_0)^{-2} \sum_{bt} \sum_{k_t} \frac{\tau \left( \begin{matrix} k_a - q & k_t \\ s & t \end{matrix} \middle| \begin{matrix} k_a & k_t - q \\ a & b \end{matrix} \right) \tau \left( \begin{matrix} k_t - q & k + q \\ b & r \end{matrix} \middle| \begin{matrix} k & k_t \\ j & t \end{matrix} \right)}{\varepsilon_a(k_a) + \varepsilon_b(k_t - q) - \varepsilon_s(k_a - q) - \varepsilon_t(k - q)} \\
 &+ (N_0)^{-2} \sum_{bt} \sum_{k_t} \frac{\tau \left( \begin{matrix} k + q & k_t \\ r & t \end{matrix} \middle| \begin{matrix} k_a & k_t - q \\ a & b \end{matrix} \right) \tau \left( \begin{matrix} k_t - q & k_a - q \\ b & s \end{matrix} \middle| \begin{matrix} k & k_t \\ j & t \end{matrix} \right)}{\varepsilon_a(k_a) + \varepsilon_b(k_t - q) - \varepsilon_r(k + q) - \varepsilon_t(k_t)} \quad (69a)
 \end{aligned}$$

$$\begin{aligned}
 U_{rab,j}^{-(2)}(k; k_r, q) &= (N_0)^{-1} \tau \left( \begin{matrix} k_r - q & k + q \\ b & a \end{matrix} \middle| \begin{matrix} k & k_r \\ j & r \end{matrix} \right) \\
 &+ \frac{1}{2} (N_0)^{-2} \sum_{st} \sum_{q'} \frac{\tau \left( \begin{matrix} k_r - q & k_r + q \\ b & a \end{matrix} \middle| \begin{matrix} k + q' & k_r - q' \\ s & t \end{matrix} \right) \tau \left( \begin{matrix} k + q' & k_r - q' \\ s & t \end{matrix} \middle| \begin{matrix} k & k_r \\ j & r \end{matrix} \right)}{\varepsilon_a(k + q) + \varepsilon_b(k_r - q) - \varepsilon_s(k + q') - \varepsilon_t(k_r - q')} \\
 &- (N_0)^{-2} \sum_{sc} \sum_{k_c} \frac{\tau \left( \begin{matrix} k_r - q & k_c \\ b & c \end{matrix} \middle| \begin{matrix} k_r & k_c - q \\ r & s \end{matrix} \right) \tau \left( \begin{matrix} k_c - q & k + q \\ s & a \end{matrix} \middle| \begin{matrix} k & k_c \\ j & c \end{matrix} \right)}{\varepsilon_b(k_r - q) + \varepsilon_c(k_c) - \varepsilon_r(k_r) - \varepsilon_s(k_c - q)} \\
 &+ (N_0)^{-2} \sum_{sc} \sum_{k_c} \frac{\tau \left( \begin{matrix} k + q & k_c \\ a & c \end{matrix} \middle| \begin{matrix} k_r & k_c - q \\ r & s \end{matrix} \right) \tau \left( \begin{matrix} k_c - q & k_r - q \\ s & b \end{matrix} \middle| \begin{matrix} k & k_c \\ j & c \end{matrix} \right)}{\varepsilon_a(k + q) + \varepsilon_c(k_c) - \varepsilon_r(k_r) - \varepsilon_s(k_c - q)}, \quad (69b)
 \end{aligned}$$

where the closed ladder and loop parts of the second-order diagrams of Figures 2(d) and 2(e) have resulted in a single summation over a momentum transfer variable,  $q'$ , and a one-particle or one-hole

momentum variable,  $k_t$  or  $k_c$ , respectively. It is important to note that, like the bielectron integral of Eq. (63) or the configuration interactions of Eq. (68), the screened bielectron interactions of Eq. (69) scale

as  $(N_0)^{-1}$  because the summations over  $q'$ ,  $k'$ , or  $k_c$  run over the  $N_0$  values of  $k$  that are permitted in the first Brillouin zone and result therefore in a scaling factor proportional to  $N_0$ . Correspondingly, in the thermodynamic limit,  $N_0 \rightarrow \infty$ , such a balance of normalization and multiplicity factors is most conveniently handled by turning the summations over momenta into integrations over the first Brillouin zone via

$$\frac{1}{N_0} \sum_k \rightarrow \frac{a_0}{2\pi} \int_{-\pi/a_0}^{+\pi/a_0} dk. \quad (70)$$

According to the expansion in  $k$ -space of its constituting elements, the ADC(3) secular equation  $H(k)X(k) = X(k)E(k)$  describing the ionization or electron attachment properties of an extended stereoregular polymer will therefore be of the form

$$\begin{bmatrix} \varepsilon(k) + \Sigma(k, \infty) & \mathbf{U}^+(k; k'_a, q') & \mathbf{U}^-(k; k'_r, q') \\ (\mathbf{U}^+(k; k'_a, q))^\dagger & F^+(k; k'_a, q, k'_a, q') & \mathbf{0} \\ (\mathbf{U}^-(k; k'_r, q))^\dagger & \mathbf{0} & F^-(k; k'_r, q, k'_r, q') \end{bmatrix} \cdot \begin{bmatrix} \mathbf{X}_1(k) \\ \mathbf{X}_3^+(k; k'_a, q') \\ \mathbf{X}_3^-(k; k'_r, q') \end{bmatrix} \\ = \begin{bmatrix} E_1(k) & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & E_3^+(k; k'_a, q, k'_a, q') & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & E_3^-(k; k'_r, q, k'_r, q') \end{bmatrix} \cdot \begin{bmatrix} \mathbf{X}_1(k) \\ \mathbf{X}_3^+(k; k'_a, q') \\ \mathbf{X}_3^-(k; k'_r, q') \end{bmatrix}, \quad (71)$$

with  $F^\pm = K^\pm + C^\pm$ . In the above equation, the following notation has been introduced to remind us that the (formally discrete) secondary momentum variables must be contracted through matrix multiplications, as follows:

$$A(k; k', k'') \cdot B(k; k', k'') \\ = \sum_{k'} \sum_{k''} A(k; k', k'') B(k; k', k''). \quad (72)$$

In Eq. (71),  $E_1(k)$  is a diagonal matrix of dimension  $M_0$ , with  $M_0$  the size of the basis of atomic functions in the reference unit cell. For an infinitely large stereoregular polymer, the eigenvalues contained in this matrix provide a correlated electron band structure in the form of  $M_0$  quasicontinuous series in  $k$ -space of one-electron binding energies. From Eq. (71), it further clearly appears that at the level of a through-third-order treatment in electron correlation such as ADC(3), each of the one-hole or one-particle eigenstates contained in these energy dispersion bands must be accompanied in the thermodynamic limit ( $N_0 \rightarrow \infty$ ) by a double continuum of  $2h - 1p$  shake-up or  $2p - 1h$  shake-on satellites. These are described by the eigenenergies contained in diagonal matrices ( $E_3^+(k; k'_a, q, k'_a, q')$  and  $E_3^-(k; k'_r, q, k'_r, q')$ ), respectively which are cast over two pairs of secondary momentum variables and are formally therefore of dimension proportional to  $N_0^2$ .

In straightforward analogy with molecular ionization or electron attachment spectra, all one-electron,  $2p - 1h$ , or  $2h - 1p$  energy dispersion bands of the polymer can be further described by a  $k$ -dependent pole strength that, regardless of cross-section

effects, amounts to an intensity function. In the framework of schemes such as ADC(3), pole strengths are derived from the Feynman–Dyson transition amplitudes contained in the set of eigenvectors  $\mathbf{X}_1(k)$ :

$$\Gamma_n(k) = \sum_{i=1}^{M_0} |\mathbf{X}_{1, in}(k)|^2 \leq 1. \quad (73)$$

$\Gamma_n(k)$  must obviously be nonvanishing for all cation or anion states resulting from a one-electron ionization or electron attachment process (for these states,  $\Gamma_n(k) = 1$ ,  $\forall n, k$ , and  $E_1(k) = \varepsilon(k)$  at the HF level). At the ADC(3) level, such states are in practice identified by pole strengths larger than  $\sim 0.80$ . On the other hand, because the coupling amplitudes  $\mathbf{U}(k; k'_a, q)$  between the  $1h$  and  $2h - 1p$  shake-up states scale like  $(N_0)^{-1}$ , it follows from Eq. (73) that the fraction of ionization intensity borrowed individually by a given shake-up state is vanishingly small [as  $(N_0)^{-2}$ ] in the limit of an infinitely large stereoregular chain. Note that for any specific value of  $k$  the total ionization intensity dispersed in shake-up states for a given one-electron eigenstate  $\phi_n(k)$  remains finite in the thermodynamic limit because the number of  $2h - 1p$  satellites associated with this state is precisely proportional to  $(N_0)^{+2}$ .

This conclusion is consistent with a number of investigations at the  $1p$ -GF/ADC(3) level of the ionization properties of oligomer series of molecular compounds of increasing size, such as model hydrogen chains [53],  $n$ -alkanes [54, 55], polyenes [56], carbon clusters [57], or polyacenes [50]. The

reader is referred in particular to a Block–Lanczos investigation [55] of the correlation bands in the ionization spectrum of  $C_nH_{2n+2}$  compounds. For these compounds, the extent of the shake-up fragmentation of ionization bands remains limited to the first one-electron levels in the inner-valence region and the correlation bands encompass therefore a number of lines practically proportional to  $n^2$ , whereas the individual shake-up intensities scale overall as  $n^{-2}$  for  $n \geq 4$ .

### Size Consistency in the Dissociation Limit

When switching off intercell interactions in a stereoregular polymer, which is equivalent to assuming that the system dissociates into  $N_0$  equivalent (closed-shell) fragments under the implicitly maintained constraints of translation symmetry and cyclic boundaries, the summations over cell indices in Eq. (64) can be restricted to the reference unit cell (0). In this limit (shortly,  $a_0 \rightarrow \infty$ ), the band structure is completely flat, i.e., does not show any dispersion in  $k$  [ $\varepsilon(k) = \varepsilon(0)$ ,  $C(k) = C(0)$ ;  $\forall k \in BZ$ ]. This implies a degeneracy of order  $N_0$  among the Bloch one-electron eigenstates describing the system in a delocalized picture. Therefore, all the needed bielectron integrals reduce to expressions of the form

$$\lim_{a_0 \rightarrow \infty} \langle \phi_l(k_l) \phi_m(k_m) | \phi_n(k_n) \phi_o(k_o) \rangle = (N_0)^{-1} \delta_{(k_n+k_o-k_l-k_m)} \tau_0 \begin{pmatrix} 0 & 0 \\ l & m \end{pmatrix} \begin{pmatrix} 0 & 0 \\ n & o \end{pmatrix}, \quad (74)$$

with

$$\tau_0 \begin{pmatrix} 0 & 0 \\ l & m \end{pmatrix} \begin{pmatrix} 0 & 0 \\ n & o \end{pmatrix} = \sum_{pqrs}^{M_0} C_{pl}^*(0) C_{qn}(0) C_{rm}^*(0) C_{so}(0) \times \langle \gamma_p^0 \gamma_r^0 | \gamma_q^0 \gamma_s^0 \rangle, \quad (75)$$

which is the equivalent of a molecular constant. More specifically, the latter is a bielectron integral over molecular orbitals localized within the reference fragment. The  $(N_0)^{-1}$  factor in Eq. (74), therefore, is obviously the direct outcome of the delocalization of the canonical orbitals over  $N_0$  distinct and noninteracting unit cells. Therefore, in the dissociation limit ( $a_0 \rightarrow \infty$ ) the coupling amplitudes and configuration interactions of Eqs. (67)–(69) are

(dropping for simplicity the constraints on momenta) correspondingly expressed in terms of molecular constants,

$$K_{ars,a'r's'}^{+(0)}(k; k_a, q, k'_a, q') = K_{ars,a'r's'}^{+(0)}(0; 0, 0, 0, 0) = K_{ars,a'r's'}^{+(0)}|_0 \quad (76)$$

$$C_{ars,a'r's'}^{+(1)}(k; k_a, q, k'_a, q') = C_{ars,a'r's'}^{+(1)}(0; 0, 0, 0, 0) = (N_0)^{-1} C_{ars,a'r's'}^{+(1)}|_0 \quad (77)$$

$$U_{ars,j}^{+(2)}(k; k_a, q) = U_{ars,j}^{+(2)}(0; 0, 0) = (N_0)^{-1} U_{ars,j}^{+(2)}|_0, \quad (78)$$

which are precisely the matrix elements encompassed in the EOM(3) or ADC(3) secular equations for the reference molecular fragment.

$$K_{ars,a'r's'}^{+(0)}|_0 = (\varepsilon_r(0) + \varepsilon_s(0) - \varepsilon_a(0)) \delta_{rr'} \delta_{ss'} \delta_{aa'} \quad (79)$$

$$C_{ars,a'r's'}^{+(1)}|_0 = \frac{1}{2} \delta_{aa'} \tau_0 \begin{pmatrix} 0 & 0 \\ s & r \end{pmatrix} \begin{pmatrix} 0 & 0 \\ s' & r' \end{pmatrix} - \delta_{rr'} \tau_0 \begin{pmatrix} 0 & 0 \\ s & a' \end{pmatrix} \begin{pmatrix} 0 & 0 \\ s' & a \end{pmatrix} - \delta_{ss'} \tau_0 \begin{pmatrix} 0 & 0 \\ r & a' \end{pmatrix} \begin{pmatrix} 0 & 0 \\ r' & a \end{pmatrix} \quad (80)$$

$$U_{ars,j}^{+(2)}|_0 = \tau_0 \begin{pmatrix} 0 & 0 \\ s & r \end{pmatrix} \begin{pmatrix} 0 & 0 \\ j & a \end{pmatrix} + \frac{1}{2} \sum_{bc} \frac{\tau_0 \begin{pmatrix} 0 & 0 \\ s & r \end{pmatrix} \begin{pmatrix} 0 & 0 \\ b & c \end{pmatrix} \tau_0 \begin{pmatrix} 0 & 0 \\ b & c \end{pmatrix} \begin{pmatrix} 0 & 0 \\ j & a \end{pmatrix}}{\varepsilon_b(0) + \varepsilon_c(0) - \varepsilon_r(0) - \varepsilon_s(0)} - (1 - P_{rs}) \sum_{bt} \frac{\tau_0 \begin{pmatrix} 0 & 0 \\ s & t \end{pmatrix} \begin{pmatrix} 0 & 0 \\ a & b \end{pmatrix} \tau_0 \begin{pmatrix} 0 & 0 \\ b & r \end{pmatrix} \begin{pmatrix} 0 & 0 \\ j & t \end{pmatrix}}{\varepsilon_a(0) + \varepsilon_b(0) - \varepsilon_s(0) - \varepsilon_t(0)}. \quad (81)$$

Note that in the latter equation one of the  $(N_0)^{-1}$  factors arising from the bielectron interactions has been cancelled out by one summation over electron momenta because Bloch eigenstates are  $(N_0)$ -tuply degenerate in the  $a_0 \rightarrow \infty$  limit.

Also, in this limit, the block diagonalization in  $k$  of the CO-1pGF/ADC(3) secular Eq. (71) implies a decoupling into  $N_0$  strictly equivalent eigenvalue problems  $[H(k)X(k) = X(k)E(k) \equiv H(0)X(0) = X(0)E(0); \forall k \in BZ]$ , one for each irreducible representation of the translation symmetry group. The one-electron energies and the associated pole strengths in the ionization and electron attachment

spectra of the dissociated polymer will therefore be  $(N_0)$ -tuply degenerate. As required by the principle of size consistency for size-intensive properties, these quantities are also independent of  $N_0$ , as is easily shown by an order-by-order analysis of the involved self-energies or one-electron densities. Taking as a main example the dynamic self-energy of Eq. (35), the first term in this power series reduces indeed in the dissociation limit into an expression of the type

$$\lim_{a_0 \rightarrow \infty} (\mathbf{U}_i^+(k))^+ (\omega - \mathbf{K}(k)^+)^{-1} \mathbf{U}_j^+(k) = \frac{1}{2} (N_0)^{-2} \sum_{k_a} \sum_q \sum_{ars} \frac{U_{i,ars}^* |0 U_{ars,j}|_0}{\omega + \varepsilon_a(0) - \varepsilon_r(0) - \varepsilon_s(0)}, \quad (82)$$

which is obviously independent of  $N_0$  because the double summation on momenta strictly results in a  $(N_0)^2$  factor in the  $a_0 \rightarrow \infty$  limit. Proceeding further, it is easy to see that this balance between the delocalization (i.e., normalization) and multiplicity properties of one-electron eigenstates will be maintained at all orders of the expansion because, with regard to the scaling properties of the configuration interactions and the constraints on momenta in Eq. (68), only one further summation over a free independent momentum variable is introduced together with an additional  $(N_0)^{-1}$  factor at each iteration over  $\mathbf{C}^\pm$  in Eq. (35).

In sharp contrast with the one-electron components of the ionization or electron attachment spectra, the shake-up or shake-on eigenspectra derived from Eq. (71) will exhibit a degeneracy of order  $(N_0)^3$  in energy and intensity, as the  $\mathbf{U}^+(k; k'_a, q')$  or  $\mathbf{U}^-(k; k'_r, q')$  vectors of coupling amplitudes of Eq. (78). As the satellite intensities individually scale like  $(N_0)^{-2}$ , according to Eqs. (73) and (78), it follows that the total intensity recovered for a given band excitation pattern is exactly proportional to  $N_0$ , as it should, demonstrating thereby the size consistency of the ADC(3) scheme for the treatment of satellites of a multiple set of molecules in a delocalized, i.e., canonical, picture (in photoionization experiments on gas-phase samples, the intensity recovered at a given binding energy is indeed obviously a linear function of the molecular concentration in the vacuum chamber of the spectrometer).

## Issue of Charge Consistency in Inhomogeneous Systems

Whatever the starting zeroth-order approximation, severe size-related difficulties must be anticipated with bielectron interactions of the  $\langle ij | ij \rangle$  type [42] when switching back long-range interactions in a canonical scheme based on orthonormal orbitals. Regardless of the associated  $N_0^{-1}$  normalization factor, these interactions, in the limit of an extended periodic system, can by proper use of translation symmetry be expanded according to the following expression:

$$\tau \begin{pmatrix} k & k' \\ i & j \end{pmatrix} \begin{vmatrix} k & k' \\ i & j \end{vmatrix} = \sum_{pqrs}^{M_0} C_{pi}^*(k) C_{qj}(k) C_{ri}^*(k') C_{sj}(k') \times \sum_{\mu\mu'\mu''}^{N_0} \left[ e^{i[k\mu+k'\mu'']a_0} \langle \gamma_p^0 \gamma_r^{\mu'} | \gamma_q^{\mu} \gamma_s^{\mu'+\mu''} \rangle - e^{i[(k-k')\mu+k''[\mu'-\mu'']]a_0} \langle \gamma_p^0 \gamma_r^{\mu'+\mu''} | \gamma_q^{\mu} \gamma_s^{\mu} \rangle \right], \quad (83)$$

in which the direct and exchange contributions have been separated at the level of the lattice summations. Assuming that atomic primitives exhibit an exponential decay in the asymptotic region, the lattice summations over the cell indices  $\mu$  and  $\mu''$  are, in the case of the direct contribution, rapidly converging because the terms involved in these summations decay like  $e^{-\mu a_0}$  and  $e^{-\mu'' a_0}$ , as the corresponding charge distributions  $(\gamma_p^0 \gamma_q^{\mu})$  and  $(\gamma_r^{\mu'} \gamma_s^{\mu'+\mu''})$ , respectively. Similarly, for the exchange term the exponential decay of the charge distributions  $(\gamma_p^0 \gamma_s^{\mu''})$  and  $(\gamma_r^{\mu'+\mu''} \gamma_q^{\mu})$  ensures a fast convergence of the lattice summations over  $\mu'$  and  $\mu''$ .

When evaluating the exchange part of Eq. (83), some care is needed to handle the remaining summation over  $\mu$  because it relates to Coulomb interactions between the charge distributions  $(\gamma_p^0 \gamma_s^{\mu''})$  and  $(\gamma_r^{\mu'+\mu''} \gamma_q^{\mu})$ , which slowly decay as  $\mu^{-1}$ . In this case, the preceding phase factor  $e^{-i(k-k')\mu a_0}$  prevents a logarithmic divergence, except at the singularity  $k = k'$ . In straightforward analogy with the treatment of the exchange pathologies at the HF level [32, 37–41], the integration over these singularities can always be exactly performed by resorting to Fourier analysis techniques. In the case of the ADC(3) scheme, because of the orthonormality of Bloch states this difficulty is only encountered [42] with the direct contribution to the “ladder” ( $\langle sr | sr' \rangle$  and  $\langle ab | a'b' \rangle$ ) renormalization terms contained in the matrices of energy shifts  $\mathbf{C}^\pm$  [Eq. (38)] and because of the exchange contribution to the



“loop” or “RPA” ( $\langle sa' | | s'a \rangle, \dots$ ) renormalization terms in the same matrices. A specific combination of diagonalization and Fourier transform algorithms will therefore be required to consistently overcome these difficulties by careful integrations over the secondary momentum variables  $q$  and  $q'$  or  $k_i$  and  $k'_i$  ( $i = a, r$ ) in Eq. (71).

Further size-related difficulties can be expected for the direct term in the electron interaction of Eq. (83) because the lattice summation over  $\mu'$  similarly runs over interaction terms decaying as  $\mu'^{-1}$ , but this time without any  $\mu'$ -dependent phase factor to ensure the convergence after integration in  $k$ -space. Therefore, whatever the relative values of  $k$  and  $k'$ , this term will, slowly but surely, diverge [42] with the number of unit cells,  $N_0$ . In many-body perturbation theory, such a divergence problem would become apparent with contributions to the energy per unit cell of a few vacuum amplitude diagrams of fifth order and beyond in electron correlation. In one-electron Green's theory, this intricate situation is already encountered at third order and occurs via the static self-energies [42, 43] or, in the ADC(3) scheme, via the corresponding inhomogeneities  $b$  [43] [Eq. (44)]. For an extended periodic chain, these quantities are indeed obtained from expressions of the type

$$\left. \begin{aligned} &\Sigma_{ij}(k, \infty) \\ &b_{ij} \end{aligned} \right\} = \sum_{lm} \sum_{k'} \langle \phi_i(k) \phi_l(k') | | \phi_j(k) \phi_m(k') \rangle Q_{ml}(k'), \quad (84)$$

in which the summation over  $k'$  systematically runs over logarithmically divergent Coulomb interactions, when  $l$  and  $m$  are equal to  $i$  and  $j$ , respectively. With regard to the absence of any phase factor for damping the divergence, it is tempting to compare this situation with the case of a classic resonance [42]. Restricting the summations over band indices to these diagonal and dominant terms, the convergence properties of Eq. (84) will follow those of

$$\begin{aligned} &\sum_l \sum_{k'} \langle \phi_i(k) \phi_l(k') | | \phi_i(k) \phi_l(k') \rangle Q_{ll}(k') \\ &= N_0^{-1} \sum_l \sum_{k'} Q_{ll}(k') \sum_{pqrs} C_{pi}^*(k) C_{qi}(k) C_{rj}^*(k') C_{sj}(k') \\ &\quad \times \sum_{\mu\mu'\mu''}^{N_S} e^{i[k\mu+k'\mu'']a_0} \langle \gamma_p^0 \gamma_r^{\mu'} | \gamma_q^{\mu} \gamma_s^{\mu'+\mu''} \rangle + \text{L.R.}, \quad (85) \end{aligned}$$

where L.R. represents the contribution arising from long-range interactions in the asymptotic region ( $\mu' \gg \mu, \mu'' \rightarrow \infty$ ):

$$\text{L.R.} = (N_0)^{-1} \sum_l \sum_{k'} Q_{ll}(k') \sum_{\mu' > N_S}^{N_0} \frac{1}{|\mu' a_0 \vec{e}_z|}. \quad (86)$$

The static self-energy [or the corresponding inhomogeneities in the ADC(3) scheme] will therefore diverge unless

$$\Delta N = \text{tr}(\mathbf{Q}) = \sum_l \sum_{k'} Q_{ll}(k') = 0. \quad (87)$$

As is well known [13], the trace of a one-electron density matrix is the ground-state expectation value of the particle number operator

$$\hat{N} = \sum_i a_i^+ a_i, \quad (88)$$

which corresponds to the exact particle number,  $N$ , if the HF or the exact one-electron density is used. Any approximated correction to the HF ground-state density may yield a possible error in the calculated number of particles,  $\Delta N$  [73]. From the presence of one summation over  $k'$  in Eq. (87), this violation in the particle number, if it occurs, is size extensive, i.e., proportional to  $N_0$  in the dissociation limit.

At this stage, it is useful to recall that for extended systems electroneutrality is an essential condition for turning individually divergent summations over nuclear attraction and Coulomb repulsion–repulsion terms into conditionally convergent Madelung series [22]. The requirement of cell electroneutrality in extended inhomogeneous systems is, for instance, clearly apparent in the analysis by Nooijen and Bartlett [49], whereas the electroneutrality constraint at any point of homogeneous systems was exploited long ago by Fetter and Walecka [7] to demonstrate the mutual cancellation of divergent terms in the Hamiltonian. In this context, any violation in the number of electrons and hence of the electroneutrality of the system implies that a spurious long-range electrostatic potential originates from each unit cell, which, in the thermodynamic limit, must obviously result into diverging results for the static self-energies. Correspondingly, a violation of size extensivity can also be anticipated for the total energy of the system. An important, but usually neglected, requirement for

the size intensivity or size extensivity of results obtained by means of advanced Green's function schemes is therefore that of charge consistency, i.e., the preservation of the exact particle number via the condition embodied in Eq. (87).

This requirement is also crucial in Green's function theories of scattering processes [62] because in this context a violation of the particle number implies that the static self-energy presents a spurious behavior at large projectile-target distances [73]:

$$\Sigma(\infty, \tilde{r}, \tilde{r}') \rightarrow \delta(\tilde{r} - \tilde{r}') \frac{\text{tr}(\mathbf{Q})}{|\tilde{r}|}. \quad (89)$$

Obviously, alterations of the electric charge of a molecule can also have serious implications when evaluating its response properties (e.g., polarizability, magnetizability, electric and magnetic shieldings, nuclear spin-spin coupling constants, optical activities, ...) to an external electric or magnetic perturbation. For instance, within the framework of the so-called coupled-perturbed one-electron propagator (CPEP) theory [74–77] the static dipole-dipole electric polarizability is dependent on the gauge, i.e., on the origin  $\tilde{r}_0$  with respect to which the dipole matrix elements  $D_{pq}$  are calculated in a molecular orbital basis:

$$\alpha = \text{tr}[\mathbf{D}\rho^{[1]}] = \sum_{pq} \langle \phi_p | \tilde{r} | \phi_q \rangle Q_{pq}^{[1]} - \tilde{r}_0 \text{tr}(\rho^{[1]}) \quad (90)$$

except if  $\text{tr}(\rho^{[1]})$  identically vanishes, as it should [76, 77]. Here,  $\rho^{[1]}$  describes the variations induced at first order by an external static homogeneous electric field in the exact one-electron density, which is formally obtained via

$$\rho^{[1]} = \frac{1}{2\pi i} \oint_C d\omega G^{[1]}(\omega), \quad (91)$$

with  $G^{[1]}(\omega)$  the first-order component of the exact Green's function in a power series over the external field.

In general, in Rayleigh–Schrödinger perturbation theory the wave function is normalized up to the last complete order attained in the expansion. Nonvanishing contributions to the particle number must therefore identically cancel [43, 76] at each order of the expansion. For instance, from the series of Eqs. (41) the charge consistency of the second-order RSPT one-electron density, and correspond-

ingly the size intensivity of the third-order static self-energy, are obviously ensured by the cancellation of the contributions of one pair of terms relating to the self-energy antigraphs  $A_1$  and  $A_2$  of Ref. [16c]:

$$\text{tr}[\mathbf{Q}^{(2)}] = \text{tr}[\mathbf{Q}_1^{(2)}] + \text{tr}[\mathbf{Q}_2^{(2)}] = 0. \quad (92)$$

Correspondingly, at second order in correlation the charge consistency of the first-order (in the external field) CPEP one-electron density and the gauge invariance of the corresponding electric or magnetic linear responses is ensured by the cancellation of 30 nonvanishing terms to  $\text{tr}[\rho^{[1](2)}]$  in four pairs and eight triplets of perturbed one-electron density diagrams [76]. When evaluating these traces, it is immediately apparent that an essential ingredient in the charge consistency of these second-order (unperturbed or perturbed) one-electron densities is the antisymmetry of the zeroth-order double-excitation and deexcitation energies related to the  $(\varepsilon_r - \mathbf{K}^{(0)-} - \mathbf{C}^{(0)-})^{-1}$  and  $(\varepsilon_a - \mathbf{K}^{(0)+} - \mathbf{C}^{(0)+})^{-1}$  matrix inverses, respectively, under an interchange of the particle and hole labels. It follows therefore that asymmetrical schemes (Table I) such as NR2 and SH2 would certainly not enable charge-consistent computations of one-electron densities, if they would be used for such purposes.

In sharp contrast with order-by-order expansions, it is also a priori impossible to guarantee the preservation of the exact particle number with expansion schemes based on a renormalization of  $\mathbf{M}^+$  and  $\mathbf{M}^-$ , as for instance ADC(2) and ADC(3), because infinite but incomplete series of higher-order contributions are incorporated. However, upon inspection of the series of Eqs. (46), for instance, it immediately appears that only two terms of opposite sign contribute to the particle number at the ADC(3) level. These terms do not necessarily exactly cancel because of the first-order energy shifts and configuration interactions embodied in the  $\mathbf{C}^\pm$  matrices, and  $\text{tr}[\mathbf{Q}^{(\text{ADC}3)}]$  might be nonvanishing. With the ADC(3) scheme, however, the error in charge consistency is of fourth order because the one-electron density is consistently recovered through third order in electron correlation. Correspondingly, the deviation from size intensivity for the static part of the ADC(3) self-energy is of fifth order and can therefore be expected to be barely noticeable in standard molecular applications. It can nonetheless be stated that, according to Eqs. (86) and (87), any failure to the requirement of size

TABLE II

Violation ( $\Delta N$ ) of the particle number with the standard ADC(3) scheme and average impact ( $\Delta I/P$ ) of the rescaling described by Eq. (94) on the computed one-electron ionization energies.

Compound	$N^a$	Basis set	$\Delta N$	$\Delta N/N$	$\Delta I/P$ (eV)
Polyacenes					
Benzene (C <sub>6</sub> H <sub>6</sub> )	30	STO-3G	$-4.577 \cdot 10^{-4}$	$-1.526 \cdot 10^{-5}$	-0.011
		6-31G	$-3.411 \cdot 10^{-4}$	$-1.138 \cdot 10^{-5}$	-0.007
		6-31G*	$+2.330 \cdot 10^{-4}$	$+7.77 \cdot 10^{-6}$	+0.005
		6-31G**	$+2.553 \cdot 10^{-4}$	$+8.51 \cdot 10^{-6}$	+0.005
		6-311G**	$+5.559 \cdot 10^{-5}$	$+1.85 \cdot 10^{-6}$	+0.001
Naphthalene (C <sub>10</sub> H <sub>8</sub> )	48	6-31G	$-4.682 \cdot 10^{-4}$	$-9.75 \cdot 10^{-6}$	-0.008(5)
		cc-pVDZ	$+2.177 \cdot 10^{-4}$	$+4.53 \cdot 10^{-6}$	+0.004
Anthracene (C <sub>14</sub> H <sub>10</sub> )	66	6-31G	$-6.725 \cdot 10^{-4}$	$-1.019 \cdot 10^{-5}$	-0.010
Naphthacene (C <sub>18</sub> H <sub>12</sub> )	84	6-31G	$-6.313 \cdot 10^{-4}$	$-7.51 \cdot 10^{-6}$	-0.008
Pentacene (C <sub>22</sub> H <sub>14</sub> )	102	6-31G	$-1.171 \cdot 10^{-3}$	$-1.148 \cdot 10^{-5}$	-0.014
Angular benzologs					
Azulene (C <sub>10</sub> H <sub>8</sub> )	48	6-31G	$-4.35 \cdot 10^{-4}$	$-9.062 \cdot 10^{-6}$	-0.007
Phenanthrene (C <sub>14</sub> H <sub>10</sub> )	66	6-31G	$-5.63 \cdot 10^{-4}$	$-8.53 \cdot 10^{-6}$	-0.008
Pyrene (C <sub>16</sub> H <sub>10</sub> )	74	6-31G	$-5.49 \cdot 10^{-4}$	$-7.42 \cdot 10^{-6}$	-0.008
Chrysene (C <sub>18</sub> H <sub>12</sub> )	84	6-31G	$-6.80 \cdot 10^{-4}$	$-8.095 \cdot 10^{-6}$	-0.009
Triphenylene (C <sub>18</sub> H <sub>12</sub> )	84	6-31G	$-5.84 \cdot 10^{-4}$	$-6.952 \cdot 10^{-6}$	-0.008

<sup>a</sup> Valence electrons only.

consistency and size intensivity should, surely but slowly, grow with system size, an assertion that has been verified with extensive series of tests on model hydrogen chains with large band gap [43]. With oligomers converging to conducting polymers, trends may complicate owing to the closure of the fundamental band gap and the presence of shake-up and shake-on states at low binding energies.

The impact of charge inconsistencies in the standard ADC(3) scheme has been evaluated in Table II for a series of polycyclic aromatic hydrocarbons, using different standard basis sets, by comparison with improved ADC(3) calculations performed using a rescaled and truly charge-consistent form of  $Q$  [43]:

$$\tilde{Q}_{ml} = \frac{N}{N + \text{tr}(Q)} \left[ Q_{ml} - n_m \delta_{ml} \frac{\text{tr}(Q)}{N} \right]. \quad (93)$$

The reader is referred to Ref. [50] for a detailed presentation (geometries, thresholds, ...) of these computations. It has been noted in this study that the above rescaling leads to small and practically uniform shifts of one-electron ionization lines ( $\Gamma > 0.7$ ) by, depending on the basis set (Table II), a few thousandths up to one hundredth of an eV. The rescaling has further practically no discernable ef-

fect on the shake-up lines with low intensity ( $\Gamma < 0.10$ ). As can be seen from Table II, standard ADC(3) computations with the minimal STO-3G and split-valence 6-31G basis lead to a slightly negative violation [ $\Delta N < 0$ ] of the total number of electrons. This implies that the ADC(3) corrections to the HF ground electron density make the molecule slightly positive, hence a minor overestimation of one-electron binding energies compared with the charge-consistent scheme. On the contrary, the violation of the particle number reverses to a small electron excess [ $\Delta N > 0$ ] when carrying out the standard ADC(3) calculations with polarized basis sets, which correspondingly results in slightly too low ionization energies. Focusing on the results obtained for benzene, it appears that in absolute value the largest charge violation occurs with the STO-3G basis. Obviously, improving the quality of the basis by incorporation of further valence and polarization shells helps limit the extent of the charge violations. In the polyacene series, these charge violations and their impact on the one-electron binding energies tend overall to increase with system size. At the ADC(3)/6-31G level, the largest charge defect ( $1.171 \cdot 10^{-3} e^-$ ) is noticed for pentacene, which implies (Table II) an average overestimation of one-electron ionization energies by 0.014 eV only.

## Conclusions and Outlook for the Future

Green's function methods, and many-body diagrammatic methods in general [13], were first developed for the study of continuous media, where the properties of interest are extensive or intensive, i.e., proportional to or independent of system size in the thermodynamic limit, respectively. Rather than size dependencies, the issue of most common interest in quantum chemistry is that of size consistency, i.e., the separability of the computed observables (or wave functions) upon dissociation in non-interacting fragments. Size consistency derives from the linked-cluster properties of these methods and can be related to the possibility to freely transform to a localized picture [13]. In this framework, the linked-cluster theorem guarantees the absence of "nonlocal" excitations in the secular equations, which ensures an equivalent treatment of "local" excitations in the whole system or in the fragments alone. Because in extended periodic and inhomogeneous systems such as stereoregular polymers or crystalline solids the total Hamiltonian can be expanded in terms of conditionally convergent Madelung summations, it is most often believed that size consistency in the dissociation limit straightforwardly ensures the correct scaling with system size, from "small" molecules up to the thermodynamic limit.

However, a major difference between inhomogeneous and homogeneous systems is that, in the latter case, a zeroth-order approximation (e.g., HF) to the one-electron density necessarily differs from the exact one-electron density because of electron correlation, whereas in homogeneous systems these densities are obviously equal. In one-particle Green's function theory, correlation corrections to the ground-state one-electron density gives rise to a troublesome static (frequency-independent) contribution to the self-energy. From the analysis described in [43] and revised in the present contribution, it appears that an essential requirement for the correct (i.e., size-intensive) scaling of the static self-energies and, thus, ionization energies in large inhomogeneous systems is that of charge consistency, namely, the preservation of the exact particle number upon correlation corrections to the zeroth-order (HF) ground-state one-electron densities. The ADC(3) scheme on which this study focuses is charge consistent through third order in electron correlation and enables thus a treatment of ioniza-

tion or electron attachment spectra that is size intensive through fourth order. Understandably, therefore, the deviations from charge consistency and size intensivity are with this scheme barely noticeable in applications on small to mid-sized systems ( $<0.02$  eV for a system as large as pentalene).

Obviously, the requirement of charge consistency in one-electron densities is also of relevance with Green's function or propagator schemes designed for characterizing electronic transitions (electron excitation, double ionization, ...) of any type beyond third order in correlation. Another implication of a failure to this requirement can be the loss of the gauge invariance of computed properties such as the electric polarizability, magnetizability, ... in theories of molecular responses based on perturbed forms of the one-particle Green's function. If the violation is not too severe, as with ADC(3), it can always be compensated by an ad hoc rescaling procedure of the one-electron densities.

In a canonical picture, size consistency in investigations of correlation bands implies that a balance must prevail both in the dissociation and thermodynamic limits between the number of satellites and the strength of configuration interactions between the main ( $1h$ ,  $1p$ ) and secondary (shake-up or shake-on) states in the cation or anion. For large molecular chains comprising  $n$  equivalent vertices, this balance can be physically traced from the size-dependence properties of the lines encompassed in these bands: Each one-electron level (orbital) gives rise to  $n^2 2h - 1p$  or  $2p - 1h$  satellites with intensity proportional to  $n^{-2}$  and the total ionization intensity to recover by convolution is proportional to  $n$  (i.e., size extensive). Correspondingly, in the limit of a chain dissociating in  $N_0$  independent and identical fragments shake-up states are  $(N_0)^3$ -tuply degenerate, with individual intensities proportional to  $(N_0)^{-2}$ .

With regard to these scaling properties, the computation of satellite bands in the ionization spectra of large or extended systems is therefore certainly not a trivial task. In further implementations of the ADC(3) scheme based on crystalline orbitals, an ideal way to tackle this problem would be to resort to Block-Lanczos diagonalization procedures [78], which are known to preserve the correct moments of the spectra and are thus precisely suited for investigating dense spectra. Further size-related complications can also be expected because of the diagonal terms in the matrices accounting for shake-up/shake-up or shake-on/shake-on configu-

rations, which give rise to singularities in the double integrations over electron momenta that are required to diagonalize the ADC(3) secular matrix in the formalism of crystalline orbitals. The convergence properties of the coefficients of the Fourier series underlying these integrations should therefore be carefully analyzed.

### ACKNOWLEDGMENTS

The author acknowledges financial support from the "Fonds voor Wetenschappelijk Onderzoek van Vlaanderen," the Flemish branch of the Belgian national science foundation, and from the "Bijzonder OnderzoeksFonds" of the Limburgs Universitair Centrum (LUC), Belgium. He is indebted to Profs. J. Delhalle (FUNDP-Namur, Belgium), B. T. Pickup (University of Sheffield, UK), J. Schirmer, and L. S. Cederbaum (University of Heidelberg, Germany) for stimulating discussions on extended systems and Green's function theories. The kind help of Prof. J.-P. Francois (LUC) and Dr. A. B. Trofimov (Irkutsk State University, Russian Federation) is also thankfully acknowledged. The computations presented in this work have been carried out on a DEC alpha 1200 station (dual processor 533-Mhz, 2-Gb core memory, 40-Gb disk space) at the Limburgs Universitair Centrum, Belgium, using the original ADC(3) code by G. Angonoa, M. K. Scheller, and J. Schirmer (contributions by A. B. Trofimov).

### References

1. Pople, J. A.; Binkley, J. S.; Seeger, R. *Int J Quantum Chem* 1976, S10, 1.
2. Brueckner, K. A. *Phys Rev* 1955, 100, 36.
3. Goldstone, J. *Proc Roy Soc Lond* 1957, 239, 267.
4. Brandow, B. H. *Rev Mod Phys* 1967, 39, 771.
5. Brueckner, K. A. *Phys Rev* 1955, 97, 1353.
6. March, N. H.; Young, W. H.; Sampatar, S. *The Many-Body Problem in Quantum Mechanics*; Cambridge University Press: Cambridge, MA, 1967 (also available as Dover reprint: New York, 1995).
7. Fetter, A. L.; Walecka, J. D. *The Quantum Mechanics of Many Particle Systems*; McGraw-Hill: New York, 1971.
8. Kelly, H. P. *Adv Chem Phys* 1969, 14, 129.
9. Freed, K. F. *Annu Rev Phys Chem* 1971, 22, 313.
10. Wilson, S. *Electron Correlation in Molecules*; Clarendon Press: Oxford, UK, 1984.
11. Hehre, W. J.; Radom, L.; von Ragué Schleyer, P.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley: New York, 1986.
12. Szabo, S.; Ostlund, N. S. *Modern Quantum Chemistry*; McGraw-Hill: New York, 1989.
13. McWeeny, R. *Methods of Molecular Quantum Mechanics*, 2nd Ed.; Academic Press: London, 1989.
14. Bartlett, R. J. *Annu Rev Phys Chem* 1981, 32, 359.
15. Stanton, R. J.; Stanton, J. F. In Lipkowitz, K. B.; Boyd, D. B., Eds. *Reviews in Computational Chemistry*, Vol. 5; VCH Publishers: New York, 1994, pp. 65–169.
16. (a) Cederbaum, L. S.; Hohlneicher, G.; von Niessen, W. *Mol Phys* 1973, 26, 1405; (b) Cederbaum, L. S.; Domcke, W. *Adv Chem Phys* 1977, 36, 205; (c) Cederbaum, L. S.; Domcke, W.; Schirmer, J.; von Niessen, W. *Adv Chem Phys* 1986, 65, 115.
17. (a) Linderberg, J.; Öhrn, Y. *Propagators in Quantum Chemistry*; Academic Press: London, 1973; (b) Öhrn, Y.; Born, G. *Adv Quantum Chem* 1981, 13, 1; (c) Öhrn, Y. *Lect Notes Chem* 1988, 50, 185.
18. Pickup, B. T.; Goscinski, O. *Mol Phys* 1973, 26, 1013.
19. (a) Ortiz, J. V. In Leszczyński, J., Ed. *Computational Chemistry: Reviews of Current Trends*, Vol. 2; World Scientific: Singapore, 1997, p. 1; (b) Ortiz, J. V.; Zakrzewski, V. G.; Dolgounitchcheva, O. In Calais, J.-L.; Kryashko, E., Eds. *Conceptual Perspectives in Quantum Chemistry*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1997, p. 465–517.
20. Tarantelli, A.; Cederbaum, L. S. *Phys Rev A* 1994, 49, 3407.
21. Calais, J.-L.; Pickup, B. T.; Deleuze, M.; Delhalle, J. *Eur J Phys* 1995, 16, 179.
22. Harris, F. E. In Henderson, D.; Eyring, H., Eds. *Theoretical Chemistry Advances and Perspectives*, Vol. 1; Academic: New York, 1975, p. 147–218.
23. Delhalle, J.; Piela, L.; Brédas, J.-L.; André, J.-M. *Phys Rev B* 1980, 22, 6254.
24. Suhai, S. *J Chem Phys* 1980, 13, 3843.
25. Piela, L.; André, J.-M.; Fripiat, J. G.; Delhalle, J. *Chem Phys Lett* 1981, 77, 143.
26. Monkhorst, H.; Kertesz, M. *Phys Rev B* 1981, 24, 3025.
27. Surjan, P. R.; Kertesz, M.; Karpfen, A.; Koller, J. *Phys Rev B* 1983, 27, 7583.
28. Dovesi, R. *Int J Quantum Chem* 1984, 26, 197.
29. Delhalle, J.; Calais, J.-L. *J Chem Phys* 1986, 85, 5286.
30. Fripiat, J. G.; Delhalle, J.; André, J.-M.; Calais, J.-L. *Int J Quantum Chem* 1990, S24, 593.
31. Delhalle, J. *Int J Quantum Chem* 1984, 26, 717.
32. Delhalle, J.; Harris, F. E. *Phys Rev B* 1985, 31, 6755.
33. Delhalle, J.; Calais, J.-L. *Phys Rev B* 1987, 35, 9460.
34. Delhalle, J.; Calais, J. L. *J Phys C Solid State Phys* 1988, 21, L499.
35. Stolarczyk, L. Z.; Jeziorska, M.; Monkhorst, H. J. *Phys Rev B* 1988, 37, 10646.
36. Jeziorska, M.; Stolarczyk, L. Z.; Paldus, J.; Monkhorst, H. J. *Phys Rev B* 1990, 41, 12473.
37. Delhalle, J.; Cizek, J.; Flamant, I.; Calais, J.-L. *J Chem Phys* 1994, 101, 10717.
38. Flamant, I.; Fripiat, J.-G.; Delhalle, J. *Int J Quantum Chem* 1996, S30, 275.
39. Flamant, I.; Fripiat, J.-G.; Delhalle, J. *Int J Quantum Chem* 1997, 63, 709.

40. Flamant, I.; Fripiat, J.-G.; Delhalle, J. *Theor Chem Acc* 1997, 98, 155.
41. Flamant, I.; Fripiat, J.-G.; Delhalle, J. *Int J Quantum Chem* 1998, 70, 1045.
42. Deleuze, M. S.; Delhalle, J.; Pickup, B. T.; Calais, J.-L. *Adv Quantum Chem* 1995, 26, 35.
43. Deleuze, M.; Scheller, M. K.; Cederbaum, L. S. *J Chem Phys* 1995, 103, 3578.
44. Schirmer, J.; Cederbaum, L. S.; Walter, O. *Phys Rev A* 1983, 28, 1237.
45. von Niessen, W.; Schirmer, J.; Cederbaum, L. S. *Comput Phys Rep* 1984, 1, 57.
46. Schirmer, J.; Angonoa, G. *J Chem Phys* 1989, 91, 1754.
47. Weikert, H.-G.; Meyer, H.-D.; Cederbaum, L. S.; Tarantelli, F. *J Chem Phys* 1996, 104, 7122.
48. Sun, J.-Q.; Bartlett, R. J. *J Chem Phys* 1997, 106, 5554.
49. Nooijen, M.; Bartlett, R. J. *Int J Quantum Chem* 1997, 63, 601.
50. (a) Deleuze, M. S.; Trofimov, A. B.; Cederbaum, L. S. *J Chem Phys* 2001, 115, 5859; (b) Deleuze, M. S. *J Chem Phys* 2002, 116, 7012.
51. (a) Cederbaum, L. S.; Hohlneicher, G.; von Niessen, W. *Chem Phys Lett* 1973, 18, 503; (b) Cederbaum, L. S. *Mol Phys* 1974, 28, 479; (c) Cederbaum, L. S. *J Chem Phys* 1975, 62, 2160; (d) Schirmer, J.; Cederbaum, L. S.; Domcke, W.; von Niessen, W. *Chem Phys* 1977, 26, 149; (e) Cederbaum, L. S.; Schirmer, J.; Domcke, W.; von Niessen, W. *Int J Quantum Chem* 1978, 14, 593; (f) Cederbaum, L. S. *J Chem Phys* 1978, 69, 1591; (g) Herman, M. F.; Freed, K. F.; Yeager, D. L. *Chem Phys* 1978, 32, 437; (h) Schirmer, J.; Domcke, W.; Cederbaum, L. S.; von Niessen, W. *J Phys B* 1978, 11, 1901; (i) Domcke, W.; Cederbaum, L. S.; Schirmer, J.; von Niessen, W.; Brion, C. E.; Tan, K. H. *Chem Phys* 1979, 40, 171; (j) Schirmer, J.; Domcke, W.; Cederbaum, L. S.; von Niessen, W.; Åsbrink, L. *Chem Phys Lett* 1979, 61, 30; (k) Cederbaum, L. S.; Domcke, W.; Schirmer, J.; von Niessen, W. *Phys Scripta* 1980, 21, 481; (l) von Niessen, W.; Bieri, G.; Schirmer, J.; Cederbaum, L. S. *Chem Phys* 1982, 65, 157.
52. Liegener, M. S. *Phys Rev B* 1993, 47, 1607.
53. Deleuze, M. S.; Cederbaum, L. S. *Phys Rev B* 1996, 53, 13326.
54. Deleuze, M. S.; Cederbaum, L. S. *J Chem Phys* 1996, 105, 7583.
55. Golod, A.; Deleuze, M. S.; Cederbaum, L. S. *J Chem Phys* 1999, 110, 6014.
56. Deleuze, M. S.; Cederbaum, L. S. *Int J Quantum Chem* 1997, 63, 465.
57. (a) Deleuze, M. S.; Giuffreda, M. G.; François, J.-P.; Cederbaum, L. S. *J Chem Phys* 1999, 111, 5851; (b) Deleuze, M. S.; Giuffreda, M. G.; François, J.-P.; Cederbaum, L. S. *J Chem Phys* 2000, 112, 5325; (c) Deleuze, M. S.; Giuffreda, M. G.; François, J.-P. *J Phys Chem A* 2002, 106, 5626.
58. Goscinski, O.; Lukman, B. *Chem Phys Lett* 1970, 7, 573.
59. (a) Löwdin, P.-O. *Phys Rev* 1965, 139, 357; (b) Löwdin, P.-O. *Int J Quantum Chem* 1977, 12 (Suppl. 1), 197; (c) Löwdin, P.-O. *Int J Quantum Chem* 1982, S16, 485.
60. Dalggaard, E. *Int J Quantum Chem* 1979, 15, 169.
61. (a) Simons, J.; Smith, W. D. *J Chem Phys* 1973, 58, 4899; (b) Purvis, G. D.; Öhrn, Y. *J Chem Phys* 1974, 60, 4063; (c) Simons, J. *Chem Phys Lett* 1974, 25, 122.
62. Cederbaum, L. S. *Ann Phys* 2001, 291, 169, and references therein.
63. (a) Baker, J.; Pickup, B. T. *Chem Phys Lett* 1980, 56, 537; (b) Baker, J.; Pickup, B. T. *Mol Phys* 1983, 49, 651.
64. (a) Coulson, C. A. *Trans Faraday Soc* 1937, 33, 338; (b) Coulson, C. A.; Longuet-Higgins, H. C. *Proc Roy Soc A* 1947, 191, 39.
65. Schirmer, J.; Cederbaum, L. S. *J Phys B* 1978, 11, 1189.
66. Herman, M. F.; Freed, K. F.; Yeager, D. L. *Adv Chem Phys* 1981, 48, 1.
67. Baker, J. *Chem Phys* 1983, 79, 117.
68. Ortiz, J. V.; Zakrzewski, V. G. *J Chem Phys* 1994, 100, 6614.
69. Ortiz, J. V. *J Chem Phys* 1998, 108, 1008.
70. Ortiz, J. V. *Int J Quantum Chem* 1998, 69, 175.
71. Mertins, F.; Schirmer, J.; Tarantelli, A. *Phys Rev A* 1996, 53, 2153.
72. Deleuze, M. S.; Pickup, B. T. *Int J Quantum Chem* 1997, 63, 483.
73. Weikert, H. G.; Cederbaum, L. S. *Few Body Sys* 1987, 2, 33.
74. Pickup, B. T. *Int J Quantum Chem* 1992, S26, 13.
75. Pickup, B. T. *Philos Mag B* 1994, 69, 799.
76. Deleuze, M.; Packer, M. J.; Pickup, B. T.; Wilson, D. J. *J Chem Phys* 1995, 102, 6128.
77. Deleuze, M. S.; Pickup, B. T.; Wilton, D. J. *Int J Quantum Chem* 2000, 77, 625.
78. (a) Parlett, B. N. *The Symmetric Eigenvalue Problem*; Prentice-Hall: Englewood Cliffs, NJ, 1980; (b) Cullum, J. K.; Wiloughby, R. A. *Lanczos Algorithms for Large Symmetric Eigenvalue Computations*; Birkhauser: Boston, 1985.