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Aspects of separability in the coupled cluster based direct methods for energy differences

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Summary. In this paper we have discussed in detail the aspects of separability of the energy differences obtained from coupled cluster based "direct" methods such as the open-shell Coupled Cluster (CC) theory and the Coupled Cluster based Linear Response Theory (CC-LRT). It has been emphasized that, unlike the state energies *per se*, the energy differences have a semi-local character in that, in the asymptotic limit of non-interacting subsystems A, B, C, etc., they are separable as ΔE_A, ΔE_B, $\Delta E_A + \Delta E_B$, etc. depending on the subsystems excited. We classify the direct many-body methods into two categories: core-extensive and core-valence extensive. In the former, we only implicitly subtract the ground state energy computed in a size-extensive manner; the energy differences are not chosen to be valence-extensive (separable) in the semi-local sense. The core-valence extensive theories, on the other hand, are fully extensive – i.e., with respect to both core and valence interactions, and hence display the semi-local separability. Generic structures of the wave-operators for core-extensive and core-valence extensive theories are discussed. CC-LRT is shown to be core-extensive after a transcription to an equivalent wave-operator based form. The emergence of valence disconnected diagrams for two and higher valence problems are indicated. The open-shell CC theory is shown to be core-valence extensive and hence fully connected. For one valence problems, the CC theory and the CC-LRT are shown to be equivalent. The equations for the cluster amplitudes in the Bloch equation are quadratic, admitting of multiple solutions. It is shown that the cluster amplitudes for the main peaks, in principle obtainable as a series in V from the zeroth order roots of the model space, are connected, and hence the energy differences are fully extensive. It is remarkable that the satellite energies obtained from the alternative solutions of the CC equations are not valence-extensive, indicating the necessity of a formal power series structure in V of the cluster amplitudes for the valence-extensivity. The alternative solutions are not obtainable as a power series in V. The CC-LRT is shown to have an effective hamiltonian structure respecting "downward reducibility". A unitary version of CC-LRT (UCC-LRT) is proposed, which satisfy both upward and downward reducibility. UCC-LRT is shown to lead to the recent propagator theory known as the Algebraic Diagrammatic Construction. It is shown that both the main and the satellite peaks from UCC-LRT for the one valence problems are core-valence extensive owing to the hermitized nature of the underlying operator to be diagonalized.

Key words: Separability – CC-based direct methods – Algebraic diagrammatic construction

1. Introduction

The Coupled Cluster (CC) approach has emerged in recent years as providing versatile methodologies for treating many particle correlation in closed [1–4] as well as open-shell [5–31] systems. The last two decades have witnessed significant developments – both formal and computational – towards formulating coupled cluster based "direct" methods [6, 10–18, 21–29] for obtaining energy differences relative to a closed-shell ground state. Since many transition quantities of physico-chemical interest are related to such energy differences as ionization potential (IP), electron affinity (EA), excitation energy (EE) or double ionization potential (DIP), the potential usefulness of coupled cluster based "direct" methods is quite clear.

The efficacy of a cluster expansion representation of a wave-function (or, of the associated wave operator) in ensuring the correct scaling behaviour of the energy seems now to be well appreciated (see, e.g. Refs. [32, 33]). There has been considerable activity in recent years in the development of open-shell CC theories for open-shell states where the extensivity of the state energies obtained are carefully examined (see, e.g. Ref. [33] for an extensive survey). Since in the direct methods, one automatically drops the common correlation terms that are present in the ground and the excited or ionized states, the emphasis is naturally on correctly modelling the *relaxation* and *differential correlation* effects. A study of the scaling behaviour of the *energy differences* relative to the ground state poses more subtle and nontrivial aspects not necessarily encountered in the analysis of the excited state energies themselves.

The aim of this paper is to highlight the recent activities of our group towards discerning and analyzing the nature of extensivity of the energy differences generated by two major classes of the open-shell CC formalisms developed and studied by us. These are the open-shell CC theory for general model spaces [11, 14–16] and the CC-based linear response theory (CC-LRT) [21, 24]. We shall emphasize in particular that the scaling behaviour of the energy differences is described differently in the above two open-shell CC formalisms. In this presentation, we shall also indicate the kinship of these formalisms with other many-body theories in vogue.

2. Separability of energy differences: core-extensive and core-valence extensive formalisms

We argue that the effective hamiltonian formulation within a model space provides a very attractive framework not only for generating direct many-body methods for energy differences but also for analyzing their scaling behaviour. Since as yet we do not seem to have a commonly accepted terminology in describing the scaling behaviour of the energy differences, we shall be careful to define our own terminology and indicate how it applies to an effective hamiltonian H_{eff} for energy differences obtained via Bloch equation [34].

Any microscopic extensive property X (such as the total energy) is *additively separable* [32] in the sense that in the limit of asymptotically vanishing interactions between the subsystems A, B, etc., one has:

$$X \to X_A + X_B + \cdots \tag{2.1}$$

where the sum is over *all* the subsystems labelled as A, B, etc. Conversely any property satisfying Eq. (2.1) may be called extensive (or size-extensive). Extensivity is obviously a *global* property since X in Eq. (2.1) receives contributions from *all* the subsystems A, B, etc. The earliest many body formulations by Goldstone [35], Hubbard [36] and Hugenholtz [37] highlighted the extensivity of the ground-state energy.

For an *exact* excited state energy E^i_{ex} corresponding to the state i, the same asymptotic property e.g. Eq. (2.1), obviously holds good, and the various open-shell formulations proposed recently [32, 33] have analyzed the behaviour of the E_{ex} obtained from them. One should, however, note carefully that for the excited states, the subsystem energies E_A, E_B, etc. need not all be *excited* state energies for A, B, etc., since it is possible to excite the system in the asymptotic limit by exciting only a few of the subsystems. As a result, the separability of the *energy differences* ΔE_{ex} assumes a peculiar *semi-local* character in the sense that all the fragment excitation energies need not contribute to the asymptotic sum. In other words:

$$\Delta E_{\text{ex}} : \to \Delta E_A, \Delta E_A + \Delta E_B, \Delta E_A + \Delta E_B + \Delta E_C, \ldots \tag{2.2}$$

depending on which and how many of the subsystems are excited. In the remarkably perceptive paper by Hugenholtz [37], it was emphasized very early on that, when *only one subsystem is excited*, ΔE_{ex} depends only on that subsystem and not on the other subsystems at all (as is evident from Eq. (2.2)) and thus should not scale linearly with the total number of particles. In fact, in this case, we should expect the excited state E_{ex} having a term E_{gr} as the base of energy, scaling with N and another term ΔE_A not scaling with N. When we want to emphasize this *semi-local nature* of the energy differences, we may even talk of their *size-intensivity*. In a recent paper, Koch et al. [29] have indeed used this term in an analogous context. For a more complete treatment, however, we also need to characterize the separability of ΔE_{ex} generally as a sum over several subsystem excitation energies, as implied by Eq. (2.2). Since the excitation energies are generated by the various hole-particle excitations out of the model space, the additive separability of ΔE_{ex} indicates a proper scaling behaviour of ΔE_{ex} with respect to the various $h-p$ excitations describing the excitation processes, rather than of the total number of particles. This aspect can be very conveniently analyzed in the effective hamiltonian framework.

Any microscopic operator Y is called extensive, if it satisfies asymptotically:

$$Y \to Y_A + Y_B + \cdots \tag{2.3}$$

where the sum runs over *all* the subsystems. Y is obviously a *global* operator, depending upon the total number of particles.

The *exact* wave-operator Ω introduced in the context of the effective hamiltonian formalism should be a *multiplicatively separable* operator:

$$\Omega \to \Omega_A \Omega_B \ldots, \tag{2.4}$$

where *all* the fragment operators Ω_A contribute. If Ω is written in an exponential or normally ordered exponential form as

$$\Omega \sim \exp(S) \tag{2.5}$$

then it follows that S is an extensive operator. Conversely, if one posits on Ω an exponential structure, and devises truncations and approximations on S, then Ω remains multiplicatively separable. It is a straightforward matter then to show that H_{eff} becomes an extensive operator (see, e.g. Refs. [32, 33] for an elaborate discussion).

The space spanned by the functions on which H_{eff} acts is conventionally called the model space [38, 39]. We also define holes, particles, and valence orbitals in the usual manner [38, 39]. We shall often use the term "active" for valence orbitals (holes or particles) and reserve the term "inactive" for the nonvalence orbitals. Operators capable of making transitions only within the model space are called "closed" [39]. We shall call an operator as "external" [32, 33, 40] when there is at least one model function which it can act on to generate a virtual function. In an effective hamiltonian formulation, the idea is to transform the hamiltonian H into another operator L via Ω:

$$L = \Omega^{-1} H \Omega \tag{2.6}$$

and demand that the external part of L is zero. This defines the external part of Ω (or of S, if the exponential form, Eq. (2.5) is used). H_{eff} is then the closed part of L. When Ω is multiplicatively separable, we have:

$$H_{\text{eff}} = L_{\text{cl}} \rightarrow H_{\text{eff}_A} + H_{\text{eff}_B} + \cdots \tag{2.7}$$

indicating clearly the extensive nature of the operator H_{eff} [32, 33, 40].

Ω satisfies the Bloch equation [34]:

$$H\Omega P = \Omega P H_{\text{eff}} P \tag{2.8}$$

If we confine ourselves to one n-electron Hilbert space sector of the Fock space, then P is the model space projector for that Hilbert space. It is also possible to adopt a Fock space strategy where the projector P can be interpreted as taking a "closed" projection on Fock space, and Eq. (2.8) stands for the pair:

$$(H\Omega)_{\text{ext}} = \Omega_{\text{ext}} H_{\text{eff}} \tag{2.9a}$$

$$(h\Omega)_{\text{cl}} = \Omega_{\text{cl}} H_{\text{eff}} \tag{2.9b}$$

Since we are interested in generating direct methods for both the excited and ionized states, the Fock space strategy is the more convenient since it can handle states with varying particle numbers [5–19]. We shall, however, often use Eq. (2.8) for the Bloch equation, although its meaning should be interpreted as in Eqs. (2.9).

It is pertinent to remark here that extensivity of an operator Y *does not automatically guarantee* extensivity of the associated property obtained after diagonalization in a *truncated* (less than complete) Hilbert space. This feature has to be borne in mind while trying to infer the extensivity or otherwise of the computed energies obtained by diagonalizing H_{eff}. In case one includes in the model space all the functions that one can generate by allocating electrons in the valence orbitals in all possible manner (i.e. the model space is full valence or *complete* [38, 39]), extensivity of H_{eff} ensures the extensivity of the associated energies. This was the principal motivation behind generating extensive H_{eff} in the earlier MBPT [38, 39] and CC [5–10] formalisms in a complete model space. For *incomplete* model spaces [41], which are almost always warranted to bypass intruder problems [42], extensivity of H_{eff} by itself is not a sufficient guarantee for the extensivity of the energies [44]. It has been proven recently [44], however,

that the fact that H_{eff} is not only extensive but also a *closed* operator is sufficient to guarantee extensivity of the energies. We shall come back to this aspect in some detail in Sects. 4 and 7 of this paper. For the present we continue with our analysis of the size-extensivity of H_{eff} generated by the open-shell CC theory and CC-LRT.

For obtaining an effective hamiltonian for the energy differences relative to a closed shell ground state, we shall posit on Ω a multiplicatively separable form:

$$\Omega = \Omega_c \Omega_v \tag{2.10}$$

where Ω_c is the wave operator for the ground state, and Ω_v is the "valence" part of Ω introducing additional correlation and relaxation effects concomitant on excitation or ionization. Ω_c satisfies:

$$H\Omega_c \Phi_0 = E_{\text{gr}} \Omega_c \Phi_0 \tag{2.11}$$

where E_{gr} is the ground state energy and Φ_0 is the hole particle vacuum for the state, conventionally called the "core" [38]. Substituting Eq. (2.10) into Eq. (2.8) and premultiplying by Ω_c^{-1}, we obtain:

$$\tilde{H}\Omega_v P = \Omega_v P H_{\text{eff}} P \tag{2.12}$$

where

$$\tilde{H} = \Omega_c^{-1} H \Omega_c \tag{2.13}$$

If we separate from $\tilde{H}$ its core or vacuum part, E_{gr} and the operator part $\bar{H}$, and introduce a modified $\bar{H}_{\text{eff}}$ defined as:

$$\bar{H}_{\text{eff}} = H_{\text{eff}} - E_{\text{gr}} \tag{2.14}$$

we then get a Bloch equation for *energy differences* [14]:

$$\bar{H}\Omega_v P = \Omega_v P \bar{H}_{\text{eff}} P \tag{2.15}$$

Clearly, the diagonalization of $\bar{H}_{\text{eff}}$ would provide us the energy differences.

Ideally, we expect $\bar{H}_{\text{eff}}$ to display the *semi-local* asymptotic behaviour in the sense that:

$$\bar{H}_{\text{eff}} \to \bar{H}_{\text{eff}_A}; \qquad \bar{H}_{\text{eff}_A} + \bar{H}_{\text{eff}_B}; \qquad \bar{H}_{\text{eff}_A} + \bar{H}_{\text{eff}_B} + \bar{H}_{\text{eff}_C} \tag{2.16}$$

depending on the types of excitations (i.e., excitations of A; A and B; A, B and C, etc.). It is obvious that for this to be true, a necessary requirement is the validity of the extensivity of E_{gr} itself:

$$E_{\text{gr}} \to E_{A_{\text{gr}}} + E_{B_{\text{gr}}} + \cdots \tag{2.17}$$

Thus, to ensure the additivity of $\bar{H}_{\text{eff}}$ in the sense of Eq. (2.16) we should maintain the extensivity of the ground state, i.e., the core. We call this the requirement of *core-extensivity* [33]. Writing Ω_c as $\exp(T)$ as is done for the CC ground state, core-extensivity is automatically respected. Since $\bar{H}_{\text{eff}}$ acts only on the model space, it has only active hole and particle creation/annihilation operators. Ω_v thus introduces interactions between the valence quasi-particles and also interaction between the valences and the core.

We analyze further the extensivity of $\bar{H}_{\text{eff}}$ in the sense of Eq. (2.16). For this to be true, it is necessary to have the multiplicative separability of Ω_v:

$$\Omega_v = \Omega_{A_v} \Omega_{B_v} \Omega_{C_v} \ldots \tag{2.18}$$

Since Ω_v involves only active holes and particles, Eq. (2.16) implies the extensivity of $\bar{H}_{\text{eff}}$ with respect to active holes and particles involved in defining the model space. Thus, Eq. (2.16) indicates the *valence-extensive* nature of $\bar{H}_{\text{eff}}$. Validity of core-extensivity (i.e. Eq. (2.17)) being always an underlying feature, we call any $\bar{H}_{\text{eff}}$ satisfying Eq. (2.16) as a *core-valence extensive* theory [33].

Since the number of valence occupancy is usually much less than the number of core electrons, one may argue that bulk of size-extensivity error in the excited states is eliminated once a theory is made core-extensive. One may then even abandon the requirement of valence-extensivity, and may posit a linear expansion structure for Ω_v as in a CI, rather than an exponential structure. In that case, Eq. (2.18) does not hold good, and as a result, Eq. (2.16) is not generally satisfied. Such theories generally do not conform to the separability requirement, Eq. (2.2), for ΔE_{ex}. We call such theories as of *core-extensive* type [33].

The open-shell CC theory for energy differences based on Fock space and quasi-Fock approach [44–45] belongs to the core-valence extensive category. The CC-based linear response theory (CC-LRT) [21, 24], developed some years ago, does not start from the Bloch equation, but we shall show in the next section that it is entirely equivalent, in its time-independent form, to a Bloch equation based formalism using a *core-extensive* choice for Ω_c, but a *valence-inextensive* choice for Ω_v. CC-LRT is thus a core-extensive theory.

We should note here, that the decoupling condition for Ω, viz $L_{\text{ext}} = 0$, defines only the external part of Ω (or of S). One still has a choice for the closed part of Ω (or of S), which is as yet quite arbitrary. To get an extensive formulation, one must choose an Ω_{cl} that is compatible with the extensivity of H_{eff} or $\bar{H}_{\text{eff}}$. We have shown recently that, for an *arbitrary model space*, a useful choice for S is to take it as an external operator only [11, 12]. Ω_{cl} is then *not* the unit operator on the model space, indicating that the conventional intermediate normalization for Ω is not a size-extensive choice [11]. In fact, for a core-valence extensive theory for EE (which use h–p model space – an incomplete one), intermediate normalization must be abandoned. $\bar{H}_{\text{eff}}$ comes out as both connected and closed with S chosen as S_{ext}. When intermediate normalization is used, disconnected valence-valence terms (or equivalently, diagrams) appear in $\bar{H}_{\text{eff}}$, spelling a break-down of the valence-extensivity [32]. However, no vacuum diagrams appear, and core-extensivity of the theory is not violated [32]. Clearly, when ensuring valence extensivity is not our goal, as in formulating a core-extensive theory for EE as in CC-LRT, one may use the intermediate normalization for Ω_v.

In the open-shell CC theory in Fock space, Ω_v is written usually as a normal ordered exponential:

$$\Omega_v = \{\exp(S)\} \tag{2.19}$$

S involves all possible excitations from valence holes and/or valence particles present in the model functions and might involve additionally nh–np excitations from the core. It has been proven [5, 6, 11, 12] that one has to invoke a Fock space strategy for uniquely defining the various components $S^{(m,n)}$ of S involving explicitly m hole and n particle destruction operators. Ω_v is "valence-universal" [6] in the sense that S involves not only $S^{(k,l)}$ for the kh–lp parent model space, but also $S^{(m,n)}$ with $m < k$, $n < l$ for the subduced model spaces. Thus, for EE, Ω_v involves – besides $S^{(1,1)}$, acting on the h–p model space – operators like $S^{(1,0)}$ and $S^{(0,1)}$ characterizing the cationic and anionic model spaces with $(N-1)$ and $(N+1)$ electrons respectively. The essential point of interest in this structure is

that for EE, the action of Ω_v on the $h-p$ model space, with the projector $P^{(1,1)}$, may be described as:

$$\Omega_v P^{(1,1)} = \{(1_v + S^{(1,0)})(1_v + S^{(0,1)}) + S^{(1,1)}\}P^{(1,1)} \tag{2.20}$$

It is the presence of *product-separable* operators $(1 + S^{(1,0)})(1 + S^{(0,1)})$ for $1h$ and $1p$ subsystems that lends the valence-extensivity to $\bar{H}_{\text{eff}}$ in the open-shell CC for EE.

The CC equations in Fock space take the form [5, 6, 11]:

$$\{\overbrace{\bar{H}\exp(S)}\}_{\text{ext}} = \{\overbrace{\exp(S)\bar{H}_{\text{eff}}}\}_{\text{ext}} \tag{2.21a}$$

$$\{\overbrace{\bar{H}\exp(S)}\}_{\text{cl}} = \{\overbrace{(\exp(S))_{\text{cl}}\bar{H}_{\text{eff}}}\}_{\text{cl}} \tag{2.21b}$$

Since all the terms in Eqs. (2.21) are connected, the extensivity of S_v and $\bar{H}_{\text{eff}}$ follows by iteration in powers of perturbation. For an incomplete model space, $(\exp(S_v))_{\text{cl}}$ is not necessarily unity [11].

In a parallel development quite distinct from the Fock-space methodology, several many-body theories have been put forward which work on an n-electron Hilbert space [41, 43, 45–47]. Hose and Kaldor [41] had been the first to formulate a Hilbert space MBPT that used an incomplete model space. The effective hamiltonian generated by them was inextensive, the origin of which can now be traced [44] to their use of intermediate normalization for Ω which is known to be a size-inextensive choice for an incomplete model space. Jeziorski and Monkhorst [43] developed a CC theory for both complete and incomplete model space in a Hilbert space framework. They used the intermediate normalization for Ω throughout. They proved that H_{eff} in their formulation is connected for a complete model space although for an incomplete model space size-inextensive terms appear. Once the importance of maintaining a size-extensive normalization for Ω for an incomplete model space is recognized, it is possible to develop size-extensive Hilbert space type of CC theories. Recently there have appeared two such formulations [45–47].

Instead of hierarchically building the higher valence cluster amplitudes all the way upto the desired parent model space in the Fock space approach, one may simply project Ω_v onto the parent model space $P^{(m,n)}$ itself. The lower valence amplitudes $S^{(k,l)}$ $((k, l) < (m, n))$ are then redundant [33] and appear always in specific combinations with the parent $S^{(m,n)}$ amplitudes. By taking each model space function Φ^μ as the vacuum for computing $\Omega_v \Phi^\mu$ in the spirit of Jeziorski and Monkhorst [43], one may work with the right number of amplitudes. These amplitudes are related to the fixed combinations of $S^{(m,n)}$ and $S^{(k,l)}$ amplitudes just mentioned. We have shown recently [45, 46] that the resultant ansatz for Ω_v, for a n-electron Hilbert space of incomplete model space, given by:

$$\Omega_v = \sum_\mu \exp(S^\mu)\big|\Phi^\mu\rangle\langle\Phi^\mu\big| \tag{2.22}$$

leads to connected expressions of $\bar{H}_{\text{eff}}$ and energy differences where S^μ is chosen to have all the "external" operators (the external operators being defined exactly as in the Fock space theory). We have denoted this theory as of quasi-Fock type, since it bypasses hierarchical generation of Ω, although an underlying Fock space separation of Ω into Ω_v and Ω_c is built in the theory. One can even envision a quasi-Hilbert space theory [45, 46], where no attempt to factorize Ω into Ω_c and

Ω_v is made and S^μ is taken to possess only external operators. This theory will generate open-shell state energies *per se*. Intermediate normalization for Ω is abandoned in both the above developments.

Meissner et al. [47a] approached the problem from a different angle. They emphasized that the requirement that a particular type of operator always leads to excitations outside the model space – independent of Φ^μ it acts upon, is not compatible with an arbitrary model space. Only for a special type of incomplete model space, known as "quasi-complete model space" [52] (vide infra) does one have this guarantee, for which a connected formulation for an H_{eff} for the state energies *per se* is possible as a generalization of the Jeziorski–Monkhorst formulation. Since for an arbitrary model space, an operator exciting from Φ^μ may lead to scattering within the model space when acting on another Φ^ν, one has a choice in either retaining or deleting this operator in S^ν. These operators are termed quasi-open by us [45, 46]. In a later paper, by analyzing the expressions for S^μ's at low order of perturbation theory, Meissner and Bartlett [47b] showed that all such operators leading to "internal excitations" should be retained for connectivity. This formulation leads to a quasi-Hilbert space CC theory. Retention of the operators discussed above in all the S^μ's is equivalent to including in S^μ's all the quasi-open operators as introduced by Mukhopadhyay and Mukherjee [45, 46]. The analogous quasi-Fock space type formulation for energy differences was not considered by these authors.

Unlike in the Fock space type of theories, if we use for Ω_v in EE a *linear expansion structure* involving various $nh-np$ excitations, then the subsystem product separability is violated, and as a result the valence separability of EE will break down. In fact in CC-LRT [21, 24] an excited or ionized state Ψ_k is written in terms of an excitation or ionization operator W_k^+ acting on the N-electron ground state Ψ_{gr} written in the CC form:

$$\Psi_k = W_k^+ \exp(T)\Phi_0 \tag{2.23}$$

where W_k^+ is indeed taken as a *linear combination* for various $mh-np$ operators to generate a Ψ_k with $(N-m+n)$ electrons. We may write the equation for the energy difference in the EOM-form as:

$$[H, W_k^+]\Psi_{\text{gr}} = \Delta E_k W_k^+ \Psi_{\text{gr}} \tag{2.24}$$

The open-shell CC theory and CC-LRT sketched above appears at first sight to be structurally quite dissimilar. The former utilizes a wave-operator Ω, while the latter – in the time-independent version [24] – uses an excitation or ionization operator W_k^+, as in the equation of motion (EOM) approach. We shall show in the next section that one can transcribe the working equations for CC-LRT to a Bloch equation form involving $\bar{H}_{\text{eff}}$ which will clearly reveal the linear expansion structure of the associated Ω_v. This will also enable us to analyze the extensivity of the energy differences from a unified framework. For earlier discussions on this point see Refs. [49].

3. Transcription of CC-LRT from the EOM form to an equivalent wave-operator based form

Utilizing the fact that W_k^+ and T have only $h-p$ creation operators and hence commute, we premultiply Eq. (2.24) by $\exp(-T)$, use Eq. (2.13) for $\tilde{H}$ and the

definition $\bar{H} = \tilde{H} - E_{gr}$ to obtain the working equation for CC-LRT for energy differences:

$$[\bar{H}, W_k^+]\Phi_0 = \Delta E_k W_k^+ \Phi_0 \tag{3.1}$$

Equation (3.1) indicates CC-LRT is a particular variant of generalized TDA employing a vertex-normalized $\bar{H}$ incorporating the ground-state correlation.

Using Wick's theorem, we may rewrite Eq. (3.1) as:

$$[\overbrace{\bar{H}\, W_k^+} - \overbrace{W_k^+ \bar{H}}]\Phi_0 = \Delta E_k W_k^+ \Phi_0 \tag{3.2}$$

where $\overbrace{AB}$ denotes contractions between creation/annihilation operators in the two operators A and B. Since in CC-LRT we choose W_k^+ to contain only *mp–nh creation operators*, $\overbrace{W_k^+ \bar{H}}$ vanishes and we have:

$$\overbrace{\bar{H}\, W_k^+}\, \Phi_0 = \Delta E_k W_k^+ \Phi_0 \tag{3.3}$$

We can now show that Eq. (3.3) can be written equivalently as:

$$\bar{H} W_k^+ \Phi_0 = \Delta E_k W_k^+ \Phi_0 \tag{3.4}$$

owing to very *special structure* of $\bar{H}$. Since $\bar{H}$ and W_k^+ are both written in normal order, we have, from Eq. (3.3):

$$\overbrace{\bar{H}\, W_k^+} = \bar{H} W_k^+ \Phi_0 - \{\bar{H} W_k^+\}\Phi_0 \tag{3.5}$$

where $\{\ \}$ denotes normal ordering of the product in the braces. Since $\{\bar{H} W_k^+\}$ acts on the physical vacuum, all those terms involving h–p destruction operators from $\bar{H}$ will give zero contribution. The only potentially non-vanishing contribution from $\{\bar{H} W_k^+\}$ can come from the term of $\bar{H}$ having h–p creation operators only. Since we solve for the ground state cluster amplitudes T by equating the various nh–np excitation terms of $\bar{H}$ to zero (these are the closed shell CC equations), all those terms of $\bar{H}$ involving only h–p creation operators are *vanishing by construction*, and we thus have the equivalence of Eq. (3.3) with Eq. (3.4). We now show the emergence of a form of Bloch equation (2.15) from Eq. (3.4).

W_k^+ can be expanded in the basis $\{Z_{m,n}^+\}$ with a fixed $(m-n)$, having mh and np creation operators:

$$W_k^+ = \sum_{m,n} C_{mn,k} Z_{m,n}^+ \tag{3.6}$$

Let us partition the operator space $\{Z_{m,n}^+\}$ into two parts. For low-lying excited/ionized states, the relaxation and change of electron correlation consequent on excitation/ionization is not drammatic, and most of these effects are dominated by the lowest rank components of $\{Z_{m,n}^+\}$. Thus for IP, EA and EE, $Z_{1,0}^+$, $Z_{0,1}^+$ and $Z_{1,1}^+$ are the dominant components respectively. In analogy with the open-shell CC theory, let us denote as the subset $\{Z_P^+\}$ those components of $\{Z_{m,n}^+\}$ that have the lowest h–p ranks and call this the model component or the primary space component [49]. The complementary subset $\{Z_Q^+\}$ will be called virtual manifold or the virtual space component, Ψ_k can then be decomposed as:

$$\Psi_k = \left[\sum_{m,n\in P} C_{mn,k} Z_{m,n}^+ + \sum_{r,s\in Q} C_{rs,k} Z_{r,s}^+\right] \exp(T)\Phi_0 \tag{3.7}$$

Introducing model functions $\Phi_{m,n} = Z^{+}_{m,n}\Phi_0$, and virtual functions $\chi_{r,s}$ we may rewrite Eq. (3.7) as:

$$\Psi_k = \exp(T)\left[\sum_{m,n\in P} C_{mn,k}\,\Phi_{m,n} + \sum_{r,s\in Q} C_{rs,k}\,\chi_{r,s}\right] \tag{3.8}$$

Introducing coefficients $d_{rs,mn}$ satisfying:

$$d_{rs,mn} = \sum_{l} C_{rs,l}[C^{-1}]_{l,mn} \tag{3.9}$$

we have:

$$\Psi_k = \exp(T)\sum_{m,n\in P} C_{mn,k}\left[\Phi_{m,n} + \sum_{r,s\in Q} d_{rs,mn}\,\chi_{m,n}\right] \tag{3.10}$$

If we now introduce a "state-universal" wave-operator Ω_v satisfying [49]:

$$\begin{aligned}\Omega_v\,\Psi^0_k &= \Omega_v \sum_{m,n\in P} C_{mn,k}\,\Phi_{m,n} \\ &= \sum_{m,n\in P} C_{mn,k}\left[\Phi_{m,n} + \sum_{r,s\in Q} d_{rs,nm}\,\chi_{m,n}\right]\end{aligned} \tag{3.11}$$

we find that Ω_v is given by:

$$\Omega_v = 1_v + \sum_{r,s\in Q}\sum_{m,n\in P} d_{rs,mn} Z^{+}_{r,s} Z_{m,n} \tag{3.12}$$

Equation (3.12) clearly indicates that CC-LRT has an underlying Ω_v that has a linear expansion structure involving valence creation and destruction operators. Since $r - s = m - n$, Ω_v preserves number of electrons, unlike W^{+}_k which changes the number of electrons by $(n-m)$ relative to the ground state.

We thus have:

$$\Psi_k = \exp(T)\,\Omega_v\,\Psi^0_k \tag{3.13}$$

with Ω_v given by Eq. (3.12), indicating the core-extensivity of CC-LRT.

We note here several features of CC-LRT which has made its equivalence with Bloch equation-based approach emerge:

(i) in CC-LRT we have used the ansatz Ψ_k as $W^{+}_k \exp(T)\Phi_0$ where *both* W^{+}_k and T contain only particle-hole creation operators, leading to commutativity of W^{+}_k and $\exp(T)$. This was crucial for generating the dressed hamiltonian $\bar{H}$ leaving W^{+}_k intact.

(ii) the imposition of the cluster structure for $\Omega_c = \exp(T)$ leads to the vanishing of all the *np–nh* excitation operators of $\bar{H}$ – a feature essential for the transcription.

In the next two sections we shall analyze the extensivity of ΔE_k's obtained from CC-LRT and compare its structure with the other Bloch equation based core-extensive theories. Since the latter invariably use an effective hamiltonian defined over a model space, we have to explicitly analyze the structure of Ω_v implied by Eq. (3.12).

We note that Ω_v is obtained as a result of "folding" the effect of the virtual manifold into the model manifold. This can be accomplished by two different procedures. One may either invoke an *eigenvalue independent partitioning tech-*

nique (EIP) [51] leading to an effective hamiltonian formalism of the *Rayleigh–Schrödinger type*. This method is very instructive in that it shows the equivalence of the CC-LRT for IP and EA problems with the analogous open-shell CC problem [14] and also indicates why for situations with more than one valence occupancy, the equivalence between the two formalisms breaks down. This is described in Sect. 4. In another approach, the folding is performed via an *eigenvalue dependent partitioning technique* (EDP)-leading to a *Brillouin–Wigner type* structure [50] for H_{eff}. We shall discuss in Sect. 5 the emergence of a Bloch–Horowitz like structure of $\bar{H}_{\text{eff}}$ using EDP.

4. Extensivity of energy differences in CC and CC-LRT

4.1. Eigenvalue independent partitioning applied to CC-LRT: A Rayleigh–Schrödinger like core-extensive formulation

The energy-independent folding in the model space of the $\{Z_Q^+\}$ operator in CC-LRT lends an energy-independent structure to the effective hamiltonian. To achieve this, we use the matrix eigenvalue-independent partitioning technique (EIP) suggested by Coope et al. [51]. Although these authors developed EIP for symmetric eigenvalue problems, ours is a generalization encompassing nonsymmetric matrices [14, 50].

Let us project Eq. (3.1) onto functions $\{Z_P^+ \Phi_0\}$ and $\{Z_Q^+ \Phi_0\}$. The working equations for CC-LRT then take the familiar eigenvalue equation form:

$$RC_k = \Delta E_k C_k \tag{4.1}$$

with R, a matrix with elements:

$$R_{ij} = \langle \Phi_0 | Z_i [\bar{H}, Z_j^+] | \Phi_0 \rangle \tag{4.2}$$

and ΔE_k's are the energy differences for the states Ψ_k, with C_k's as the eigenvectors. Z_i^+ etc. denotes generically both the operators $Z_{m,n}^+$ and $Z_{r,s}^+$. Let us assume now that we are interested in only those roots which are dominated by the *subset* of the operator manifold: $\{Z_{m,n}^+\}$. The rest of the set $\{Z_{r,s}^+\}$ is the "virtual space". The matrix R then naturally gets partitioned into the form:

$$R \equiv \begin{bmatrix} R_{PP} & R_{PQ} \\ R_{QP} & R_{QQ} \end{bmatrix} \tag{4.3}$$

and similarly the vectors C_k get partitioned as:

$$C \equiv \begin{bmatrix} C_{PK} \\ C_{QK} \end{bmatrix} \tag{4.4}$$

Our intention now is to focus on n_P roots ΔE_k which are dominated by the subset $\{Z_P^+\}$, n_P in number. If we write all the n_P vectors in successive columns, and call this $(n_P + n_S) \times n_P$ matrix as C_P, then the eigenproblems for n_P roots ΔE_k may be compactly written as:

$$RC_P = C_P \, \Delta E_P \tag{4.5}$$

where ΔE_P is the diagonal matrix of the roots. C_P, from Eq. (4.4), partitions as:

$$C_P \equiv \begin{bmatrix} C_{PP} \\ C_{QP} \end{bmatrix} \tag{4.6}$$

Since the roots in ΔE_P are dominated by the subspace P, the projections of the vectors C_K on P – C_{PK}'s – are expected to be linearly independent, so that the $n_P \times n_P$ matrix C_{PP} is *invertible*. In case this is not so (i.e., C_{PP} is precariously close to being singular), we may always make this nonsingular by suitably expanding the operator manifold (i.e., by redefining our model space). We now write Eq. (4.5) in long hand, using Eq. (4.3) as:

$$R_{PP}C_{PP} + R_{PQ}C_{QP} = C_{PP}\,\Delta E_P \tag{4.7a}$$

$$R_{QP}C_{PP} + R_{QQ}C_{QP} = C_{QP}\,\Delta E_P \tag{4.7b}$$

Let us now introduce a *partitioning matrix* X_{QP}, defined by:

$$X_{QP} = C_{QP}C_{PP}^{-1}$$

Thus from Eqs. (4.7), we have:

$$R_{PP} + R_{PQ}X_{QP} = C_{PP}\,\Delta E_P C_{PP}^{-1} = \Sigma_{PP} \tag{4.8a}$$

$$\begin{aligned} R_{QP} + R_{QQ}X_{QP} &= X_{QP}\Sigma_{PP} \\ &= X_{QP}R_{PP} + X_{QP}R_{PQ}X_{QP} \end{aligned} \tag{4.8b}$$

Solution of Eq. (4.8b), *which is quadratic* in X_{QP}, gives us the $n_Q \times n_P$ matrix X_{QP}, whose substitution in Eq. (4.8a) furnishes us an effective hamiltonian-like matrix Σ_{PP}. The roots of Σ_{PP} are the ΔE_k's with eigenvectors C_{PK}. Since Σ_{PP} does not parametrically depend on ΔE_k's, this partitioning is called EIP. We could have obtained X_{QP} and Σ_{PP} directly from Eq. (3.11), using Eq. (3.12), by identifying X_{QP} with the matrix of $d_{rs,mn}$ and Σ_{PP} as $\bar{H}_{\text{eff}}$. The above formulation, however, is more concrete and indicates the matrices that are really involved in the computation.

X_{QP} may be solved from Eq. (4.8b) in orders of perturbation, which in turn generates a perturbative expansion for Σ_{PP}. It is obvious that this expansion for Σ_{PP} is of Rayleigh–Schrödinger type. Let us assume that $\bar{H}$ may be decomposed into the Hartree–Fock part F and the perturbation $\bar{H}^{(1)}$. Then R decomposes into $R^{(0)} + R^{(1)}$, where $R^{(0)}$ is a diagonal matrix. Equation (4.8b) leads to:

$$[X_{QP}, R^{(0)}]_{QP} = R_{QP}^{(1)} + R_{QQ}^{(1)}X_{QP} - X_{QP}[R_{PP}^{(1)} + R_{PQ}^{(1)}X_{QP}] \tag{4.9}$$

Equation (4.9) is the matrix form of the Bloch equation (3.12) in the fixed Hilbert space spanned by $\{Z_i^+\}$. Although this is strongly reminiscent of an analogous equation used for generating open-shell MBPT [38, 39] or CC theory [6–8], we should remember that for a truncated theory, the Hilbert space spanned by $\{Z_i^+\}$ is not complete. This spoils the valence-extensivity of CC-LRT as we shall presently see.

Let us analyze the extensivity of the corresponding ΔE_k's obtained by diagonalizing Σ_{PP}. We shall study two concrete cases: the one valence problems (IP/EA) and the two-valence problems (EE and DIP).

In what follows, it would be convenient to define two different types of external operators: quasi-open and open [32, 33, 40]. The former has meaning only for incomplete model spaces. For an incomplete model space, P, one may define its completion R which together with P forms the complete model space.

An operator is quasi-open if there is at least one model function on which its action leads to an excitation to the space R. These operators have only active (valence) operators like the closed ones, but they have special valence labels on them. Open operators cause transitions to the space $(Q - R)$, and hence has at least one inactive creation operator.

For an arbitrary incomplete model space, quasi-open operators may induce transitions within the model space when acting on some model functions. In contrast, an open-operator can never induce transitions within the model space. There is, however, a very special incomplete model space for which a quasi-open operator cannot induce transitions within the model space. This model space, introduced by Lindgren and called quasi-complete by him [52], is generated in a special manner: one groups the valence orbitals into groups A, B, C, etc. and assigns fixed occupancies n_A, n_B, n_C for each group; one then constructs all the possible determinants with the above occupancy. These determinants span the quasi-complete model space. A quasi-open operator then, by the very nature of this model space, has to change the occupancy of at least one group and thus, by construction, cannot lead to transition within the model space. Such model space plays *very special roles* in generating extensive energies, as we shall see.

For IP(EA) computations, there is only one valence occupancy in the model space. $\bar{H}$ is a connected hence extensive operator. The model space being complete, X_{QP} is of open category. An order by order expansion of X_{QP} generates $X_{QP}^{(n)}$'s which have operator structure like $Z_{2,1}^{+}Z_{1,0}$, $Z_{3,2}^{+}Z_{1,0}$, etc. for the IP problem. Since R has no vacuum terms, and no $nh-np$ excitations, at no stage of iteration can we generate disconnected vacuum terms in X_{QP}. Σ_{PP} also then can have no vacuum terms. Also in Σ_{PP}, X_{QP} has to be connected to R_{PQ} in Eq. (4.8a), since otherwise X_{QP} would induce a transition to the Q space, it being an open operator. As a result, Σ_{PP} for IP is a connected operator. Since the model space for a one-valence problem is necessarily complete, the associated energies have no disconnected terms. The IP's computed for the *main peaks*, i.e., those dominated by the manifold $Z_{1,0}^{+}$ are thus core-valence extensive. This, of course, is only expected. CC-LRT is core-extensive any way, and for one valence problems we cannot further subdivide the valence occupancies into subsystems [14, 49]. The same is true likewise for the EA problem.

We now show that a nonperturbative solution of Eqs. (4.8) generates the same roots as those obtained from open-shell CC theory for IP(EA) [14, 49]. S_v operators of the type $S_v^{(1,0)}$, $(S_v^{(0,1)})$ for the IP(EA) introduce single shake-up, double shake-up etc. excitations from the model space. Since Ω_v is chosen in normal ordered form, the exponential like structure terminates after the linear term when acting on $P^{(1,0)}$ (or $P^{(0,1)}$). Thus, for IP, we have:

$$\{\exp(1 + S_v^{(1,0)})\}P^{(1,0)} = \{1 + S_v^{(1,0)}\}P^{(1,0)} \tag{4.10}$$

By comparing Eq. (4.10) with Eq. (3.12), it becomes clear that Ω_v for the open-shell CC formalism has also a linear expansion structure as in CC-LRT, and thus has the same underlying extensivity property. For the same truncation of the operator manifold in CC-LRT theory and CC theory, this equivalence obviously will continue to hold good.

One might wonder that we have a contraction of information of sorts here, in the sense that the original CC-LRT equations have potentially $(n_P + n_Q)$ roots, as is evident from Eq. (4.3), while the corresponding Bloch equation based formulation generates only n_P roots from Σ_{PP}. We should note however, that the Bloch equation, Eq. (4.8), for X_{QP} is quadratic – allowing *multiple solutions*. The

same is true of the analogous equations for S_v amplitudes in the CC formalism. The shake-up roots can thus be obtained in principle by homing on to these alternative solutions. Such a procedure was in fact adopted by us to generate shake-up roots from the open-shell CC formalism [14]. Since these roots are dominated by the $2h-p$ ($h-2p$) determinants for the IP (EA) problem – having more than one valence occupancy – the question naturally arises regarding their extensivity.

4.2. Core-extensivity of satellite energies obtained as alternative solutions to CC equations

We first note that we cannot generally infer the core-valence extensivity of these roots even if we solve for the alternative roots for X_{QP} from Eqs. (4.8) or (4.9), since the connectivity of $\bar{H}_{\text{eff}}$ for the main roots were obtained by an iteration in order of perturbation. The alternative roots *are not obtainable* from a perturbation series. To look into the nature of extensivity of the roots for the shake-up peaks we follow a different strategy.

We write the complete eigenproblem for the matrix R in Eq. (4.3) as follows:

$$\begin{bmatrix} R_{PP} & R_{PQ} \\ R_{QP} & R_{QQ} \end{bmatrix} \begin{bmatrix} C_{PP} & C_{PQ} \\ C_{QP} & C_{QQ} \end{bmatrix} = \begin{bmatrix} C_{PP} & C_{PQ} \\ C_{QP} & C_{QQ} \end{bmatrix} \begin{bmatrix} E_P & 0 \\ 0 & E_Q \end{bmatrix} \tag{4.11}$$

Introducing a matrix K with elements:

$$K = \begin{bmatrix} 1_{PP} & 0 \\ X_{QP} & 1_{QQ} \end{bmatrix} \tag{4.12}$$

and its inverse K^{-1} as:

$$K^{-1} = \begin{bmatrix} 1_{PP} & 0 \\ -X_{QP} & 1_{QQ} \end{bmatrix} \tag{4.13}$$

we may rewrite Eq. (4.11) as:

$$\begin{bmatrix} \Sigma_{PP} & R_{PQ} \\ 0 & \Sigma_{QQ} \end{bmatrix} \begin{bmatrix} C_{PP} & D_{PQ} \\ 0 & D_{QQ} \end{bmatrix} = \begin{bmatrix} C_{PP} & D_{PQ} \\ 0 & D_{QQ} \end{bmatrix} \begin{bmatrix} E_P & 0 \\ 0 & E_Q \end{bmatrix} \tag{4.14}$$

where

$$\Sigma_{QQ} = R_{QQ} - X_{QP} R_{PQ} \tag{4.15}$$

and

$$\begin{aligned} D_{PQ} &= C_{PQ} \\ D_{QQ} &= C_{QQ} - X_{QP} C_{PQ} \end{aligned} \tag{4.16}$$

Equation (4.14) indicates that the shake-up roots can be obtained by diagonalizing Σ_{QQ}, with eigenvectors generated as D_{QQ}, once X_{QP} for the main roots gets known. Σ_{QQ} is *not* an effective hamiltonian for the shake-up roots, however, since the component D_{PQ} outside the Q-space remains non-zero. Since X_{QP} admits of a power series expansion (being obtained from the main roots), Σ_{QQ} can be analyzed as a power series in $R^{(1)}$. As a matter of fact, we have:

$$\Sigma_{QQ}^{(n)} = R_{QQ}^{(1)} \delta_{1,n} - X_{QP}^{(n-1)} R_{PQ}^{(1)} \tag{4.17}$$

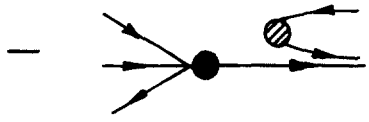

Fig. 1. Disconnected valence diagram contributing to Σ_{QQ} for the satellite roots. The filled circle indicates the vertex stemming from X_{QP}. In the second order it is simply an $R^{(1)}$ vertex with an energy denominator

Already at the second order, we have a disconnected valence diagram of the type shown in Fig. 1. The cross-hatched circle stands for the $R^{(1)}$ vertices, and the X_{QP} operator is indicated by solid vertex. This indicates that the shake-up roots obtained from CC-LRT are *not valence extensive*. The same conclusion is hence also valid *ipso facto* for the alternative roots from the CC equations for IP. However, since R has no $nh-np$ excitation terms, at no stage of diagonalization of Σ_{QQ}, would we encounter disconnected vacuum diagrams. The *core extensivity of the shake-up roots* is thus guaranteed. The demonstration of lack of valence-extensivity of the energies obtained as alternative solutions of the CC equations is, in our opinion, a rather nontrivial result. The same situation prevails for the multivalence problems in CC theory. For a more extensive treatment, we refer to one of our forthcoming papers [53].

4.3. *Core-extensivity of* CC-LRT *vs core-valence extensivity of* CC *theory*

For two and higher valence problems, the above equivalence of CC-LRT and CC-theory does no longer hold good. For these situations, the CC-LRT continues to use a linear expansion of W_k^+ in terms of $\{Z_i^+\}$ operator, and hence the associated Ω_v has also a linear expansion structure. In contrast, the CC theory uses an exponential structure which does not terminate after the linear term, unlike what we encountered in Eq. (4.10). This difference is crucial in ensuring valence extensivity of the ΔE_k's in CC theory, while this is no longer so in CC-LRT.

To illustrate this, we take a typical example from EE. Let us assume that the Hilbert space Q is spanned by $2h-2p$ determinants, and consider a fourth order diagram of Σ_{PP} stemming from a typical third order $X_{QP}^{(3)}$ diagram from the term $X_{QP}^{(1)}R_{PQ}^{(1)}X_{QP}^{(1)}$ of Eq. (4.9) having $2h-2p$ intermediate illustrated in Fig. 2a. This generates a $\Sigma_{PP}^{(4)}$ of the type shown in Fig. 2b. This is a *manifestly disconnected diagram* which spoils the valence extensivity of the energies. This term remains non-vanishing even if there is very little interaction between "hole" part and "particle" part of the subdiagrams. The *counter-terms* which would have cancelled this disconnected term at fourth order can emanate only from diagrams having $3h-3p$ excited states in Q-space – *which are absent* in truncated calculations. These diagrams for $\Sigma_{PP}^{(4)}$ are of the types as shown in Fig. 3. Using the Franz–Mills identity [54], it is easy to show that the two diagrams of Fig. 3 will

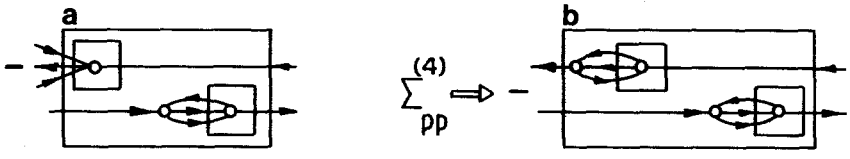

Fig. 2. **a** A disconnected norm-correction type diagram contributing to $X_{QP}^{(3)}$ for EE in CC-LRT. **b** Its contribution to $\Sigma_{PP}^{(4)}$, generating a disconnected valence diagram

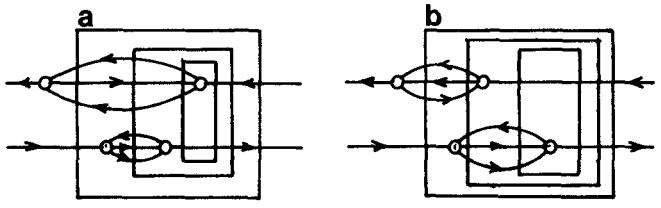

Fig. 3. Disconnected diagrams with $4h-4p$ intermediates stemming from the sum over states which could cancel the diagram of Fig. 2b

cancel the terms shown in Fig. 2b. Since, using the Hartree–Fock orbitals for the ground state, the first one body term of $R^{(1)}$ appears at second order, the first disconnected diagrams appear at fourth order, as in $\Sigma_{PP}^{(4)}$. This feature was also noted by Meissner and Bartlett, as announced in the Harvard Symposium in CC theory [55].

For the CC theory, however, even if we assume that there are only $S_v^{(1,0)}$ and $S_v^{(0,1)}$ operators in the calculation for EE, which excites $2h-2p$ determinants from the $h-p$ model space $P^{(1,1)}$, the presence $\{S^{(1,0)}S^{(0,1)}\}$ in Ω_v will induce the $3h-3p$ excited determinants, and this will automatically generate the counter terms of the type shown in Fig. 3. Even in a perturbative calculation, this cancellation will remain valid, if we invoke a perturbative construction of S_v, rather than of Ω_v itself.

Koch et al. [29] have very recently demonstrated that CC-LRT for EE generates ΔE_k's that are size-intensive in the sense that when the system consists of subsystems A and B, $\Delta E_{\text{ex}A}$ and $\Delta E_{\text{ex}B}$ are possible solutions of CC-LRT. We reanalyze this example for EE, taking a Hilbert space of $h-p(P)$ and $2h-2p(Q)$ determinants, to shed further light on the extensivity. For CC-LRT, the matrix R is defined in the $P+Q$ space above, while we take as our model space this $(P+Q)$ space for the CC theory. In both cases, we diagonalize a matrix in the space of $h-p$ and $2h-2p$ determinants.

We discuss the CC theory first. Since $h-p$ excitations from $2h-2p$ functions lead to $3h-3p$ functions lying outside the model space, they are external (actually quasi-open) operators, and we have to introduce S_v operators to eliminate the corresponding $L_{q\text{-open}}$ operators. Since these same types of excitations connect the $h-p$ model functions to the $2h-2p$ model functions, there is a *null entry* in the blocks for the matrix of $\bar{H}_{\text{eff}}$ connecting the $h-p$ and $2h-2p$ functions. The matrix is thus of structure shown in Fig. 4. The energies for the roots corresponding to dominance of $h-p$ determinants are obtained by diagonalizing the block marked *I*, while those dominated by the $2h-2p$ determinants are obtained by diagonalizing the block marked *II*. In both cases, we diagonalize a matrix of a connected operator in the *quasi-complete model* space $nh-np$, for $n=1$ and 2. The operator by construction is closed.

We now prove that a matrix of a connected operator defined in a quasi-complete model space generates *valence-extensive* energies. The proof is by perturba-

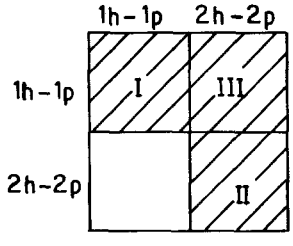

Fig. 4. The block structure of the matrix of H_{eff} in the $h-p+2h-2p$ model space in the open-shell CC theory. Note the appearance of the null-matrix in the lower off-diagonal block

tive reasoning. We may follow the diagonalization as a perturbation series for each root. The norm correction terms can generate manifestly disconnected diagrams. We may juggle these terms, using Franz–Mills identity [54] to rewrite them as disconnected terms having various intermediate states reached by the operator, which is closed by construction. Since a closed operator always scatters only within the model space, the intermediates are all of model space type, since the model space is quasi-complete. These terms are hence cancelled by the disconnected term containing general sum over the functions of the quasi-complete model space. Another way of looking at the problem is to note that, unlike CC-LRT, we can never have terms corresponding to the Fig. 2b or 3, since the vertices leading from $h-p$ to $2h-2p$ functions correspond to quasi-open operators, *which are zero* by construction (these conditions are used to find the corresponding S_v amplitudes). This is reflected in the lower block-diagonal structure of the effective hamiltonian matrix. Thus, the energy differences obtained for EE from CC theory (or DIP by a similar reasoning) are core-valence extensive.

We shall now analyze the semi-local separability in the sense of Eq. (2.2) of the energy differences obtained from CC and CC-LRT. Continuing with our example, we go to the limit of two non-interacting subsystems A and B. A thus have $h-p$ and $2h-2p$ excitations. The joint excitations on AB can have at most $2h-2p$ excitations.

For the case of CC-LRT, we explicitly show, using arguments similar to those of Koch et al. [29], the blocks marked A, B and AB to indicate the subsystems excited. Owing to the connectivity of $\bar{H}$, the matrix R assumes the block structure shown in Fig. 5a. Clearly then, possible solutions from CC-LRT are ΔE_A and ΔE_B indicating the size-intensive nature of the theory. To see the separability properties of EE when A and B are both excited, we explicitly show the structure of the AB block. As we pull the two subsystems apart, the functions in the AB block may be of four different types: (i) one valence occupancy on A and one valence occupancy on B, denoted as A_1B_1 (an example: $1h$ on A, $1p$ on B) (ii) three valence occupancy on A and one valence occupancy on B, denoted by A_3B_1 (iii) occupancy of the type A_1B_3 and (iv) occupancy of the type A_2B_2. The structure of the AB block is shown in Fig. 5b. Clearly, when we have single excitation on A and single excitation on B (A_2B_2 type), $\Delta E_A + \Delta E_B$ is a possible

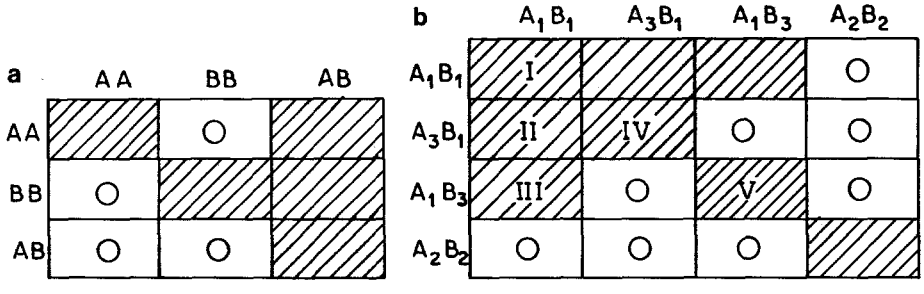

Fig. 5. **a** The block structure of the matrix R in CC-LRT for EE showing explicitly the subblocks corresponding to the subsystems A, B. **b** The detailed structure of the subblock AB of Fig. 5a showing the possible valence excitations in the subsystems A, B

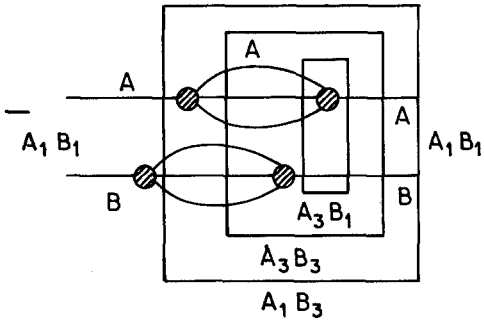

Fig. 6. Generation of disconnected valence diagram in the AB block with $3h-3p$ intermediate of the type A_3B_3

solution. However, when we have excitation of the type A_1B_1 (i.e. one hole on A/B and one particle on A/B), we have disconnected diagrams of the type shown in Fig. 6, when we fold the effects of A_3B_1 and A_1B_3 blocks into A_1B_1 block. This stems from a norm correction type diagram coming from A_1B_3, A_3B_1, and A_1B_1 coupling, juggled using Franz–Mills identity to have an intermediate state of A_3B_3 type. Since there are no A_3B_3 intermediates in the general sum, this term *will remain uncancelled* and will spoil the additivity of one valence energies $\Delta E_A + \Delta E_B$ when one valence is a hole and the other is a particle. Similarly, for the DIP process, we expect some solutions for $\Delta E_{\mathrm{DIP}} \neq \Delta E_{\mathrm{IP},A} + \Delta E_{\mathrm{IP},B}$ when we ionize singly on two subsystems A and B, when they are non-interacting. Figure 6 shows that there is a spurious dispersion type interaction between subdiagrams for A and B. In contrast, the corresponding block structure for the $\bar{H}_{\mathrm{eff}}$ matrix in the CC formulation will be entirely different. The blocks *II* and *III* will be additionally *zero* in the $\bar{H}_{\mathrm{eff}}$ matrix, since they correspond to quasi-open excitations. As a result, even for A_1B_1 block, $\Delta E_k = \Delta E_A + \Delta E_B$ will hold good. The other zero entries will remain, lending complete subsystem separability of the ΔE_k's.

5. Eigenvalue-dependent partitioning applied to CC-LRT: a Brillouin–Wigner like core-extensive formulation (variant of Bloch–Horowitz theory)

We now show a way to fold the effect of the virtual manifold $\{Z_Q^+\}$ in a manner reminiscent of the Brillouin–Wigner theory [49b]. Since CC-LRT is a core-extensive theory, this will generate a Brillouin–Wigner theory involving only the *energy-shifts* ΔE_k, i.e. a theory of Bloch–Horowitz type.

For this, we use Eq. (3.8) to rewrite the function Ψ_k as:

$$\Psi_k = \exp(T)\Omega_v \Psi_k^0 \tag{5.1a}$$

with

$$\Omega_v \Psi_k^0 = \sum_{m,n\in P} C_{mn,k}\, \Phi_{mn} + \sum_{r,s\in Q} C_{rs,k}\, \chi_{rs}$$

$$= \Psi_k^0 + U_k; \qquad \langle \Psi_k^0 | U_k \rangle = 0 \tag{5.1b}$$

and attempt to generate $C_{rs,k}$ in a perturbative manner as follows. We rewrite Eq. (2.12) in terms of F and $R^{(1)}$ as:

$$[\Delta E_k - F]\Psi_k^0 + [\Delta E_k - F]U_k = R^{(1)}\Psi_k^{(0)} + R^{(1)}U_k \tag{5.2}$$

where from Sect. 4 we have F and $R^{(1)}$ as:

$$\bar{H} = F + \bar{H}^{(1)} \quad \text{and} \quad R = R^{(0)} + R^{(1)}$$

Hence U_k is given by:

$$U_k \equiv QU_k = Q[\Delta E_k - F]^{-1}[R^{(1)}\Psi_k^0 + R^{(1)}U_k] \tag{5.3}$$

From Eq. (5.3), U_k can be solved by iteration. From the structure of U_k it is clear that U_k can have no vacuum diagrams (since $R^{(1)}$ has no vacuum terms) and hence $\bar{H}_{\text{eff}} = P\bar{H}\Omega_v P$ will also have no vacuum diagrams. $\bar{H}_{\text{eff}}$ in this *energy dependent* partitioning satisfies:

$$\bar{H}_{\text{eff}}\Psi_k^0 = F + R_{PQ}^{(1)} \sum_{n=1} [Q(\Delta E_k - F)^{-1}R_{QP}^{(1)}]^n \Psi_k^0 = \Delta E_k \Psi_k^0 \tag{5.4}$$

where Q contains only those manifolds *which are retained in the truncated* CC-LRT *computations*. We note here that the same equation follows by using the partitioning technique of Löwdin straight way to Eq. (4.7) *for each* ΔE_k. In fact, we have:

$$C_{QK} = (\Delta E_k - R_{QQ})^{-1}R_{QP}C_{PK} \tag{5.5}$$

and

$$\bar{H}_{\text{eff}} = R_{PP} + R_{PQ}(\Delta E_k - R_{QQ})^{-1}R_{QP} \tag{5.6}$$

Using the partitioning of R into $R^0 + R^{(1)}$, the Brillouin–Wigner series follows by iteration. Since $\bar{H}_{\text{eff}}$ in Eq. (5.4) or (5.6) has only the *energy-shifts* ΔE_k, this perturbative theory is of *Bloch–Horowitz* type [50]; and likewise has no vacuum terms. Again as in the EIP technique, we may envisage either a power series expansion in $R^{(1)}$, or in V. In the former we generate a Bloch–Horowitz theory involving the normalized $R^{(1)}$ ("dressed" vertices including ground state correlation). In the latter we generate a particular variant of the Bloch–Horowitz type, where core excitation type of dangling blocks from the right have *local Rayleigh–Schrödinger like denominator*, while the rest of the diagram have Bloch–Horowitz type denominators. The genesis of this *hybrid structure* can be traced to the fact that $R^{(1)}$ contains T, and T has the Rayleigh–Schrödinger power series in terms of V. The series in V for T has the same structure of core excitation described above, while the factor $Q[\Delta E_k - F]^{-1}$ generate the usual Bloch–Horowitz like denominators. Thus a third order diagram like the one shown in Fig. 7a will appear in the series of $\bar{H}_{\text{eff}}$ of Eq. (5.4) or (5.5). The right going core-excitation stems from a T_1 and has a local denominator of the Rayleigh–Schrödinger type. The other denominator is global and is of Brillouin–Wigner type. The *conjugate diagram of Fig. 7a, will have an altogether different structure*. This is illustrated in Fig. 7b. Since this diagram has no core-excitation from the right, they cannot stem from T-diagrams, hence has only Bloch–Horowitz denominators, denoted by double line boxes. This unsymmetrical structure of the series owes itsorigin to the fact that the series of T in power series of V has only core-excitation from the right, and none from the left. Hence core-excitation from the left do not come from the T and acquire from Bloch–Horowitz denominators. A more telling demonstration of this fact can be given by

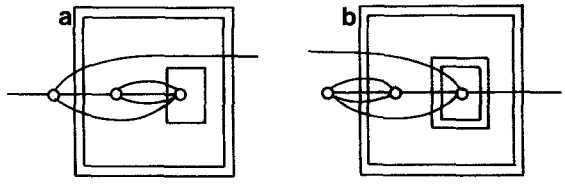

Fig. 7. a A third order diagram in the $B-W$ form of $\bar{H}_{\text{eff}}$ in the CC-LRT. The two vertices from the right contribute to a T_1, and has a local $R-S$ intermediate. The other denominator is global and is of $B-W$ type. **b** The conjugate diagram having global $B-W$ denominator only

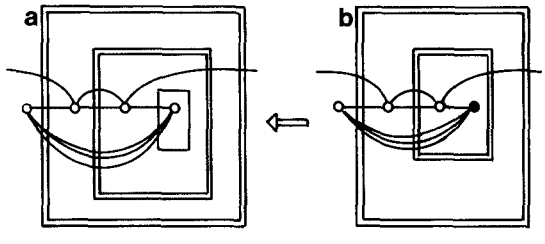

Fig. 8. a A diagram with a self-conjugate skeleton. The right-most vertex, with a right-going core-excitation, has a local $R-S$ denominator. The rest are all global $B-W$ denominators. Note that the left-most vertex, with a left-going core-excitation is traced differently from the right-most vertex. **b** The genesis of the diagram of Fig. 8a from a T_2-vertex

considering the diagram of Fig. 8a. The two projected core-excitations (on the right and left) have completely different denominators. The one on the right stems from a T_2-vertex (Fig. 8b), and thus has a Rayleigh–Schrödinger denominator. Using the terminology of Brandow [38], we may say that the series has *only downward reducibility*. We may remark here that $\bar{H}_{\text{eff}}$ generated from the EIP also clould have been expanded orderwise in V (i.e. $R^{(1)}$ expanded in power of V). In that case all the denominators would have been of Rayleigh–Schrödinger type. However, in that case the right going core-insertions would have *local* denominators, while the left going ones would have *global* denominators. Thus the diagrams of Figs. 7 and 8 would have resulted, with the difference that the double-barred denominators have to be interpreted as global Rayleigh–Schrödinger denominators.

We shall show in Sect. 6 that one may achieve both downward and upward reducibility provided we use a unitary cluster operator for Ω_c. This generates a unitarized version of CC-LRT, which we shall discuss only by way of illustration and to show the emergence of Algebraic Diagrammatic Construction (ADC). The extensivity of the ΔE_k's are also somewhat different.

6. Relation of CCLRT-like theories with ADC

In recent years, Schirmer, Cederbaum and others [56] have proposed a modified Green's function theory, currently known as the Algebraic Diagrammatic Construction (ADC), where the space in which the poles of Green's function are sought (roughly equivalent to the space of inner projection of the associated superoperator resolvent $(w-\hat{H})^{-1}$) is *systematically expanded* depending on the order of perturbation. Also, to analyze the pole structure of G, it is recommended in ADC to split the forward and backward components [56] of G, G_+ and G_-, and analyze each of these separately. It was shown recently [57] that

ADC follows from the Green's function theory if Ψ_{gr} is represented in terms of a *unitary cluster operator* of the form:

$$\Psi_{gr} = \exp(\sigma)\Phi_0 \tag{6.1}$$

where

$$\sigma = T - T^+ \tag{6.2}$$

This indicates that a comparison of ADC with the CC-LRT as formulated and discussed by us is not possible. However, we may envisage a *new formulation of linear response theory* where the essential spirit of CC-LRT could be retained. This will be a *unitarized formulation* of CC-LRT(UCC-LRT) which still keeps the renormalized TDA-like structure of the working equations.

In this modified formulation, we make use of an ansatz of the form:

$$\Psi_k = \exp(\sigma) W_k^+ \Phi_0 \tag{6.3}$$

where W_k^+ is written in terms of the operators $\{Z_1^+\}$ of the traditional CC-LRT. Using the same type of arguments as in CC-LRT, we ultimately find:

$$R^h C_k = \Delta E_k C_k \tag{6.4}$$

where R^h is a matrix with elements:

$$R^h_{k1} = \langle \Phi_0 | Z_k [\bar{H}^h, Z_1^+] | \Phi_0 \rangle \tag{6.5}$$

where:

$$\bar{H}^h = \exp(-\sigma) H \exp(\sigma) - E_{gr} \tag{6.6}$$

and is the *hermitian* "dressed" operator. It then follows that R^h itself is hermitian. This formulation obviously is core-extensive, since E_{gr} is generated from a unitary cluster operator $\exp(\sigma)$ for the core.

The chief difference between UCC-LRT and CC-LRT are (i) the nonterminating nature of the series for $\bar{H}^h$, since $\exp(\sigma)$ has both T and T^+; (ii) more complicated equation for T (and T^+) for the ground state, since the unitarized CC equations for the ground state contain again non-terminating series of T (and T^+). Despite the more complicated structure, UCC-LRT has certain redeeming features which are interesting.

One important aspect is the emergence of ADC, as we shall show now. Since $\exp(\sigma)$ is unitary, the expression for G_{ab} for Green's function may be written as [57]:

$$\begin{aligned} G_{ab} = &\langle \Phi_0 | \exp(-\sigma) a (\omega - \hat{H})^{-1} b^+ \exp(\sigma) | \Phi_0 \rangle \\ &\pm \langle \Phi_0 | \exp(-\sigma)(\omega - \hat{H})^{-1} b^+ a \exp(\sigma) | \Phi_0 \rangle \end{aligned} \tag{6.7}$$

Let us note that the nature of poles in the two terms in Eq. (6.7) is dictated by the types of functions reached by $b^+ \exp(\sigma)$ and $a \exp(\sigma)$ respectively, acting on $|\Phi_0\rangle$. Following Prasad et al. [58], we introduce a complete set of functions $|\eta_k\rangle \equiv \exp(\sigma) Z_k^+ |\Phi_0\rangle$, $\langle \eta_k | = \langle \Phi_0 | Z_k \exp(-\sigma)$ for all k in the resolution of identity. We further subdivide them as $|\eta_k^+\rangle$ and $|\eta_k^-\rangle$ for representing states reached by $b^+ \exp(\sigma)$ and $a \exp(\sigma)$, respectively. They have the properties:

$$\langle \Phi_0 | \exp(-\sigma) a | \eta_k^+ \rangle = \langle \Phi_0 | \tilde{a} Z_{k+}^+ | \Phi_0 \rangle = \langle \Phi_0 | [\tilde{a}, Z_{k+}^+] | \Phi_0 \rangle \tag{6.8}$$

and there is a similar equation for Z_{k-}^+. Here $\tilde{a}$ is the unitary transform of a:

$$\tilde{a} = \exp(-\sigma) a \exp(\sigma) \tag{6.9}$$

Introducing the transformed superoperator $\hat{\bar{H}}$ via:

$$\hat{\bar{H}} = \exp(-\sigma)\hat{H}\exp(\sigma) \tag{6.10}$$

we obtain

$$G_{ab} = \langle\Phi_0|[\tilde{a}, Z^+_{k+}]|\Phi_0\rangle[\omega - R^h_+]^{-1}_{kl}\langle\Phi_0|[Z^+_{l+}, \tilde{b}^+]|\Phi_0\rangle$$
$$\pm\langle\Phi_0|[\tilde{b}^+, Z^+_{k-}]|\Phi_0\rangle[\omega + R^h_-]^{-1}_{kl}\langle\Phi_0|[Z^-_{l-}, \tilde{a}]|\Phi_0\rangle \tag{6.11}$$

where the matrices R^h_+ and R^h_- are the same as the ones introduced in Eq. (6.5). For excited states Ψ^+_l, we have the basis $\exp(\sigma)Z^+_{k+}$, and for Ψ^-_l we have the basis $\exp(\sigma)Z^+_{k-}$. The corresponding matrices are then R^h_+ and R^h_-. Equation (6.11) indicates that the poles of G_{ab}, utilizing the unitary cluster ansatz for Ψ_{gr}, would generate the same poles as those obtained by diagonalizing the matrix R^h (for + and − separately). Thus UCC-LRT has the same information content about energy differences as the Green's function where Ψ_{gr} is given as a unitary cluster ansatz. The poles of the Green's function are also obtainable from Eq. (6.11) as a bonus.

Let us expand σ in powers of V, and also retain in the expression of $\tilde{a}$ terms upto order n in the residues. It is interesting to note, that $\tilde{a}^{[n]}$ contains a *finite number* of operators Z^+_k upto order n, and hence the dimension of the matrix R^h and the manifold defining R^h is automatically defined at each order n. Clearly, at higher n's the rank of Z^+_k will increase, and as a result the dimension of R^h also will likewise increase. For consistency at a given order, it is reasonable then to truncate $\hat{\bar{H}}$ also at the order n, and evaluate the matrix $R^{h[n]} \equiv \langle\Phi_0|[Z, \bar{H}^{[n]}Z^+]|\Phi_0\rangle$.

ADC will emerge from UCC-LRT if we enclose the operator manifold $\{Z^+_k\}$ depending on the order of perturbation V. Operationally this will mean that we first define a primary manifold defined by a, b^+. For example for IP/EA, these manifolds are $1h/1p$ types, and for EE $1p$-$1h$ types. Depending on the order of perturbation, the transformed operators $\tilde{a}^{[n]}$, $\tilde{b}^{+[n]}$ will generate $\{Z^{+[n]}_k\}$. If we truncate our manifold after those Z^+_k's generated by $\tilde{a}^{[n]}$ and $\tilde{b}^{[n]}$, and construct the matrix $R^{h[n]}$ using $\bar{H}^{[n]}$, then ΔE_i's obtained from UCC-LRT[n] are the same as those obtained from ADC(n).

The other interesting aspect of UCC-LRT is its ability to generate a Rayleigh–Schrödinger or Brillouin–Wigner series, depending on whether EIP or EDP is used, in a model space that respects *both* upward and downward reducibility. In contrast to Σ_{PP} obtained from EIP, the Σ^h_{PP} that will be generated by the EIP on R^h will have an $R^{(1)}$ involving σ which has both T and T^+. Thus, Σ^h_{PP} has both upward and downward going core excitations with local denominators, indicating both upward and downward reducibility [38]. With EDP, an energy dependent $\bar{H}_{\text{eff}}$ follows, having upward and downward reducibility for the core-excitations with the rest of the denominators as of Brillouin–Wigner type.

Finally, we make a comment on the nature of extensivity of the satellite peaks obtainable from the UCC-LRT for the IP/EA problem. Since R^h is hermitian, it has neither nh–np excitations nor de-excitations. As a result, when solving for the shake-up roots by diagonalizing Σ^h_{QQ} using the analogue of Eq. (4.15), we would never encounter terms of Fig. 1. Thus, the satellite roots will be *core-valence extensive* in UCC-LRT, since Σ^h_{QQ} then contains a connected operator acting in a quasi-complete space. We note that this feature is due to the hermitian nature of R^h, and is very special. For EE and other higher valence problems, the energy differences will remain core-extensive. We also mention

here that UCC theories for the closed shell are proving to be efficacious for property and gradient calculations for the closed shells [59].

7. Aspects of extensivity of energy differences of the quasi-Fock CC theory

When we are interested in the energy differences involving states obtained from multi-valence model functions and the ground state, it appears somewhat extravagant to invoke a Fock space strategy and generate the cluster amplitudes of the parent model space by proceeding hierarchically upwards. A more desirable approach is to invoke the factorizability, Eq. (2.10), for Ω and solve for Ω_v for the parent model space only – bypassing the hierarchical generation. Recently we have shown [45, 46] that such a formulation is possible by choosing a Hilbert space type approach. Ω_v has the form of a Fock space valence wave-operator *projected on the desired incomplete model space*. Since the full Ω has also in it the wave operator of the closed shell ground state, which generally differ in the number of electrons as compared to the excited or ionized state, we may call such a formulation as a *quasi-Fock* CC theory [45, 46]. One may even delete all references to the ground state itself and can generate a CC theory for the full Ω directly [45], which may be called a *quasi-Hilbert* CC theory. This latter formulation is closely related to the development of the quasi-Hilbert type put forward by Meissner et al. [47a] and Meissner and Bartlett [47b], to be discussed later.

In the quasi-Fock formulation, we write Ω as:

$$\Omega = \Omega_c \Omega_v \tag{7.1}$$

with

$$\Omega_v = \sum_{\mu} \exp(S^{\mu}) |\Phi^{\mu}\rangle\langle\Phi^{\mu}| \tag{7.2}$$

where S^{μ} has all the quasi-open and open operators involving excitations out of $|\Phi^{\mu}\rangle$. Since a quasi-open operator may generally induce transition to another Φ^{ν} by its action on a Φ^{μ}, it is tempting to drop from a S^{μ} such quasi-open operators. This would then violate the decoupling conditions on Fock space, Eq. (2.19) since there Ω_v contains all the possible quasi-open operators. We thus have to keep all the quasi-open operators in S^{μ} regardless of whether some of them make transitions within the model space. $\bar{H}_{\text{eff}}$ by construction come out as closed, and pairs of functions (Φ^{ν}, Φ^{μ}) joined by a quasi-open operator would have *zero-entry* in the matrix of $\bar{H}_{\text{eff}}$ in the Hilbert space. The quasi-Fock space Bloch equation for energy differences may be written as:

$$\exp(-S^{\mu})\bar{H} \exp(S^{\mu})|\Phi^{\mu}\rangle = \sum_{\nu} \exp(-S^{\nu}) \exp(S^{\mu})|\Phi^{\nu}\rangle\langle\Phi^{\nu}|\bar{H}_{\text{eff}}|\Phi^{\mu}\rangle \tag{7.3}$$

In using Eq. (7.3) for each Φ^{μ}, we shall take Φ^{μ} as the vacuum for the manipulations. It has been proved [45, 46] that S^{μ} and $\bar{H}_{\text{eff}}$ are both connected. To be more precise, we should label $\bar{H}_{\text{eff}}$ by μ (i.e., $\bar{H}^{\mu}_{\text{eff}}$) when it acts on Φ^{μ}, since while rewriting $\bar{H}_{\text{eff}}$ in normal order with respect to Φ^{μ}, only the potentially nonvanishing terms are retained, leading to an explicit μ dependence. Thus:

$$\bar{H}_{\text{eff}}|\Phi^{\mu}\rangle \equiv \bar{H}^{\mu}_{\text{eff}}|\Phi^{\mu}\rangle \tag{7.4}$$

Since $\bar{H}_{\text{eff}}$ is a closed operator by construction, it has the same block structure in the matrix representation for the model space. As an example, with the model space of $1h-1p+2h-2p$ for EE, we have the block structure of the

type shown in Fig. 4. One may imagine then that the core-valence extensivity of the associated energies would follow in a way exactly analogous to what was found for the Fock space using a perturbative solution of the diagonalization. There is, however, a subtle but nontrivial difficulty. $\bar{H}_{\text{eff}}$ in the Fock space theory was a *unique* operator, written in normal order, with respect to a fixed vacuum. $\bar{H}^{\mu}_{\text{eff}}$ in the quasi-Hilbert space theory has a structure dependent on Φ^{μ} it is acting upon. Thus the familiar use of Franz–Mills identity [54], invoked in proving the cancellation of the disconnected norm correction terms with similar terms from the general sum at each order of perturbation, cannot be used. We cannot juggle an $\bar{H}^{\mu}_{\text{eff}}$ and make it act on a Φ^{ν}, to effect a cancellation. A rather tricky and involved proof using the concept of "connected" entities [45] was, in fact, needed in this case.

We may, however, propose a rather simple alternative proof of the connectivity of the energies. The proof does not allow us to calculate the values for the energy differences at each order of perturbation unlike the more elaborate proof [45]. It is, however, sufficient to prove the extensivity.

Since the matrix elements $\langle \Phi^{\nu} | \bar{H}^{\mu}_{\text{eff}} | \Phi^{\mu} \rangle$ are all connected, we may infer that *there exists a connected closed operator* h_{eff} written in normal order with respect to a fixed vacuum, whose matrix-elements satisfy:

$$\langle \Phi^{\nu} | \bar{H}^{\mu}_{\text{eff}} | \Phi^{\mu} \rangle = \langle \Phi^{\nu} | h_{\text{eff}} | \Phi^{\mu} \rangle \tag{7.5}$$

The important point to note here is that h_{eff} must be a *connected closed* operator, since a disconnected h_{eff} would violate connectedness of the matrix elements of $\langle \Phi^{\nu} | \bar{H}^{\mu}_{\text{eff}} | \Phi^{\mu} \rangle$, and presence of quasi-open operators in h_{eff} would violate Eq. (7.5). The right side would thus be non-zero for the pairs (Φ^{ν}, Φ^{μ}) joined by a quasi-open operator, while the left side would be zero by construction. There need not be a unique h_{eff} for our subsequent proof, although the existence of a unique h_{eff} seems pretty clear.

Using Eq. (7.5), one may interpret the matrix involving elements $\langle \Phi^{\nu} | \bar{H}^{\mu}_{\text{eff}} | \Phi^{\mu} \rangle$ as involving the operator h_{eff}. The block structure and null entries in the matrix remain exactly the same. Since there is now a unique operator h_{eff}, we may invoke the Franz–Mills identity to prove the connectivity of the energy differences in a way exactly analogous to what was done for the Fock space CC theory. For a recent application of the formalism, we refer to the Ref. [46].

In their development of quasi-Hilbert type CC theory, Meissner et al. [47a] analyzed the consequence of including in S^{μ} only those operators leading to excitations from Φ^{μ} to functions outside the model space. This appears at first sight to be an eminently sensible choice for a Hilbert space type of formulation. An order by order expansion for S^{μ} was, however, shown to lead to disconnected diagrams stemming from the terms $[S^{\mu} - S^{\nu}]$ whenever if S^{ν} does not include the same excitations as those considered in S^{μ}. Clearly only quasi-open operators are the ones that either excite out of the model space or lead to scattering within the model space. The origin of the disconnectedness stems thus from partial inclusion of the quasi-open operators. For consistency, one has two choices: (a) to consider only special type model spaces where a quasi-open operator exciting out a Φ^{μ} can never lead to scattering within the model space and thus avoid the situation described above; (b) to include all the quasi-open operators in all the S^{μ}'s. We should note that the choice (a) corresponds to working with quasi-complete model spaces only, and Meisner et al. [47a] proved the connectivity of H_{eff} first utilizing this model space. Meissner and Bartlett in a subsequent communication [47b] choose the option (b), the same choice as that of Mukhopadhyay

and Mukherjee [45, 46], where S^{μ}'s are chosen as consisting of "open" and "quasi-open" type, and proved the connectivity of H_{eff}. A connected formulation of MBPT in the same spirit has also been considered by the same group [48].

8. Conclusions

We conclude this paper by summarizing our principal findings:

(1) We have discussed in detail the separability property of energy differences, emphasizing its *semi-local* nature in that, in the asymptotic limit of their noninteracting subsystems, ΔE becomes additively separable as ΔE_A, $\Delta E_A + \Delta E_B$, etc. depending on the subsystems excited. When only one subsystem is excited, ΔE depends only on the ΔE_A, and is *size-intensive* in this sense. When more than one subsystem is excited, we talk of additive separability of ΔE, and this may be viewed as *valence-extensivity* in the effective hamiltonian framework.

(2) For the separability of ΔE, it is essential to have the extensivity of E_{gr}, taken as the base of energy. This aspect of separability has been termed by us as *core-extensivity*.

(3) When both valence-extensivity and core-extensivity is satisfied, we have a *core-valence extensive* theory for energy differences. In contrast, when only the core-extensivity is satisfied, we have called these theories as core-extensive. The open-shell CC theory is core-valence extensive and the CC-LRT is core-extensive.

(4) We have analyzed and illustrated the core-extensivity of CC-LRT and core-valence extensivity of the CC theory for one valence and two-valence problems. An essential aspect in this analysis has been unified treatment of CC-LRT and CC theories in the effective hamiltonian framework using Bloch equation. Generic nature of the wave-operators in CC-LRT and CC theory have been indicated.

(5) It is shown that the CC-LRT is equivalent to CC theory for IP/EA (one-valence problem), both of which generate core-valence extensive energy differences. The satellite roots, in contrast, are only of the core-extensive type. A novel partitioning technique has been proposed in this paper to analyze perturbatively this aspect of the problem.

(6) It is remarkable that even for the one valence model space in the CC theory, the satellite energies obtained from the alternative solutions of the CC equations are not valence-extensive. This indicates the necessity of the existence of an analytic series (even if formal) of S_v in powers of V in proving the connectivity of $\bar{H}_{\text{eff}}$. The alternative solutions are not obtainable as power series in V.

(7) CC-LRT and CC theories have been shown to be inequivalent for two-valence problems and their behaviourial differences have been analyzed. Perturbative analysis has been carried out both in the Rayleigh–Schrödinger and in the Brillouin–Wigner form.

(8) An energy dependent partitioning produces an energy dependent effective hamiltonian. A perturbative expansion generates a Bloch–Horowitz type of series having a hybrid structure: the core-excitations from the right side have Rayleigh–Schrödinger local denominators (downward reducibility) while the rest of the terms have Bloch–Horowtiz denominators. Since there is no "upward reducibility" there is an inherent asymmetry in the treatment of the conjugate diagrams.

(9) A unitarized version of CC-LRT is formulated where a unitary cluster operator is used to construct Ψ_{gr}. This leads to UCC-LRT which has an underlying hermitian matrix R. It is pointed out that an energy independent

partitioning on UCC-LRT will lead to a Rayleigh–Schrödinger theory having both upward and downward reducibility.

(10) ADC is shown to emerge from the UCC-LRT at any given order of perturbation.

(11) The satellite peaks from UCC-LRT for IP/EA have been shown to be of core-valence extensive variety despite the fact that the underlying wave-operator has a linear expansion structure, owing to the hermitian nature of the matrix to be diagonalized.

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