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An alternative definition of the electron propagator in the superoperator form and its relation to linear response theory in a coupled-cluster framework

M DURGA PRASAD, SOURAV PAL and D MUKHERJEE*
Department of Physical Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India
*Present address: Department of Chemistry, University of Utah, Salt Lake City, Utah, U.S.A.

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Abstract. In this paper it is shown that (i) there exists an alternative definition of the superoperator resolvent for calculation of difference energy satisfying linked cluster theorem for a coupled-cluster choice of the ground-state function which may even be approximate; (ii) the pole-structure of this propagator-like function in superoperator form is shown to contain information similar to that contained in the conventional propagator. (iii) It is demonstrated that suitable "Killer conditions" and completeness of the "operator manifold"—essential for understanding the pole-structure of the propagator—can be established both for an exact and an approximate ground state function in a coupled-cluster form. (iv) It is also demonstrated that difference energies calculated with these propagator-like functions are identical to those obtained from a linear response theory in a coupled-cluster form put forward recently by Mukherjee *et al* and Monkhorst.

Keywords. Difference energies; atoms; molecules; linear response theory; propagators; electron propagator; superoperator; coupled-cluster framework.

1. Introduction

Many quantities of chemical interest are differences of two large numbers. Examples of such quantities are the excitation energies (EE), ionisation potentials (IP) and the electron affinities (EA). The conventional method of computation of such quantities is the configurational interaction (CI) method, in which the energies of both the levels involved (such as the ground state, and the excited state or the ionic state) are calculated to some degree of accuracy separately, and the difference is taken. This procedure has a serious drawback in the sense that the quantity of interest is calculated as the difference of two large quantities and the difference energies of interest are of the same order of magnitude as the error involved in the calculation of the original quantities.

An obvious way of overcoming this drawback is to calculate the difference quantity directly. The essential philosophy behind this approach is the realisation that the common correlation terms of both the parent ground state and the daughter state energies cancel out exactly in such difference, and need not be calculated explicitly. Only the difference terms which are by far the smaller of the two need be calculated.

A plethora of such theories have been developed over the past few years. These

include (a) the Green's function methods (Linderberg and Ohrn 1973; Jorgenson 1975; Pickup and Goscinski 1973; Cederbaum and Domcke 1977; Freed and Yeager 1977) and the related equations of motion (EOM) methods (Simons 1977; McCurdy *et al* 1977), (b) Rayleigh-Schrödinger many-body perturbation theory (Kvasnicka 1977; Brandow 1967; Kaldor 1975), and (c) the cluster expansion methods (Mukherjee *et al* 1977; Mukherjee and Mukherjee 1979; Mukhopadhyay *et al* 1979; Lindgren 1978; Monkhorst 1977; Reitz and Kutzelnigg 1979; Paldus *et al* 1979).

While all these methods lead to similar results, attempts to study the structural correspondence between them are sporadic in literature and include only (i) order by order comparison of the Greens functions approach to Rayleigh-Schrödinger theory (Brandow 1967; Hernandez and Langhoff 1977, Freed and Yeager 1977) (ii) delineation of a procedure by which the propagator method in the superoperator formalism may be mapped under certain approximations with the Green's function methods (Born and Ohrn 1980) and (iii) a formal demonstration of the structural equivalence of the open shell coupled cluster methods with that of the folded diagram perturbation theory (Mukherjee 1979; Lindgren 1978).

In this paper we analyse the structural correspondence between two specific theories belonging to classes (a) and (c) above. These theories are the propagator method in superoperator formalism and the linear response theory in CC-framework. We show that the superoperator formalism can be generalised to satisfy the linked cluster theorem. Such a superoperator formalism connects in a natural way with the cluster expansion method in the framework of linear response theory (Mukherjee and Mukherjee 1979). We also indicate that the alternative choice of superoperator offers immediate advantage over the conventional one for a possible extension to multi-configurational ground state.

In § 2 we discuss the alternative choice of the superoperator resolvent and discuss its properties *vis-a-vis* the conventional choice. In § 3 we rewrite the coupled cluster linear response theory in an EOM form and show that the two theories are connected. In § 4 we briefly indicate that there exist other possible choices of the superoperator resolvent which have as yet no counterparts in CC-linear response theory.

2. Alternative choice of the propagator in the superoperator resolvent

In what follows, we use the definition of the propagator as introduced by Goscinski *et al* 1980 (Goscinski and Lukman 1970). The n-electron propagator or G_n in an orbital representation is written in the form

$$G^n_{IJ} = \langle 0 | [C^n_I (E - \hat{H})^{-1} C^{n\dagger}_J]_{\pm} | 0 \rangle, \tag{1}$$

where C^n_I and $C^{n\dagger}_J$ are respectively products of n-destruction and n-creation operators, $\hat{H}$ is the Hamiltonian superoperator acting on a manifold of creation and annihilation operators $\{A_K\}$ satisfying $\hat{H} A_K = [A_K, \hat{H}]$ for A_K, and $| 0 \rangle$ is the exact ground state of the system. Depending on whether n is odd or even, the anticommutator (+) or the commutator (—) in (1) has to be taken. Inserting the

complete set of states in (1), it is a straightforward matter to show that (1) leads to a spectral resolution of the form

$$G^n_{IJ} = \sum_{K,M} \left[\frac{\langle 0 | C^n_I | \psi^M_K \rangle \langle \psi^M_K | C^{n\dagger}_J | 0 \rangle}{E - E_0 + E^M_K} \right.$$

$$\left. \pm \frac{\langle 0 | C^{n\dagger}_J | \psi^M_K \rangle \langle \psi^M_K | C^n_I | 0 \rangle}{E + E_0 - E^M_K} \right], \tag{2}$$

where the sum runs over all the eigenstate ψ^M_K of $\hat{H}$ belonging to various M electron spaces that would have non-vanishing matrix-elements like

$$\langle \psi^M_K | C^{n\dagger}_J | 0 \rangle \text{ or } \langle \psi^M_K | C^n_I | 0 \rangle$$

Clearly G^n_{IJ} would have simple poles as

$$E = E_0 - E^M_K \text{ or } E^M_K - E_0$$

depending on which range of E we are scanning.

The standard procedures for seeking the poles for practical calculations have mostly concentrated on choosing appropriately a suitable operator manifold $\{A_K\}$ for explicitly representing the superoperator inverse $(E-H)^{-1}$ in a matrix form, and a recipe for choosing an approximate reference state $|0\rangle$ for evaluating the expectation values (for a critical discussion, see *e.g.* Goscinski and Weiner 1980). Formally speaking, the propagators G^n_{IJ} may be interpreted as IJ element of a whole matrix G^n. It has been proved, using the completeness theorem for an operator manifold (Manne 1977; Dalgaard 1979), that G^n admits of a representation (see *e.g.* Goscinski and Weiner 1980):

$$G^n = K L^{-1} M, \tag{3a}$$

where
$$K = [\langle 0 | [C, B^\dagger]_\pm | 0 \rangle, \quad \langle 0 | [C, B]_\pm | 0 \rangle] \tag{3b}$$

$$L = \begin{bmatrix} (E \langle 0 | [B, B^\dagger]_\pm | 0 \rangle & -\langle 0 | [B, \hat{H} B]_\pm | 0 \rangle \\ -\langle 0 | [B, \hat{H} B^\dagger]_\pm | 0 \rangle) & \\ & (E \langle 0 | [B^\dagger, B]_\pm | 0 \rangle \\ -\langle 0 | [B^\dagger \hat{H}, B^\dagger]_\pm | 0 \rangle & -\langle 0 | [B^\dagger, \hat{H} B]_\pm | 0 \rangle) \end{bmatrix} \tag{3c}$$

$$M = \begin{bmatrix} \langle 0 | [B, C^\dagger]_\pm | 0 \rangle \\ \langle 0 | [B^\dagger, C^\dagger]_\pm | 0 \rangle \end{bmatrix} \tag{3d}$$

where the operator manifold $B^\dagger = \{B_K^\dagger\}$ is complete in the sense that $\{B_K^\dagger \mid 0\rangle\}$ is complete, and is chosen to satisfy the so-called 'Killer condition' for the adjoints:

$$B_K \mid 0\rangle = 0, \tag{4}$$

for all K.

The location of poles of G^n thus reduces to finding zeros of the matrix L which can be easily cast into an eigenvalue equation. For practical computation, one specifies an approximate ground state ψ_0, *i.e.* $\mid 0\rangle = \mid \psi_0\rangle$ a truncated operator manifold $\{B_K'^\dagger\}$ and finds the zeros of a truncated matrix L'. However, it is important to note that, for an arbitrary approximate ground state function ψ_0, choice of an appropriate operator manifold satisfying 'Killer condition' (equation (4)) is far from trivial. In fact, one can show that for an exact G^n, the off-diagonal blocks having $\langle 0 \mid [B, \hat{H} B^\dagger]_\pm \mid 0\rangle$ and $\langle 0 \mid [B^\dagger, \hat{H} B^\dagger]_\pm \mid 0\rangle$ should be exactly zero—a situation never encountered in practice for the conventional choices $\{B_K'^\dagger\}$ for which (4) is not satisfied. This is the reason why the matrix eigenvalue problem $L = 0$ for an approximate ground state ψ_0 and the set $\{B_K^\dagger\}$ has the dimension twice as large as that in a corresponding CI problem.

Clearly, then, for a practical calculation involving ψ_0 and an approximate set $\{B_K'^\dagger\}$ several inaccuracies and uncertainties creep in, whose extent is difficult to analyse in close terms. Furthermore, except when ψ_0 is just the exact ground state $\mid 0\rangle$, or a single determinant state $\mid \phi_0\rangle$ the matrix L involves calculation of expectation values like $\langle \psi_0 \mid [B, \hat{H} B^\dagger]_\pm \mid \psi_0\rangle$, etc. This would lead to appearance of unlinked terms as one would have in any CI calculation involving less than full CI. Thus, the accepted recipe for an approximate calculation of the superoperator resolvent runs afoul of two discrepancies: (i) Killer condition is not satisfied—vitiating the accuracy of the representation implied by (3); (ii) generalisation of the theory to an multi-configuration approximate ground state function ψ_0 leads to unlinked terms. Although very recently attempts are being made to use multiconfiguration functions in propagator methods in superoperator resolvents (Banerjee *et al* 1978; Albertson and Jorgenson 1979; Chuljian and Simons 1980), the two difficulties mentioned above have not been touched upon.

We would now like to introduce an alternative choice of the superoperator propagator which has the same pole-structure as the conventional (*e.g.* equation (1)), but which is amenable to calculation involving Killer condition to be satisfied for even approximate choice of the ground state. The choice also leads to inclusion of linked terms only for an approximate ψ_0-provided it is chosen in a particular (*e.g.* coupled cluster) form. It is now widely appreciated (Cizek 1966, 1969; Harris 1977) that even an approximate function $\psi_0 = e^T \phi_0$ with ϕ_0 a single determinant and T are hole-particle excitations leading to linked terms only for a transition formula like $\langle \phi_0 \mid A\, e^T \mid \phi_0\rangle$, where A is an arbitrary operator. The reason is simple: as $\langle \phi_0 \mid T = 0$, we may write $\langle \phi_0 \mid A\, e^T \mid \phi_0\rangle = \langle \phi_0 \mid e^{-T} A\, e^T \mid \phi_0\rangle$ and use Hausdorff expansion to show that $e^{-T} A e^T$ consists of multiple commutators which are linked (Mukherjee *et al* 1975 a, b). We take cue from this observations and would like to construct an alternative $\overline{G^n}$ which would have transition formulae like $\langle \phi_0 \mid [\ ]\, e^T \mid \phi_0\rangle$ rather than expectation values $\langle 0 \mid [\ ] \mid 0\rangle$.

Let us note that the choice G^n_{IJ} in (1) could have been rewritten as

$$G^n_{IJ} = \langle 0 | C^n_I (E - \hat{H})^{-1} C^{n\dagger}_J | 0 \rangle \mp \langle 0 | C^{n\dagger}_J (-E - \hat{H})^{-1} C^n_I | 0 \rangle, \quad (5)$$

where use has been made of the fact that $|0\rangle$ is an exact eigenstate of H. We now introduce a $\overline{G^n_{IJ}}$ defined as

$$\overline{G^n_{IJ}} = \langle \phi_0 | C^n_I (E - \hat{H})^{-1} C^{n\dagger}_J | 0 \rangle \mp \langle \phi_0 | C^{n\dagger}_J (E - \hat{H})^{-1} C^n_I | 0 \rangle, \quad (6)$$

where $\langle \phi_0 |$ is a single determinant and $| 0 \rangle$ is the exact ground state, written as $| 0 \rangle = e^T | \phi_0 \rangle$; the choice (6) is clearly generalisation of (5). We have kept E rather than $-E$ in the second term of (6) in contrast to that in (5) as it would look more symmetric and would merely change the sign of the poles without affecting the values. We show that $\overline{G^n}$ has the same pole-structure as G^n. For this we use the same kind of spectral resolution as used in getting (2), and obtain

$$\overline{G^n_{IJ}} = \sum_{K,M} \left[\frac{\langle \phi_0 | C^n_I | \psi^M_K \rangle \langle \psi^M_K | C^{n\dagger}_J | 0 \rangle}{E - E_0 + E^M_K} \mp \frac{\langle \phi_0 | C^{n\dagger}_J | \psi^M_K \rangle \langle \psi^M_K | C^n_I | 0 \rangle}{E - E_0 + E^M_K} \right] \quad (7)$$

Thus (7) provides us with the same kinds of poles (apart from signs) as those given by (2). The residues are, of course, different, but they do not affect the calculation of difference energies at all. Following Goscinski and Lukman (1970), we now show that there exists a vector space defined over an operator manifold which allows scalar product, resolution of identity, etc, and derive a completeness relation within the definition of the scalar product. This would lead to a representation of $\bar{G}$ in a way similar to (3a) and we would thus get an eigenvalue equation of the form $L=0$ for the choice (6). In § 3 we show that this equation yields the same difference energies as the ones provided by the linear response theory in a coupled cluster framework (Mukherjee *et al* 1979).

We define an identify superoperator $\hat{I}$ satisfying the relation $\hat{I} A_K = A_K$ for all operator manifolds $\{A_K\}$. If we now classify all the orbitals involved in the calculation (assumed complete) as holes or particles depending on whether they are occupied or not in ϕ_0, then we may induce a hole-particle transformation $\{a_\alpha\} \equiv \{b_\alpha\}$, α holes $\{a_p\} \equiv \{b_p\}$, p particles such that

$$b_i | \phi_0 \rangle = 0; \; i = \text{holes or particles.}$$

Then all possible products of a number of $b^\dagger$ would generate a complete set of determinants acting on $|\phi_0\rangle$ (Manne 1977), and we may call it a manifold $\{q^\dagger_K\}$ which is complete. The adjoint set $\{q_K\}$ satisfies the 'Killer condition' on ϕ_0

$$q_K | \phi_0 \rangle = 0, \quad (9)$$

but not (4). Let us now introduce another set of operators defined through the relation

$$Q_K = e^T q_K e^{-T}. \tag{10}$$

Note that for a representation of $|0\rangle$ as $|0\rangle = e^T|\phi_0\rangle$ Q_K satisfies the Killer condition on $|0\rangle$

$$Q_K|0\rangle = e^T q_K e^{-T} e^T|\phi_0\rangle = 0 \tag{11}$$

We show that both the set $\{q_K^\dagger|0\rangle\}$ and $\{Q_K^\dagger|\phi_0\rangle\}$ are complete, and together they define a bi-orthogonal set.

We note that, by construction, $\{q_K^\dagger|\phi_0\rangle\}$ is complete. Thus, any combination satisfying

$$\sum_K a_K q_K^\dagger|\phi_0\rangle = 0, \tag{12}$$

would imply $a_K = 0$, following from linear independence. From (12), we may write

$$\sum_K a_K e^T q_K^\dagger|\phi_0\rangle = 0, \tag{13a}$$

and, as both T and $q_K^\dagger$ consists only of excitation operators $b^\dagger$, they commute, so that a combination

$$\sum_K a_K q_K^\dagger e^T|\phi_0\rangle = \sum_K a_K q_K^\dagger|0\rangle = 0, \tag{13b}$$

would imply $a_K = 0$. Thus $\{q_K^\dagger|0\rangle\}$ are linearly independent. As their number coincides with those in $\{q_K^\dagger|\phi_0\rangle\}$ they must be complete.

For the set $\{Q_K^\dagger|\phi_0\rangle\}$, assume they are not linearly independent. Then there exists a set of nonzero a_K's such that

$$\sum_K a_K Q_K^\dagger|\phi_0\rangle = 0. \tag{14a}$$

Using the relation (10), and the fact that $T^\dagger|\phi_0\rangle = 0$ we have

$$\sum_K a_K e^{-T^\dagger} q_K^\dagger|\phi_0\rangle = 0. \tag{14b}$$

Premultiplying (14b) with $e^{T^\dagger}$, we have

$$\sum_K a_K q_K^\dagger|\phi_0\rangle = 0, \tag{14c}$$

with nonzero a_K's, which is a contradiction. Thus, the assumption of linear dependence of the set $\{Q_K^\dagger \mid \phi_0 \rangle\}$ was wrong. Again, as the number of $\{Q_K^\dagger \mid \phi_0 \rangle\}$ are the same as in $\{q_K^\dagger \mid \phi_0 \rangle\}$, they must be complete.

The scalar product $\langle \phi_0 \mid Q_K\, q_L^\dagger \mid 0 \rangle$ may be evaluated easily using (10), and this leads to

$$\begin{aligned}\langle \phi_0 \mid Q_K\, q_L^\dagger \mid 0 \rangle &= \langle \phi_0 \mid e^T\, q_K\, e^{-T}\, q_L^\dagger\, e^T \mid \phi_0 \rangle \\ &= \langle \phi_0 \mid q_K\, e^{-T}\, e^T\, q_L^\dagger \mid \phi_0 \rangle, \\ &= \delta_{KL},\end{aligned} \tag{15}$$

where commutability of T and $q_L^\dagger$ and the relation $\langle \phi_0 \mid T = 0$ has been made use of. The sets $\{q_K^\dagger \mid 0 \rangle\}$ and $\{Q_K^\dagger \mid \phi_0 \rangle\}$ are biorthogonal to each other.

Let us now introduce the following two definitions:

(A) Scalar product:

$$((\lambda_i \mid \lambda_j)) = ((\lambda_i \mid \hat{I} \mid \lambda_j)) = \langle \phi_0 \mid [\lambda_i, \lambda_j^\dagger]_\pm \mid 0 \rangle. \tag{16a}$$

(B) Scalar product involving a super operator other than $\hat{I}$:

$$((\lambda_i \mid \hat{A} \mid \lambda_j)) = \langle \phi_0 \mid [\lambda_i\, \hat{A}\, \lambda_j^\dagger \mp \lambda_i^\dagger\, \hat{A}\, \lambda_j] \mid 0 \rangle. \tag{16b}$$

Let us first establish that there exists a resolution of identity in the scalar product space defined above. For (16a), we may rigorously use the sets $\{q_K^\dagger \mid 0 \rangle\}$ and $\{Q_K^\dagger \mid \phi_0 \rangle\}$ in the resolution of identity in the ordinary (Dirac-) scalar product sense and get:

$$\begin{aligned}((\lambda_i \mid \lambda_j)) &= \langle \phi_0 \mid \lambda_i\, \lambda_j^\dagger \mid 0 \rangle \pm \langle \phi_0 \mid \lambda_j^\dagger\, \lambda_i \mid 0 \rangle \\ &= \sum_K [\langle \phi_0 \mid \lambda_i\, q_K^\dagger \mid 0 \rangle \langle \phi_0 \mid Q_K\, \lambda_j^\dagger \mid 0 \rangle \pm \\ &\quad \langle \phi_0 \mid \lambda_j^\dagger\, q_K^\dagger \mid 0 \rangle \langle \phi_0 \mid Q_K\, \lambda_i \mid 0 \rangle].\end{aligned} \tag{17a}$$

As $\langle \phi_0 \mid q_K^\dagger = Q_K \mid 0 \rangle = 0$ we may rewrite (17a) as

$$\begin{aligned}((\lambda_i \mid \lambda_j)) &= \sum_K [\langle \phi_0 \mid [\lambda_i, q_K^\dagger]_\pm \mid 0 \rangle \langle \phi_0 \mid [Q_K, \lambda_j^\dagger]_\pm \mid 0 \rangle \\ &\quad \pm \langle \phi_0 \mid [\lambda_j^\dagger, q_K^\dagger]_\pm \mid 0 \rangle \langle \phi_0 \mid [Q_K, \lambda_i]_\pm \mid 0 \rangle \\ &\equiv \sum_K [((\lambda_i \mid q_K))\, ((Q_K \mid \lambda_j)) \pm ((\lambda_i \mid Q_K^\dagger))\, ((q_K^\dagger \mid \lambda_j)).\end{aligned} \tag{18}$$

Thus it appears that there is a resolution of identity

$$\hat{I} = \sum_K [\,|\,q_K)) ((Q_K\,| + |\,Q_K^\dagger)) ((q_K^\dagger\,|\,]. \tag{19}$$

Let us note that, just as in the conventional superoperator formalism, the dimension of the expansion (19) equals twice the number of independent functions $\{q_K^\dagger|0\rangle\}$, etc.

Now, we show that the same resolution of identity may be inserted in the scalar product (16b) provided $\hat{A}$ is or is a function of the Hamiltonian superoperator $\hat{A} = F(\hat{H})$. We have,

$$\begin{aligned}((\lambda_i\,|\,F(\hat{H})\,|\,\lambda_j)) &= \langle\phi_0\,|\,\lambda_i\,F(\hat{H})\,\lambda_j^\dagger\,|\,0\rangle \mp \langle\phi_0\,|\lambda_j^\dagger\,F(\hat{H})\,\lambda_i\,|\,0\rangle,\\ &= \langle\phi_0\,|\,\lambda_i\,(F(E_0) - F(\hat{H}))\,\lambda_j^\dagger\,|\,0\rangle \mp \langle\phi_0|\,\lambda_j^\dagger\,(F\,(E_0) - F(\hat{H}))\,\lambda_i\,|\,0\rangle.\end{aligned} \tag{20}$$

If we insert resolution of identity in Dirac-sense after $\langle\phi_0\,|\,\lambda_i$ and $\langle\,\phi_0\,|\,\lambda_j^\dagger$ in (20), and use the same manipulation as in (18), we get

$$\begin{aligned}((\lambda_i\,|\,F(\hat{H})\,|\,\lambda_j)) = \sum_K [&((\lambda_i\,|\,q_K))\,((Q_K\,|\,F(\hat{H})\,|\,\lambda_j))\\ &+ ((\lambda_i\,|\,Q_K^\dagger))\,((q_K^\dagger|\,F(\hat{H})\,|\,\lambda_j))\cdot]\end{aligned} \tag{21}$$

Similarly, inserting resolution of identity in Dirac-sense after $(F(E_0) - F(\hat{H}))$ in (20), we have

$$\begin{aligned}((\lambda_i\,|\,F(\hat{H})\,|\,\lambda_j)) = \sum_K [&((\lambda_i\,|\,F(\hat{H})|q_K))\,((Q_K\,|\,\lambda_j))\\ &+ ((\lambda_i|\,F(\hat{H})|\,Q_K^\dagger))\,((q_K^\dagger\,|\,\lambda_j))\end{aligned} \tag{22}$$

Thus, when $\hat{A}$ is a function of $\hat{H}$, the resolution of identity (19) is generally valid for both (16a) and (16b). We would compactly write (19) as

$$I = \sum_K |\,X_K))\,((X_K\,|. \tag{23}$$

Using the definitions (16), the superoperator propagator $\overline{G^n}$ takes the form

$$\overline{G^n} = ((C^n\,|\,(E\hat{I} - \hat{H}^{-1})\,|\,C^n)) \tag{24}$$

Using the resolution of superoperator identity (23), we have

$$\overline{G^n} = ((C^n\,|\,X))\,((X|\,E\hat{I} - \hat{H}|\,X))^{-1}\,((X|\,C^n)). \tag{25}$$

Equation (25) is the analogue of (3) for the alternative choice $\overline{G^n}$, and it shows that poles of $\overline{G^n}$ would be obtained if we solve for the zeros of the matrix $((X|\,E\hat{I}-\hat{H}\,|X))$.

Let us now take a closer look at the structure of the matrix $L_x = ((X|E\hat{I}-\hat{H}\,|X))$:

$$L_x = ((X|\,E\hat{I}-\hat{H}\,|X))$$

$$= \begin{pmatrix} (Q|\,E\hat{I}-\hat{H}\,|q) & (Q|\,E\hat{I}-\hat{H}\,|Q^\dagger) \\ (q^\dagger|\,E\hat{I}-\hat{H}\,|q) & (q^\dagger|\,E\hat{I}-\hat{H}\,|Q^\dagger) \end{pmatrix}$$

$$= \begin{pmatrix} E(Q\,|\,q)-A & E(Q\,|\,Q^\dagger)-B \\ E(q^\dagger\,|\,q)-C & E(q^\dagger\,|\,Q^\dagger)-D \end{pmatrix} \tag{26}$$

and try to simplify the expressions for the matrices A, B, C and D. We show one such simplification explicitly and give results for the rest:

$$A_{KL} = (Q_K\,|\,\hat{H}\,|\,q_L),$$

$$= \langle\,\phi_0|\,e^T q_K\, e^{-T}\,[q_L^\dagger,\ H]\,e^T\,|\,\phi_0\,\rangle. \tag{27a}$$

Using $\langle\phi_0|\ e^T = \langle\,\phi_0|$, $Q_K\,|\,0\,\rangle = 0$, and the fact T commutes with $q^\dagger$ operators, we have

$$A_{KL} = \langle\,\phi_0\,|\,q_K\,[q_L^\dagger,\ e^{-T}\,H\,e^T]\,|\,\phi_0\,\rangle$$

$$= \langle\,\phi_0\,|\,q_K\,[q_L^\dagger,\ \bar{H}]\,|\,\phi_0\,\rangle, \tag{27b}$$

where we define a transformed Hamiltonian $\bar{H}$ as

$$\bar{H} = e^{-T}\,H\,e^T \tag{27c}$$

Similar to what is done in coupled cluster theory.

The matrix-elements of B, C and D are likewise given by

$$B_{KL} = (Q_K\,|\,\hat{H}\,|\,Q_L^\dagger) = \langle\,\phi_0|\,q_K\,[\bar{H},\,q_L]\,|\,\phi_0\,\rangle$$

$$\mp\,\langle\,\phi_0\,|\,q_L\,[\bar{H},\,q_K]\,|\,\phi_0\,\rangle \tag{28}$$

$$C_{KL} = (q_K^\dagger\,|\,\hat{H}\,|\,q_L) = \langle\,\phi_0\,|\,q_K^\dagger\,[H,\,q_L^\dagger]\,|\,0\,\rangle$$

$$\mp\,\langle\,\phi_0\,|\,q_L^\dagger\,[H,\,q_K^\dagger]\,|\,0\,\rangle = 0 \tag{29}$$

$$D_{KL} = (q_K^\dagger\,|\,\hat{H}\,|\ Q_L^\dagger) = -\,\langle\,\phi_0\,|\,q_L\,[\bar{H},\,q_K^\dagger]\,|\,\phi_0\,\rangle = -\,A_{LK}. \tag{30}$$

Thus zeros of L_x defined by (26) may be cast into an eigenvalue equation of the form

$$\begin{pmatrix} A & B \\ O & -A^T \end{pmatrix} \begin{pmatrix} U \\ V \end{pmatrix} = E \begin{pmatrix} U \\ V \end{pmatrix} \tag{31}$$

This is the equation analogous to $L=0$ as used in conventional superoperator theory. Let us note that A, B, C and D all contains linked terms only as H is itself linked.

3. Relation with the coupled-cluster linear response theory

There exist both a time-independent (Mukherjee *et al* 1979) time-dependent (Monkhorst 1977) version of the coupled-cluster linear response theory for calculating difference energies. The time-dependent version suffers from the appearance of spurious 'secular' terms just like its perturbative counterparts, while the time-independent version does not involve these terms at all. For our purpose, we would therefore make use of the time-independent version. The theory (only formally) introduces an external photon field and an interaction between this field and the electronic ground state of the system and evaluates the linear response function of the system in the presence of the photon field. The difference energies of interest are then obtained by seeking the poles of the linear response function. The ground state as well as the perturbed state in this theory is given a coupled-cluster representation.

In what follows, we shall recast the theory in a way analogous to EOM. For this transcription, it suffices to note the structure of the eigenvalue equation generated by the C-C linear response theory (see, *e.g.* equations C. 1 of Mukherjee *et al* 1979). The matrix whose eigenvalues are sought contains matrix-element of a transformed Hamiltonian $\bar{H}=e^{-T} H e^{T}$ between states like $\langle \phi_i^* |$ and $|\phi_0\rangle$, where $\langle \phi_i^* |$'s are the excited states obtained through action of an excitation operator acting on $|\phi_0\rangle$. Thus, at least in the linear response framework, we can cast the theory quite akin to a Tamm-Dancoff theory as shown below.

We write the ground state of the system in a coupled-cluster form

$$H e^{T} | \phi_0 \rangle = E_0 e^{T} | \phi_0 \rangle, \tag{32}$$

and T's are solved from

$$\langle \phi_i^* | e^{-T} H e^{T} | \phi_0 \rangle = \langle \phi_i^* | \bar{H} | \phi_0 \rangle = 0. \tag{33}$$

We write the excited states as

$$|\psi_{ex}\rangle = e^{T} S | \phi_0 \rangle, \tag{34}$$

and write the corresponding Schrödinger equation as in an EOM:

$$H | \psi_{ex} \rangle = H e^{T} S | \phi_0 \rangle = (E_0 + \triangle E) e^{T} S | \phi_0 \rangle \tag{35}$$

leading to $[\bar{H}, S] | \phi_0 \rangle = \triangle E S | \phi_0 \rangle$.

Now, we may easily show that the set $\{e^T q^\dagger \mid \phi_0\rangle\}$ is complete. This is because, had they not been linearly independent it would be possible to find non-zero a_K' s satisfying

$$\sum_K a_K \, e^T q_K^\dagger \mid \phi_0\rangle = 0. \tag{36}$$

Premultiplying by e^{-T}, (36) leads to
$\sum_K a_K \, q_K^\dagger \mid \phi_0\rangle = 0$ for non zero a_K's. But $\{q_K^\dagger \mid \phi_0\rangle\}$ is complete. So $\{e^T q_K^\dagger \mid \phi_0\rangle\}$ are linearly independent. As their number equals that in $\{q_K^\dagger \mid \phi_0\rangle\}$ they must be complete.

Thus, we write

$$S = \sum_L q_L^\dagger X_L, \tag{37}$$

and project (35b) on to all the excited states to get

$$\begin{aligned} \sum_L \bar{H}_{KL} \, X_L &= \sum_L \langle \phi_0 \mid q_K \, [\bar{H}, q_L^\dagger] \mid \phi_0\rangle \, X_L, \\ &= \triangle E \sum_L \langle \phi_0 \mid q_K \, q_L^\dagger \mid \phi_0\rangle X_L, \\ &= \triangle E \, X_K \end{aligned} \tag{38}$$

Now, the matrix $\bar{H}_{KL}$ whose eigenvalues are the difference energies of interest is precisely the matrix $-A$, as is evident on comparison of (27b) and (38)

$$\bar{H} = -A\,.$$

Let us assume that the eigenvalues of (38) are the roots and the right and left eigenvectors are χ_i^R and χ_i^L

$$\begin{aligned} \bar{H} \, \chi_i^R &= \omega_i \, \chi_i^R, \\ \chi_i^L \, \bar{H} &= \omega_i \, \chi_i^L. \end{aligned} \tag{40a}$$

This indicates that from (39)

$$A \, \chi_i^R = -\omega_i \, \chi_i^R. \tag{40b}$$

But, (31) implies that

$$AU + BV = EU, \tag{41a}$$

$$-A^T V = EV. \tag{41b}$$

But (41b) leads to

$$\bar{H}^T V = E V,$$

or
$$V^T \bar{H} = E V^T. \tag{42}$$

Thus, from (41b) roots E are the same roots ω_i and V^T's are χ_i^L. As the dimension of the problem (31) is twice that of (40), half the roots of (31) are thus ω_i. We now show by demonstration, that there exist an equal number of roots $-\omega_i$.

For a choice $\begin{pmatrix} U \\ V \end{pmatrix} = \begin{pmatrix} \chi_i^R \\ O \end{pmatrix}$

right hand side of (41a) and (41b) would look like $A\ \chi_i^R$ and O. The left hand sides are correspondingly, $E\chi_i^R$ and O. We know, that for χ_i^R, $E = -\omega_i$ from (40). Thus, for eigenvalues $-\omega_i$, the choice of $\begin{pmatrix} U \\ V \end{pmatrix}$ as $\begin{pmatrix} \chi_i^R \\ O \end{pmatrix}$ are consistent. The other possible roots of (31) are thus $-\omega_i$. This exhausts the total number of possible roots also.

Clearly the solution of (31), as in RPA, provides with both $+\omega_i$ and $-\omega_i$ as difference energies, though as $B=0$, the problem could have been decoupled to yield only ω_i by solving (41b), but that would be doing just the C-C linear response theory (eq. 40). Use of C-C linear response theory in a truncated space $\{q'_K\}$ involving single and double excitation for excitation energies (Mukherjee *et al* 1979, Adnan *et al* 1980 a, b) have produced encouraging results, and applications to *IP* calculations are under way (Ghosh *et al*, to be published).

4. Discussion

We have shown in §§ 2 and 3, how the definition of the superoperator as introduced in (6) leads in a natural way to expressions containing linked terms only. This desirable feature is retained for any practical calculation involving approximate ground state ψ_0. Because in that case the form of the function $|\psi_0\rangle = e^T \phi_0$ is still retained, and as a result, $\bar{H} = e^{-T} H e^{-T}$ remains still linked. Further, the Killer conditions $Q_K|0\rangle = 0$ gets replaced by $Q_K|\psi_0\rangle = 0$, with Q_K still defined as in (10), and thus the of the matrix (31) remains the same. This indicates that, so long as one sticks to (6) and (10), but uses a coupled-cluster representation for an approximate function $|\psi_0\rangle$, the simplifications inherent in Killer condition and linked nature of $\bar{H}$ may be made use of. To date, satisfying Killer condition in an approximate function has been considered to be quite awkward to be of any practical utility.

We should mention that the scalar product (16b) containing the superoperator is not mathematically analogous to the corresponding quantity as introduced by Goscinski and Lukman. In (16b), $\hat{H}$ is not strictly a linear superoperator as it acts both on λ_i and $\lambda_j^\dagger$ in $((\lambda_i | \hat{H} | \lambda_j))$. This does not introduce any mathematical problem so long as bounds to difference energies are not considered. In any case, bounds

to difference energies is a topic about which very little is known and there does not seem to be any theory which sheds light on this problem.

The choice (16b) is not the only possible choice for the scalar product $((\lambda_i \mid \hat{H} \mid \lambda_j))$ however. It is possible to retain the linear nature of $\hat{H}$—in the same spirit as in Goscinski and Lukman (Mukherjee and Simons to be published)—and work in such a direction is in progress.

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