Polarization Propagator and Equation of Motion Methods

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June 21, 2013

1 Derivation of general propagator methods

We have derived earlier a response function, or frequency dependent polarizability,

$$\Pi(BA|\omega) = \lim_{\eta \to 0} \left(\frac{1}{\hbar}\right) \sum_{n \neq 0} \left\{ \frac{\langle 0|B|n\rangle\langle n|A|0\rangle}{\omega + i\eta - \omega_{0n}} - \frac{\langle 0|A|n\rangle\langle n|B|0\rangle}{\omega + i\eta + \omega_{0n}} \right\} \tag{1}$$

where A is the applied perturbation, and B is the observable, and both are assumed to be Hermitian. ω_{0n} is the excitation energy for the change between states 0 and n. It should be clear that the response function has poles when ω — the applied field frequency – equals to the excitation energy ω_{0n}. Finding these poles is precisely the goal of polarization propagator methods. In the polarization propagator approach, the above equation has η set to 0, and the response function (the 'propagator'), defined as:

$$\langle\langle B; A\rangle\rangle_\omega \equiv \sum_{n \neq 0} \left\{ \frac{\langle 0|B|n\rangle\langle n|A|0\rangle}{\hbar\omega - \hbar\omega_{0n}} + \frac{\langle 0|A|n\rangle\langle n|B|0\rangle}{-\hbar\omega - \hbar\omega_{0n}} \right\} \tag{2}$$

Now we want to describe the propagator in terms of commutators between A and B. Make the observation that $\frac{ab}{c+d} = \frac{ab}{c} - \frac{d}{c}\left(\frac{ab}{c+d}\right)$, and applying to the first term of eq. (2) yields:

$$\sum_{n \neq 0} \frac{\langle 0|B|n\rangle\langle n|A|0\rangle}{\hbar\omega - \hbar\omega_{0n}} = \sum_{n \neq 0} \frac{\langle 0|B|n\rangle\langle n|A|0\rangle}{\hbar\omega} - \sum_{n \neq 0} \frac{-\hbar\omega_{0n}\langle 0|B|n\rangle\langle n|A|0\rangle}{\hbar\omega\left(\hbar\omega - \hbar\omega_{0n}\right)} \tag{3}$$

Do the same for the second term of eq. (2) and combine, recognizing that the $n = 0$ term vanishes in the first part (thus we get a sum over all n):

$$\begin{aligned}\langle\langle B; A\rangle\rangle_\omega = {} & \frac{1}{\hbar\omega} \sum_n \left\{ \langle 0|B|n\rangle\langle n|A|0\rangle - \langle 0|A|n\rangle\langle n|B|0\rangle \right\} \\ & - \frac{1}{\hbar\omega} \sum_{n \neq 0} \left\{ \frac{-\hbar\omega_{0n}\langle 0|B|n\rangle\langle n|A|0\rangle}{\hbar\omega - \hbar\omega_{0n}} - \frac{-\hbar\omega_{0n}\langle 0|A|n\rangle\langle n|B|0\rangle}{-\hbar\omega - \hbar\omega_{0n}} \right\}\end{aligned} \tag{4}$$

Making use of the fact that $1 = \sum_n |n\rangle\langle n|$ and $H|n\rangle = E_n|n\rangle$ and $\hbar\omega_{0n} = E_n - E_0$:

$$\langle\langle B; A\rangle\rangle_\omega = \frac{1}{\hbar\omega}\langle 0|\left[B, A\right]|0\rangle + \frac{1}{\hbar\omega} \sum_{n \neq 0} \left\{ \frac{\langle 0|B|n\rangle\langle n|\left[H, A\right]|0\rangle}{\hbar\omega - \hbar\omega_{0n}} + \frac{\langle 0|\left[H, A\right]|n\rangle\langle n|B|0\rangle}{-\hbar\omega - \hbar\omega_{0n}} \right\} \tag{5}$$

Which is to say that

$$\langle\langle B; A\rangle\rangle_\omega = \frac{1}{\hbar\omega}\langle 0|\left[B, A\right]|0\rangle + \frac{1}{\hbar\omega}\langle\langle B; \left[H, A\right]\rangle\rangle_\omega \tag{6}$$

Or, as we will use it:

$$\hbar\omega\langle\langle B;A\rangle\rangle_\omega = \langle 0|\,[B,A]\,|0\rangle - \langle\langle [H,B];A\rangle\rangle_\omega \tag{7}$$

As you may have started to see, we can define the propagator iteratively in terms of commutator expectation values of ever-increasing complexity. This is what is known as the so-called "moment expansion" of the propagator. Thus by iteration:

$$\langle\langle B;A\rangle\rangle_\omega = \frac{1}{\hbar\omega}\left\{\langle 0|\,[B,A]\,|0\rangle + \left(\frac{-1}{\hbar\omega}\right)\langle 0|\,[[H,B]\,,A]\,|0\rangle + \left(\frac{-1}{\hbar\omega}\right)^2\langle 0|\,[[H,[H,B]]\,,A]\,|0\rangle + \cdots\right\} \tag{8}$$

We introduce the "superoperator" (analogous to the Liouville operator in Statistical Mechanics), which acts on operators to give their commutator:

$$\hat{H}B = [H,B]\,, \qquad \hat{H}^2 B = [H,[H,B]]\,, \qquad \hat{H}^3 B = [H,[H,[H,B]]]\,, \qquad \cdots \tag{9}$$

With this definition, we have the power series

$$\langle\langle B;A\rangle\rangle_\omega = \frac{1}{\hbar\omega}\sum_{n=0}^{\infty}\left(\frac{-1}{\hbar\omega}\right)^n\langle 0|\left[\hat{H}^n B, A\right]|0\rangle \tag{10}$$

At this point we make two useful observations. First, recognize that

$$\langle 0|\left[\hat{H}B, A\right]|0\rangle = -\langle 0|\left[B, \hat{H}A\right]|0\rangle \tag{11}$$

and so $\hat{H}$ can be applied to A instead of B insofar as we introduce a factor of $(-1)^n$. Furthermore, note that the power series is equivalent to

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \cdots \tag{12}$$

Making use of these two observations (and using $\hat{1}X = X$ and $\hat{H}^0 = \hat{1}$, where $\hat{1}$ is the unit superoperator), we have

$$\langle\langle B;A\rangle\rangle_\omega = \langle 0|\left[B, \left(\hbar\omega\hat{1} - \hat{H}\right)^{-1} A\right]|0\rangle \tag{13}$$

Which is merely a cosmetic change at this point, as the superoperator resolvent is defined by the series expansion. We need to find a matrix representation of the resolvent, which implies that we find a complete basis set of operators. To do this, we are going to develop an "operator space", where $\hat{H}$ is defined by its effect on operators instead of vectors. Introducing the notation

$$(X|Y) = \langle 0|\left[X^\dagger, Y\right]|0\rangle \tag{14}$$

and it follows that $(Y|X) = (X|Y)^*$. As defined, we now have

$$\langle\langle B;A\rangle\rangle_\omega = \left(B^\dagger|\left(\hbar\omega\hat{1} - \hat{H}\right)^{-1}|A\right) \tag{15}$$

Which is formally exact, albeit useless until we develop approximations. However, the form of the above equation *does* look similar to ordinary vector spaces in Hartree-Fock, *etc.* methods. Truncation of a basis in linear vector space V to n elements produces a subspace V_n, and truncation of a general vector corresponds to finding its projection onto the subspace. It follows, then, that we need to find a projection operator ρ, associated with the truncated basis. If the basis ($\mathbf{e}$, say) is orthonormal we write

$$\rho = \sum_i e_i e_i^* = \mathbf{e}\mathbf{e}^\dagger \tag{16}$$

which in a complete basis gives:

$$\rho = \sum_i |e_i\rangle\langle e_i| = \mathbf{1} \tag{17}$$

If it is not an orthonormal basis, we must include the metric matrix $\mathbf{S} = \mathbf{e}^\dagger\mathbf{e}$ (or Löwdin basis $\bar{\mathbf{e}}\mathbf{S}^{-1/2}$):

$$\rho = \mathbf{e}\mathbf{S}^{-1}\mathbf{e}^\dagger = \sum_{ij} e_i (S^{-1})_{ij} e_j^* \tag{18}$$

When using a truncated basis in *operator space*, two kinds of projections are useful (Löwdin, 1977, 1982),

$$A' = \rho A \rho, \qquad A'' = A^{1/2}\rho A^{1/2} \tag{19}$$

which are the *outer projection* and *inner projection*, respectively, onto space V_n defined by ρ. Note that $AB = C \;\not\Longrightarrow\; A'B' = C' \;\not\Longrightarrow\; A''B'' = C''$. Plugging the metric into A'':

$$A'' = A^{1/2}\mathbf{e}\mathbf{S}^{-1}\mathbf{e}^\dagger A^{1/2} \tag{20}$$

and we define

$$\mathbf{f} \equiv A^{1/2}\mathbf{e} = \begin{pmatrix} A^{1/2}\mathbf{e}_1 & A^{1/2}\mathbf{e}_1 & \cdots \end{pmatrix} \tag{21}$$

We assume that A is Hermitian and positive-definite, so that $A^{1/2}$ can be defined. Note that $\mathbf{S} = \mathbf{e}^\dagger\mathbf{e} = \left(A^{-1/2}\mathbf{f}\right)^\dagger \left(A^{-1/2}\mathbf{f}\right) = \mathbf{f}^\dagger A^{-1}\mathbf{f} \implies A'' = \mathbf{f}\left(\mathbf{f}^\dagger A^{-1}\mathbf{f}\right)^{-1}\mathbf{f}^\dagger$. Because A is arbitrary, replace it with A^{-1}, and since $\mathbf{f}^\dagger A\mathbf{f} = \mathbf{A}$ with $A_{ij} = \langle f_i|A|f_j\rangle$:

$$\left(\mathbf{A}^{-1}\right)'' = \mathbf{f}\left(\mathbf{f}^\dagger A\mathbf{f}\right)^{-1}\mathbf{f}^\dagger = \mathbf{f}\mathbf{A}^{-1}\mathbf{f}^\dagger \tag{22}$$

As the basis $V_n \to V$, the inner projection $\to \mathbf{A}^{-1}$, else it is simply a finite basis approximation to the inverse. This is the operator inverse in terms of a matrix inverse. Since $\mathbf{e}$ was an arbitrary basis defining V_n, let $\mathbf{f}$ define n-dimensional subspace V_n'. Thus:

$$\mathbf{A}^{-1} \approx \mathbf{e}\mathbf{A}^{-1}\mathbf{e}^\dagger = \sum_{ij} e_i (\mathbf{e}^\dagger\mathbf{A}\mathbf{e})^{-1}_{ij}\mathbf{e}_j^* \tag{23}$$

Thus the inner projection leads to an approximation for the projector. Let us define the (as of yet undefined) operator basis:

$$\mathbf{n} = (\mathbf{n}_1 \quad \mathbf{n}_2 \quad \mathbf{n}_3 \quad \cdots) \tag{24}$$

Given that the binary product (compare with $\langle x|y\rangle = x^*y$ for vectors)

$$X^\dagger \cdot Y = (X|Y) = \langle 0| \left[X^\dagger, Y\right] |0\rangle \tag{25}$$

then for our resolvent superoperator we have

$$\hat{R}(\omega) = (\hbar\omega\hat{1} - \hat{H})^{-1} = \mathbf{n}R(\omega)\mathbf{n}^\dagger = \sum_{r,s} \mathbf{n}_r [R(\omega)]_{rs}\mathbf{n}_s^\dagger \tag{26}$$

where $\mathbf{n}_r$ and $\mathbf{n}_s^\dagger$ are the analogues of $\mathbf{e}$ and $\mathbf{e}^*$ in operator space. Finally, if

$$R(\omega) = M(\omega)^{-1}, \qquad M(\omega) = \mathbf{n}^\dagger(\hbar\omega\hat{1} - \hat{H})\mathbf{n} \tag{27}$$

then we have

$$\langle\langle B; A\rangle\rangle_\omega = B \cdot R(\omega) \cdot A = B \cdot \mathbf{n}R(\omega)\mathbf{n}^\dagger \cdot A \tag{28}$$

which is the key to calculating approximations to response properties. The matrix M is determined once we have chosen an operator basis. This approximation depends on two things: 1) the basis $\mathbf{n}$ (and its truncations), and 2) the reference function, that is not the exact ground state. Any approximations to these two things are where we get out various response methods.