Calculating response functions in time domain with non-orthonormal basis sets

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II. NONORTHONORMAL BASIS SET

In this section, let us review the description of a system with a Hilbert space spanned by finite numbers of linearly independent nonorthonormal bases \{|\varphi_\alpha\}. We distinguish a vector in the Hilbert space from its components by using the bracket notation for a vector in the Hilbert space and the tensor notation \[24\] and the matrix notation \[26\] for its components.

The overlap matrix is defined as a Hermitian matrix with subscripts,

\[ S_{\alpha\beta} \equiv \langle \varphi_\alpha | \varphi_\beta \rangle = S^*_{\beta\alpha}. \] (1)

Then the inverse matrix is defined as a matrix with superscripts that satisfies

\[ \sum_\beta (S^{-1})^{\alpha\beta} S_{\beta\gamma} = \delta^\gamma_{\alpha}, \] (2)

where \( \delta^\gamma_{\alpha} \) is Kroneker’s delta. Then the dual basis set \( \langle \varphi^\alpha | \) is defined by

\[ |\varphi^\alpha \rangle = \sum_\beta |\varphi_\beta \rangle (S^{-1})^{\beta\alpha}, \] (3)

which is used only in formal description, but not in real numerical calculations. These two basis sets are biorthogonal and bicomplete,

\[ \langle \varphi^\alpha | \varphi_\beta \rangle = \sum_\gamma (S^{-1})^{\alpha\gamma} S_{\gamma\beta} = \delta_\beta^\alpha, \] (4)

\[ \sum_\alpha |\varphi_\alpha \rangle \langle \varphi^\alpha | = I, \] (5)

where \( I \) is the identity operator.

An arbitrary state \( |\phi \rangle \) can be expressed in original or dual basis set,

\[ |\phi \rangle = \sum_\alpha \phi^\alpha |\varphi_\alpha \rangle = \sum_{\alpha,\beta} \phi^\alpha |\varphi^\beta \rangle S_{\beta\alpha} = \sum_\beta \phi_\beta |\varphi^\beta \rangle, \] (6)

where \( \phi^\alpha \) and \( \phi_\alpha \) are the components in each basis set, which are related to each other by

\[ \phi_\beta = \sum_\alpha S_{\beta\alpha} \phi^\alpha. \] (7)

The components of \( |\phi \rangle \) are represented by a column vector \( \phi = [\phi^1, \phi^2, \ldots, \phi^N] \), where \( t \) indicates the transpose of a vector or matrix, and its dual \( \langle \hat{\phi} | \) is represented by a row vector \( \hat{\phi} = [\phi_1^1, \phi_2^2, \ldots, \phi_N^N] \).

The lower-indexed components of an operator, the Hamiltonian \( \hat{H} \) for example, are defined in the original basis set by
\[ H_{\alpha\beta} = \langle \varphi_\alpha | \hat{H} | \varphi_\beta \rangle. \]  

Then the mixed-indexed components are defined by
\[ H^\alpha_\beta = \langle \varphi^\alpha | \hat{H} | \varphi_\beta \rangle = \sum_\gamma (S^{-1})^{\alpha\gamma} H_{\gamma\beta}. \]

The manipulation of state vectors and operators is most conveniently expressed in the mixed representation. For example, \(|\psi\rangle = \hat{H}|\phi\rangle\) becomes \(\psi^\alpha = \sum_\beta H^\alpha_\beta \phi^\beta\). Therefore, we can introduce the matrix notation, \(\psi = \bar{H}\phi\) where the bar over the matrix symbol indicates the raise of the first index \(\bar{H} = \{H^\alpha_\beta\}\). Then Eq. (1) is rewritten as
\[ \bar{H} = S^{-1} H, \]

where \(H\) is the matrix \(\{H_{\alpha\beta}\}\). Now \(\bar{H}\) is not Hermitian matrix anymore, since
\[ \bar{H}^\dagger = (S^{-1} H)^\dagger = H^\dagger (S^{-1})^\dagger = HS^{-1} = \bar{S}H \bar{S}^{-1} \neq \bar{H}. \]

Note that the full calculation of \(S^{-1}\), which costs \(O(N^3)\) CPU time, is not necessary to obtain a good approximant of \(\bar{H}\) from a sparse \(H\) \[25,26\]. One of the advantages of \(\bar{H}\) over \(H\) is that power of \(H\) is easily calculated without explicitly multiplying \(S^{-1}\) \[25\],
\[ \hat{H}^n |\phi\rangle = \sum_\beta \hat{H}^n |\varphi_\beta\rangle \phi^\beta = \sum_\alpha \sum_\beta \langle \varphi_\alpha | (\bar{H}^\dagger)^n |\varphi_\beta\rangle \phi^\beta \]
\[ = \sum_\alpha \langle \varphi_\alpha | \left( \bar{H}^\dagger \right)^n \phi \rangle^\alpha. \]

The matrix form of the eigenvalue problem
\[ \sum_\beta H^\alpha_\beta \phi^\beta = E \phi^\alpha \]
becomes
\[ \bar{H} \phi (E_\beta) = E_\beta \phi (E_\beta) \]
and the dual of Eq. (16) becomes
\[ \phi^\dagger (E_\beta) \bar{H} = E_\beta \phi^\dagger (E_\beta). \]

The eigenvectors, Eqs. (16) and (17), define the eigenstates
\[ |E_\beta\rangle = \sum_\alpha \langle \varphi_\alpha | \phi^\alpha (E_\beta), \]
\[ \langle \bar{E}_\beta | = \sum_\alpha \phi^\dagger_\alpha (E_\beta) \langle \varphi^\alpha |, \]

which satisfy the biorthonormality and the bicompleteness
\[ \langle \bar{E}_\alpha | E_\beta \rangle = \delta_{\alpha\beta}, \]
\[ \sum_\alpha |E_\alpha\rangle \langle \bar{E}_\alpha| = I. \]

### III. RANDOM VECTORS

Let us define random states \[22,23\] by
\[ |\Phi\rangle = \sum_\beta \langle \varphi_\beta | \phi^\beta, \]
\[ \langle \bar{\Phi} | = \sum_\alpha \phi^\dagger_\alpha \langle \varphi^\alpha |, \]

where \(\{|\varphi_\beta\rangle\}\) and \(\{\langle \varphi^\alpha |\}\) are the basis set used in the computation and its dual basis set, respectively.

Their components
\[ \Phi^\alpha = \tilde{\Phi}^\alpha = \xi_\alpha \]
are the pseudorandom numbers that satisfy the statistical relation
\[\langle \xi_\alpha ^* \xi_\beta \rangle \rangle = \delta_{\alpha\beta} \]
where \(\langle \cdot | \cdot \rangle \rangle \) indicates the statistical average. Note that the transformation of the random vector to its dual does not contain the overlap matrix \(S\) in Eq. (24), unlike the general rule for usual vectors in Eq. (1).

These random vectors may be also expressed by the eigenvectors of \(\bar{H}\) by substituting Eq. (21) into Eqs. (22) and (23),
\[ |\Phi\rangle = \sum_\beta \langle E_\beta | \varphi_\gamma \rangle \xi_\gamma = \sum_\beta |E_\beta\rangle \zeta_\beta, \]
\[ \langle \bar{\Phi} | = \sum_\alpha \zeta^*_\alpha \langle \varphi^\dagger_\alpha | E_\alpha \rangle = \sum_\alpha \zeta^*_\alpha |E_\alpha\rangle, \]

where
\[ \zeta_\beta = \sum_\gamma \langle \bar{E}_\beta | \varphi_\gamma \rangle \xi_\gamma, \]
\[ \zeta^*_\alpha = \sum_\delta \xi^*_\delta \langle \varphi^\dagger_\alpha | E_\alpha \rangle. \]

Although we do not know the actual value of \(\zeta^*_\alpha\), \(\zeta_\beta\), \langle \bar{E}_\beta |\), or \(|E_\alpha\rangle\), we can derive the statistical relation of the random variables \(\zeta_\beta\) as follows:
\[ \langle \langle \zeta_\alpha \zeta_\beta \rangle \rangle = \sum_\gamma \sum_\delta \langle \varphi^\dagger_\alpha | E_\alpha \rangle \langle E_\beta | \varphi_\gamma \rangle \zeta^*_\delta \xi_\gamma = \delta_{\alpha\beta}. \]

This relation is very important, as we will see later.

One of the useful features of random states is that the expectation value of an operator \(\hat{X}\) in terms of the random states gives trace of the operator,
\[ \langle \langle \langle \hat{X} | \Phi \rangle \rangle \rangle = \sum_{\alpha\beta} \langle \langle \xi_\alpha \xi_\beta \rangle \rangle \langle \varphi^\alpha | \hat{X} | \varphi_\beta \rangle = \sum_\alpha X^\alpha, \]

which is identical to the trace calculated with an orthonormal basis set \(|n\rangle\) because
\[ \langle \hat{X} \rangle = \text{tr} [\hat{X}] = \sum_{n,\alpha,\beta} \langle n | \varphi_{\alpha} \rangle X^{\alpha}_{\beta} \langle \varphi^{\beta} | n \rangle \]  
\[ = \sum_{\alpha,\beta} \langle \varphi^{\beta} | \varphi_{\alpha} \rangle X^{\alpha}_{\beta} = \sum_{\alpha} X^{\alpha}_{\alpha}. \]  

IV. PROJECTED RANDOM VECTORS

Then the projected random vectors are defined by
\[ \Phi_{E_f} = \theta (E_f - \mathbf{H}) \Phi = \sum m c_m \psi_m \]  
\[ \tilde{\Phi}_{E_f} = \tilde{\Phi} \theta (E_f - \mathbf{H}) = \sum m c_m \tilde{\psi}_m \]  

where \( c_m \) are the coefficients for the Chebyshev polynomial expansion of the step function \( \theta (x) = \begin{cases} 0 & (x < 0) \\ 1 & (x > 0). \end{cases} \)  

The random vectors multiplied by the Chebyshev polynomial \( T_m (\mathbf{H}) \)
\[ \psi_m = T_m (\mathbf{H}) \Phi, \]  
\[ \tilde{\psi}_m = \tilde{\Phi} T_m (\mathbf{H}), \]  
are calculated by using the recursion formulas

\[ \psi_{m+1} = 2 \Phi \psi_m - \psi_{m-1}, \]  
\[ \tilde{\psi}_{m+1} = 2 \tilde{\Phi} \tilde{\psi}_m - \tilde{\psi}_{m-1}. \]

The coefficient vectors, Eqs.(33) and (eq:step.def), define the projected random states
\[ |\Phi_{E_f}\rangle \equiv \sum_{\alpha} |\varphi_{\alpha}\rangle \langle \Phi_{E_f}\rangle_{\alpha} = \sum_{E_{\beta} \leq E_f} |E_{\beta}\rangle \zeta_{\beta}, \]  
\[ \langle \tilde{\Phi}_{E_f}\rangle \equiv \sum_{\alpha} \langle \tilde{\Phi}_{E_f}\rangle_{\alpha} \langle \varphi^{\alpha}\rangle = \sum_{E_{\beta} \leq E_f} \zeta_{\beta}^{\ast} \langle \tilde{E}_{\beta}\rangle. \]

One of the useful features of projected random states is that the expectation value of an operator \( \hat{X} \) with them gives the trace of the operator over the Fermi occupied states,

\[ \langle \langle \tilde{\Phi}_{E_f} | \hat{X} | \Phi_{E_f} \rangle \rangle = \sum_{E_{\alpha} \leq E_f} \langle \langle \zeta_{\alpha}^{\ast} \zeta_{\alpha} \rangle \rangle \langle \tilde{E}_{\alpha} | \hat{X} | \tilde{E}_{\beta} \rangle \]  
\[ = \sum_{E_{\alpha} \leq E_f} X^{\alpha}_{\alpha}, \]

where the statistical relation Eq. (30) is used.

V. TIME EVOLUTION

The time-dependent Schrödinger equations corresponding to the eigenvalue equations (10) and (17) become
\[ + \frac{d}{dt} \Phi (t) = \mathbf{H} \Phi (t), \]
\[ - \frac{d}{dt} \tilde{\Phi} (t) = \tilde{\Phi} (t) \mathbf{H}. \]

The formal solutions of the time-dependent equations become
\[ \Phi (t) = e^{-i \mathbf{H} t} \Phi (0), \]
\[ \tilde{\Phi} (t) = e^{-i \tilde{\mathbf{H}} t} \tilde{\Phi} (0). \]

For numerically calculating the time evolution of the coefficients, we use the leap frog method \[ \Phi (t + \Delta t) = -2i \Delta \mathbf{H} \Phi (t) + \Phi (t - \Delta t), \]
\[ \tilde{\Phi} (t + \Delta t) = +2i \Delta \tilde{\mathbf{H}} \tilde{\Phi} (t) + \tilde{\Phi} (t - \Delta t), \]  
where \( \Delta t \) is the time step.

VI. LINEAR RESPONSE FUNCTION

When an impulse of perturbation \( \hat{A} \delta (t) \) is applied to the system described by the Hamiltonian \( \hat{H} \), the time evolution of the wave function is described by the time-dependent Schrödinger equation in the matrix form
\[ \frac{d}{dt} \Phi (t) = \{ \mathbf{H} + \mathbf{A} \delta (t) \} \Phi (t), \]
\[ - \frac{d}{dt} \tilde{\Phi} (t) = \{ \tilde{\Phi} (t) \mathbf{H} + \mathbf{A} \delta (t) \}. \]

where \( \mathbf{A} = S^{-1} \mathbf{A} \) is the matrix of \( \hat{A} \) in the mixed representation. Note that the impulse \( \mathbf{A} \delta (t) \) contains all frequency components \( \mathbf{A} e^{-i\omega t} \). Assuming that the system was in a projected random state \( \Phi (0) = \Phi_{E_f} \) before the perturbation, the wave function after the perturbation \( t > 0 \) becomes
\[ \Phi (t) = \Phi (0) + \delta \Phi (t), \]
\[ \tilde{\Phi} (t) = \tilde{\Phi} (0) + \delta \tilde{\Phi} (t), \]
where
\[ \Phi (0) = e^{-i \mathbf{H} t} \Phi_{E_f}, \]
\[ \delta \Phi (t) = (-i) e^{-i \mathbf{H} t} \theta (\mathbf{H} - E_f) \mathbf{A} \Phi_{E_f}, \]
and
\[ \tilde{\Phi} (0) = \tilde{\Phi}_{E_f} e^{+i \tilde{\mathbf{H}} t}, \]
\[ \delta \tilde{\Phi} (t) = (+i) \tilde{\Phi}_{E_f} e^{+i \tilde{\mathbf{H}} t} \mathbf{A} e^{-i \mathbf{H} t}. \]
are the time evolution of unperturbed and perturbed vectors. In Eqs. (55) and (57), projection operators \( \theta(\mathbf{H} - E_f) \) have been introduced to ensure that the excited states should be higher than the Fermi energy.

The linear response of an observable \( \hat{B} \) from all electrons is calculated as

\[
\delta B(t) = 2 \text{Re} \left\{ \Phi_{E_f}(t) \mathbf{B} \Phi_{E_f}^{(0)}(t) \right\},
\]

where \( \mathbf{B} = \mathbf{S}^{-1} \mathbf{B} \) is the matrix of \( \hat{B} \) in the mixed representation. Then the Fourier transformation of \( \delta B(t) \) gives the linear response of the noninteracting many-electron system to the perturbation \( \mathbf{X} e^{-i \omega t} \),

\[
\chi_{BA}(\omega + i \eta) = \left\langle \int_0^T dt \ e^{i(\omega + i \eta)t} \delta B(t) \right\rangle,
\]

where the imaginary part of frequency \( \eta \) is introduced to limit the integration time to a finite value \( T = -\ln \delta/\eta \), with \( \delta \) being the relative numerical accuracy of Eq. (59). Here \( \left\langle (\cdot) \right\rangle \) indicates the statistical average.

\section{VII. Summary}

We presented a generalized version of the projection method for linear and nonlinear response functions developed by Iitaka and others [13–21]. The method can now be used with nonorthonormal basis sets such as local basis sets, for order-\( N \) total energy calculations. As a result, it became possible to calculate the response functions of very large systems by applying the projection method to the optimized Hamiltonian with a local nonorthonormal basis set.

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