Efficient Algorithms for Estimating the Absorption Spectrum within Linear Response TDDFT

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Supporting Information

ABSTRACT: We present a special symmetric Lanczos algorithm and a kernel polynomial method (KPM) for approximating the absorption spectrum of molecules within the linear response time-dependent density functional theory (TDDFT) framework in the product form. In contrast to existing algorithms, the new algorithms are based on reformulating the original non-Hermitian eigenvalue problem as a product eigenvalue problem and the observation that the product eigenvalue problem is self-adjoint with respect to an appropriately chosen inner product. This allows a simple symmetric Lanczos algorithm to be used to compute the desired absorption spectrum. The use of a symmetric Lanczos algorithm only requires half of the memory compared with the nonsymmetric variant of the Lanczos algorithm. The symmetric Lanczos algorithm is also numerically more stable than the nonsymmetric version. The KPM algorithm is also presented as a low-memory alternative to the Lanczos approach, but the algorithm may require more matrix-vector multiplications in practice. We discuss the pros and cons of these methods in terms of their accuracy as well as their computational and storage cost. Applications to a set of small and medium-sized molecules are also presented.

1. INTRODUCTION

Time-dependent density functional theory (TDDFT) has emerged as an important tool for reliable excited-state calculations for a broad spectrum of applications from molecular to materials systems. The most common formulation of TDDFT in quantum chemistry is in the frequency domain via linear response theory or the Casida formulation. This approach is also known as linear-response (LR) TDDFT and is widely used to calculate absorption spectra. Computing the absorption spectrum with this approach involves solving a non-Hermitian eigenvalue problem. Formally, the numerical cost to diagonalize the full LR-TDDFT matrix equations scales as $O(N^6)$, where $N$ is the total number of molecular orbitals (MO). As a result, for large systems, this approach becomes expensive if a large number of excitations ($\sim 10^5$) are needed. It can be shown that the original matrix equation can be unitarily transformed into a form that decouples into two equivalent product eigenvalue problems half of the size of the original problem. The iterative eigensolvers are typically used to solve the lowest lying excited states or the excited states within a given energy window. In the worst-case scenario, these algorithms scale as $O(N^6)$, and more advanced techniques including Krylov subspace approaches and linear-scaling methods, can reduce the cost to $O(N^5)$ or less. We refer the reader to more comprehensive reviews of LR-TDDFT.

In many cases, like large molecular complexes and high density of states (DOS) materials, excitations over a wider energy range may be required. This often results in a very demanding calculation, even when iterative eigensolvers are used. Over the years, several approaches have been developed to tackle this problem including the complex polarization, damped response approaches, multishift linear solvers, variational DFT approach of Ziegler and co-workers, the simplified approaches from Grimme and co-workers, and the efficient LR approach of Neuhauser and Baer. Alternative approaches like real-time time-dependent density functional theory (RT-TDDFT) in combination with a weak delta-function field have also been used to tackle this problem in the time domain. Despite these algorithmic developments, it is

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desirable to look for novel approximate, yet accurate, excited-state approaches for large systems.

In this paper, we explore efficient ways to estimate the absorption spectrum of a finite system in the frequency domain. Specifically, we are interested in methods that do not explicitly compute the eigenvalues and eigenvectors of the full LR-TDDFT matrix. Within the Tamm–Dancoff approximation (TDA),\(^{26}\) the matrix to be diagonalized becomes Hermitian. In this case, the absorption spectrum can be approximated by the kernel polynomial method (KPM), originally proposed to estimate the density of states of a symmetric matrix.\(^{27}\) This approach has been discussed in ref 28. By casting the full LR-TDDFT eigenvalue problem as a product eigenvalue problem, we show that the KPM can be extended to the full LR-TDDFT equations. To the best of our knowledge, the product form has not been utilized in the computation of absorption spectra.

A “two-sided” Lanczos procedure was proposed in ref 29 to approximate the absorption spectrum in the full LR-TDDFT framework. This approach treats the Casida Hamiltonian as a non-Hermitian matrix and can be numerically unstable. We show that it is possible to use a more standard Lanczos algorithm with a properly chosen inner product to obtain an accurate approximation of the absorption spectrum. This approach improves the numerical stability and reduces the memory and computational cost compared with a two-sided Lanczos procedure.

The rest of the paper is organized as follows. For completeness, we first derive the expression to be computed in the absorption spectrum estimation using matrix notation. Although this result is well-known (see, e.g., ref 29), our derivation highlights the relationship between several quantities associated with the LR-TDDFT eigenvalue problem. We then present the Lanczos and KPM algorithms for estimating the absorption spectrum in Section 3. We also discuss how to use the Lanczos and KPM algorithms to compute the density of states (DOS) of the LR-TDDFT eigenvalue problem. Computational results that demonstrate the effectiveness of the Lanczos algorithm are presented in Section 6, where we compare the accuracy and cost of the Lanczos and KPM approaches. All algorithms discussed in this paper have been implemented in a development version of the NWChem\(^{30}\) program.

2. LINEAR RESPONSE AND ABSORPTION SPECTRUM

In the linear response regime of TDDFT, the optical absorption spectrum of a finite system can be obtained from the trace of the 3 × 3 dynamic polarizability tensor \(\alpha_{\mu\nu}(\omega)\) defined as

\[
\alpha_{\mu\nu}(\omega) = \langle \psi \mid -\frac{1}{\pi} \text{Im} \chi(\omega) \upsilon \rangle = -\frac{1}{\pi} \text{Im} (\mu | \chi(\omega) | \nu)
\]

where \(\mu\) and \(\nu\) are one of the coordinate variables \(x, y, \) and \(z\), and \(\chi(\omega)\) characterizes the linearized charge density response \(\Delta \rho(r; \omega)\) of the ground state Kohn–Sham Hamiltonian in the frequency domain, i.e.

\[
\Delta \rho(r; \omega) = \int \chi(r', r; \omega) \delta \rho_{\omega}(r'; \omega) dr'
\]

The symbol \(\text{Im} \chi\) denotes the imaginary part of \(\chi\), which is also called the spectral function of \(\chi\). Further discussion about the imaginary part is given in Appendix A.

It is well-known\(^{14}\) that \(\chi\) can be expressed as

\[
\chi(r, r'; \omega) = \int e^{-i(\omega, r''; \omega)} \chi_{0}(r'', r'; \omega) dr''
\]

where \(\omega\) is called the dielectric operator defined as

\[
\epsilon(r, r'; \omega) = \delta(r, r') - \int \chi_{0}(r, r'; \omega) f_\text{Huc}(r', r) dr'
\]

and \(\omega^{-1}\) is the inverse of the dielectric operator in the operator sense. In TDDFT, within the adiabatic approximation, the Hartree–exchange–correlation kernel \(f_\text{Huc}\) is frequency-independent and is defined as

\[
f_\text{Huc}(r, r') = \frac{1}{|r - r'|} + \frac{\delta v_{\omega}(|r|)(r)}{\delta \rho(r')}
\]

with \(v_{\omega}\) being the static exchange–correlation potential. The retarded irreducible independent-particle polarization function \(\chi_{0}\) is defined by

\[
\chi_{0}(r, r'; \omega) = \sum_{j} \sum_{a} \frac{\phi_{a}(r) \phi_{a}(r') \phi_{j}(r) \phi_{j}(r')}{\omega - \Delta \epsilon_{aj} + i\eta} - \frac{\phi_{a}(r) \phi_{a}(r') \phi_{j}(r) \phi_{j}(r')}{\omega + \Delta \epsilon_{aj} + i\eta}
\]

where \((\epsilon_{a}\phi_{a})\) and \((\epsilon_{j}\phi_{j})\) are eigenpairs of the ground state self-consistent Kohn–Sham Hamiltonian. Here \(j\) and \(a\) are indices of the occupied and virtual Kohn–Sham eigenfunctions (orbitals), \(\Delta \epsilon_{aj} \equiv \epsilon_{j} - \epsilon_{a}\) and \(\Delta \epsilon_{aj} > 0\) by definition. Also \(\eta > 0\) is an infinitesimally small constant to keep \(\text{eq} \pm \text{well-defined for all}\ \omega\).

Since we consider the excitation properties of finite systems, without loss of generality we can assume that all Kohn–Sham eigenfunctions \(\phi_{j}\) and \(\phi_{a}\) are real. To simplify the notation, we will use \(\Phi(r)\) to denote a matrix that contains all products of occupied and virtual wave function pairs, i.e., \(\Phi(r) = [\phi_{j}(r) \phi_{a}(r) \cdot \cdot \cdot]\) and \(D_{0}\) to denote a diagonal matrix that contains \(\Delta \epsilon_{aj}\) on its diagonal. Using this notation, we can rewrite \(\chi_{0}\) as

\[
\chi_{0}(r, r'; \omega) = [\Phi(r), \Phi(r)]\begin{bmatrix}
\omega + i\eta & D_{0} \\
0 & 0
\end{bmatrix}^{-1} D_{0}^{-1} [\Phi(r), \Phi(r)]
\]

To simplify the notation further, we define

\[
C = \begin{bmatrix}
I & 0 \\
0 & -I
\end{bmatrix}, \quad D = \begin{bmatrix}
D_{0} & 0 \\
0 & D_{0}
\end{bmatrix}, \quad \tilde{\Phi}(r) = [\Phi(r), \Phi(r)]
\]

which allows us to rewrite \(\chi_{0}\) succinctly as

\[
\chi_{0}(r, r'; \omega) = \tilde{\Phi}(r) \tilde{\Delta}(\omega + i\eta) C - D)^{-1} \tilde{\Phi}(r')
\]

We denote by \(\Phi, \tilde{\Phi}\) the finite dimensional matrices obtained by discretizing \(\Phi(r), \tilde{\Phi}(r)\) on real space grids, respectively. Similarly, the discretized \(\tilde{\Phi}(r')\) can be viewed as the matrix transpose of \(\tilde{\Phi}\). Replacing all integrals with the matrix–matrix multiplication notation and making use of the Sherman–Morrison–Woodbury formula for manipulating a matrix inverse, we can show that (see Appendix B for a detailed derivation)

\[
\chi(\omega) = \tilde{\Phi}((\omega + i\eta) C - \Omega)^{-1} \tilde{\Phi}^T
\]

where
Here $\Phi^T f_{\text{Huc}} \Phi$ is an $n_\alpha n_\alpha \times n_\alpha n_\alpha$ matrix commonly known as the coupling matrix, where $n_\alpha$ and $n_\alpha$ are the number of occupied and virtual states, respectively. The $(\mu, \nu)$th element of the matrix is evaluated as

$$\int dr dr' \psi(\mu, r) \psi^*(\nu, r') \Phi^T f_{\text{Huc}}(r, r') \Phi \phi_\mu(r) \phi_\nu(r')$$

It follows from eq. 6 that

$$\langle x \chi(\omega) | x \rangle = \hat{x}^T \left[ (\omega + i\eta) C - \Omega \right]^{-1} \hat{x}$$

where $\hat{x} = [\hat{x}_{\alpha, 1}, \hat{x}_{\alpha, 2}]^T$ and $\hat{x}_\alpha = \Phi^T x$ is a column vector of size $n_\alpha n_\alpha$. The $(\mu, \nu)$th element of $\hat{x}_\alpha$ can be evaluated as

$$\int x \phi_\mu(r) \phi_\nu(r) dr$$

It can be verified that

$$\langle x \chi(\omega) | x \rangle = \hat{x}^T \left[ (\omega + i\eta) I - H \right]^{-1} C \hat{x}$$

where

$$H = \begin{bmatrix} A & B \\ -B & -A \end{bmatrix}$$

and is also referred to as the Casida or LR-TDDFT matrix equations. Although $H$ is non-Hermitian, it has a special structure that has been examined in detail in previous work. In particular, when both $K \equiv A-B$ and $M \equiv A + B$ are positive definite, it can be shown that the eigenvalues of $H$ come in positive and negative pairs ($-\lambda_i), \lambda_i > 0, i = 1, 2, ..., n_\alpha n_\alpha$. If $[u_i^+, v_i^-]^T$ is the right eigenvector associated with $\lambda_i$, the left eigenvector associated with the same eigenvalue is $[u_i^-, v_i^+]^T$.

It follows from the eigendecomposition of $H$ (see Appendix C) and (10) that

$$\langle x \chi(\omega) | x \rangle = \sum_{i=1}^{n_\alpha n_\alpha} \left( \frac{[\hat{x}_{\alpha, 1}^T (u_i + v_i)]^2}{\omega - \lambda_i + i\eta} - \frac{[\hat{x}_{\alpha, 2}^T (u_i + v_i)]^2}{\omega + \lambda_i + i\eta} \right)$$

where the eigenvectors satisfy the normalization condition $u_i^+ u_i^- - v_i^+ v_i^- = 1$. In the limit of $\eta \rightarrow 0^+$, $\alpha_{\alpha, \nu} = -\frac{1}{\pi} \text{Im}(\langle x \chi(\omega) | x \rangle)$ becomes

$$\sum_{i=1}^{n_\alpha n_\alpha} [\hat{x}_{\alpha, 1}^T (u_i + v_i)]^2 \delta(\omega - \lambda_i) - [\hat{x}_{\alpha, 2}^T (u_i + v_i)]^2 \delta(\omega + \lambda_i)$$

$$= \hat{x}^T \delta(\omega I - H) C \hat{x}$$

Hence, the absorption spectrum has the form

$$\sigma(\omega) = -\frac{1}{\pi} \lim_{\eta \rightarrow 0^+} \text{Im}(\langle x \chi(\omega) | x \rangle (\chi(\omega) | y) + (y | \chi(\omega) | x)))$$

$$= \frac{1}{\pi} \sum_i f_i^2 \delta(\omega - \lambda_i) - \delta(\omega + \lambda_i)$$

(13)

where $f_i^2 = [\hat{x}_{\alpha, 1}^T (u_i + v_i)]^2 + [\hat{x}_{\alpha, 2}^T (u_i + v_i)]^2 + [\hat{x}_{\alpha, 1}^T (u_i - v_i)]^2$ is known as the oscillator strength.

It is not difficult to show that $\omega_i \equiv u_i + v_i$ is the $i$th eigenvalue of the $n_\alpha n_\alpha \times n_\alpha n_\alpha$ matrix $MK$, associated with the eigenvalue $\lambda_i$. The corresponding right eigenvector is in the direction of $u_i - v_i$. Therefore, the absorption spectrum can be obtained by computing the eigenvalues of $KM$, which is half of the size of $H$. It can be shown that $\alpha_{\alpha, \nu}$ can be expressed as

$$\alpha_{\alpha, \nu}(\omega) = 2 \text{sign}(\omega) \hat{x}_i^T K \delta(\omega^2 - \omega^2 I - MK) \hat{x}_i$$

(14)

where the matrix function $\delta(\omega^2 I - MK)$ should be understood in terms of the eigendecomposition of $MK$, i.e., $\delta(\omega^2 I - MK) = \sum_k \delta(\omega - \lambda_k^2) (u_i - v_i) (u_i + v_i)^T$. The derivation can be found in the Appendix C. In (13), the value of $\omega = \lambda_i > 0$ is often referred to as the $i$th excitation energy, whereas $\omega = -\lambda_i < 0$ is often referred to as the $i$th deexcitation energy. Because the oscillator strength factors associated with these energy levels are identical in magnitude and opposite in signs, it is sufficient to focus on just one of them. Here, we will only be concerned with excitation energies, i.e., we assume $\omega > 0$.

3. ALGORITHMS FOR APPROXIMATING THE ABSORPTION SPECTRUM

If the eigenvalues and eigenvectors of $H$ or $MK$ are known, the absorption spectrum defined in (13) is easy to construct. However, because the dimensions of $H$ and $MK$ are $O(n_\alpha n_\alpha)$, computing all eigenvalues and eigenvectors of these matrices is prohibitively expensive for large systems due to the $O(n_\alpha^3 n_\alpha^3)$ complexity.

If we only need the excitation energies and oscillator strengths of the first few low excited states, we may use an iterative eigensolver such as Davidson’s method or a variant of the locally optimal block preconditioned gradient method (LOBPCG) to compute the lowest few eigenpairs of $MK$. These methods only require the user to provide a procedure for multiplying $A$ and $B$ with a vector. The matrix $A$ or $B$ does not need to be explicitly constructed. However, these methods tend to become prohibitively expensive when the number of eigenvalues within the desired energy range becomes large.

In this section, we introduce two methods that do not require computing eigenvalues and eigenvectors of the Casida Hamiltonian explicitly. In addition, these methods only require a procedure for multiplying $A$ and $B$ with a vector. Both approaches provide a satisfactory approximation to the overall shape of the absorption spectrum from which the position and the height of each major peak with a desired energy range can be easily identified.

3.1. Lanczos Method. One way to estimate $\alpha_{\alpha, \nu}$ is to use the Lanczos algorithm. Because $MK$ is self-adjoint with respect to the inner product induced by $K$, i.e.,

$$\langle v, MKv \rangle_K = u^T MKv = \langle MKv, v \rangle_K$$

(15)

we can use the $K$-inner product to generate a $k$-step Lanczos factorization of the form

$$MKQ_k = Q_k T_k + f_k \xi_k^T$$

(16)

where

$$Q_k^T K Q_k = I$$

and $T_k$ is a tridiagonal matrix of size $k \times k$. The major steps of the $K$-inner product Lanczos procedure is shown in Algorithm 1. We use the MATLAB notation $Q(i,j)$ to denote the $j$th column of the matrix $Q$. In principle, because $T_k$ is tridiagonal in exact arithmetic, columns of $Q_k$ can be generated via a three-term recurrence. However, it is well-known that as some of the eigenvalues of $T_k$ converge to those of $MK$, and loss of
orthogonality among columns of \( Q_k \) can occur due to potential instability in the numerical procedure. As a result, \( T_k \) may become singular with several spurious eigenvalues near zero.\(^{35}\)

To avoid loss of orthogonality, we perform full reorthogonalization as shown in steps 5–7 of Algorithm 1. Unless \( k \) is extremely large, the cost of full reorthogonalization is relatively small compared to the cost of multiplying \( A \) and \( B \) with vectors. However, full reorthogonalization does require keeping all columns of \( Q_k \) in memory.

If we choose the starting vector for the Lanczos iteration to be \( \mathbf{e}_1 \), i.e., \( Q_k \mathbf{e}_1 = \mathbf{e}_1 / \sqrt{\lambda_1} K \mathbf{e}_1 \), then \( e_1^T \delta (\omega^2 I - T_k) \mathbf{e}_1 \) serves as a good approximation of \( \alpha_{\omega,\omega}(\omega) \).

To see why this is the case, let us first assume that \( \delta (\omega^2 I - MK) \) can be formally approximated by a \( k \)-th degree polynomial of the form \( p_k(MK; \omega^2) \), i.e.

\[
\delta (\omega^2 I - MK) \approx p_k(MK; \omega^2) = \sum_{i=0}^{k} \gamma_i (\omega^2)(MK)^i
\]

It follows from eq 16 that

\[
p_k(MK; \omega^2) Q_k = Q_k p_k(T_k; \omega^2) + R_k
\]

where \( R_k \) is a residual matrix that vanishes when \( k = n \).

Algorithm 1: A \( k \)-step Lanczos method in the \((A - B)\)-inner product.

\[
\begin{align*}
\text{Input:} & \quad \text{Real symmetric matrices } A \text{ and } B \text{ defined in (7); } A \text{ starting vector } \mathbf{v}_0; \text{ the number of steps } k. \\
\text{Output:} & \quad \text{Matrices } Q_k \text{ and } T_k \text{ that satisfy (16) and (17).}
\end{align*}
\]

1. \( Q_k(:,1) = \mathbf{v}_0 / \sqrt{\sum_i (A - B)v_0^2} \); 
2. for \( j = 1, \ldots, k \) do 
3. \( w = (A - B)Q_k(:,j) \); 
4. \( w = (A + B)w \); 
5. \( h = Q_k(:,1:j)^T(A - B)w \); 
6. \( h(1:1:j) = h \); 
7. \( w = w - Q_k(:,1:j)h \); 
8. if \( j < k \) then 
9. \( Q_k(:,j+1) = w / \sqrt{w^T(A - B)w} \); 
10. end if 
11. end for 

Consequently, we can show that

\[
\lim_{\eta \to \infty} -\frac{1}{\pi} \text{Im} \langle \mathbf{x} | \chi(\omega) | \mathbf{x} \rangle = 2 \tilde{\xi}_1 K (\omega^2 I - MK) \tilde{\xi}_1 = e_1^T Q_k^T K p_k(Q_k p_k(T_k; \omega^2) + R_k) e_1
\]

\[
= e_1^T Q_k^T K (Q_k p_k(T_k; \omega^2) + R_k) e_1
\]

\[
\approx e_1^T p_k(T_k; \omega^2) e_1
\]

\[
= \sum_{j=1}^{k} \gamma_j (\omega^2 - \theta_j),
\]

where \( \theta_j > 0 \) is the \( j \)-th eigenvalue of the \( k \times k \) tridiagonal matrix \( T_k \) sorted in increasing order and \( \tau_j \) is the first component of the \( j \)-th eigenvector of \( T_k \).

As shown in the Appendix C, \( \delta (\omega^2 - \theta_j) \) can be rewritten as

\[
\delta (\omega^2 - \theta_j) = \frac{1}{2\sqrt{\theta_j}} \delta (\omega - \sqrt{\theta_j}), \quad (\omega > 0)
\]

Therefore

\[
\alpha_{\omega,\omega}(\omega) \approx \sum_{j=1}^{k} \tau_j^2 \delta (\omega^2 - \theta_j) = \sum_{j=1}^{k} \frac{\tau_j^2}{2\sqrt{\theta_j}} \delta (\omega - \sqrt{\theta_j})
\]

holds.

The cost of the Lanczos algorithm is proportional to the number of steps \( k \) in the Lanczos iterations. We would like to keep \( k \) as small as possible without losing desired information in eq 19. However, when \( k \) is small, eq 21 gives a few spikes at the square root of the eigenvalues of \( T_k \), also called Ritz values. No absorption intensity is given at other frequencies. To estimate the intensity of the absorption at these frequencies, we replace \( \delta (\omega^2 - \theta_j) \) by either a Gaussian or a Lorentzian. The use of these regularization functions allows us to interpolate the absorption intensity from the square root of the Ritz values to any frequency. Replacing \( \delta (\omega^2 - \theta_j) \) with a Lorentzian is equivalent to not taking the \( \eta \to 0^+ \) limit in eq 19. It is also equivalent to computing the \((1,1)\) entry of the matrix inverse \( [(\omega^2 + \eta I - T_k)]^{-1} \). This entry can be computed by using a recursive expression that is related to continued fractions.\(^{36}\)

This is the method of Haydock.\(^{37}\) However, since the cost of computing the inverse and the eigenvalue decomposition of a small tridiagonal matrix is negligibly small, we do not gain much by using the Haydock recursion.

3.2. Kernel Polynomial Method. Another approach follows the kernel polynomial method (KPM) reviewed in ref 27. To use this method, it is convenient to consider the case of \( \omega > 0 \) and view \( \alpha_{\omega,\omega}(\omega) \) as a function of \( \mathbf{w} = \omega^2 \). The general idea relies in expressing \( \alpha_{\omega,\omega}(\omega) \) (and similarly \( \alpha_{\omega,\nu} \) and \( \alpha_{\nu,\omega} \)) formally by a polynomial expansion of the form

\[
\hat{\alpha}_{\omega,\omega}(\mathbf{w}) = \sum_{k=0}^{\infty} \gamma_k T_k(\mathbf{w})
\]

where

\[
\hat{\alpha}_{\omega,\omega}(\mathbf{w}) = \frac{\sqrt{1 - \mathbf{w}^2}}{2} \alpha_{\omega,\omega}(\mathbf{w}) = \frac{\sqrt{1 - \mathbf{w}^2} \tilde{\xi}_1 K \delta (\mathbf{w} I - MK) \tilde{\xi}_1}{\sqrt{1 - \mathbf{w}^2}} = \frac{\sqrt{1 - \mathbf{w}^2}}{\sqrt{1 - \mathbf{w}^2}} \sum_{j=1}^{k} \lambda_j (\tilde{\xi}_1^T \mathbf{w}) \delta (\mathbf{w} - \lambda_j^2)
\]

with \( \mathbf{w} \) being the \( i \)-th left eigenvector of \( MK \) and \{\( T_k(\mathbf{w}) \)\} being a set of orthogonal polynomials of degree \( k \).

For instance, we choose \{\( T_k(\mathbf{w}) \)\} to be Chebyshev polynomials. Using the identity

\[
\int T_k(\mathbf{w}) \delta (\mathbf{w} - \lambda_j^2) = T_k(\lambda_j^2)
\]

we can compute the expansion coefficients \( \gamma_k \)'s by

\[
\gamma_k = \frac{2 - \delta_{00}}{\pi} \int_{-1}^{1} \frac{1}{\sqrt{1 - \mathbf{w}^2}} T_k(\mathbf{w}) \alpha_{\omega,\omega}(\mathbf{w}) d\mathbf{w}
\]

\[
= \frac{2 - \delta_{00}}{\pi} \frac{1}{\sqrt{1 - \mathbf{w}^2}} \sum_{i=1}^{\infty} \lambda_i w_i T_k(\lambda_i^2) \mathbf{w}_1^T \mathbf{x}_1
\]

\[
= \frac{2 - \delta_{00}}{\pi} \frac{1}{\sqrt{1 - \mathbf{w}^2}} \sum_{i=1}^{\infty} \left( K(\mathbf{u}_i - \mathbf{v}_i) T_k(\lambda_i^2)(\mathbf{u}_i + \mathbf{v}_i) \right) \mathbf{x}_1
\]

\[
= \frac{2 - \delta_{00}}{\pi} \frac{1}{\sqrt{1 - \mathbf{w}^2}} K T(MK) \mathbf{x}_1.
\]

Here \( \delta_{00} \) is the Kronecker \( \delta \) symbol so that \( 2 - \delta_{00} \) is equal to 1 when \( k = 0 \) and to 2 otherwise. In deriving eq 23 from the line before, we use the property that \( \mathbf{w}_i = \mathbf{u}_i + \mathbf{v}_i \) is a left eigenvector of \( MK \) and the corresponding right eigenvector is in the direction of \( \mathbf{u}_i - \mathbf{v}_i = \mathbf{K}^{-1}(\mathbf{u}_i + \mathbf{v}_i) \).

Because Chebyshev polynomials \( T_k(\mathbf{w}) \) can be generated recursively using the three-term recurrence

\[ T_{k+1}(\mathbf{w}) = 2 \mathbf{w} T_k(\mathbf{w}) - T_{k-1}(\mathbf{w}). \]
\[ T_0(\sigma) = 1 \]

\[ T_1(\sigma) = \sigma \]

\[ T_{k+1}(\sigma) = 2T_k(\sigma) - T_{k-1}(\sigma) \]

for \( \sigma \in [-1,1] \), we do not need to construct \( T_k(\sigma) \) explicitly. We can apply \( T_k(\sigma) \) recursively using a three-term recurrence also. This three-term recurrence allows us to implement the KPM by storing 3 or 4 vectors depending on whether an intermediate vector is used to hold intermediate matrix vector products. Pseudocode for the KPM is given in Algorithm 2. The cost of the KPM is dominated by the multiplication of the matrices \( A \) and \( B \) with vectors, and proportional to the degree of the expansion polynomial or the number of expansion terms in \( (22) \).

The derivation above requires \( \sigma \in [-1,1] \). To generate Chebyshev polynomials on an interval \([a,b]\) where \( a \) and \( b \) are the estimated lower and upper bounds of the eigenvalues of \( MK \), a proper linear transformation should be used to map \( \sigma \) to \([-1,1]\) first.

In eq \( 22 \), we assume that the \( \eta \to 0^+ \) limit has been taken. Because the left-hand side is a sum of Dirac-\( \delta \) distributions, which is discontinuous, a finite least-squares polynomial expansion will produce the well-known Gibbs oscillations as shown e.g. in ref 38 and lead to larger errors near the point of discontinuity. This effect is more pronounced for molecules of solids whose excitation energies are more closely spaced. To reduce the effects of the Gibbs oscillation, we can set \( \eta \) to a small positive constant (instead of taking the \( \eta \to 0^+ \) limit.) This is equivalent to replacing each Dirac-\( \delta \) distribution with a Lorentzian of the form

\[ g_\eta(\omega - \lambda_i) = \frac{1}{\pi} \frac{\eta}{(\omega - \lambda_i)^2 + \eta^2} \]

In this case, the expansion coefficients \( \gamma_i \)'s need to be computed in a different way. We may also replace the Dirac-\( \delta \) distributions on the left-hand side of eq \( 22 \) with Gaussians of the form

\[ g_\sigma(\omega - \lambda_i) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(\omega-\lambda_i)^2/(2\sigma^2)} \]  

(24)

where \( \sigma \) is a smoothing parameter that should be chosen according to the desired resolution of \( \alpha_{kx} \). We refer to the technique of replacing Dirac-\( \delta \) distributions with Lorentzians or Gaussians as regularization. In ref 38, we show how the expansion coefficients \( \gamma_i \)'s can be computed recursively when Dirac-\( \delta \) distributions are replaced with Gaussians, and \( T_k(\sigma) \) is taken to be the \( k \)th degree Legendre polynomial. We referred to this particular expansion as the Delta–Gaussian–Legendre (DGL) expansion. Another technique for reducing the Gibbs phenomenon is the use of Jackson damping.\(^3^9\) However, it has been shown in ref 38 that Jackson damping can lead to an over-regularized spectrum.

### 4. ESTIMATING THE DENSITY OF STATES OF THE LR-TDDFT MATRIX EQUATIONS

In some cases, the oscillator strength associated with some of the excitation energies are negligibly small. These are sometimes referred to as dark states.\(^1\) To reveal these states, it is sometimes useful to examine the density of states (DOS) associated with the LR-TDDFT matrix eqs 11.

In the review paper,\(^1^6\) several numerical algorithms for estimating the DOS of symmetric matrices are presented and compared. To apply these techniques, we make use of the fact that eigenvalues of \( H \) can be obtained from that of \( MK \) or \( K^{1/2}MK^{1/2} \) which is Hermitian. As a result, the DOS can be written as

\[ \phi(\omega) = \text{trace}(\omega^2 I - K^{1/2}MK^{1/2}) \]  

(25)

We assume that \( \omega \geq 0 \) since \( \phi(-\omega) = \phi(\omega) \).

If we use the KPM to approximate \( (25) \), i.e.

\[ \phi(\omega) \approx \sum_{k=0}^{\alpha_{max}} \gamma_k T_k(\omega^2) \]  

(26)

the expansion coefficients \( \gamma_k \) can be computed as

\[ \gamma_k = \frac{2 - \delta_{0k}}{n\pi} \text{trace}[T_k(K^{1/2}MK^{1/2})] = \frac{2 - \delta_{0k}}{n\pi} \text{trace}[T_k(MK)] \]  

(27)

Thus, apart from the scaling factor \( (2 - \delta_{0k})/(n\pi) \), \( \gamma_k \) is the trace of \( T_k(MK) \), and such a trace can be estimated through a statistical sampling technique that involves computing

\[ \zeta_k = \frac{1}{n_{\text{vec}}} \sum_{l=1}^{n_{\text{vec}}} (\eta_l^{(0)})^2 K T_k(MK) \eta_l^{(0)} \]  

(28)

for a set of randomly generated vectors \( \eta_l^{(0)}, \eta_l^{(2)}, \ldots, \eta_l^{(n_{\text{vec}})} \). One possible choice of the random vectors is that each entry of \( \eta_l^{(0)} \) follows an independent Gaussian distribution \( N(0,1) \) for all \( l = \)
1,...,nvec The method only requires multiplying A and B with a number of vectors, and the multiplication of $T_k(MK)$ with a vector can be implemented through a three-terme recurrence.

To estimate the DOS by the Lanczos method, we can simply use the $K$-orthogonal Lanczos factorization shown in eq 16 to obtain a sequence of tridiagonal matrices $T_k$, $l = 1,2,...,nvec$, using a set of randomly generated starting vectors $q^{(1)}, q^{(2)}, ...$ as mentioned above. The approximate DOS can be expressed as

$$\phi(\omega) \approx \frac{1}{n_{vec}} \sum_{l=1}^{nvec} \sum_{i} (\varepsilon_{i}^{(l)})^2 \delta(\omega^2 - \varepsilon_{i}^{(l)})$$

(29)

where $\varepsilon_{i}^{(l)}$ is the $i$th eigenvalue of $T_k$, $\varepsilon_{i}^{(0)}$ is the first component of the corresponding eigenvector. To regularize the approximate DOS, we rewrite $\delta(\omega^2 - \varepsilon_{i}^{(l)})$ in the form of eq 20, and replace $\delta(\omega - \sqrt{\varepsilon_{i}^{(l)}})$ with the properly defined Gaussian $g_{\sigma}(\omega - \sqrt{\varepsilon_{i}^{(l)}})$.

5. FROZEN ORBITAL AND TAMM–DANCOFF APPROXIMATION

When $\omega$ is relatively small compared with $\Delta E_{\epsilon,\rho}$, the contribution of the corresponding term in eq 4 is relatively insignificant. Thus, it is reasonable to leave out these terms which constitute indices $j$'s that correspond to the lowest occupied orbitals often known as the core orbitals. By using this frozen core approximation (FCA), we effectively reduce the dimension of $A$ and $B$ matrices in eq 7 from $n_{\nu}n_{\nu}$ to $(n_{\nu} - n_{f})n_{\nu}$, where $n_{f}$ is the number of lowest occupied orbitals that are excluded (or “frozen”) from eq 4. It is well-known that the FCA preserves the low end of the absorption spectrum while removing poles of $\chi(\omega)$ at higher frequencies. Therefore, it is extremely useful to combine FCA with the Lanczos algorithm to obtain an accurate approximation to the absorption spectrum in the low excitation energy range at a reduced cost, as we will show in the next section.

Another commonly used technique to reduce the computational cost of estimating the absorption spectrum is to set the matrix B in eq 7 to zero. This approximation is often referred to as the Tamm–Dancoff approximation (TDA). It reduces the eigenvalue problem to a symmetric eigenvalue problem that involves the matrix $A$ only. We do not consider the TDA in this paper.

6. COMPUTATIONAL RESULTS

We now present computational results to demonstrate the quality of the approximate absorption spectrum obtained from the algorithms presented in Section 3 and the efficiency of these algorithms. In particular, we compare the absorption spectrum obtained from the new algorithms with that obtained from a traditional diagonalization based approach and that obtained from a real-time TDDFT (RT-TDDFT) simulation that can be readily performed with the released version of the NWChem open source code. It has been shown that absorption spectra from RT-TDDFT simulations in the weak delta-function field limit are consistent with those obtained from LR-TDDFT calculations for both UV/vis and core-level excitations.9,13 In addition, RT-TDDFT has been shown to provide a reasonable approximation of the entire spectrum for large molecular complexes and high DOS systems. For these reasons and since our goal is to demonstrate the applicability of our new approaches to large systems, we have chosen the RT-TDDFT spectra as our reference where full diagonalization is prohibitive. For details of the RT-TDDFT approach, we refer the reader to refs 24,25. We also compare the efficiency of the new algorithms with the aforementioned approaches and show that the algorithms presented in Section 3 are much faster.

6.1. Test Systems. Our test systems include two small dyes: 2,3,5-trifluorobenzaldehyde (TFBA) and 4’-hydroxybenzylidene-2,3-dimethylimidazoline (HDBMI) as well as two relatively large molecules F2N12S and P3B2, respectively. The atomic configurations of these molecular systems are shown in Figure 1. All geometries were optimized in the ground state.
Figure 2. Comparison of the approximate absorption spectrum obtained from the Lanczos algorithm with that obtained from an exact LR-TDDFT calculation and RT-TDDFT calculation for (a) TFBA (b) HBDMI.

Figure 3. (a) Density of states of $H$ with and without the FCA (b) The absorption spectrum obtained from 400 Lanczos iterations with and without the FCA.

Figure 4. Resolution improvement with respect to the number of Lanczos iterations $k$ for (a) TFBA (b) HBDMI.
The Lanczos algorithm is prohibitively expensive. Directly for larger problems, where the traditional diagonalization approach is only feasible, the Lanczos algorithm is preferred. When comparing the absorption spectrum obtained from the Lanczos algorithm with that obtained from RT-TDDFT, it is reasonable to compare the absorption spectrum obtained from the Lanczos algorithm with that obtained from RT-TDDFT for both the F2N12S and P3B2 molecules. If we see from this figure that the LR-TDDFT absorption spectrum matches well with that obtained from RT-TDDFT for both TFBA and HBDMI, the nearly perfect match indicates the validity of linear response approximation. Therefore, it seems reasonable to compare the absorption spectrum obtained from the Lanczos algorithm with that obtained from RT-TDDFT directly for larger problems where the traditional diagonalization approach is prohibitively expensive.

6.3. Effect of FCA. In Figure 3, we illustrate the effect of using the frozen core approximation (FCA) for TFBA by setting \( n_j \) to eq 11. That effectively reduces the dimension of the A and B matrices in eq 11 from \( n_n = 4800 \) to \( n_n - n_j \) \( n_e = 3480 \). We can clearly see from the DOS shown in Figure 3a that FCA preserves the small eigenvalues of the original matrix, but the largest eigenvalues are absent. The absence of these eigenvalues allows the Lanczos algorithm to obtain more Ritz values in the low energy range (e.g., [0,20] eV) in fewer iterations, thereby producing an accurate absorption spectrum with lower cost. The cost reduction in FCA results from both the reduction in the dimension of the matrix and the reduction in the steps of Lanczos iterations required to achieve a desired resolution in the absorption spectrum.

6.4. Resolution and the Number of Lanczos Steps. In Figure 4, we show that the resolution of the absorption spectrum obtained from the Lanczos algorithm clearly improves as we take more Lanczos iterations for TFBA and HBDMI. In this set of experiments, we use FCA for all test runs.

When \( k = 400 \) iterations are performed, the Lanczos approximation is nearly indistinguishable from traditional diagonalization. When \( k \) is as small as 100, the general features of the absorption spectrum are clearly captured.

6.5. Approximation for Larger Molecules. In Figure 5, we compare the absorption spectra obtained from the Lanczos-based LR-TDDFT calculation with those obtained from RT-TDDFT simulations for both the F2N12S and P3B2 molecules. We can see from this figure that without the FCA, the Lanczos algorithm can capture the basic features of the F2N12S absorption spectrum exhibited by the RT-TDDFT simulation after \( k = 1200 \) iterations, but it does not clearly reveal all the peaks. However, when the FCA is used, the result matches extremely well with that produced by RT-TDDFT. For the P3B2 molecule, we need to run 1200 Lanczos iterations to obtain the result that matches well with that produced by RT-TDDFT. When the FCA is used, only 400 Lanczos iterations are needed to achieve essentially full resolution in the computed absorption spectrum.

6.6. Computational Efficiency. Clearly, the most expensive method for estimating the absorption spectrum is the full diagonalization approach, which constructs a full Casida matrix of size \( O(n_n^3) \) and performs a diagonalization that requires \( O((n_n)^3) \) floating point operations (flops). The Davidson, Lanczos, and KPM algorithms are iterative methods that require one multiplication of vector(s) by matrices \( K \) and \( M \) per iteration. These multiplications are the most expensive operations relative to other linear algebra operations. The efficiency of these methods depends on the number of iterations required to reach convergence, and the number of eigenvalues to be computed in the case of the Davidson algorithm because the number of matrix vector multiplications performed in each Davidson iteration is proportional to the number of eigenvalues to be computed. For the Davidson method, the error of each eigenvector can be estimated by computing the residual norm of each eigenpair. For the Lanczos and KPM algorithm, we do not yet have an efficient estimator to estimate the error of the absorption spectrum directly. In the results presented in this paper, we use a visual inspection of the approximate absorption spectrum to determine whether sufficient resolution is reached after \( k \) steps. A more systematic approach to terminate these
To illustrate the computational efficiency of the implementation of Lanczos algorithm, we compare the wall clock time taken by 400 Lanczos steps with that used by the Davidson algorithm to compute the lowest 200 eigenvalues of the matrix $K_{M}$, as well as with that used by the RT-TDDFT to run a 24.2 fs trajectory with a 4.8 attosecond time step (5000 time steps). For these settings, the RT-TDDFT gives a similar resolution of spectra as those obtained by Lanczos. All calculations were performed with a development version of the NWChem 30 program on the Cascade system, which is equipped with 1440 Xeon E5−2670 8C 2.6 GHz 16-core CPUs plus Xeon Phi “MIC” accelerators, 128 GB memory per compute node, and an Infiniband FDR network, and the system is maintained at the EMSL user facility located at the Pacific Northwest National Laboratory. The Xeon Phi accelerators were not utilized in this work.

Each calculation was performed using 1536 cores. In both the Lanczos and RT-TDDFT methods, the $xx$, $yy$, and $zz$ components of the dynamic polarizability can be computed simultaneously. We use 512 cores for each component. The Lanczos calculation required 2.5 h, whereas Davidson required 4 h and RT-TDDFT 15 h.

6.7. Lanczos vs KPM and DGL. In Figure 6a, we compare the absorption spectrum obtained from the Lanczos algorithm, KPM, and DGL for the TFBA dye. We ran 400 Lanczos steps, which produces a relatively high resolution approximation to the absorption spectrum produced by exact diagonalization. To make the computational cost of the KPM and DGL method comparable to that of the Lanczos algorithm, we set the degree of the polynomial approximation to 400 also in this test. We can see from Figure 6a that the absorption spectra produced by the KPM and DGL algorithm match with “exact” solution reasonably well in the [0,10] eV energy range. However, they miss some of the peaks beyond 10 eV. We can see that the approximate absorption spectra produced by the KPM and the DGL algorithm are not strictly non-negative, which is an undesirable feature. Furthermore, KPM tends to produce some artificial oscillations and peaks in the approximate absorption spectrum, which may be misinterpreted as real excited states. These artificial oscillations and peaks are the result of the Gibbs oscillation that are present when a discontinuous function, such as the sum of a number of Dirac-$\delta$ distributions, is approximated by a high degree polynomial. This observation is consistent with that reported in ref 38. Because the absorption spectrum associated with molecules contain well isolated peaks, the KPM, which is based on polynomial approximation in a continuous measure, often exhibit Gibbs oscillation when degree of the polynomial is high. The Gibbs oscillations are clearly visible on Figure 6 between 0−5 eV and also create pseudopeak around 5.5 eV (Figure 6b). This problem is reduced in the DGL algorithm.

Figure 6b shows that as the degree of the kernel polynomial increases, for example, to 600, all major peaks of the absorption spectrum in [0,30] eV are correctly resolved.

6.8. DOS by Lanczos. In Figure 7, we plot the DOS approximation for the FTBA dye obtained from the Lanczos algorithm and compare it with that obtained from a full diagonalization of the $K_{M}$ matrix. The FCA is used to show the DOS in the energy range [0,125] eV. We use $n_{w} = 10$ randomly generated vectors to run the Lanczos algorithm. When 200 Lanczos steps are used in each run, the DOS approximation obtained from (29) is nearly indistinguishable from that constructed from the eigenvalues of the $K_{M}$ matrix. The total number of matrix vector multiplications used in this...
is defined to be
\[ s(\omega) = \sum_i a_i \delta(\omega - \lambda_i) \]

It is an elegant way to describe the numerator (or weighting factor) associated with each pole of \( f(\omega) \).

An alternative way to express \( s(\omega) \) is through the expression
\[
s(\omega) = -\frac{1}{\pi} \lim_{\eta \to 0} \text{Im} f(\omega + i\eta) = \frac{1}{\pi} \lim_{\eta \to 0} \sum_i a_i \frac{\eta}{(\omega - \lambda_i)^2 + \eta^2}
\]

This is the expression we used in eq 1 to define the dynamic polarizability tensor \( \alpha \).

B. Derivation for \( \chi \)

The expression of \( \chi(\omega) \) given in eq 2 can be derived in a number of ways, (e.g. through the Liouville super-operator presented in ref 29). We give a simple derivation of this expression here using basic linear algebra.

We start from a matrix representation of eq 2
\[ \chi(\omega) = \varepsilon^{-1} \chi_0(\omega) = [I - \chi_0(\omega)]^{-1} \chi_0(\omega) \]

and substitute \( \chi_0 \) with (5) to obtain
\[ \chi(\omega) = [I - \Phi((\omega + i\eta)C - D)^{-1} \Phi^T]^{-1} \Phi(\omega + i\eta)(C - D)^{-1} \Phi^T \]

Using the Sherman–Morrison–Woodbury formula for the following matrix inverse
\[
[I - \Phi((\omega + i\eta)C - D)^{-1} \Phi^T]^{-1} = I + \Phi[(\omega + i\eta)C - D]^{-1} \Phi^T \Phi \Phi^T [\omega + i\eta] C - D\]^{-1} \Phi^T
\]

where \( \Omega \) is defined by (7). We obtain
\[ \chi(\omega) = \left[I + \Phi((\omega + i\eta)(C - D)^{-1} \Phi^T \Phi(\omega + i\eta)(C - D)^{-1} \Phi^T\right]^{-1} \]

C. Eigendecomposition of the Casida Matrix

It is known (see, e.g., ref 47) that when both \( M \equiv A + B \) and \( K \equiv A - B \) are positive definite, the Casida matrix, \( H \), defined in eq 11 admits a eigendecomposition of the form
\[
\begin{bmatrix}
A & B \\
-B & -A
\end{bmatrix} =
\begin{bmatrix}
U & V \\
V & U
\end{bmatrix} \Lambda \begin{bmatrix}
U & V \\
V & U
\end{bmatrix}^{-1} =
\begin{bmatrix}
U & V \\
V & U
\end{bmatrix} \Lambda \begin{bmatrix}
U & -V \\
-V & U
\end{bmatrix}^T
\]

where \( U \) and \( V \) are real \( n_\pi \times n_\pi \) matrices satisfying \( U^T U = V^T V = I \), \( U^T V = V^T U = 0 \), and \( \Lambda = \text{diag} \{ \lambda_1, \ldots, \lambda_{n_\pi} \} \). Let \( U = [u_{1,\pi}, \ldots, u_{n_\pi,\pi}] \) and \( V = [v_{1,\pi}, \ldots, v_{n_\pi,\pi}] \). Then the right and left eigenvectors of \( H \) associated with \( \lambda_i \) are \([u_i, v_i]^T\) and \([u_i^T, v_i^T]^T\), respectively. In addition, we have
$\langle \chi | \omega | x \rangle = -\hat{T}^* \left[ (\omega + i\eta)I - H \right]^{-1} C \hat{T}^*$

$= [\hat{T}^* \hat{T}], I$ (with $\omega = \lambda$)

$= [\hat{T}^* \hat{T}], U V U^T \left[ (\omega + i\eta)I - \Lambda \right]^{-1} \left[ U V U^T \right], U^T \hat{T}^*$

$= [\hat{T}^* (U + V), \hat{T}^* (U + V)] \left[ (\omega + i\eta)I - \Lambda \right]^{-1} \left[ (U + V)^T \hat{T}^* \Lambda \right]

= \sum_{i=1}^{N} \left[ \frac{\hat{T}^* (U + V)(\omega - \lambda_i + i\eta)}{\omega - \lambda_i + i\eta} - \frac{\hat{T}^* (U + V)(\omega + \lambda_i - i\eta)}{\omega + \lambda_i + i\eta} \right]. \tag{31}$

In the limit of $\eta \to 0^+$, the imaginary part of eq 31 becomes

$$\lim_{\eta \to 0^+} \text{Im}(\chi(\omega)|x) = \frac{-\pi}{\omega} \sum_{i=1}^{N} \left( \hat{T}^* (U + V)(\omega - \lambda_i + i\eta) \right)$$

$$= -2\pi \text{sign}(\omega) \sum_{i=1}^{N} \lambda_i \hat{T}^* (U + V)(\omega + \lambda_i - i\eta)$$

Hence, we make use of the identity

$$\delta(\omega + \lambda_i) = 2\Lambda H(\pm \omega) \delta(\omega^2 - \lambda_i^2)$$

where $H(x) = \left[1 + \text{sign}(x)\right]/2$ is the Heaviside step function. This identity can be proved by showing

$$\xi(\lambda_i) = \int_{-\infty}^{\infty} \frac{2\lambda_i \delta(\omega^2 - \lambda_i^2)}{2\Lambda H(\pm \omega)} \xi(\omega) d\omega$$

$$\xi(-\lambda_i) = \int_{-\infty}^{\infty} \frac{2\lambda_i \delta(\omega^2 - \lambda_i^2)}{2\Lambda H(\pm \omega)} \xi(\omega) d\omega$$

for any continuous function $\xi(\omega)$, through a change of variable $\omega = \omega' \pm i\eta$, and $d\omega = \pm d\omega'$. It can be verified that the normalization condition $U^T U V^T V = I$ implies that $(U + V)^T (U - V) = I$ and $(U + V)^T M (U + V) = \Lambda$. Consequently, we have

$$M = (U - V) \Lambda (U - V)^T, \quad K = (U + V) \Lambda (U + V)^T$$

The eigendecompositions of $MK$ and $KM$ are thus given by

$$MK = (U - V) \Lambda^2 (U - V)^T = (U - V) \Lambda^2 (U + V)^T$$

$$KM = (U + V) \Lambda^2 (U + V)^T = (U + V) \Lambda^2 (U + V)^T$$

Therefore, the vectors $u_i + v_i$ ($i = 1, 2, \ldots, n_n$) in eq (31) are the right eigenvectors of $KM$, as well as the left eigenvector of $MK$, both associated with the eigenvalues $\lambda_i^2$. These results lead to

$$\alpha_{e_i}(\omega) = 2\pi \text{sign}(\omega) \sum_{i=1}^{N} \lambda_i \hat{T}^* (U + V)(\omega + \lambda_i - i\eta)$$

$$= 2\pi \text{sign}(\omega) \hat{T}^* (U + V)(\omega + \lambda_i - i\eta) \hat{T}^* (U + V)(\omega + \lambda_i + i\eta)$$

Thus, we have proved eq 14, which is an expression for $\alpha_{e_i}(\omega)$ that involves matrices of dimension $n_n \times n_n (n_n \times 2n_n )$ instead of $2n_n \times 2n_n$ in eq 8.

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(45) See Supporting Information for geometries.


(47) Ref 46, Theorem 3.