Variational Principles and Computation of Linear Response Eigenvalue Problems with Application to Excited State Calculations

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joint work with
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Review: variational principles for the symmetric eigenproblem

For $A = A^T \in \mathbb{R}^{n \times n}$ with eigenvalues $\lambda_1 \leq \lambda_2 \leq \cdots \leq \lambda_n$:

1. The minimization principle:

$$\lambda_1 = \min_{x^T x = 1} x^T A x.$$

2. Ky Fan’s trace minimization principle is

$$\lambda_1 + \lambda_2 + \cdots + \lambda_k = \min_{U_k \in \mathbb{R}^{n \times k}, U_k^T U_k = I_k} \text{trace}(U_k^T A U_k),$$

3. Cauchy’s interlacing inequalities:

$$\lambda_i \leq \mu_i \leq \lambda_{i+n-k},$$

where $\mu_i$ are the eigenvalues of $U_k^T A U_k$ in ascending order

These results establish the theoretical foundation for the development of efficient methods for symmetric eigenproblems such as SD, CG and Lanczos.
Linear Response (LR) eigenvalue problems

- LR eigenvalue problems:
  \[
  \begin{bmatrix}
  A & B \\
  -B & -A
  \end{bmatrix}
  \begin{bmatrix}
  u \\
  v
  \end{bmatrix}
  = \lambda
  \begin{bmatrix}
  \Sigma & \Delta \\
  \Delta & \Sigma
  \end{bmatrix}
  \begin{bmatrix}
  u \\
  v
  \end{bmatrix}
  \]

  where \( A^T = A, B^T = B, \Sigma^T = \Sigma \) and \( \Delta^T = -\Delta \).

- Eigenvalue problems of doubly structured matrix pencils

- Known as the RPA (Random Phase Approximation) eigenvalue problem for studying collective motion of many particle systems since 1950s.
  [Bohm and Pines’53, Thouless’61, Olsen et al’88, ...]

- Other forms of LR eigenvalue problems, see e.g.
  [List et al’14, Shao et al’15]

- Eigenvalue problems of doubly structured matrix pencils
  [Mehl, Mehrmann and Xu’00,’04, Mostafazadeh’02]
An origin of LR eigenvalue problems

Electronic structure calculations: DFT to TD-DFT

- The density functional theory (DFT) of Hohenberg and Kohn’64 and Kohn and Sham’65 is a remarkably successful theory to describe ground-state properties of condensed matter systems such as molecules and crystal.

- Runge and Gross’84 generalizes DFT to time-dependent DFT (TDDFT) to study the excited state properties [Casida’95].
TD-DFT for excited states calculation: a road map

Photovoltaic Conversion  
(collective motion of many particles)

\[ \downarrow \]

**TDDFT (TDKS)**  
\[
\left[ -\frac{1}{2} \nabla^2 + V_{KS}(r, t) \right] \Phi_i(r, t) = i \frac{\partial}{\partial t} \Phi_i(r, t)
\]

\[ \downarrow \]

Linear Response Perturbation Theory

\[ V_{KS}^0(r) \sim V_{KS}^0(r) + \delta v(r, t) \]

\[ \downarrow \]

Excited (eigen) States Calculations  
(Linear Response Eigenvalue Problem)
Immense recent interests

Immense recent interests in the excited states calculations of molecules for materials design and energy science

- Special issue of *Materials Research Society Bulletin* on High-performance computing for materials design to advance energy science. (solar, electrochemical batteries, ...)

- SIAM News article “Mathematicians Gone Solar!”

- Grond *et al* (2013): Excitation spectra of many-body systems by linear response: general theory and applications to trapped condensates
  linear response of Gross-Pitaeskii equation = Bogoliubov-de Gennes equation

two-particle Green’s function = Bethe-Salpeter equation

- [Baroni *et al’14, Challacombe’14, List *et al’14]
Multiple Exciton Generation and Charge Extraction in All-Inorganic Nanostructured Solar Cells (DMR-1035468 - SOLAR Collaborative)

Gergely T. Zimanyi, G. Galli, S. Kauzlarich, D. Larsen, Z. Bai, D. Paul, all University of California, Davis

S. Carter, University of California, Santa Cruz

Goals

(1) Study the Multiple Exciton Generation (MEG) pathway for solar energy conversion
(2) Analyze the competition of quantum confinement and charge extraction
(3) Focus on all-inorganic nanostructured solar cells

Project triad

(P1) Synthesize pure, doped and alloyed Si and Ge core-shell NPs to analyze their chemistry, quantum states and absorption spectrum in a wide range of size, doping, and structure, in a comparative analysis relative to PbS NPs
(P2) Explore the impact of complex factors such as the relaxation of the NP surface, the various core-shell structures, the exciton interaction and the NP-NP interaction on the chemistry and spectra of the NPs as well as on the MEG
(P3) Analyze the competing design principles of maintaining quantum confinement to preserve the strong Coulomb interaction and thus the efficiency of the MEG while embedding the NPs into the charge-transport layers of the solar cell for an effective extraction of the photo-charge carriers

Interdisciplinary triad

(1) Chemical effort: synthesize and characterize a wide variety of NPs
(2) Material science effort: compute the single NP spectrum with high accuracy to model the MEG process, to describe charge transfer from the NPs to the electrodes, and to optimize the photovoltaic (PV) properties when embedding the NPs on nanosstructured surfaces
(3) Mathematical effort: invent transformative mathematical breakthroughs for a qualitatively better description of the exciton interaction effects in the NPs and to develop methods of global statistical analysis to extract previously hidden dynamics from ultra-high dimensional spectro-temporal datasets

Experimental triad

(E1) Synthesize pure, doped and alloyed Si and Ge based NPs, including core-shell composites, terminate the surface bonds with inorganic shells, manipulate the surface of the NPs in a controlled manner
(E2) Characterize the multielexiton generation in the NPs by transient absorption and photoluminescence with femtosecond resolution and perform a comparative analysis of the results in relation to PbS NP solar cells
(E3) Optimize the charge transport by embedding the NPs into charge transport layers of PV devices while maintaining quantum confinement

Theoretical triad

(T1) Surface reconstruction and energetics of NPs will be described by density functional theories (DFT)
(T2) Exciton interaction effects will be described via time dependent DFT and Bethe-Salpeter methods
(T3) Competing MEG theories will be compared based on these results; and non-equilibrium rate equations will be developed to determine the full rate of MEG

Mathematical framework

(M1) Lanczos coefficient extrapolation method will be developed, dramatically reducing the computational workload by replacing direct matrix manipulations with matrix by vector products
(M2) Global statistical methods will be developed to qualitatively improve the analysis and extraction of the hidden dynamics from the noisy, ultra-high dimensional spectro-temporal dataset, obtained by the optical methods of (E3)

Convergence of the absorption spectrum of benzene, calculated by the Padé-extrapolated Lanczos method. N=number of recursive steps.
The rest of this talk

1. Variational principles of the LR eigenvalue problem
2. Computation of the LR eigenvalue problem
Variational principles of LR eigenvalue problem
Standard Linear Response (LR) eigenvalue problem

- In this talk, for simplicity, we focus on the standard LR eigenvalue problem

\[
\begin{bmatrix}
A & B \\
-B & -A \\
\end{bmatrix}
\begin{bmatrix}
u \\
v \\
\end{bmatrix}
= \lambda
\begin{bmatrix}
u \\
v \\
\end{bmatrix}
\]

where \( A^T = A, \ B^T = B \) and \( \begin{bmatrix} A & B \\
B & A \end{bmatrix} > 0 \)

- Under a symmetric orthogonal similarity transformation, \( J = \frac{1}{\sqrt{2}} \begin{bmatrix} I & I \\
I & -I \end{bmatrix} \)

The LR eigenvalue problem is equivalent to

\[
Hz \equiv \begin{bmatrix}
0 & A-B \\
A+B & 0 \\
\end{bmatrix}
\begin{bmatrix}
y \\
x \\
\end{bmatrix}
\equiv
\begin{bmatrix}
0 & K \\
M & 0 \\
\end{bmatrix}
\begin{bmatrix}
y \\
x \\
\end{bmatrix}
= \lambda
\begin{bmatrix}
y \\
x \\
\end{bmatrix}
\equiv \lambda z,
\]

- \( \begin{bmatrix} A & B \\
B & A \end{bmatrix} > 0 \iff K > 0 \) and \( M > 0 \).
Basic facts

1. Eigenvalues of $H$ are real and

$$-\lambda_n \leq \cdots \leq -\lambda_2 \leq -\lambda_1 < 0 < \lambda_1 \leq \lambda_2 \leq \cdots \leq \lambda_n$$

2. Eigen-decomposition

$$H = \begin{bmatrix} Y\Lambda & Y\Lambda \\ X & -X \end{bmatrix} \begin{bmatrix} \Lambda & \Lambda \\ -\Lambda & -\Lambda \end{bmatrix} \begin{bmatrix} Y\Lambda & Y\Lambda \\ X & -X \end{bmatrix}^{-1}$$

where $X = Y^{-T}$ and $\Lambda = \text{diag}(\lambda_1, \lambda_2, \ldots, \lambda_n)$. 
3. Let $\mathcal{U}, \mathcal{V} \subseteq \mathbb{R}^n$ be a pair of *deflating subspaces* of $\{K, M\}$, namely

$$K\mathcal{U} \subseteq \mathcal{V} \quad \text{and} \quad M\mathcal{V} \subseteq \mathcal{U}.$$ 

Then

(a) If $\{\mathcal{U}, \mathcal{V}\}$ is a pair of *deflating subspaces* of $\{K, M\}$, then $\mathcal{V} \oplus \mathcal{U}$ is an *invariant subspace* of $H$.

(b) Let $\mathcal{Z}$ be *invariant subspace* of $H$ and let $\mathcal{Z} = \begin{bmatrix} \mathcal{V} \\ \mathcal{U} \end{bmatrix}$ be a basis matrix of $\mathcal{Z}$, then $\{\text{span}(U), \text{span}(V)\}$ is a pair of *deflating subspaces* of $\{K, M\}$. 
4. Structure-preserving subspace projection

Let $U, V \in \mathbb{R}^{n \times k}$ be basis matrices of a pair of deflating subspaces $\mathcal{U}$ and $\mathcal{V}$, and

$$U^T V \equiv W = W_1^T W_2$$

Define $2k \times 2k$ block Rayleigh quotient matrix:

$$H_{SR} = \begin{bmatrix}
W_1^{-T} U^T & W_2^{-T} V^T \\
W_2^{-T} V^T & W_2^{-T} V^T
\end{bmatrix}
\begin{bmatrix}
0 & K \\
M & 0
\end{bmatrix}
\begin{bmatrix}
V W_2^{-1} \\
U W_1^{-1}
\end{bmatrix}$$

Then

$$H_{SR} \begin{bmatrix}
\hat{y} \\
\hat{x}
\end{bmatrix} = \lambda \begin{bmatrix}
\hat{y} \\
\hat{x}
\end{bmatrix} \implies \begin{bmatrix}
0 & K \\
M & 0
\end{bmatrix}
\begin{bmatrix}
V W_2^{-1} \hat{y} \\
U W_1^{-1} \hat{x}
\end{bmatrix} = \lambda
\begin{bmatrix}
V W_2^{-1} \hat{y} \\
U W_1^{-1} \hat{x}
\end{bmatrix}. $$
Thouless minimization principle

1. Recall: eigenvalues of $H$:

\[-\lambda_n \leq \cdots \leq -\lambda_2 \leq -\lambda_1 < 0 < \lambda_1 \leq \lambda_2 \leq \cdots \leq \lambda_n\]

2. Thouless functional [Thouless’61]

\[\rho(x, y) = \frac{x^T K x + y^T M y}{2|xTy|}\]

3. Minimization principle [Thouless’61, Tsiper’99,’01]

\[\lambda_1 = \min_{x, y \in \mathcal{D}} \rho(x, y)\]

$\mathcal{D}$ consists of all $x$ and $y$ such that either $x^T y \neq 0$ or $x^T y = 0$ but $x^T K x + y^T M y > 0$. This removes those $x$ and $y$ that vanish both the numerator and the denominator from the domain. In particular $x = y = 0$ is not in the domain $\mathcal{D}$. 
Review: variational principles for the symmetric eigenproblem

For $A = A^T \in \mathbb{R}^{n \times n}$ with eigenvalues $\lambda_1 \leq \lambda_2 \leq \cdots \leq \lambda_n$:

1. The minimization principle:
   $$\lambda_1 = \min_{x^T x = 1} x^T A x.$$

2. Ky Fan’s trace minimization principle is
   $$\lambda_1 + \lambda_2 + \cdots + \lambda_k = \min_{U_k \in \mathbb{R}^{n \times k}, U_k^T U_k = I_k} \text{trace}(U_k^T A U_k),$$

3. Cauchy’s interlacing inequalities:
   $$\lambda_i \leq \mu_i \leq \lambda_{i+n-k},$$
   where $\mu_i$ are the eigenvalues of $U_k^T A U_k$ in ascending order.

These results establish the theoretical foundation for the development of efficient methods for symmetric eigenproblems, such as SD, CG and Lanczos.
1. Extension of Thouless minimization principle:

(a) If one of $K$ and $M$ is positive definite, then

$$\lambda_1 = \inf_{x,y} \rho(x, y)$$

where $x, y$ is taken such that $x^Ty \neq 0$.

(b) “inf” can be replaced by “min” $\iff K > 0$ and $M > 0$.

(c) When both $K$ and $M$ are definite, the optimal argument pair $(x_1, y_1)$ gives to an eigenvector $z_1 = \begin{bmatrix} y_1 \\ x_1 \end{bmatrix}$ of $H$ associated with $\lambda_1$. 
2. The trace minimization principle

(a) If one of $K$ and $M$ is positive definite,

$$\lambda_1 + \lambda_2 + \cdots + \lambda_k = \inf_{U_k, V_k \in \mathbb{R}^{n \times k}} \frac{1}{2} \text{trace}(U_k^T K U_k + V_k^T M V_k).$$

(b) “inf” can be replaced by “min” $\Leftrightarrow K > 0$ and $M > 0$.

(c) When both $K$ and $M$ are definite and if also $\lambda_k < \lambda_{k+1}$, then for any $U_k$ and $V_k$ that attain the minimum, \{span($U_k$), span($V_k$)\} is a pair of deflating subspaces of \{$K$, $M$\} and the corresponding $H_{SR}$ has eigenvalues $\pm \lambda_i$ ($1 \leq i \leq k$).
3. Let $H_{SR}$ be the block Rayleigh quotient, and $\mu_i$ be eigenvalues of $H_{SR}$.

(a) Cauchy-like interlacing inequalities:

$$
\lambda_i \leq \mu_i \leq \beta \lambda_{i+n-k} \quad \text{for } 1 \leq i \leq k,
$$

where $\beta = \min\{\kappa(K), \kappa(M)\}^{1/2}/\cos \theta(U, V)$.

(b) If $U \subseteq M V$ when $M$ is definite, or $V \subseteq K U$ when $K$ is definite, then

$$
\lambda_i \leq \mu_i \leq \lambda_{i+n-k} \quad \text{for } 1 \leq i \leq k,
$$
These theoretical results

- parallel to the symmetric eigenvalue problem
- establish theoretical justification for the best approximation of the smallest positive eigenvalues of \( H \) via approximate deflating subspaces.
Computation of the LR eigenvalue problem
LR eigensolvers in Physics and Chemistry

1. QR on “KM” via Cholesky decomposition [Chi’70]
2. Davidson-like algorithms applied to $KM$ and $H$ [Rettrup’82, Olsen et al’88, Stratman, Scuseria and Frisch’98]
3. Lanczos-like algorithms [Tsiper’99,’01, Gruning et al’09,’11]
4. CG via a Thouless variational principle [Muta et al’02, Lucero et al’08, Challacombe’10,’14]
5. Contour-integral SS-method [Tsuchimochi et al’08]
6. Algorithm survey and comparison [Tretiak et al’08]
LR eigensolvers developed in Numerical Linear Algebra

1. The generalized symmetric definite eigenproblems of types 2 and 3 [Wilkinson’65, LAPACK routines xSYGVD]
2. QZ-like algorithm [Flaschka and W-W Lin’92]
3. GR algorithm: generalized QR algorithm [Watkin’07]
4. ScaLAPACK-enabled dense solver [Shao, da Jornada, Yang et al’14]
5. Generalized Lanczos scheme for $A = CB$ [Van der Vorst’82]
6. Sympletic Lanczos, Hamiltonian Krylov-Schur [Benner et al’97, ... Benner et al’09]
7. Krylov-Schur algorithms for the product eigenproblems [Kressner’06]
8. Jacobi-Davidson algorithm for the product eigenproblems [Hochstenbach’08]
9. Indefinite variant of LOBPCG [Kressner, Pandur and Shao’13]
Line and dual-channel search based SD/CG methods

1. Line search [Muta et al’02, Lucero et al’08]:
   look for the best possible scalar argument $t$ on the line
   \[
   \begin{bmatrix} y_+ \\ x_+ \end{bmatrix} = \begin{bmatrix} y_- \\ x_- \end{bmatrix} + t \begin{bmatrix} q \\ p \end{bmatrix}
   \]
   to minimize the Thouless functional $\rho(x_+, y_+)$:
   \[
   \min_t \rho(x_+, y_+)
   \]

2. Dual-channel search [Challacombe’10,’14]:
   \[
   \min_{s,t} \rho(x + sp, y + tq)
   \]

3. Both search schemes
   - *cannot* be related to a smaller projected problem of the same kind
   - *no* justification for optimality
   - *not* readily extensible to the subspace search for simultaneously computing few smallest positive eigenvalues and corresponding eigenvectors of $H$. 
New 4-D SD/CG methods

1. 4-D search: find scalars $\alpha$, $\beta$, $s$, and $t$ to minimize

$$\rho(\alpha x + sp, \beta y + tq)$$

i.e., the search space is

$$\text{span} \left\{ \begin{bmatrix} y \\ 0 \end{bmatrix}, \begin{bmatrix} q \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ x \end{bmatrix}, \begin{bmatrix} 0 \\ p \end{bmatrix} \right\}$$

2. Let $U = (x, p)$ and $V = (y, q)$, then

$$\min_{\alpha, \beta, s, t} \rho(\alpha x + sp, \beta y + tq) = \min_{u \in \text{span}(U), v \in \text{span}(V)} \rho(u, v) = \lambda_1(H_{SR}),$$

where $H_{SR}$ is a $4 \times 4$ structure-preserving projection of $H$:

$$H_{SR} = \begin{bmatrix} 0 & K_{SR} \\ M_{SR} & 0 \end{bmatrix}$$
3. 4-D search:

- yields the **best approximation** based on $U$ and $V$
  ... justified by the minimization principle
- is readily applicable for computing multiple eigenpairs, ⇒ block SD/CG.
  ... led by the trace minimization principle
- is easy to incorporate the **preconditioning**
4-D search steepest descent algorithm

0. Given initial approximations $z_0 = \begin{bmatrix} y_0 \\ x_0 \end{bmatrix}$

1. for $i = 0, 1, \ldots$ until convergence

2. $f_i = \rho(x_i, y_i)$

3. $p_i = K x_i - f_i y_i$, $q_i = M y_i - f_i x_i$

4. $\begin{bmatrix} q_i \\ p_i \end{bmatrix} \leftarrow \Phi \begin{bmatrix} p_i \\ q_i \end{bmatrix}$ if pre-conditioner $\Phi$ selected

5. $W = U^T V = W_1^T W_2$, where $U = (x_i, p_i)$, $V = (y_i, q_i)$

6. Compute the smallest positive eigenpair of $H_{SR}$

7. $x_{i+1} = U W_1^{-1} \hat{x}_1$, $y_{i+1} = V W_2^{-1} \hat{y}_1$

8. Normalization: $x_{i+1} \leftarrow \alpha x_{i+1}$, $y_{i+1} \leftarrow \alpha y_{i+1}$
4-D search steepest descent algorithm – block version

0  Given initial approximations \( Z_0 = \begin{bmatrix} Y_0 \\ X_0 \end{bmatrix} \)

1  for \( i = 0, 1, \ldots \) until convergence:

2  \( \rho_j = \rho((X_i)_{(:,j)}, (Y_i)_{(:,j)}), 1 \leq j \leq k \)

3  \( P_i = K X_i - Y_i D_i, Q_i = M Y_i - X_i D_i, \) where \( D_i = \text{diag}(\rho_1, \ldots, \rho_k) \)

4  \( \begin{bmatrix} Q_i \\ P_i \end{bmatrix} \leftarrow \Phi \begin{bmatrix} P_i \\ Q_i \end{bmatrix} \) if the pre-conditioner \( \Phi \) is selected

5  Compute \( W = U^T V = W_1^T W_2, \) where \( U = (X_i, P_i), Y = (Y_i, Q_i) \)

6  Compute the \( k \) smallest positive eigenpairs of \( H_{SR} \)

7  \( X_{i+1} = U W_1^{-1}(\hat{x}_1, \ldots, \hat{x}_k), Y_{i+1} = V W_2^{-1}(\hat{y}_1, \ldots, \hat{y}_k) \)

8  Normalize each column of \( Z_{i+1} = \begin{bmatrix} Y_{i+1} \\ X_{i+1} \end{bmatrix} \)
Numerical results

1. Quantum-ESPRESSO
   
   [http://www.quantum-espresso.org](http://www.quantum-espresso.org)

   an integrated suite of open-source computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials.
Silane molecule SiH₄

Dimension of $K$ and $M$: 5660
Compute 4 smallest positive eigenpairs: $0 < \lambda_1 < \lambda_2 < \lambda_3 < \lambda_4$

Residual norms

Eigenvalue accuracy

![Graph showing residual norms and iteration](image)

![Graph showing relative error of eigenvalues and iteration](image)
TDDFT excitation spectrum of benzene: Comparison with previous calculations and experiments

<table>
<thead>
<tr>
<th>Transitions</th>
<th>This work</th>
<th>Ref. 1 6-31+G*</th>
<th>Ref. 1 AUG-cc-pVTZ</th>
<th>Ref. 2 pVTZ+</th>
<th>Exp. [2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{2u}$ (π → π*)</td>
<td>5.39</td>
<td>5.31</td>
<td>5.26</td>
<td>5.28</td>
<td>4.90</td>
</tr>
<tr>
<td>$E_{1g}$ (π → 3s)</td>
<td>5.95</td>
<td>6.36</td>
<td>6.19</td>
<td>5.99</td>
<td>6.33</td>
</tr>
<tr>
<td>$B_{1u}$ (π → π*)</td>
<td>6.10</td>
<td>6.10</td>
<td>6.02</td>
<td>6.10</td>
<td>6.20</td>
</tr>
<tr>
<td>$E_{2u}$ (π → 3p)</td>
<td>6.58</td>
<td>6.98</td>
<td>6.80</td>
<td>6.45</td>
<td>6.95</td>
</tr>
<tr>
<td>$A_{2u}$ (π → 3p)</td>
<td>6.58</td>
<td>6.99</td>
<td>6.80</td>
<td>6.44</td>
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</tr>
<tr>
<td>$E_{1u}$ (π → π*)</td>
<td>6.95</td>
<td>6.94</td>
<td>n.a.</td>
<td>6.92</td>
<td>6.94</td>
</tr>
</tbody>
</table>

Details
• Low-lying TDDFT (LDA) excitations of benzene in eV
• Supercell: 30 x 30 x 20 $a_0^3$
• Cutoff: 60 Ry
• TDDFT matrix dimension: $2,117,910 \times 2,117,910$ (never built explicitly)
• Results after 2500 iterations


Convergence of the normalized residual for benzene

Normalized Residual

\[ \frac{||\mathcal{H}'_{RPA}z_j^f - \lambda_j z_j^f||}{||r_j^{(0)}||} \]

A preconitoning scheme for the 4-D Steepest Descent algorithm (preliminary results)

In the density matrix perturbation theory implementation of TDDFT and BSE a preconitoning scheme based on the kinetic energy can be used, as usually done in plane-wave implementations:

\[ H_{G,G'}^{-1} \approx \frac{2m}{\hbar^2 G'^2} \delta_{G,G'} \quad \text{for} \quad G \to \infty \]

4-D SD without preconitoning

**TDDFT for benzene**

2,117,910 x 2,117,910 matrix

4-D SD with preconitoning

**TDDFT for benzene**

2,117,910 x 2,117,910 matrix

THE FINAL RESULT IS UNCHANGED BUT THE TOTAL NUMBER OF NECESSARY ITERATIONS IS DECREASED BY A FACTOR 10
Application of the preconditioned 4-D Steepest Descent algorithm to the TDDFT excitation energies of fullerene $C_{60}$

4-D SD with preconditioning

$\frac{\|H_{\text{RPA}}^\prime z_j^\ell - \lambda_j z_j^\ell\|}{\|r_j^{(0)}\|}$

$22 \text{ million} \times 22 \text{ million}$ TDLDA matrix (not built explicitly)
Concluding remarks

1. New minimization principles for the LR eigenvalue problem
2. Structure-preserving Rayleigh-Ritz like subspace projection $H_{SR}$ of $H$
3. Cauchy-like interlacing inequalities
4. 4-D SD and CG algorithms
5. Numerical experiments for Quantum-ESPRESSO based excited state calculations