Title: Correlated Electronic States in Conjugated Polymers: A DMRG Approach

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Correlated Electronic States in Conjugated Polymers: A DMRG Approach

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Plan of the Talk

1. Introduction to conjugated systems
2. Noninteracting model and its limitations
3. Introduction to interacting model
4. The DMRG method for excited states
5. Some applications
6. Dynamic DMRG method
7. Summary
Conjugated Electronic Materials

Organic molecules with extended $\pi$ - conjugation

Examples – polymers and large molecules

Poly Acetylene (PA), Poly Para Phenylene Vinylene (PPV)

Oligo thiophenes, Oligo acenes, Porphines, Phthalocyanines . . .

Applications:

Organic Light Emitting Diodes (OLEDs)

Organic Photovoltaics (OPVs)

Organic Transistors (OTFTs, OFETs)
Examples of Conjugated Polymers

From top: Poly acetylene \((\text{CH})_x\), poly para phenylene (PPP) poly acene and poly para phenylene vinylene (PPV)
Theoretical Models for $\pi$-Conjugated Systems

Hückel Model:

Carbon atoms are in $sp^2$ hybridization.

Assumes one $p_z$ orbital at every Carbon site involved in conjugation.
Assumes transfer integral only between bonded Carbon sites.

\[ \hat{H_o} = \sum_{ij} t_{ij} (\hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} + H.c.) + \sum_i \alpha_i \hat{n}_i \]

$t_{ij}$ is resonance / transfer integral between bonded sites and $\alpha_i$, the site energy at site ‘$i$’.
(CH)$_x$ and Symmetries in the MO picture

- (CH)$_x$ has charge conjugation or electron-hole or alternancy symmetry. Carbon sites when subdivided into two sublattices, no bond exists between carbon atoms on same sublattice.

  \[ C^A=C^B \quad C^A=C^B \quad C^A=C^B \quad C^A=C^B \]

- The polymer also has inversion symmetry.
- Weak spin-orbit interactions; states can be classified by total spin.
- Symmetries lead to strong experimental predictions.
$(CH)_x$ and Symmetries in the MO picture

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Consequences of Symmetry

- Pairing theorem follows from alternancy symmetry predicts that for a $\pi$ bonding state at energy $-\varepsilon_k$, there exists a $\pi^*$ anti-bonding state at $+\varepsilon_k$.

- Symmetry of states alternate between $a^+$ and $b^-$, so lowest energy excitation is dipole allowed.

- Pairing theorem implies, $(\text{CH})_x$ with odd number of carbon atoms should have a mid-gap state and a mid-gap absorption since lowest energy excitation is dipole allowed.
Schematic MO Picture of Even and Odd Polyenes

Even polyene

Odd polyene
Polymer or Band Limit

C.B.  \[ \text{Optical Gap} \quad E_g \]
V.B.  

C.B.  \[ \text{Dipole allowed} \quad E_g/2 \]
V.B.  

Dipole allowed  \[ E_g/2 \]

The kink in odd polyene is a topological soliton and is associated with a mid gap state.
Experimental Status

- Polyacetylene is a semiconductor due to Peierls’ distortion. Valence $\pi$ band is filled and conduction $\pi^*$ band is empty.

- The optical gap $\sim 1.7\text{eV}$. Dimerization required to obtain this gap twice the observed bond length alternation.

- Evidence for dipole forbidden states below $E_g$.

- No evidence for mid-gap absorption in polyene radicals.

- $esr$ studies of polyene radicals show evidence for both positive and negative spin densities.
Symmetric Cyanine Dyes: An intrigue

\[ \text{SCD} = \begin{array}{c}
\text{R} \\
\text{N} \\
\text{C} \\
\text{C} \\
\text{C} \end{array} \times \begin{array}{c}
\text{R} \\
\text{N} \\
\text{C} \\
\text{C} \\
\text{R} \end{array} \]

SCD similar to \((\text{CH})_x\) except for end groups.

Qualitatively different \(E_g\) vs \(1/x\) extrapolation in \((\text{CH})_x\) and SCD.

\(E_g\) for Infinite chains in \((\text{CH})_x\) is nonzero, but in SCD it is zero.
Hückel model for molecules \quad \rightarrow \quad \text{Single band tight – binding model in Solids}

**Drawbacks of Hückel model:**

- Gives incorrect ordering of energy levels in polyenes.
- Fails to account for negative spin densities in radicals and yields wrong spin-spin correlations.
- Fails to reproduce qualitative differences between closely related systems.
- Mainly of pedagogical value. Ignores explicit electron-electron interactions.
Interacting π–Electron Models

- Explicit electron – electron interactions essential for realistic modeling

\[ \hat{H}_{\text{Full}} = \hat{H}_0 + \frac{1}{2} \sum_{ijkl} [ij|kl] (\hat{E}_{ij}\hat{E}_{kl} - \delta_{jk}\hat{E}_{il}) \]

\[ \hat{E}_{ij} = \sum_{\sigma} \hat{a}_{i,\sigma}^\dagger \hat{a}_{j,\sigma} \]

\[ [ij|kl] = \int \phi_i^*(1) \phi_j(1) \left( \frac{e^2}{r_{12}} \right) \phi_k^*(2) \phi_l(2) \, d^3r_1 d^3r_2 \]

This model requires further simplification to enable routine solvability.
Zero Differential Overlap (ZDO) Approximation

\[ [ij|kl] = \int \phi_i^*(1) \phi_j(1) \left( \frac{e^2}{r_{12}} \right) \phi_k^*(2) \phi_l(2) \, d^3r_1 \, d^3r_2 \]

\[ [ij|kl] = [ij|kl] \delta_{ij} \delta_{kl} \]
Pariser-Parr-Pople (PPP) Model

\[ [ii][jj] \text{ parametrized by } V( r_{ij} ) \]

\[ \hat{H}_{PPP} = \hat{H}_{Hub} + \sum_{ij} V(r_{ij}) \left( \hat{n}_i - z_i \right) \left( \hat{n}_j - z_j \right) \]

\( z_i \) are local chemical potentials.

- Ohno parametrization:

\[ V(r_{ij}) = \left\{ \frac{2}{(U_i + U_j)} \right\}^2 + r_{ij} \}^{-1/2} \]

- Mataga-Nishimoto parametrization:

\[ V(r_{ij}) = \left\{ \frac{2}{(U_i + U_j)} \right\} + r_{ij} \}^{-1} \]
PPP Hamiltonian (1953)

$$\hat{H}_{PPP} = \sum_{<ij>\sigma} t_{ij} (\hat{a}_{i\sigma}^{\dagger} \hat{a}_{j\sigma} + H.c.) + \sum_i (U_i/2) \hat{n}_i (\hat{n}_i - 1) + \sum_{i>j} V(r_{ij}) (\hat{n}_i - 1) (\hat{n}_j - 1)$$
Hubbard Model (1964)

- Hückel model + on-site repulsions

\[ [ii|jj] = 0 \text{ for } i \neq j ; \]

\[ [ii|jj] = U_i \text{ for } i=j \]

\[ \hat{H}_{\text{Hub}} = \hat{H}_o + \sum_i U_i \hat{n}_i (\hat{n}_i - 1)/2 \]
Exact Diagonalization (ED) Methods

- Hilbert space of PPP Hamiltonian is finite for molecules.
- PPP model conserves total S and $M_s$.
- Hilbert space factorized into definite total S and $M_s$ spaces using Rumer-Pauling VB basis.
- Rumer-Pauling VB basis is nonorthogonal, but complete, and linearly independent.
- Recent development allows exploiting full spatial symmetry of any point group.

S. Sahoo and SR, Int. J. Quantum Chem DOI 10.1002/qua.23097
Exact Diagonalization (ED) Methods

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Necessity and Drawbacks of ED Methods

- ED methods are size consistent. Good for energy gap extrapolations to thermodynamic or polymer limit.

- Hilbert space dimension explodes with increase in no. of orbitals
  
  \[ N_{\text{electrons}} = 14, \quad N_{\text{sites}} = 14, \quad \# \text{ of singlets} = 2,760,615 \]
  
  \[ N_{\text{electrons}} = 16, \quad N_{\text{sites}} = 16, \quad \# \text{ of singlets} = 34,763,300 \]

  hence for polymers with large monomers (e.g. PPV), ED methods limited to small oligomers.

- ED methods rely on extrapolations. In systems with large \( \pi \) coherence length, ED methods may not be reliable.

- ED methods provide excellent check on approximate methods.
Approximate Methods

- Restricted CI methods
- Coupled Cluster methods
  - Quantum Monte Carlo methods
  - Renormalization Group Methods
    - Energy eigenvalue based methods
    - Density matrix eigenvalue based methods
Density matrix based methods.

- Natural orbital basis: eigenfunctions of one-particle density matrix with large densities (density matrix eigenvalues) were used as orbitals for CI calculations.

- DMRG uses eigenstates of many-body density matrices to span the Fock space of the many-particle subsystem. Besides, it also uses a renormalization procedure to extend the system size.
The Density Matrix Renormalization Group (DMRG) Technique

- DMRG method involves iteratively building a large system starting from a small system.

- The eigenstate of superblock consisting of system and surroundings is used to build density matrix of system.

- Dominant eigenstates ($10^2 \sim 10^3$) of the density matrix are used to span the Fock space of the system.

- The superblock size is increased by adding new sites.

- Very accurate for one and quasi-one dimensional systems such as Hubbard, Heisenberg spin chains and polymers.

S.R. White (1992)
Entanglement Entropy and the Area Law.

\[ \rho_x | \mu_x \rangle = | \mu_x \rangle | \mu_x \rangle \]

\[ S = - \sum_x \mu_x \log_2 \mu_x \]

Area Law \quad S \sim \text{Area between system and environment}

DMRG cut-off \quad m \sim \sigma^3 \quad \text{Hence DMRG most accurate for 1-D systems. At criticality, there are log corrections to } S \text{ leading to higher cut-off for desired accuracy.}
Exact entanglement entropy of Hubbard (U/t=4) and PPP eigenstates of a chain of 16 sites

DMRG technique is accurate for long-range interacting models with diagonal density-density interactions

DMRG and Matrix Product States

DMRG wavefunction at the end of right sweep

\[ \Psi = \sum_{Z^{(N-2)}, \sigma_{N-1}} A^{(N-2)}_{Z^{(N-2)}, \sigma_{N-1}} \left| Z^{(N-2)}, \sigma_{N-1} \right\rangle \]

\[ \left| Z^{(N-1)} \right\rangle = \sum_{Z^{(N-2)}, \sigma_{N-1}} A^{(N-2)}_{Z^{(N-2)}, \sigma_{N-1}} \left| Z^{(N-2)}, \sigma_{N-1} \right\rangle \]

\[ \Psi = \sum_{Z^{(N-2)}} \sum_{Z^{(N-1)}} \sum_{\sigma_{N-1}} \sum_{\sigma_{N}} A^{(N-1)}_{Z^{(N-1)}, \sigma_{N}} A^{(N-2)}_{Z^{(N-2)}, \sigma_{N-1}} \left| Z^{(N-2)}, Z^{(N-1)}, \sigma_{N-1}, \sigma_{N} \right\rangle \]
Continuing

\[ \Phi = \sum_{\sigma_1, \sigma_2, \ldots, \sigma_N} \sum_{2^{(1)}, 2^{(2)}, \ldots, 2^{(N-1)}} \]

\[ \begin{array}{c}
A^{(1)}_{2^{(1)}}, \sigma_1 \\
A^{(2)}_{2^{(2)}}, 2^{(2)} \sigma_2 \\
\vdots \\
A^{(N-1)}_{2^{(N-1)}}, \sigma_{N-1}
\end{array} \cdot \left| \sigma_1, \sigma_2, \ldots, \sigma_{N-1}, 10, \sigma_N \right\rangle \\
= \begin{array}{c}
A^{(1)} \\
A^{(2)} \\
A^{(3)} \\
\vdots \\
A^{(N-1)}
\end{array}
\]

Matrix Product States (MPS)
Symmetrized DMRG Method

Why do we need to exploit symmetries?

- Important states in conjugated polymers:
  - Ground state ($1^1A_g^+$);
  - Lowest dipole excited state ($1^1B_u^-$);
  - Lowest triplet state ($1^3B_u^+$);
  - Lowest two-photon state ($2^1A_g^+$);
  - mA$_g^+$ state (large transition dipole to $1^1B_u^-$);
  - nB$_u^-$ state (large transition dipole to mA$_g^+$)

- In unsymmetrized methods, too many intruder states between desired eigenstates.

- In large correlated systems, only a few low-lying states can be targeted; important states may be missed altogether.
Symmetries in the PPP and Hubbard Models

Electron-hole symmetry:

- When all sites are equivalent, for a bipartite system, electron-hole or charge conjugation or alternancy symmetry exists, at half-filling.

- At half-filling the Hamiltonian is invariant under the transformation

\[ \hat{a}_i^\dagger = \hat{b}_i; \text{‘} i\text{’ on sublattice A} \]
\[ \hat{a}_i^\dagger = -\hat{b}_i; \text{‘} i\text{’ on sublattice B} \]
E-h symmetry divides $N = N_e$ space into two subspaces: one containing both ‘covalent’ and ‘ionic’ configurations, other containing only ionic configurations. Dipole operator connects the two spaces.
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Spin symmetries

- Hamiltonian conserves total spin and $z$-component of total spin.

\[ [\hat{H}, \hat{S}^2] = 0 \ ; \ [\hat{H}, \hat{S}_z] = 0 \]

- Exploiting invariance of the total $\hat{S}_z$ is trivial, but of the total $\hat{S}^2$ is hard.

- When $M_s^{\text{tot}} = 0$, $\hat{H}$ is invariant when all the spins are rotated about the $y$-axis by $\pi$. This operation flips all the spins of a state and is called spin inversion.
Spin inversion divides the total spin space into spaces of even total spin and odd total spin.
\[^{\hat{C}_2}\] Operation on the DMRG basis yields,
\[\hat{C}_2 | \mu,\sigma,\sigma',\mu' > = (-1)^\gamma | \mu',\sigma',\sigma,\mu >;\]
\[\gamma = (n_{\sigma'} + n_{\mu'})(n_{\sigma} + n_{\mu})\]

and from this, we can construct the matrix for \[^{\hat{C}_2}\].

\[^{\hat{J}, \hat{P}}\] and \[^{\hat{C}_2}\] form an Abelian group

Irr. representations, \[^{e}A^+, eA^-\], \[^{o}A^+, oA^-\], \[^{e}B^+, eB^-\], \[^{o}B^+, oB^-\];

‘e’ and ‘o’ imply even and odd under parity;

‘+’ and ‘-’ imply even and odd under e-h symmetry.

Ground state lies in \[^{e}A^+\],
dipole allowed optical excitation in \[^{e}B^-\],
the lowest triplet in \[^{o}B^+\].
Checks on SDMRG

- Optical gap ($E_g$) in Hubbard model known analytically. In the limit of infinite chain length, for

$$U/t = 4.0, \ E_g^{\text{exact}} = 1.2867\ t \ ; \ U/t = 6.0 \ E_g^{\text{exact}} = 2.8926\ t$$

![Graph showing optical gap as a function of inverse chain length for Hubbard chains with $U=4.0t$ and $U=6.0t$. $m$ corresponds to the number of density matrix eigenvectors retained in the DMRG procedure. Arrows indicate the model exact gaps for infinite chains.]

$$E_{g,N\to\infty}^{\text{DMRG}} = 1.278, \ U/t = 4$$

$$E_{g,N\to\infty}^{\text{DMRG}} = 2.895, \ U/t = 6$$

The spin gap in the limit $U/t \to \infty$ should vanish for the Hubbard model.

**FIG. 2.** Spin gap (defined in the text) as a function of $1/n$ for Hubbard chains with $U=4.0t$ and $U=6.0t$. $m$ corresponds to the DMRG cutoff. Model exact spin gaps vanish for infinite chains.

**FIG. 3.** Energy gaps (measured from the ground state) of the lowest state in each subspace for chain length varying from 40 to 50, for two different values of $U/t$. The level ordering is $E_{uA} < E_{gA} < E_{gB} < E_{uB} < E_{gA} < E_{uB} < E_{gA}$. 

PRB, **54**, 7598 (1996).
Ordering of Low-lying Excitations

- Two important low-lying excitations in conjugated Polymers:
  - lowest one-photon state \( (1^1B_u) \)
  - lowest two-photon state \( (2^1A_g) \).

- Kasha rule in organic photochemistry – fluorescent light emission occurs from lowest excited state.

- Implications for level ordering
  \[
  E (1^1B_u) < E (2^1A_g) \quad \text{... Polymer is fluorescent}
  \]
  \[
  E (2^1A_g) < E (1^1B_u) \quad \text{... Polymer nonfluorescent}
  \]

- Level ordering controlled by polymer topology, correlation strength and conjugation length

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  \]

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Small $U/t$:

$1^1B_u$ below $2^1A_g$

Large $U/t$:

$2^1A_g$ below $1^1B_u$

Reason:

$1^1B_u$ has no covalent Contribution: Its energy increases with $U/t$.

PRB 56, 9298 (1997)

FIG. 1. Crossover on $U$ for $\delta=0.07$. 
1^1B_u - 2^1A_g crossover also occur as a function of $\delta$.

As $U/t$ increases, crossover occurs at higher value of $\delta$.

2^1A_g state described as two triplets at large $U/t$ and small $\delta$. 
- 2A -1B crossover occurs as a function of chain length for intermediate \( U/t \).

2A above 1B for long chains
2A below 1B for short chains.

2A state is more localized than 1B state. As system size increases 1B descends below 2A.

*PRB 56, 9298 (1997)*
Polyacenes

- Crossover in the two-photon and optical gap at pentacene - experimentally seen.
- One photon state more localized than two photon state.
- Unusually small triplet or spin gap.

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Molecular Multiferroics

Fused azulene

- Azulenes have fused seven and five membered rings.
- Frustration is expected to lower the spin gap.
- Hückel (4n+2) rule predicts positive charge on seven membered ring and negative charge on five membered ring.
Spin Gaps in Azulene

- $\Delta_1 = E(M_S=1) - E(M_S=0)$
- $\Delta_2 = E(M_S=2) - E(M_S=0)$
- $\Delta_3 = E(M_S=3) - E(M_S=0)$

$n$ is # of azulenes in fused azulene

S. Thomas, D. Garcia, K. Hallberg and SR (preprint)
Spin gaps for a $s=1/2$ Heisenberg antiferromagnetic system on the fused azulene lattice
Spin Gaps in Azulene

- Oligomers up to five azulene units ground state is singlet, $S=0$.

- Ground state for oligomers with $(n>5)$ is a triplet, $S=1$.

- Gap $\Delta_2$ appears to vanish for 10 or 11 azulene units, leading to ground state spin $S=2$.

- From the slopes of the gaps, it appears that in the polymer limit, a ferromagnetic ground state will result.
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- From the slopes of the gaps, it appears that in the polymer limit, a ferromagnetic ground state will result.
Odd(Even) ring index corresponds to seven(five) membered ring of the azulene.
Computing dynamic response involves calculating

\[ I(\omega) = \langle \Psi_0 | \hat{O}^\dagger \frac{1}{E_0 + \omega + i\epsilon - H} \hat{O} | \Psi_0 \rangle \]

where \( \hat{O} \) is the operator corresponding to the response property. This can be solved by the Lanczos scheme, the sum over states technique or the correction vector technique.
Lanczos method:

We obtain the tridiagonal matrix representation of the Hamiltonian

$$H_L = \begin{pmatrix} c_0 & d_1 & 0 & 0 & \cdots \\ d_1 & c_1 & d_2 & 0 & 0 \\ 0 & d_2 & c_2 & d_3 & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots \\ 0 & 0 & 0 & 0 & \cdots & d_n & c_n \end{pmatrix}$$

and obtain the ground state of the Hamiltonian $|\Phi_0\rangle$. We then repeat the Lanczos scheme with the starting vector $|\Phi_0\rangle = 0 |\psi_0\rangle / [\langle \psi_0 | \hat{t}_0^+ \hat{t}_0 | \psi_0 \rangle]^{1/2}$ to get $|\Phi_L\rangle$.
\[ x_0 = \langle \Phi_0 | \frac{1}{2 \pi - \tilde{H}_L} | \Phi_0 \rangle \]

\[ = \langle \Phi_0 | \sigma^+ \frac{1}{2 \pi - \tilde{H}_L} \sigma | \Phi_0 \rangle / [\langle \Phi_0 | \Phi_0 \rangle]^{1/2} \]

with \[ \tilde{H}_L = \begin{pmatrix}
  a_0 & b_1 & 0 & 0 & \cdots \\
  b_1 & a_1 & b_2 & 0 & \cdots \\
  0 & b_2 & a_2 & b_3 & \cdots \\
  \vdots & \vdots & \vdots & \vdots & \ddots \\
  0 & 0 & \cdots & b_{n-1} & b_n
\end{pmatrix} \]

\[ I(\omega) = -\frac{1}{\pi} \text{Im} \begin{pmatrix}
  \langle \Phi_0 | (\sigma^+ \sigma) | \Phi_0 \rangle \\
  \frac{2 - a_0 - b_1^2}{2 - a_1 - b_2^2} \\
  \frac{2 - a_2 - b_3^2}{2 - a_3 - b_4^2} \\
  \vdots
\end{pmatrix} \]

Karen Hillberg
PRB 1995
Lanczos Technique is numerically fast and efficient, but not very accurate as it involves truncation of the Hilbert space. In quantum chemistry literature $I(\omega)$ is obtained by computing a small $(10^2 \sim 10^3)$ excited state of the Hamiltonian $|\Psi\rangle$ and obtaining $I(\omega)$ as

$$I(\omega) = -\frac{1}{\pi} \text{Im} \left[ \frac{\langle \Psi_0 | \hat{O}^+ | R \rangle \langle R | \hat{O} | \Psi_0 \rangle}{E_R - E_0 + \hbar \omega + i\epsilon} \right]$$
The Correction Vector Technique

We can define a vector \( \phi^{(i)}(\omega) \) as

\[
(H - E_0 - i\varepsilon) |\phi^{(i)}(\omega)\rangle = 0 |\ell_0\rangle
\]

If \( \phi^{(i)}(\omega) \) is expanded in the eigenstates of \( \hat{H} \)

\[
\phi^{(i)}(\omega) = \sum_R c_R |\ell_R\rangle
\]

with \( \hat{H} |\ell_R\rangle = E_R |\ell_R\rangle \), we can show that

\[
c_R = \frac{\langle \ell_R | \partial \delta | \ell_0 \rangle}{E_R - E_0 - i\omega - i\varepsilon}
\]
Lanczos Technique is numerically fast and efficient, but not very accurate as it involves truncation of the Hilbert space. In quantum chemistry literature, $I(\omega)$ is obtained by computing a small ($10^2$ ~ $10^3$) excited states of the Hamiltonian $|R\rangle$ and obtaining $I(\omega)$ as

$$I(\omega) = -\frac{1}{\pi} \text{Im} \left[ \frac{\langle \Psi_0 | \hat{D}^+ | R \rangle \langle R | \hat{D} | \Psi_0 \rangle}{E_R - E_0 + \hbar \omega + i \epsilon} \right]$$
The Correction Vector Technique

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If \( \phi^{(i)}(\omega) \) is expanded in the eigenstates of \( \hat{H} \)

\[
\phi^{(i)}(\omega) = \sum R \ket{R}
\]

with \( \hat{H}\ket{R} = E_R \ket{R} \), we can show that

\[
C_R = \frac{<R|\hat{A}|\psi_0>}{E_R - E_0 - \hbar\omega - i\epsilon}
\]
and \( I(\omega) = \frac{-1}{\pi} \text{Im} \langle \Psi_g \mid \delta \mid \Phi^{(1)}(\omega) \rangle \)

Since we already know \( \hat{H} \) in a chosen basis (DMRG basis, VB basis, Stabilizer determinants), we can solve for \( \Phi^{(1)}(\omega) \) in that basis. If

\[ \Phi^{(1)}(\omega) = \sum_{k} c_k |k\rangle \]

then we can write the equation for \( \Phi^{(1)}(\omega) \) as

\[ A^c \rightarrow b \]
\[ A_{ij} = (E_0 + \hbar \omega + i\epsilon) \delta_{ij} - H_{ij} \]

and \[ b_i = \sum_j O_{ij} a_j \]

\[ |\Psi_0\rangle = \sum_j q_j |j\rangle \]

Solution \( \vec{c} \) can be obtained in the full basis of the Hamiltonian and

\[ I(\omega) = -\frac{1}{\pi} \text{Im} \langle \Psi_0 | \hat{D}_I | \Phi^{(1)}(\omega) \rangle \]

in exact within the chosen basis.

Solution of \( \vec{A} \vec{c} = \vec{b} \) can be obtained by a small matrix algorithm similar to Davidson's

SR J. Comp. Chem 11, 545 (1990)
If \( 0 \) is the dipole displacement operator, \( \hat{\alpha}_i \), then polarizability

\[
\alpha_{ij}(\omega) = \frac{1}{2} \left[ \langle \phi_i^{(1)}(\omega) | \hat{\alpha}_j | \phi_j \rangle + \langle \phi_j^{(1)}(\omega) | \hat{\alpha}_i | \phi_i \rangle \right]
\]

To obtain higher order nonlinear response coefficients, we define the next order equation

\[
(\hat{H} - E_0 + i\omega_2 + i\xi) \phi_{ij}^{(2)}(\omega_1, \omega_2) = \hat{\alpha}_i \phi_j^{(1)}(\omega_1)
\]

and

\[
\gamma_{ijkl} = \hat{P} \langle \phi_i^{(1)}(\omega_1) | \hat{\alpha}_j | \phi_k^{(2)}(\omega_1 - \omega_2, -\omega_1) \rangle
\]

where \( \hat{P} \) is intrinsic permutation symmetry operator.
In the DMRG scheme, we can improve the accuracy by constructing an average density matrix which includes the density matrix from $\rho^{(0)}(\omega)$.

The method, though more accurate than the Lanczos scheme, is more compute intensive. It involves solving algebraic equations for every $\omega$.

To test the technique, we compare the rotationally averaged linear polarizability $\overline{\alpha}$ and THG coefficient $\overline{\gamma}$

$$\overline{\alpha} = \frac{1}{3} \sum_{i=1}^{3} \alpha_{ii}; \quad \overline{\gamma} = \frac{1}{15} \sum_{i,j=1}^{3} (2 \gamma_{iijj} + \gamma_{ijji})$$

Computed at $\omega = 0.1t$ exactly for a Hubbard chain of 12 sites at $U/t=4$ with DMRG computation with $m=200$

<table>
<thead>
<tr>
<th>$\overline{\alpha}_{\text{exact}}$</th>
<th>$\overline{\alpha}_{\text{DMRG}}$</th>
<th>$\overline{\gamma}_{\text{exact}}$</th>
<th>$\overline{\gamma}_{\text{DMRG}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.343</td>
<td>5.317</td>
<td>598.3</td>
<td>591.1</td>
</tr>
</tbody>
</table>

The dominant $\alpha$ ($\alpha_{xx}$) is 14.83 (exact) and 14.81 (DMRG) and $\gamma$ ($\gamma_{xxxx}$) 2873 (exact) and 2872 (DMRG).

$\alpha$ in $10^{-24}$ esu and $\gamma$ in $10^{-36}$ esu in all cases

Table 6.4: Calculation of tumbling averaged polarizabilities and hyperpolarizabilities by two-state model (TSM) and correction vector (CV) techniques.

| Model | System | $\bar{\alpha}$ ($\times 10^{-23}$ esu) | $\vec{\beta}_i$ ($\times 10^{-30}$ esu) | $|\vec{\beta}|$ ($\times 10^{-30}$ esu) |
|-------|--------|-------------------------------------|-------------------------------------|---------------------------------|
|       |        |    | $\beta_x$ | $\beta_y$ | $\beta_z$ | $\beta_x$ | $\beta_y$ | $\beta_z$ | $\beta_x$ | $\beta_y$ | $\beta_z$ |
| TSM   | TTA    | 29.00 | 17.20 | 20.42 | -19.70 | 33.18 |
|       | TSA    | 106.81 | 17.60 | 190.40 | -131.20 | 231.90 |
|       | TSA1   | 139.05 | -65.82 | 208.09 | 242.06 | 325.92 |
| CV    | TTA    | 163.97 | 13.02 | -19.24 | 15.93 | 28.17 |
|       | TSA    | 465.13 | 15.41 | 22.34 | -29.78 | 40.29 |
|       | TSA1   | 642.39 | -28.11 | 16.35 | 38.69 | 50.54 |

Real Time Dynamics

Important to understand processes such as
spin-charge separation
electron-hole recombination
fluorescent resonant energy transfer

Study involves propagating a wavepacket \( \Psi(t) \)
at zero time using time dependent Schrödinger Equation

\[
\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = \hat{H} \Psi
\]
\( \Psi \) is the desired wavepacket, e.g. a hole doped at site 1 in the ground state

\[ |\Psi\rangle = a_1 |4g\rangle \]

we follow the time evolution of \( \Psi \) and calculate evolution of properties such as

\[ n_i(t) = \langle \Psi(t) | \hat{n}_{i\sigma} + \hat{n}_{i,-\sigma} | \Psi(t) \rangle \]

and

\[ S_i^z(t) = \langle \Psi(t) | \hat{n}_{i\sigma} - \hat{n}_{i,-\sigma} | \Psi(t) \rangle \]

at various sites 'i' of the system.
Multistep Differencing (MSD) Techniques

MSD4:

\[
e^{i2\hat{H}t/\hbar} - e^{-i2\hat{H}t/\hbar} = \frac{i\hat{H}t}{\hbar} \left( -4 + \frac{8}{3} \frac{\hat{H}^2 \Delta t^2}{\hbar^2} \right) + O(\Delta t^5)
\]

\[
\frac{\hat{H}^2 \Delta t^2}{\hbar^2} = 2 - e^{i\hat{H}t/\hbar} - e^{-i\hat{H}t/\hbar}
\]

\[
e^{-i2\hat{H}t/\hbar} \approx e^{i2\hat{H}t/\hbar} - \frac{4i\hat{H}t}{3\hbar} \left[ I + 2(e^{i\hat{H}t/\hbar} + e^{-i\hat{H}t/\hbar}) \right]
\]

operating on \(\psi(0)\)

\[
\Psi(t+2\Delta t) \approx \Psi(t-2\Delta t) - \frac{4i\hat{H}t}{3\hbar} \left[ \Psi(t) + 2(\Psi(t-\Delta t) + \Psi(t+\Delta t)) \right]
\]

Fast - involves only one sparse matrix multiplication for time propagation. Time dependent quantities evaluated as \(\langle O(t) \rangle = \langle \psi(t)|O|\psi(t) \rangle.\)
The DMRG space at time $t=0$ rapidly fails to satisfactorily describe the wave packet at later times $t \gg t_0$. 

[Diagram showing the transition from initial DMRG space to wave packet evolution over time, labeled as $\Psi(t)$ and $t$-DMRG space.]
Double Time Window Targeting (DTWT) is a hybrid of LXW and TST schemes, which is at least twice as fast and more accurate than either

Charge and spin transport in PPP chains

\[ \langle n_a(t) \rangle \]

\[ \langle n_b(t) \rangle \]

\[ \langle n_c(t) \rangle \]

\[ \langle n_d(t) \rangle \]

\[ \text{time (fs)} \]

\[ L = 40 \]

\[ L = 30 \]

\[ L = 20 \]

\[ L = 14 \]
Spin transport in PPP model

\[ \langle S^z_{40}(t) \rangle \]
\[ \langle S^z_{30}(t) \rangle \]
\[ \langle S^z_{20}(t) \rangle \]
\[ \langle S^z_{14}(t) \rangle \]

\( L = 40 \)
\( L = 30 \)
\( L = 20 \)
\( L = 14 \)

Time (fs)
Summary

- Molecular electronic materials based on conjugated organics are strongly correlated systems.

- Electron states in these systems are modeled by long range interacting models like the PPP model.

- Entanglement entropy of eigenstates of PPP chains are comparable to those of Hubbard models. Hence DMRG method is best suited for solving these models.

- DMRG method is extended to target desired excited states, obtain frequency dependent linear and nonlinear responses.

- Efficient real time DMRG algorithm has been developed for wave-packet dynamics.
Thank You