Coupled cluster approaches to wave packet dynamics

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The Goals

To develop **viable approximations** to calculate

$$U = \exp(-iHt)$$

$$C(t) = \langle 0 | U(t) | 0 \rangle$$

$$P(\omega) = \int \mathrm{d}t \, C(t) \exp(i\omega t)$$

The hamiltonian

$$H = \Sigma\, |e_i\rangle\, (\varepsilon_i + H_i)\, \langle e_i| \;+\; V_c$$

$$H_i = \Sigma\; [\, \omega_n (p_n^2 + q_n^2)/2 + k_{in} q_n] \;+\; X$$

$$V_c = \; |e_1\rangle\, \lambda_c q_c\, \langle e_2| \;+\; \text{h.c.} \;+\; Y$$

The TDSCF Approximation

The Ansatz : $\psi_{SCF} = \varphi_{ec} \Pi \varphi_n \exp(S_o)$

The method : Frenkel variational principle

$$< \delta\psi_{SCF} \mid H - i\partial/\partial t \mid \psi_{SCF} > = 0$$

Working equations

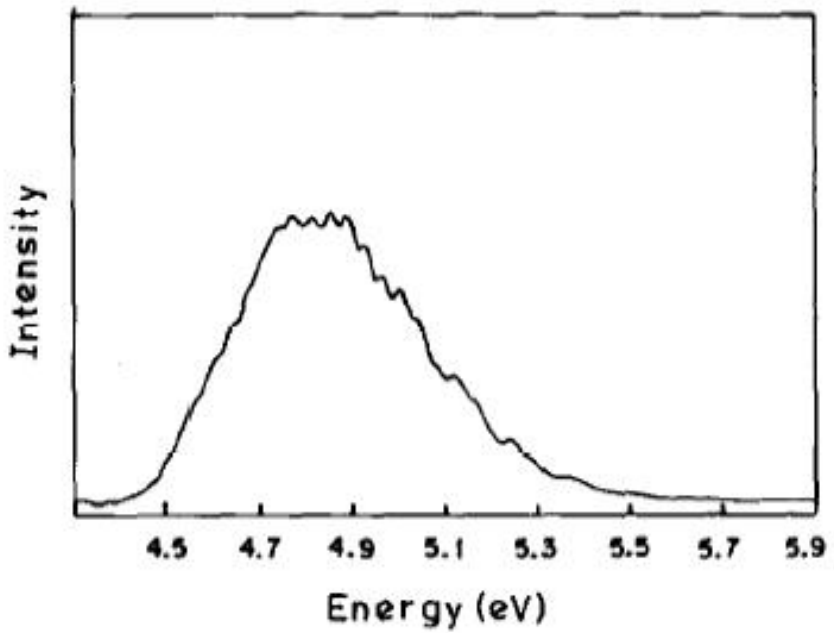
$$i d\varphi_n/dt = h_n^{SCF}\varphi_n$$

$$h_n^{SCF} = \omega_n(p_n^2 + q_n^2)/2 + \Sigma |\langle\varphi_{ec}|e_i\rangle|^2 k_{in}q_n$$

$$i d\varphi_{ec}/dt = h_{ec}^{SCF}\varphi_{ec}$$

$$\varphi_{ec} = \Sigma'_{i,n}|e_i\rangle \varphi_{cn}(q_c)\, c_{in}(t)$$

Application : Pyrazine S_2 band



The TDSCF+TDCCM Approach

The Ansatz : $\psi_{CCM} = \exp(S)\,\psi_{SCF}$

The method:

$$i\langle\psi_e|dS/dt|\,\psi_{SCF}\rangle = \langle\psi_e|\exp(-S)\,H\exp(S)|\,\psi_{SCF}\rangle$$

The Representation : **Mixed**

The Approximation : $S = S_o + S_1 + S_2$

Application : Pyrazine S_2 band

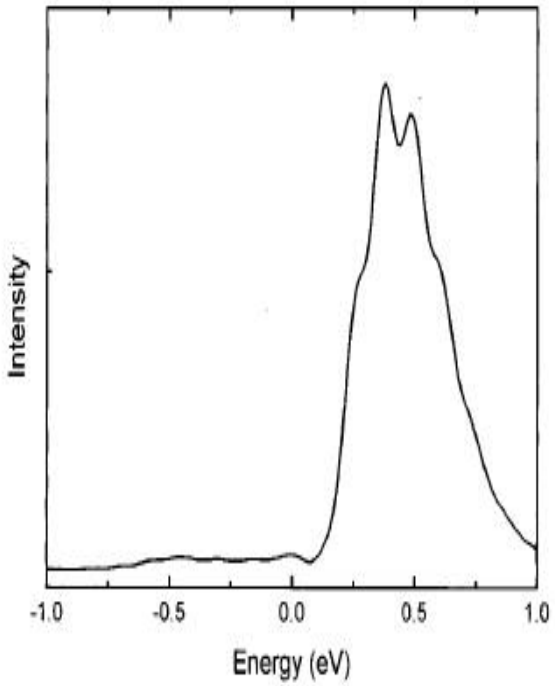
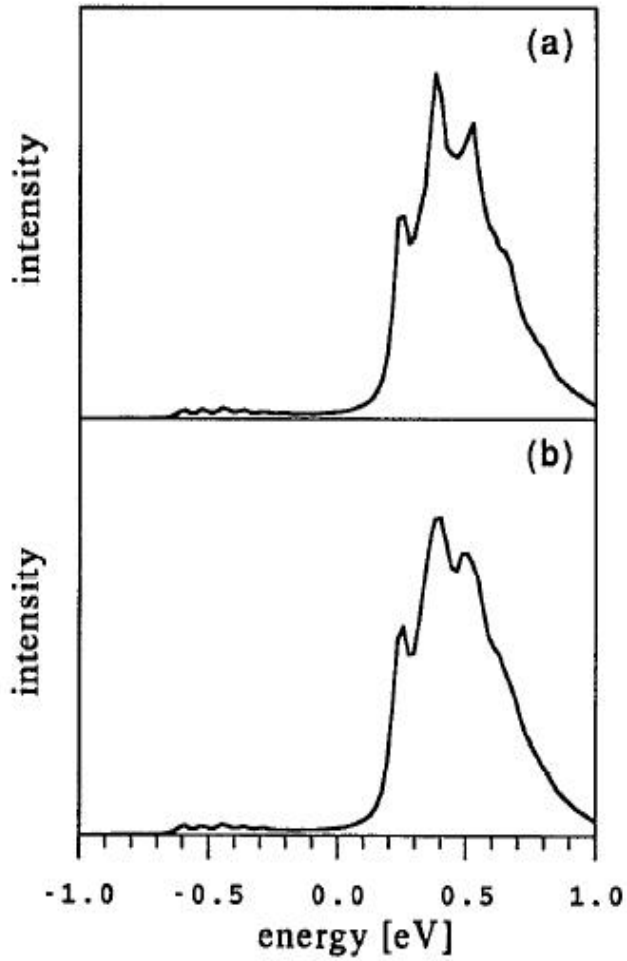
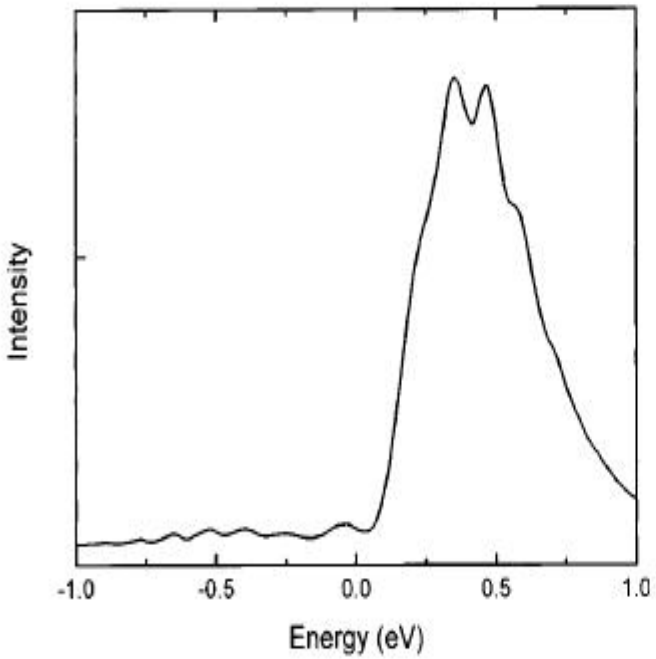
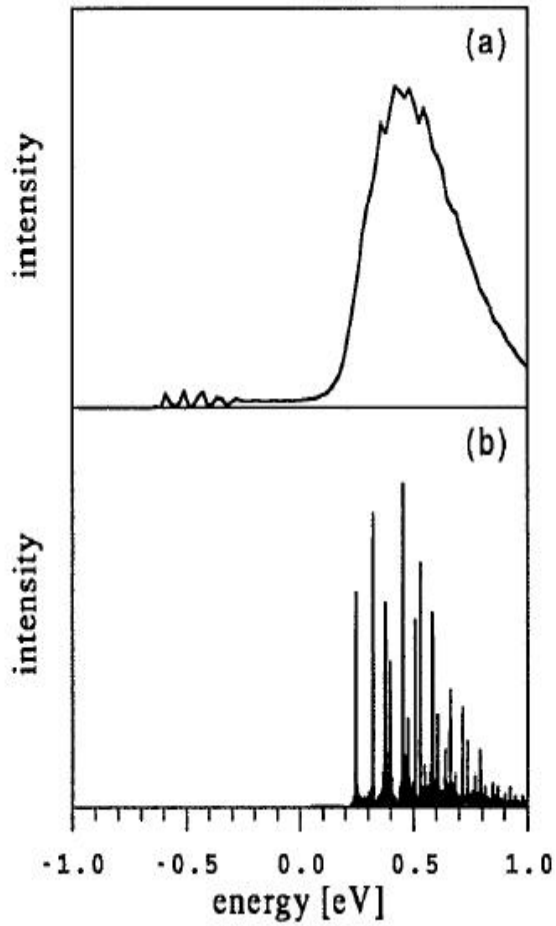


FIG. 2. The absorption spectrum of the S_2 state of pyrazine by the TDCCM approach.



Application : Pyrazine like 24 mode system S_2band





Limitations and Problems

1. Valid for Short times (~120 fs)

2. Stiff equations due to the singular nature of *S*

$$S_e \sim C_e C_o^{-1}$$

$$C_o \sim 0$$

The MRTDCCM Approach

The Model space: should contain the essential part of the wave packet such that C_o^{-1} does not become singular.

The method: Include all the strongly coupled modes (***Active modes***) in the definition of the model space.

Treat the excitations in the weekly coupled modes (***Passive modes)*** by cluster expansion.

The Ansatz : $\psi_{CCM} = \exp(S^o) \exp(S^1) \exp(S^2) \ldots\ldots \psi_M$

(S^k is the k-active particle excitation operator.)

$$\psi_M = \Sigma_M \varphi_i C_{oi}$$

The method:

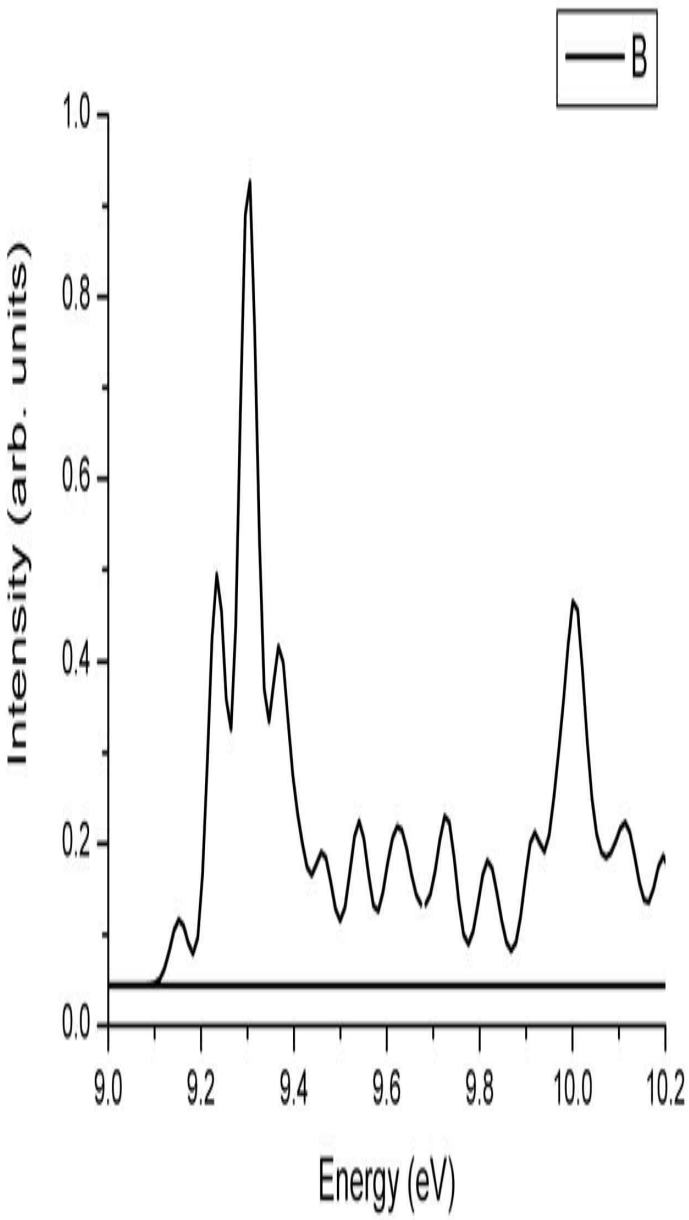
Similarity transformation followed by projection on to states outside the model space as in the case of the single reference CCM, with additional imposition of subsystem embedding condition to decouple the equations of S^k from all S^{k+l} .

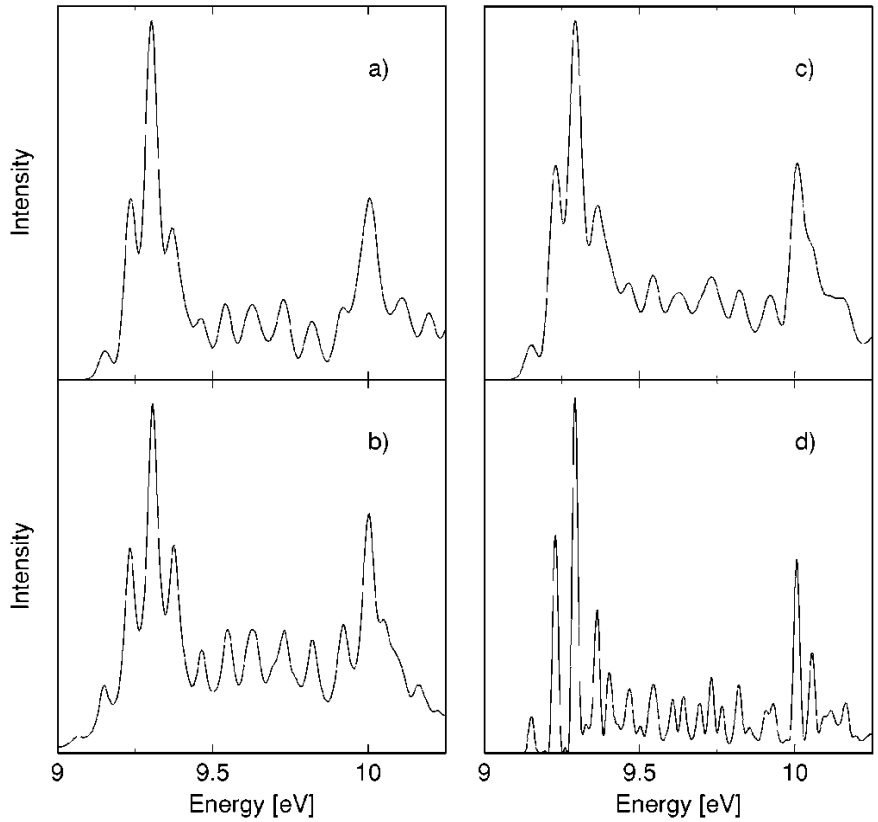
Application : 5-mode model of Butatriene

Active modes : **ν_5 (coupling) , ν_{14} (tuning)**

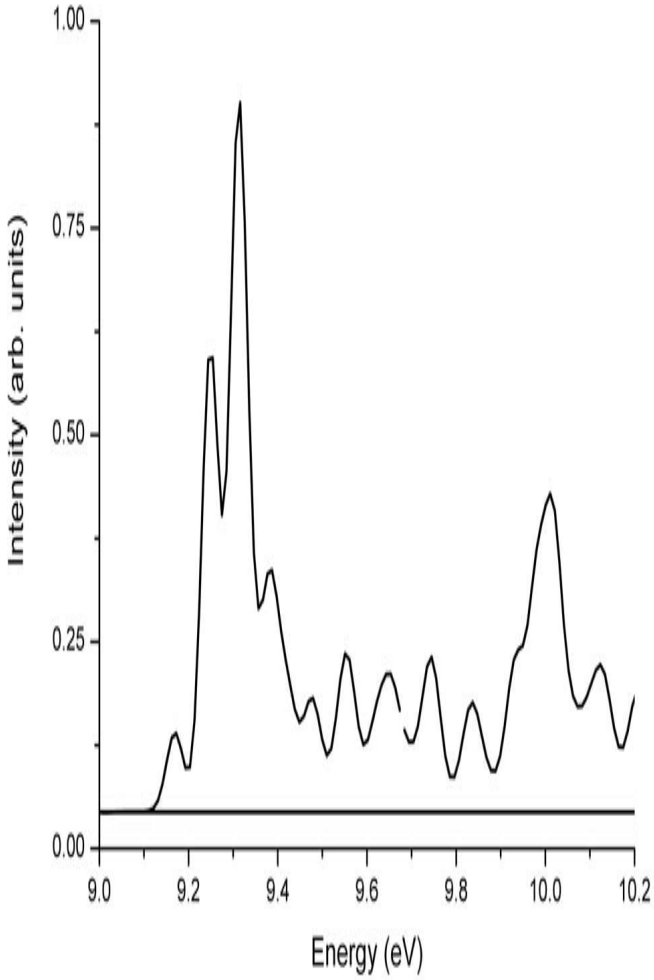
Passive modes : **ν_8, ν_{12}, ν_{15}, (tuning)**

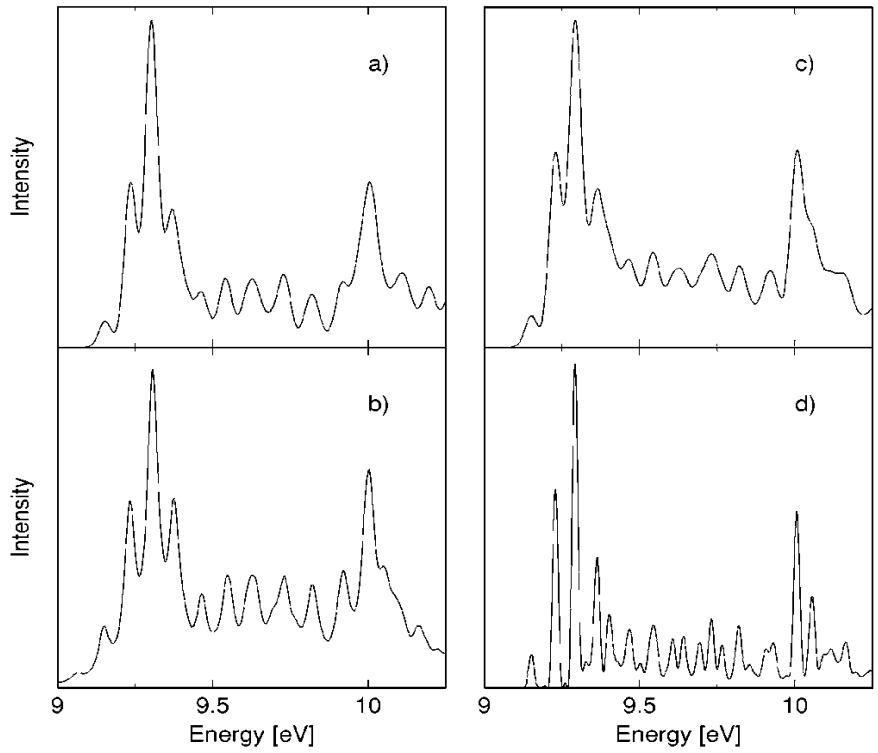
Single valence excitation approximation





Unitarized Single valence excitation approximation





Unanswered Questions

1. Balance between propagator and vertex renormalization.
2. Convergence with increasing active particle excitation operators S^k.
3. Long time behavior of the working equations.
4. Other observables : Ability to describe the vibrational dephasing.
5. Can we push some coupling modes into the passive mode list ?
6. Ability to handle quadratic and bilinear coupling terms

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Audience	Patience

The Solution : $\psi_{CCM} = \exp(S^o) \exp(S^1) \exp(S^2) \ldots\ldots \psi_M$

(S^k is the k-active particle excitation operator.)

1. $S^o = 0$ for this class of hamiltonians.
2. If the passive modes are all tuning modes, e.g. diagonal in the electronic states, then, for the linear and bilinear coupling models, the S^1 operator belongs to a finite dimensional Lie-algebra. Hence closed set of equations can be obtained for them.
3. However, S^2 onward do not belong to a finite dimensional Lie-algebra. At S^2 level, only electronic-coupling mode subsystem has non-zero excitations.