Modeling Nonadiabatic Dynamics on Many Electronic States

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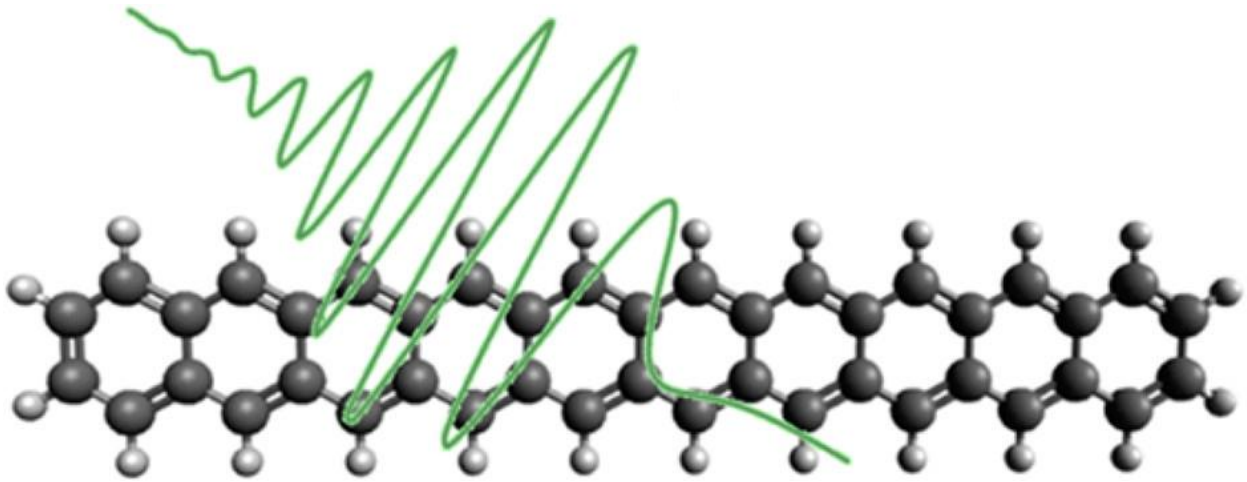
Stony Brook University IACS and Chemistry Departments

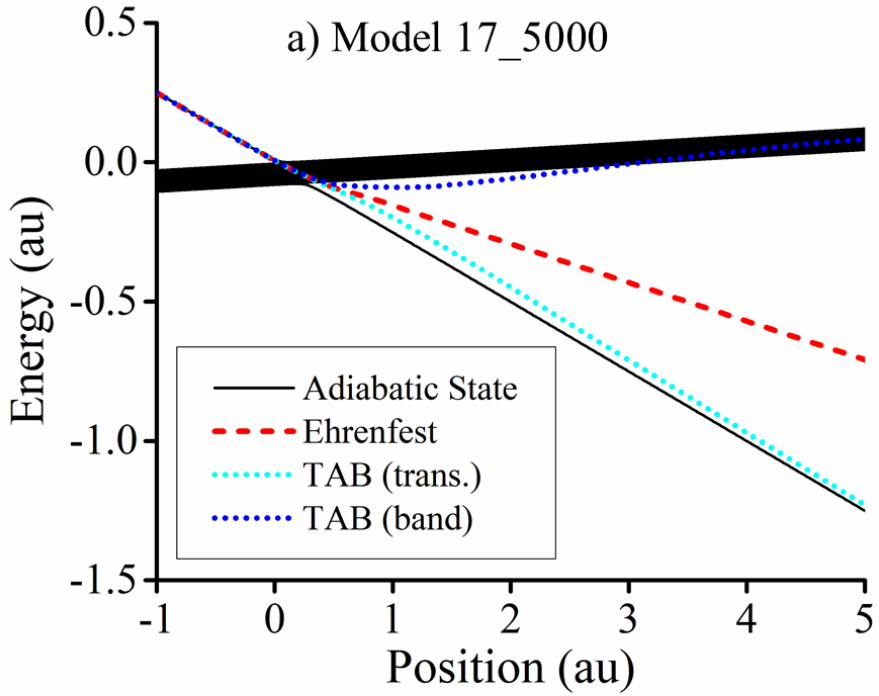


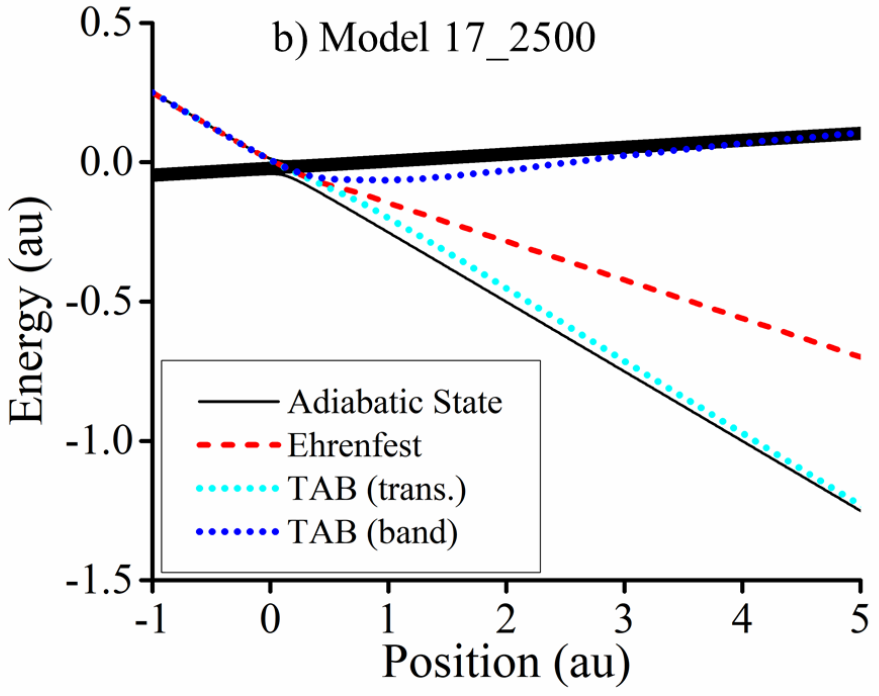
Decoherence Corrected Ehrenfest Dynamics using Approximate Electronic States

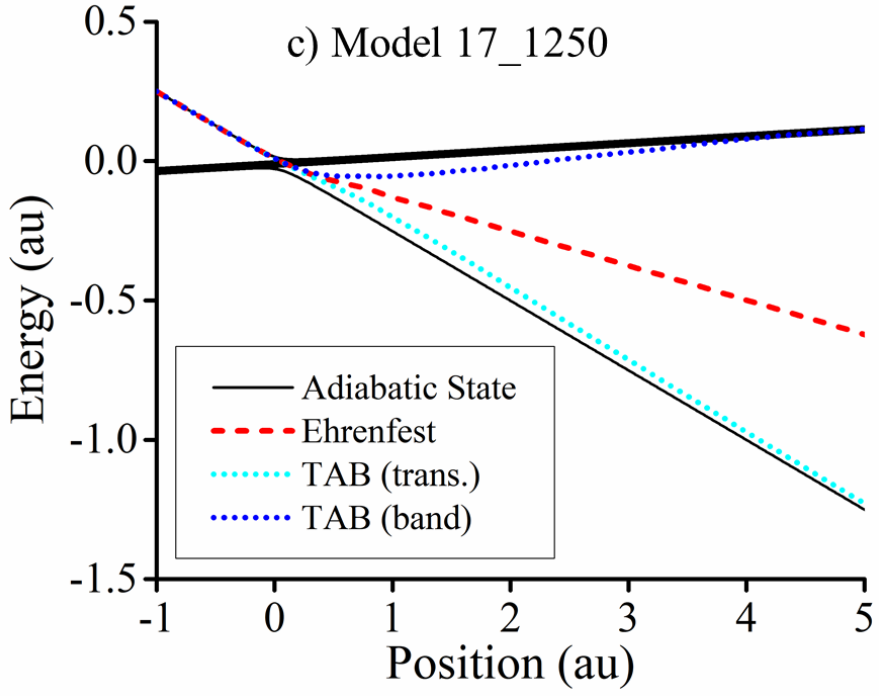
- Efficient propagation of classical degrees of freedom on the Ehrenfest potential energy surface (PES)

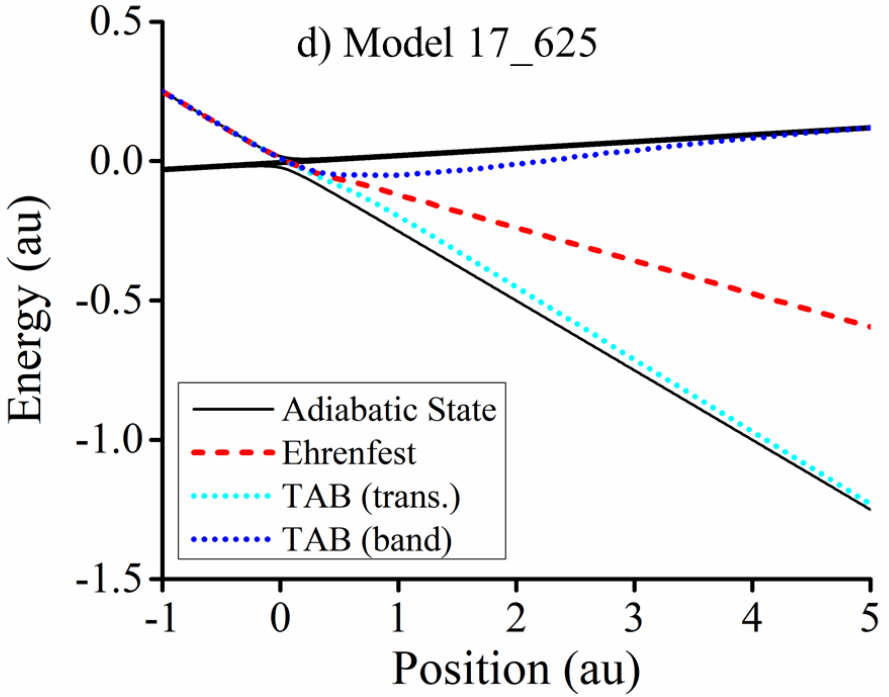
- Refines trajectory dynamics with properties of the approximate electronic states to avoid the qualitative error of mean-field PES propagation of standard Ehrenfest

- Refinements from the decoherence correction are applied without computing the full electronic eigenspectrum!


a) Model 17_5000
Energy (au)
Position (au)
Adiabatic State
Ehrenfest
TAB (trans.)
TAB (band)


b) Model 17_2500
Energy (au)
Position (au)
Adiabatic State
Ehrenfest
TAB (trans.)
TAB (band)


c) Model 17_1250
Energy (au)
Position (au)
Adiabatic State
Ehrenfest
TAB (trans.)
TAB (band)


d) Model 17_625
Energy (au)
Position (au)
Adiabatic State
Ehrenfest
TAB (trans.)
TAB (band)

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- Refinements from the decoherence correction are applied without computing the full electronic eigenspectrum!

- Can be applied to systems where computing the full eigenspectrum would cause dynamics simulations to become intractable!

Correcting Dynamics for Electronic Coherence Loss

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2) E. R. Bittner and P. J. Rossky, J. Chem. Phys. **103**, (1995) 8130.
3) B. J. Schwartz, E. R. Bittner, O. V. Prezhdo, P. J. Rossky The Journal of Chemical Physics **104** (1996) 5942.
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7) M. Ben-Nun, J. Quenneville, and T. J. Martínez, The Journal of Physical Chemistry A **104** (2000) 5161.
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17) D. V. Makhov, T. J. Martinez, and D. V. Shalashilin, Faraday Discuss. **194** (2016) 81.
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19) L. J. Wang, A. Akimov, and O. V. Prezhdo, J. Phys. Chem. Lett. **7**, (2016) 2100.
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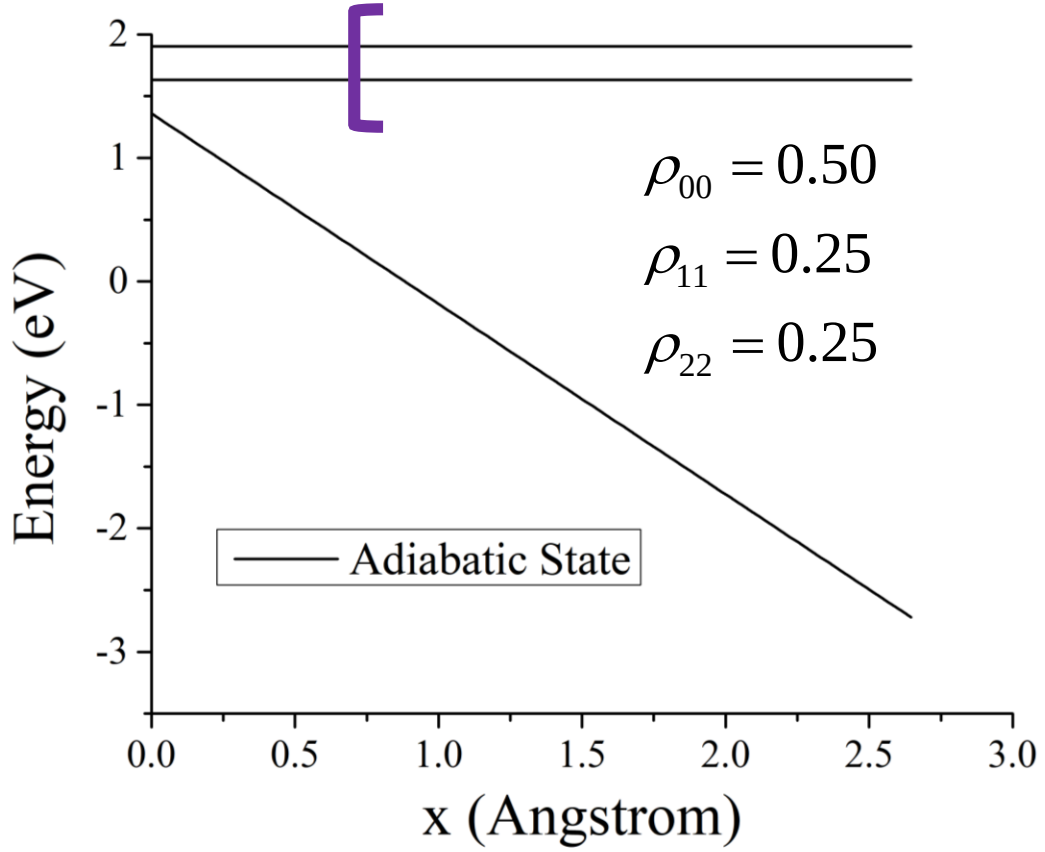
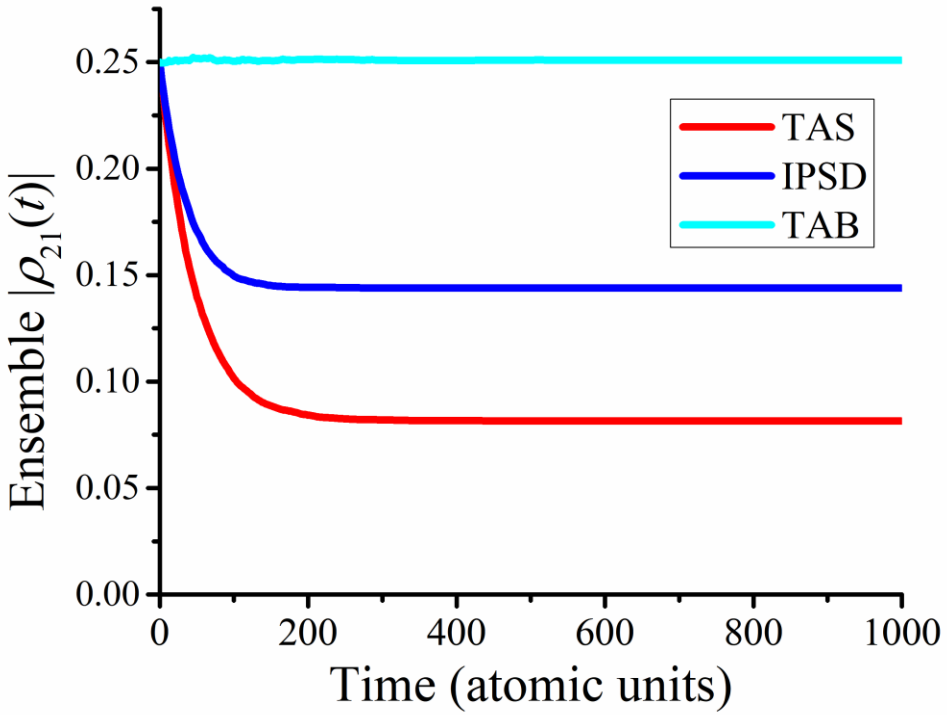
21) D. A. Fedorov, and B. G. Levine, The Journal of Physical Chemistry Letters **10** (2019) 4542.
22) P. Nijjar, J. Jankowska, and O. V. Prezhdo, J. Chem. Phys. **150**(20), (2019) 204124.

Collapse ‘to a block’ (TAB) corrected Ehrenfest Dynamics





M. P. Esch, and B. G. Levine, The Journal of Chemical Physics **152** (2020) 234105.

TAB wave function collapse procedure inputs

1) The trajectory density matrix generated from the Ehrenfest wave function

$$\boldsymbol{\rho}^{c} = \mathbf{c}(t)\mathbf{c}^{*}(t)$$

2) The state-pairwise decoherence times

$$\tau_{ij}^{-2} = \sum_{\eta} \frac{\left(F_{\eta,i}^{avg} - F_{\eta,j}^{avg}\right)^{2}}{\hbar^{2}\alpha_{\eta}}$$

B. J. Schwartz *et al.*, The Journal of Chemical Physics **104** (1996) 5942.

3) The adiabatic electronic states

$$\mathbf{HV} = \mathbf{EV}$$

What to use instead of the complete adiabatic electronic basis?

- Will generate a reduced rank approximate adiabatic basis using the history of the time-dependent Ehrenfest electronic wave function $\mathbf{c}(t)$
- Contains information of the dominant electronic states in the dynamics
- Calculated at every electronic time step, so no additional computation is required to obtain it

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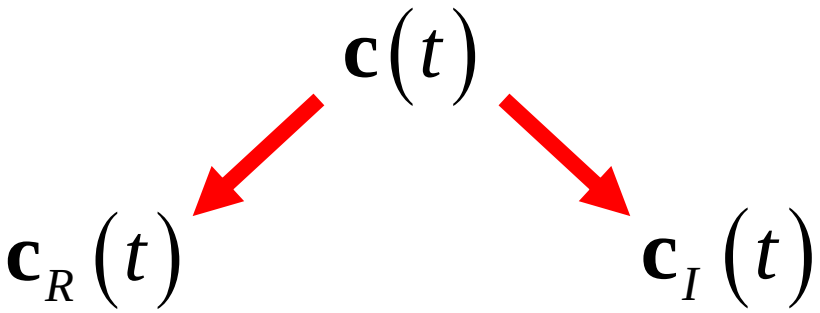
For those familiar with recent Levine group developments…

D. A. Fedorov, and B. G. Levine, The Journal of Physical Chemistry Letters **10** (2019) 4542.

Basis reduction using time history of the electronic wave function

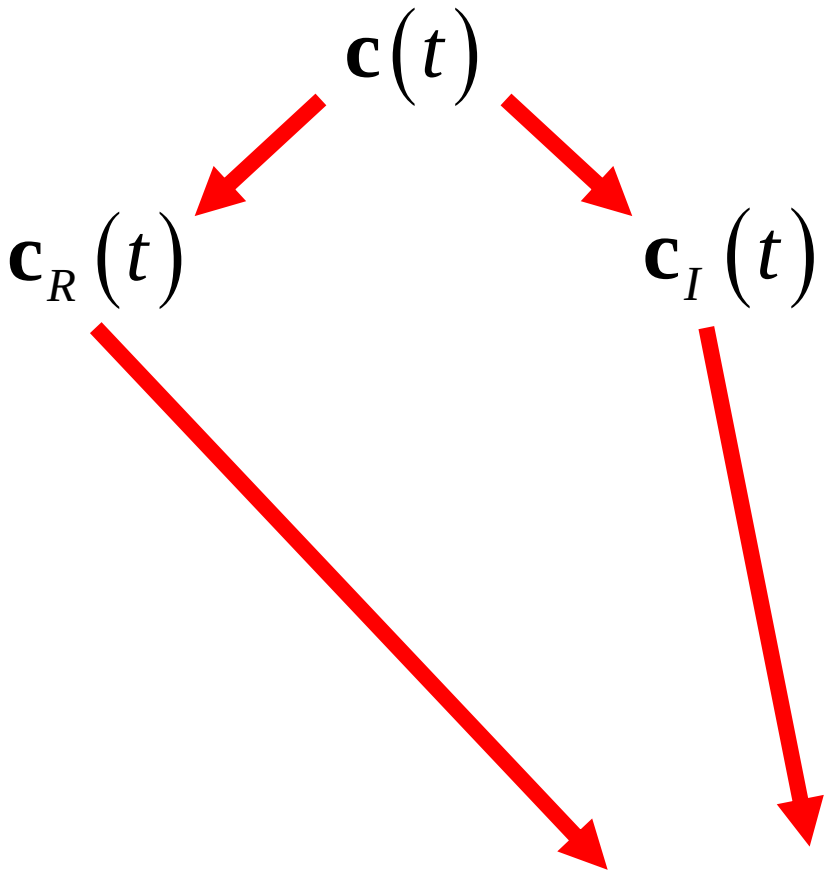
1) Split the wave function into its real and imaginary parts at electronic time steps



Basis reduction using time history of the electronic wave function

1) Split the wave function into its real and imaginary parts at electronic time steps

2) Store the most recent N time steps in an array $\mathbf{X}$

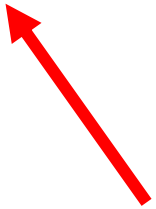


$$\mathbf{X}_{M,2N} = \left[\mathbf{c}_R\left(t-\left(N-1\right)\Delta t_e\right), \mathbf{c}_I\left(t-\left(N-1\right)\Delta t_e\right), \cdots, \mathbf{c}_R\left(t-\Delta t_e\right), \mathbf{c}_I\left(t-\Delta t_e\right), \mathbf{c}_R\left(t\right), \mathbf{c}_I\left(t\right)\right]$$

Basis reduction using time history of the electronic wave function

$$\mathbf{X}_{M,2N} = \left[\mathbf{c}_R\left(t-\left(N-1\right)\Delta t_e\right), \mathbf{c}_I\left(t-\left(N-1\right)\Delta t_e\right), \cdots, \mathbf{c}_R\left(t-\Delta t_e\right), \mathbf{c}_I\left(t-\Delta t_e\right), \mathbf{c}_R\left(t\right), \mathbf{c}_I\left(t\right) \right]$$

$$\mathbf{X}_{M,2N} = \mathbf{Q}_{M,2N}\mathbf{R}_{2N,2N}$$

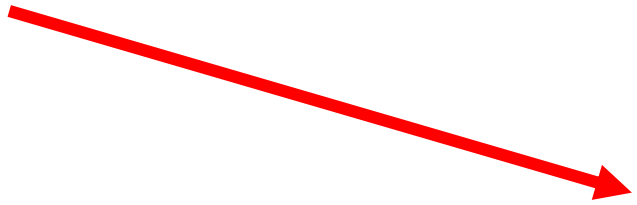


transformation matrix into the orthogonalized basis

Basis reduction using time history of the electronic wave function

$$\mathbf{X}_{M,2N} = \left[\mathbf{c}_R\left(t-\left(N-1\right)\Delta t_e\right),\mathbf{c}_I\left(t-\left(N-1\right)\Delta t_e\right),\cdots,\mathbf{c}_R\left(t-\Delta t_e\right),\mathbf{c}_I\left(t-\Delta t_e\right),\mathbf{c}_R\left(t\right),\mathbf{c}_I\left(t\right)\right]$$

$$\mathbf{X}_{M,2N} = \mathbf{Q}_{M,2N}\mathbf{R}_{2N,2N}$$



$$\mathbf{Q}^{\mathrm{T}}{}_{2N,M}\mathbf{c}\left(t\right)_{M,1} = \mathbf{c}^k\left(t\right)_{2N,1}$$

$$\mathbf{Q}^{\mathrm{T}}\mathbf{H}\mathbf{Q} = \mathbf{H}^k$$

$$\mathbf{H}^k\mathbf{V}^k = \mathbf{E}^k\mathbf{V}^k$$

Basis reduction using time history of the electronic wave function

$$\mathbf{X}_{M,2N} = \left[\mathbf{c}_R\left(t-\left(N-1\right)\Delta t_e\right),\mathbf{c}_I\left(t-\left(N-1\right)\Delta t_e\right),\cdots,\mathbf{c}_R\left(t-\Delta t_e\right),\mathbf{c}_I\left(t-\Delta t_e\right),\mathbf{c}_R\left(t\right),\mathbf{c}_I\left(t\right)\right]$$

$$\mathbf{X}_{M,2N} = \mathbf{Q}_{M,2N}\mathbf{R}_{2N,2N}$$

$$\mathbf{Q}^{\mathrm{T}}{}_{2N,M}\mathbf{c}\left(t\right)_{M,1} = \mathbf{c}^k\left(t\right)_{2N,1}$$

$$\mathbf{Q}^{\mathrm{T}}\mathbf{H}\mathbf{Q} = \mathbf{H}^k$$

$$\mathbf{H}^k\mathbf{V}^k = \mathbf{E}^k\mathbf{V}^k$$

★ $$\rho_{ij}^k\left(t\right) = \mathbf{V}_i^{k\mathrm{T}}\left(t\right)\mathbf{Q}^{\mathrm{T}}\left(t\right)\mathbf{c}\left(t\right)\mathbf{c}^*\left(t\right)\mathbf{Q}\left(t\right)\mathbf{V}_j^k\left(t\right)$$

M. P. Esch, and B. G. Levine, The Journal of Chemical Physics **153** (2020) 114104.

TAB-DMS Inputs (TAB using an approximate electronic basis)

1) The trajectory density matrix generated from the Ehrenfest wave function

$$\boldsymbol{\rho}^{k} = \mathbf{V}^{k\mathrm{T}}\left(t\right)\mathbf{Q}^{\mathrm{T}}\left(t\right)\mathbf{c}\left(t\right)\mathbf{c}^{*}\left(t\right)\mathbf{Q}\left(t\right)\mathbf{V}^{k}\left(t\right)$$

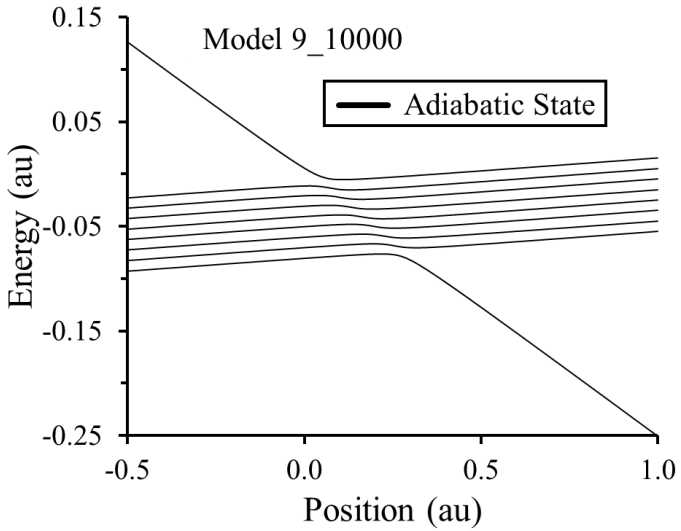
2) The state-pairwise decoherence times

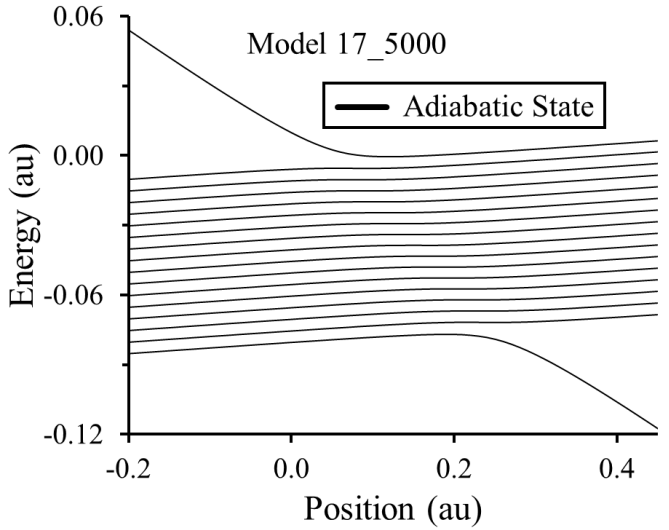
$$\left(\tau_{ij}^{k}\right)^{-2} = \sum_{\eta}\frac{\left(F_{\eta,i}^{k,avg} - F_{\eta,j}^{k,avg}\right)^{2}}{\hbar^{2}\alpha_{\eta}}$$

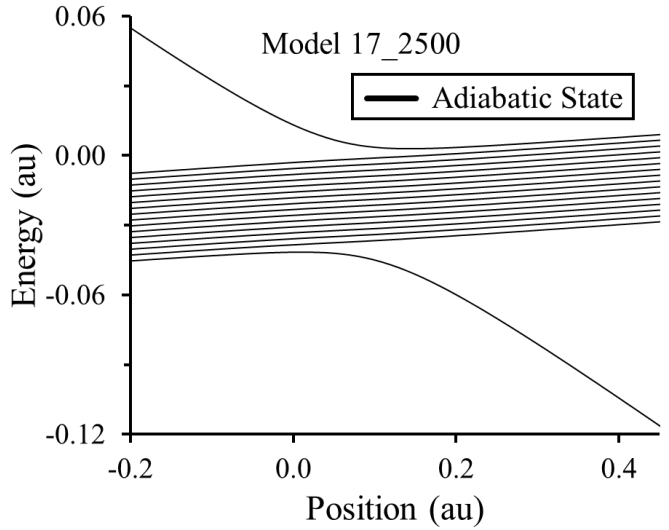
3) The approximate adiabatic electronic states

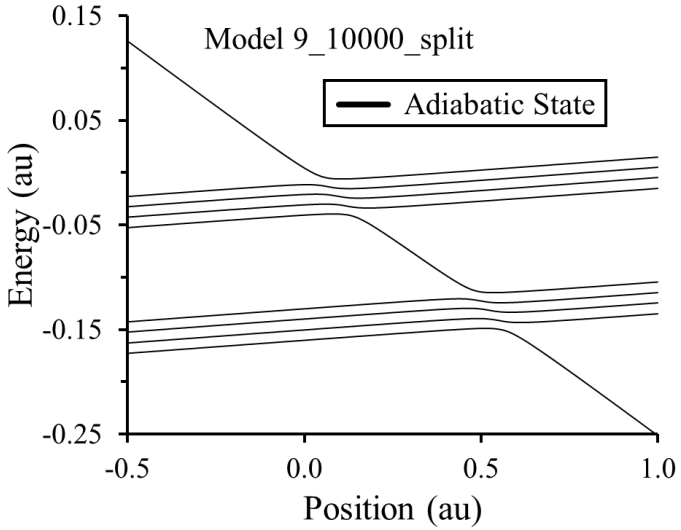
$$\mathbf{H}^{k}\mathbf{V}^{k} = \mathbf{E}^{k}\mathbf{V}^{k}$$

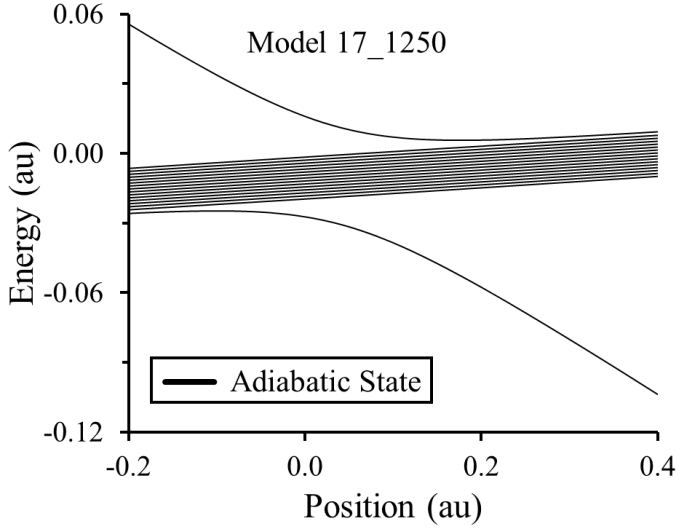
Model PESs for Probabilities of Transmission

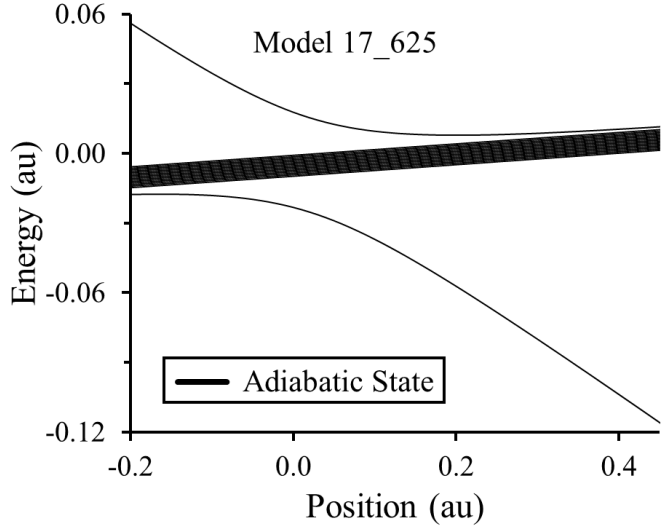


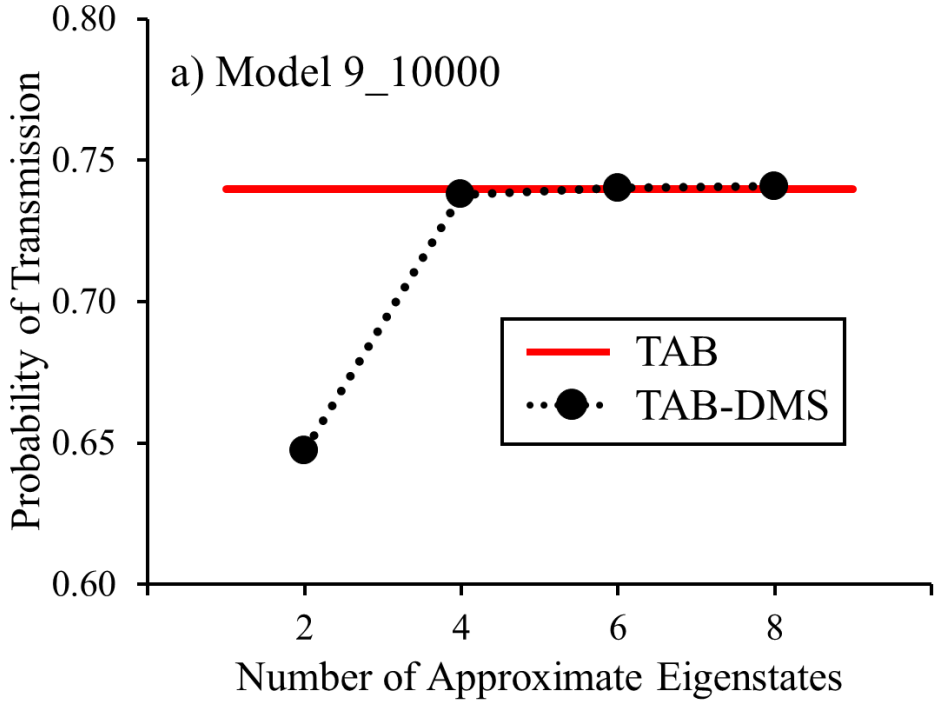


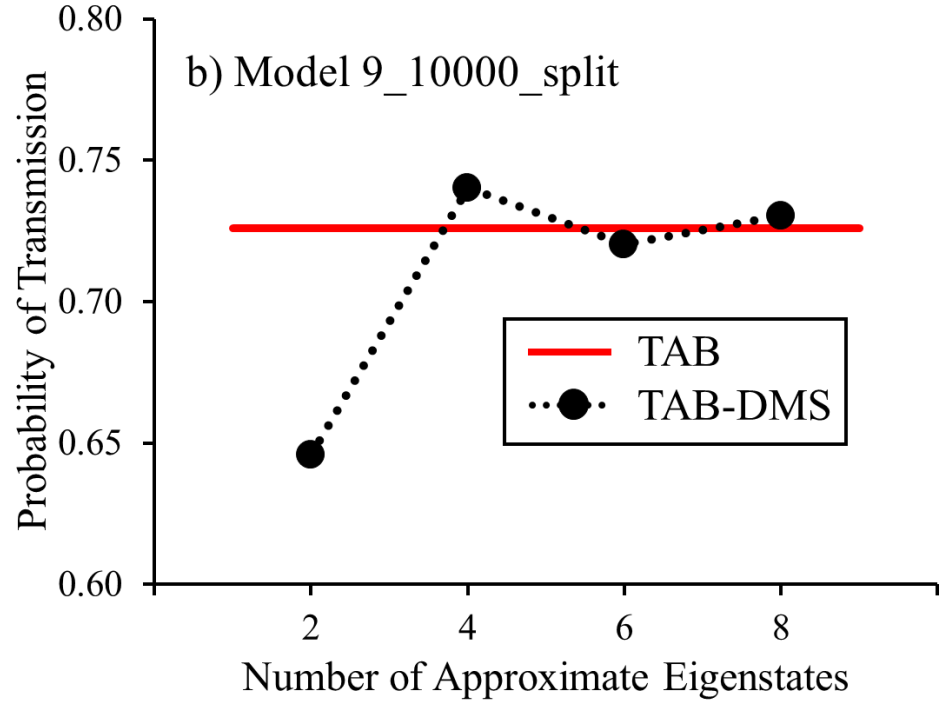


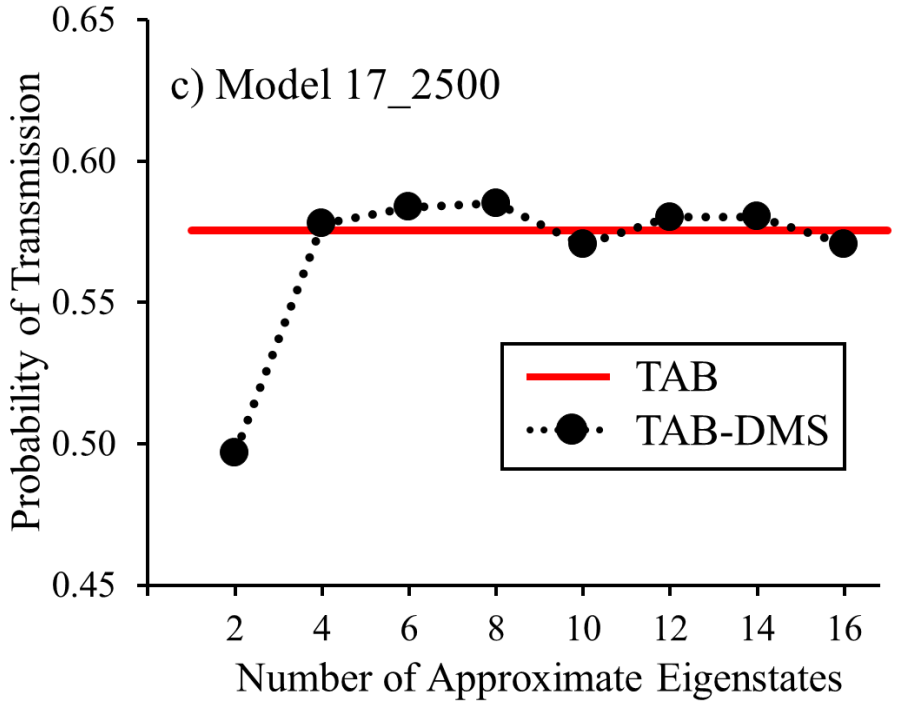


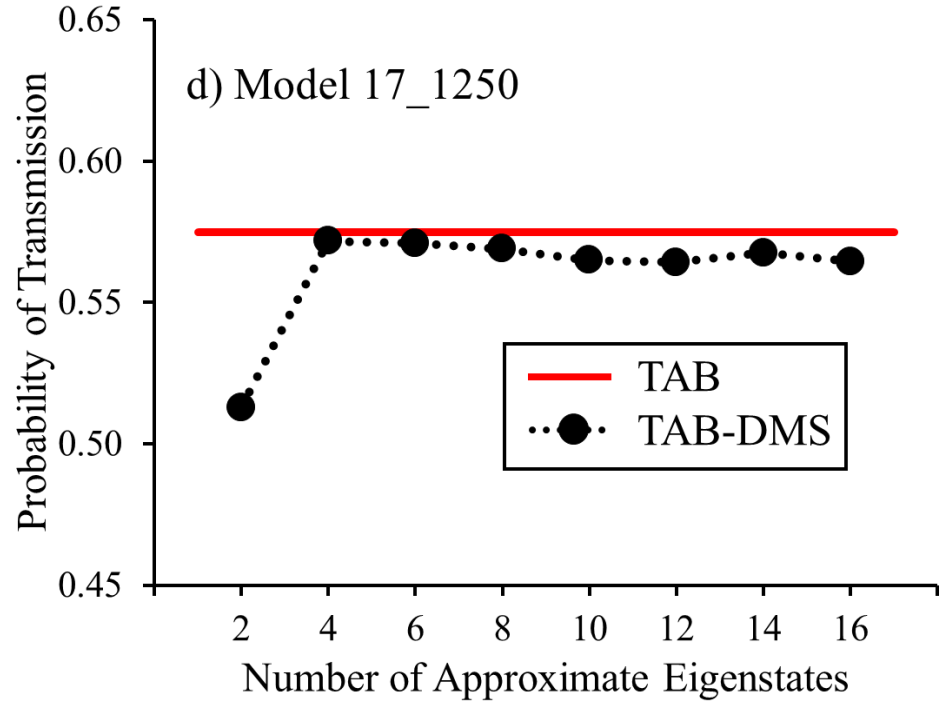





a) Model 9_10000
Probability of Transmission
0.80
0.75
0.70
0.65
0.60
2
4
6
8
Number of Approximate Eigenstates
TAB
TAB-DMS


b) Model 9_10000_split
Probability of Transmission
0.80
0.75
0.70
0.65
0.60
2
4
6
8
Number of Approximate Eigenstates
TAB
TAB-DMS


c) Model 17_2500
Probability of Transmission
0.65
0.60
0.55
0.50
0.45
2
4
6
8
10
12
14
16
Number of Approximate Eigenstates
TAB
TAB-DMS


d) Model 17_1250
Probability of Transmission
0.65
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0.55
0.50
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4
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16
Number of Approximate Eigenstates
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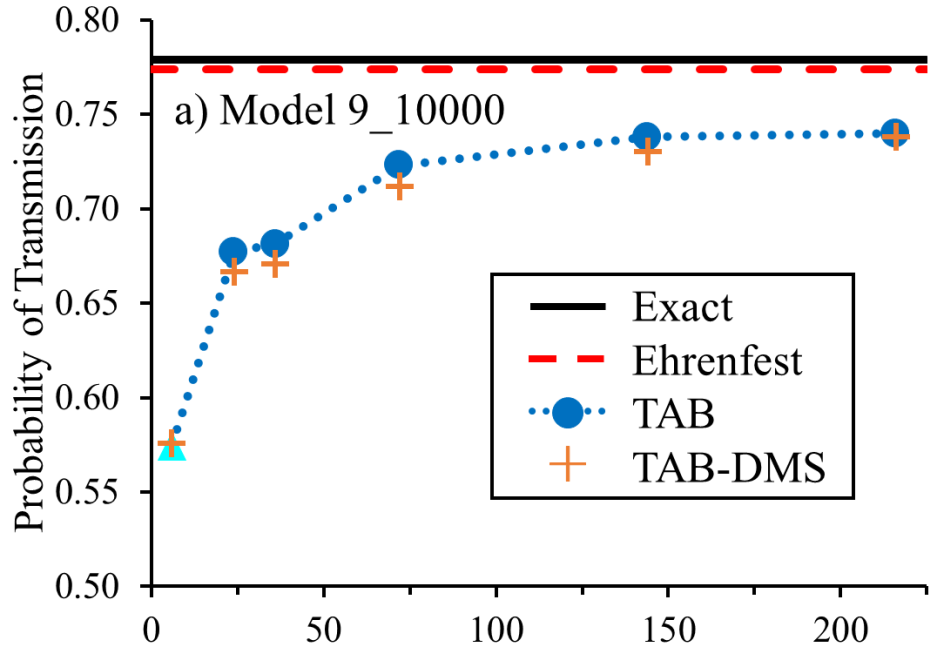
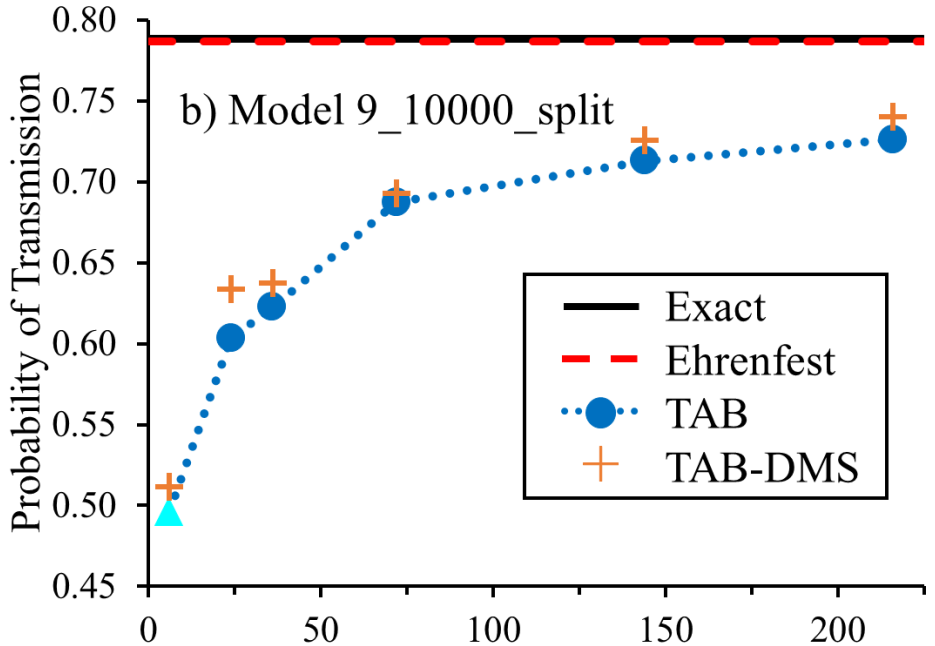
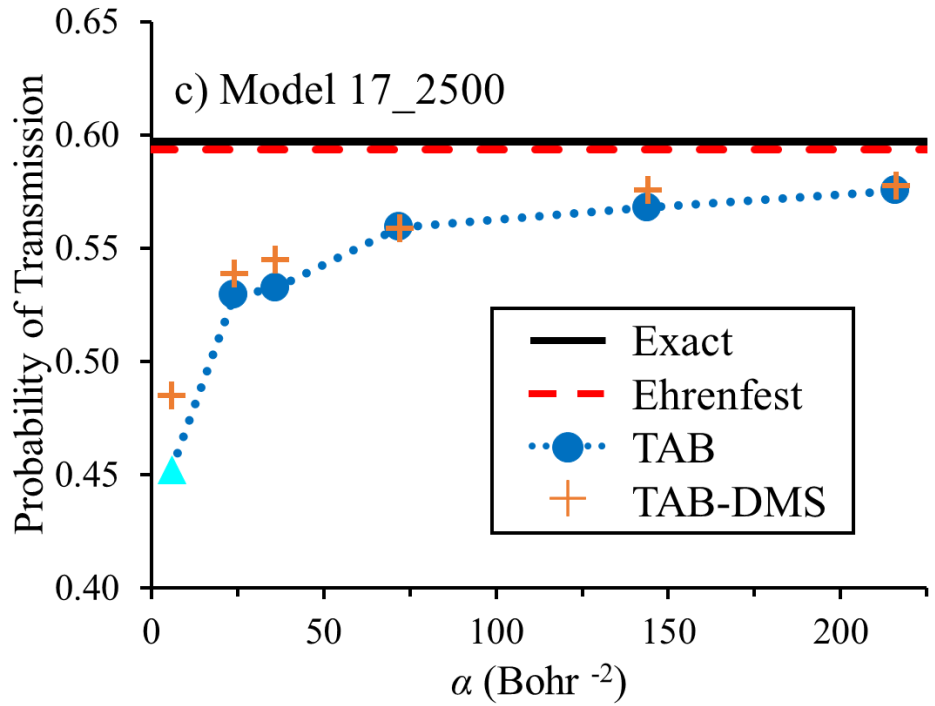
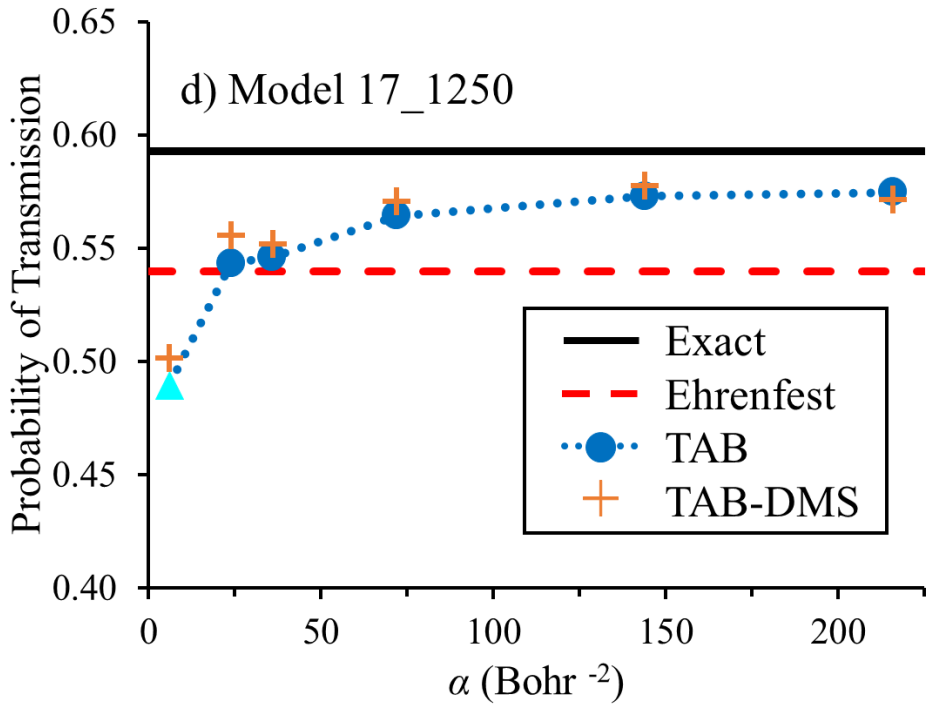
TAB-DMS

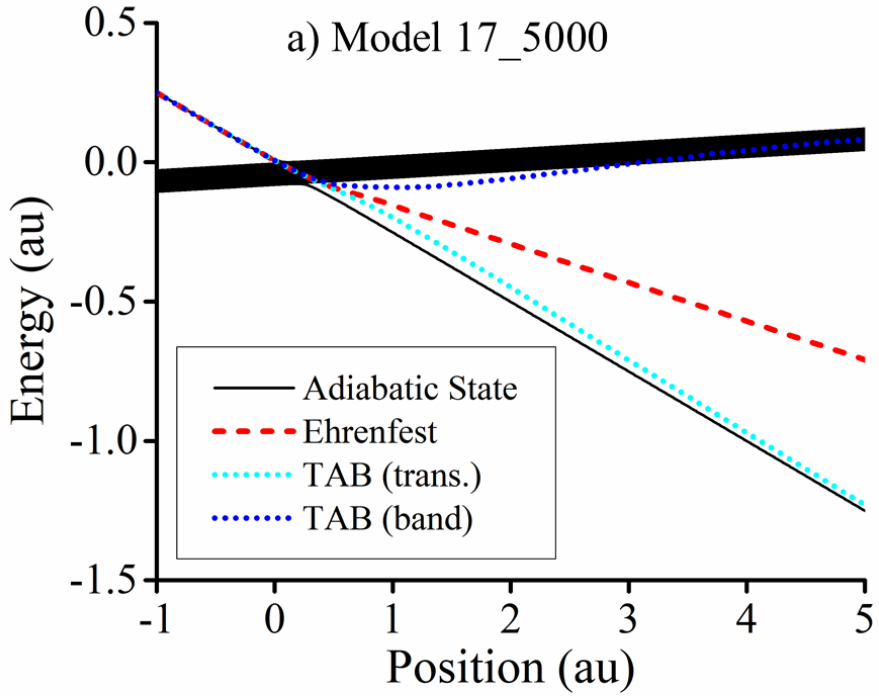




Decoherence Parameter →



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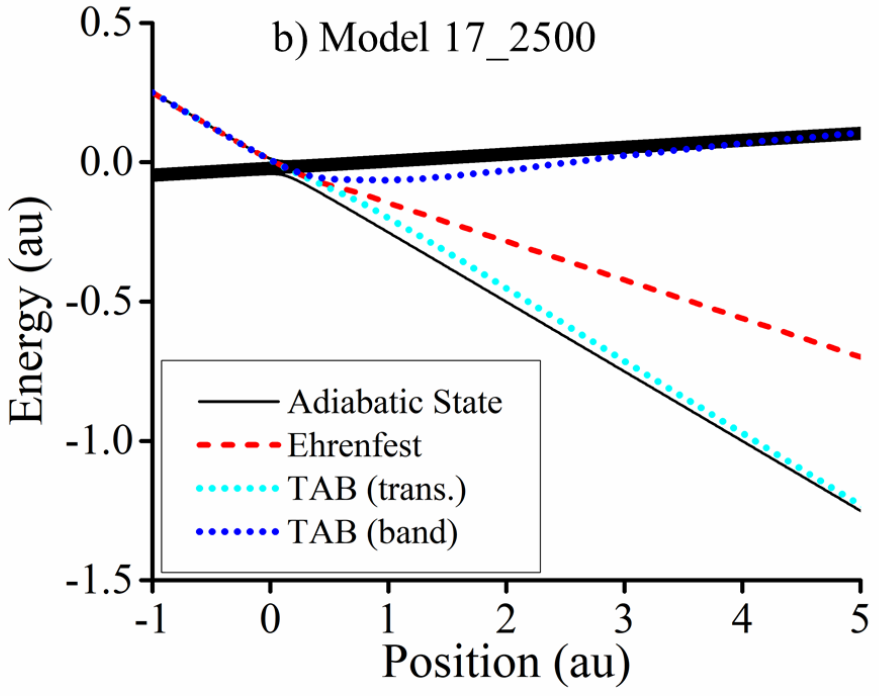
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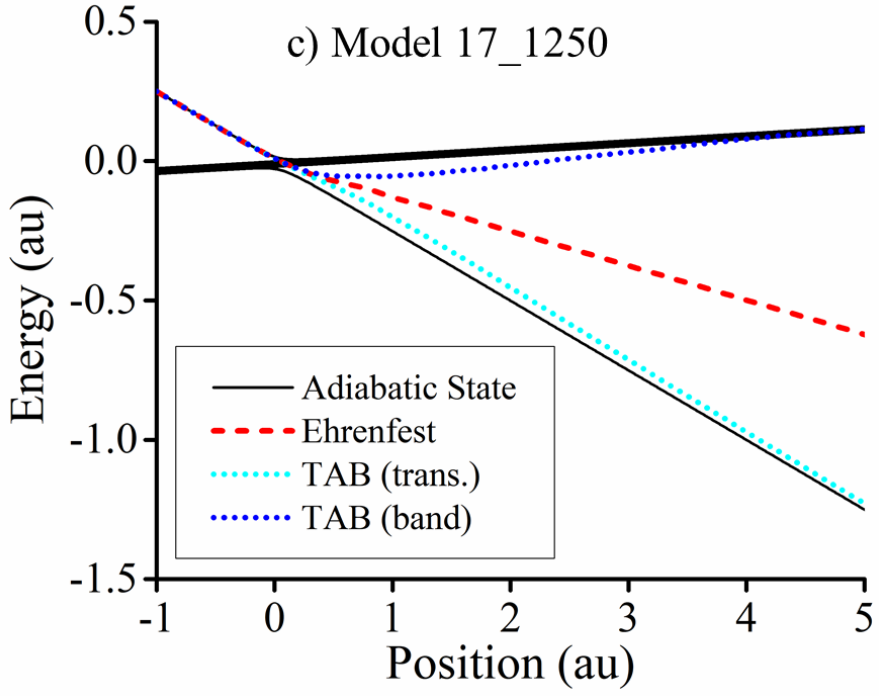
Energy (au)
Position (au)
Adiabatic State
Ehrenfest
TAB (trans.)
TAB (band)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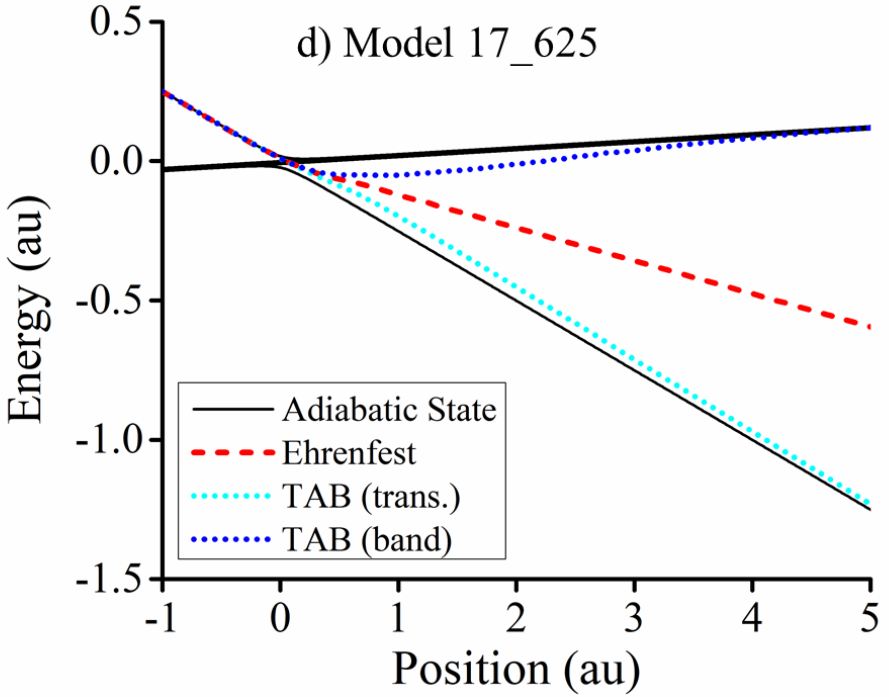
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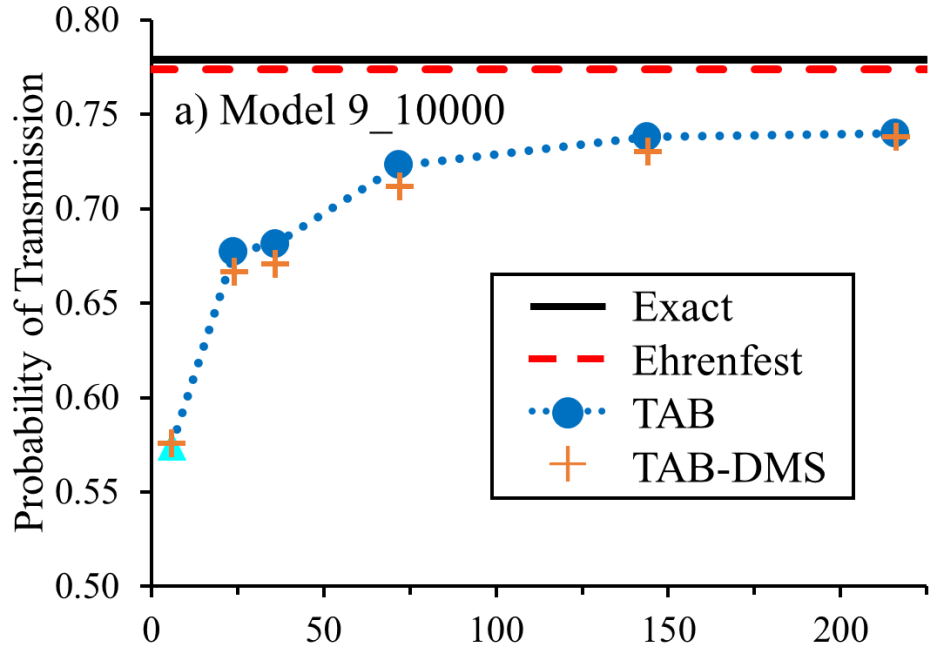
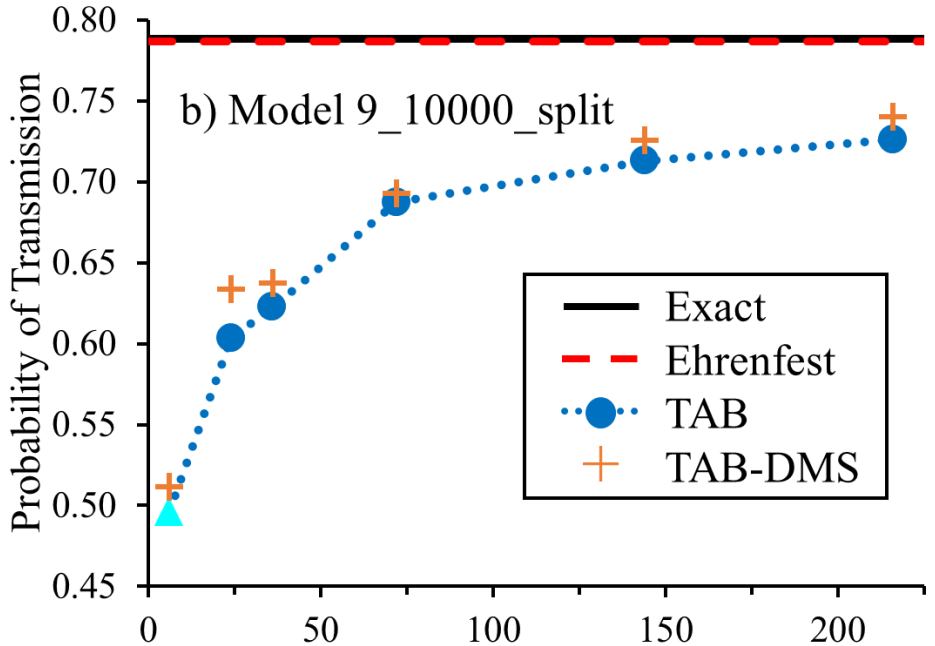
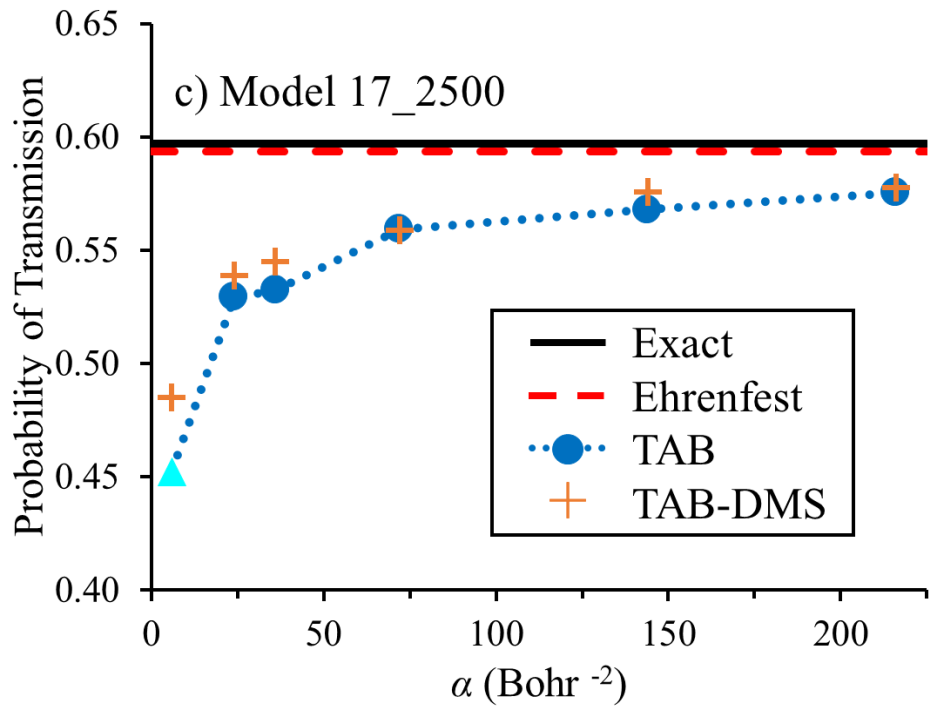
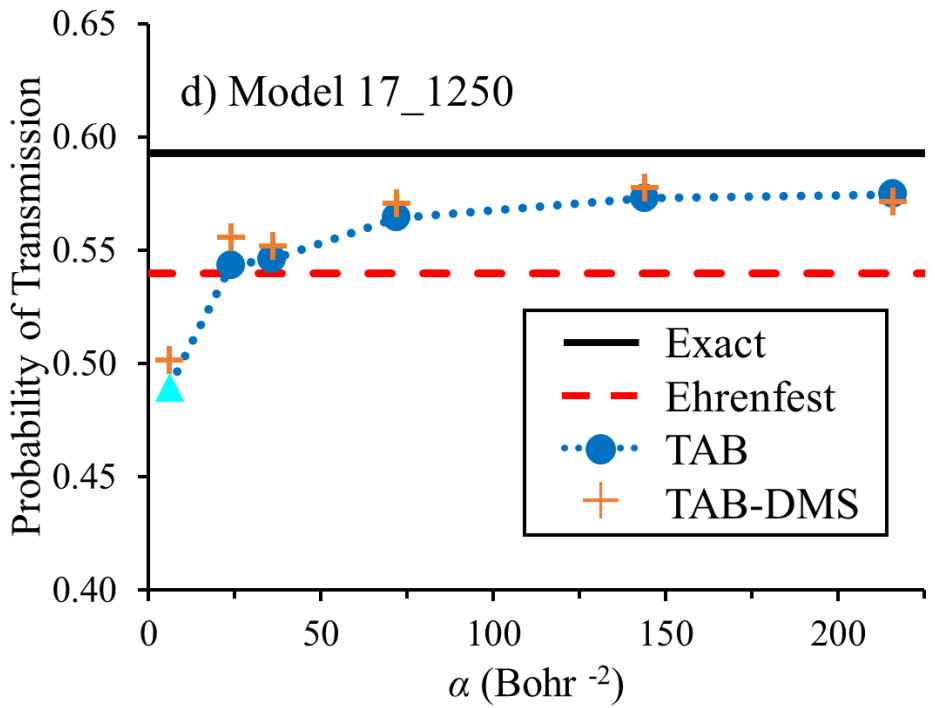




Decoherence Parameter →





Conclusions

- We have demonstrated the history of the time-dependent Ehrenfest wave function can be used to generate a small approximate electronic basis that can be used by compatible decoherence corrections to Ehrenfest dynamics

- Using a modest fraction of the total number of real electronic states TAB-DMS produces results in statistical agreement to TAB

- Well parameterized TAB and TAB-DMS ensembles reasonably reproduce fully quantum mechanical probabilities of transmission

- Work is being done to improve the accuracy of intuitive parameter TAB ensembles, since the intuitive parameters can be reasonably approximated for real systems using the ground state harmonic vibrational wave function.

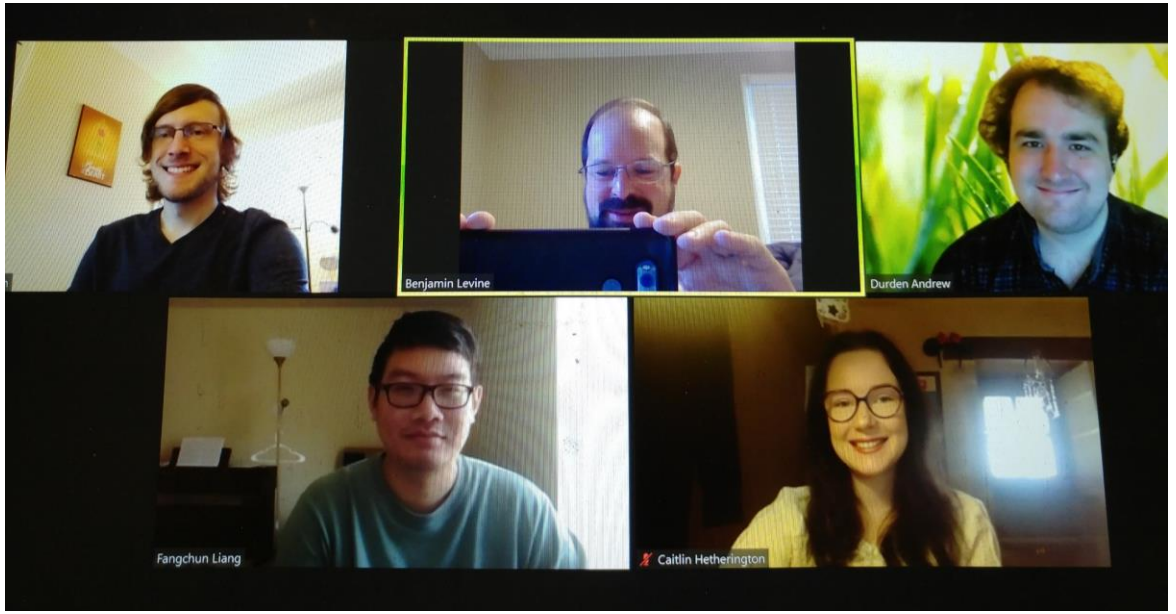
Acknowledgments

Dr. Benjamin G. Levine

Current Group Members: Andy Durden, Fangchun Liang, Caitlin Hetherington, Katy Humphries

Former Group Members: Yinan Shu, Garrett Meek, B. Scott Fales, Wei-tao Peng, Dmitry Fedorov, Brandon Child, Dylan Hardwick, Adam Hartley

The VISTA organizers and all of you!



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