**Ab Initio Multiple Spawning Dynamics**

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### Ab Initio Molecular Dynamics Terminology

<table>
<thead>
<tr>
<th>Dynamics</th>
<th>Extended Lagrangian?</th>
<th>Dynamics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Dynamics</td>
<td>DFT</td>
<td>Any</td>
</tr>
<tr>
<td>BOMD Born-Oppenheimer Molecular Dynamics</td>
<td>DFT</td>
<td>Any</td>
</tr>
<tr>
<td>CPMMD Car-Parrinello Molecular Dynamics</td>
<td>DFT</td>
<td>Plane Wave</td>
</tr>
<tr>
<td>ADMP Atom-Centered Density Matrix Propagation</td>
<td>DFT or SCF</td>
<td>Gaussian</td>
</tr>
</tbody>
</table>

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#### Electronic Basis Sets

- **Plane waves** - $e^{i\mathbf{k}\cdot \mathbf{r}}$
  - Natural for periodic systems
  - Hellman-Feynman Forces are exact
  - Very inefficient for nonperiodic systems (large empty spaces between periodic replicas; in almost all cases, this empty space is filled with basis functions)
  - Obvious, well-defined convergence hierarchy

- **Gaussian** - $e^{-\alpha r^2}$
  - Periodicity is more difficult to incorporate (but not impossible, e.g. **Crystkal**)
  - Generally atom-centered (“floating” Gaussians also possible)
  - Electrons like to be near nuclei!
  - Pulay terms in forces for atom-centered Gaussians
  - Convergence hierarchy more subtle, but now well-understood (Dunning)

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#### Pulay Terms

\[
\frac{\partial E}{\partial \mathbf{R}} = \frac{\partial}{\partial \mathbf{R}} \left\{ \psi_{\text{ion}} (\mathbf{r}, \mathbf{R}) \left| \hat{H}_{\text{ion}} \right| \psi_{\text{ion}} (\mathbf{r}, \mathbf{R}) \right\},
\]

- “Hellmann-Feynman Force”

\[
= \left\{ \psi_{\text{ion}} (\mathbf{r}, \mathbf{R}) \left| \hat{\partial}_{\mathbf{R}} \right| \psi_{\text{ion}} (\mathbf{r}, \mathbf{R}) \right\} + \left\{ \psi_{\text{ion}} (\mathbf{r}, \mathbf{R}) \left| \hat{H}_{\text{ion}} \right| \psi_{\text{ion}} (\mathbf{r}, \mathbf{R}) \right\}.
\]

- “Pulay Force”

Pulay force apparently requires derivatives of electronic wavefunctions! Actually, often it does not, but it is always more expensive than HF Force

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#### Extended Lagrangian Technique

- **What is it?**  
  - Electronic degrees of freedom are propagated under a new Lagrangian, instead of using the variational principle to determine them at each new geometry

- **Benefits**  
  - Wavefunction does not need to be converged at each time step
    - “1” iteration vs. typical 10-15 iterations (apparently)
    - But, good BOMD codes require < 5 per h’s geometry change in one time step is small

- **Disadvantages**  
  - Need to ensure that the electronic coefficients are always “cold” and nuclei are always “hot”
    - Energy transfer between ions and “fictitious” degrees of freedom is unphysical
  - Time step needs to be smaller than in BOMD – fictitious degrees of freedom are high-frequency relative to nuclei

- **Bottom line** (according to TJM)  
  - EL schemes have ½ time step to save 5 iterations/time step. Works out to a 2.5x speed advantage in favor of EL
  - But need to be careful to maintain adiabatic separation of nuclei and electrons.
  - Both are reasonable and choice depends on taste

EL expands dynamic range of frequencies to reduce SCF iterations

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#### Electronic Excited States

**Chemical Synthesis**

**Energy Conversion**

**Vision**
**Light-Driven Molecular Devices**

Switch electron transport on and off


More Light-Driven Devices


**Breakdown of Born-Oppenheimer Approximation**

Avoided Crossings

Degeneracy lifted in N-dimensional space

Conical Intersections

Degeneracy lifted in 2-dimensional space

CIs are the rule, not the exception: e.g., Michl, Yarkony, Robb, ...

**Including Quantum Effects**

- Classical with "ad hoc corrections"
  - Not guaranteed to converge to the right answer…
  - No well-defined nuclear wavefunction
- Mixed Quantum/Classical (See Iyengar Talk)
  - Based on time-dependent self-consistent field approximation
  - Not obvious that QM and CM are strictly compatible!
- Fully Quantum Mechanical
  - Approach is well-defined
  - But difficult (in fact, exponentially difficult in general case)
  - Basis set and path integral approaches
    - Feynman Path integrals
      - Imaginary time (quantum statistics) is easy
      - “Sign” problem in real time – progress, but still unsolved
    - Basis set
      - What kind of functions?
      - How to choose them?

**Nonadiabatic Dynamics**

- Ehrenfest Methods
  \[ \dot{c}_i = -\sum H_{ij}(\hat{R}) c_j, \quad V_{ee}(\hat{R}) = \sum \beta_{ij}^2 c_i^* \bar{H}_{ij}(\hat{R}) \]
  Hamilton’s Eqs with \( V_{ee} \) for R and P
  \( V_{ee} \) is unphysical asymptotically!
  Why? - Wavepacket splits into two parts and averaging becomes senseless
- Surface Hopping (Tully, Truhlar, many more…)
  Avoid unphysical averaging
  Stochastic "hops"
  No systematic hierarchy to improve approximations

**Ab initio Quantum Dynamics**

- \textit{Ab initio} Quantum Dynamics \( \rightarrow \) "On-the-fly" solution of electronic and nuclear Schrödinger equations
  - Multiple electronic states/Tunneling \( \rightarrow \) Need quantum nuclear dynamics
  - Bond rearrangement \( \rightarrow \) Need to solve electronic Schrödinger equation
- Exact numerical solution of the nuclear Schrödinger equation is impractical for large systems.
  - \textit{Ab initio} quantum chemistry is local
  - Nuclear Schrödinger equation is global
  - Not a problem in Car-Parrinello b/c Newtonian mechanics is local…

Further considerations:

- Need PEIs for both ground and excited states
- Matrix elements which couple electronic states
- Minimize the number of PEIs evaluations b/c of extreme expense.

Tailor the requirements of quantum dynamics to quantum chemistry and vice-versa!
### Basis Set Approaches to Quantum Dynamics

#### Orthogonal basis of $\delta$ functions

$\psi(x) = \sum c_i \delta(x - x_i)$

Determine $c_i(t)$ using FFT method, as described by Batista yesterday.

For cognoscenti – the basis functions in the FFT method are actually sinc functions.

#### Nonorthogonal basis

$\psi(x,t) \approx \sum \psi_i(x,t) c_i(t)$

Insert ansatz into t-Dep Schrödinger Equation:

$$\frac{d}{dt} \langle \psi | t \rangle = -i \mathbf{H} \langle \psi | t \rangle$$

Note this is NOT the time derivative of the overlap matrix!

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### Ideal Basis Set

- Ideally, our basis set would be:
  - Compact
  - Accurately describe the wavefunction at all times
  - Easily determined at any point in time

- Fixed basis sets (orthogonal and nonorthogonal):
  - Must span all Hilbert space which is sampled by the wavefunction from beginning to end of simulation!
  - Recall Batista’s example of a Gaussian basis function evolving in a harmonic potential – it does not deform and its center follows classical mechanics.
  - With a fixed basis set, we must cover the entire configuration space accessed.
  - Even in 1D, the problem is much worse if wavefunction is unbound – for free particle, we MUST have basis functions covering ALL space uniformly.

### Time Evolution

- Batista already showed us one way to get around this – adaptively expanding a Gaussian basis set at each point in time.
- Could we make a good guess at the evolution of these basis functions?
- If we really believe that classical mechanics is usually sufficient, there should be a way to take advantage of it!
- Why Gaussians (“coherent states”)?
  - Exhibit classical motion without deformation in harmonic potential
  - Minimum uncertainty states – as $p/q$ localized as possible in QM
- Localization is good for scaling – analogy to local bases in quantum chemistry.
- Localization lends itself well to numerical approximations (e.g. integrals)
- Localization is needed for interface to electronic structure!
- Overcomplete if all $p,q$ allowed – this will be good for us!
- Would a basis set of Gaussians with classical EOM be sufficient in principle?
  - Need to have classical energy width!
  - Otherwise, energy conservation will restrict allowed space
  - If no hidden conserved quantities and all energies are allowed, infinite basis by this prescription will be overcomplete, hence the answer is YES.

### Principle to Practice

- In principle, we do not need to do anything special – just to have enough “trajectory basis functions”
- But who cares if the basis set prescription would be sufficient in principle?!
- Our computers have limited memory and we have limited lifespans…
- Our basis set needs to be able to adapt to the problem!
Adaptive Basis Set

New Basis Functions added to augment classical mechanics and accelerate convergence

Time Discretization

- Basis set is small because crossing time is typically short.
- Each basis function is “responsible” for a portion of the population transfer.

Time Discretization – Long Events

Each trajectory basis function can be in “spawning” mode. In this case, it knows not to spawn again until a certain time is reached.

Time Discretization

Central discretization point should be chosen at maximum coupling, not midway in time interval.

Other discretization points chosen to be equispaced in time

MultiSpawn \(\rightarrow\) Number of discretization points per event

Time Discretization

Avoid many small spawning regions

Start of “event”

End of “event”

CSThresh > CFThresh

Usually chosen to be very close to each other

Time Discretization

Maximum time for discretization

Spawn separately in each time interval
**More Sophisticated Spawning Schemes**

“Constant Area” Spawning
Invariant to time step; Under development

**Where to Spawn?**

- Want largest matrix element connecting new and old basis functions
- Demand classical energy conservation — still have freedom

**Energy for Spawned Trajectories**

Energy for Spawned Trajectories

**Wigner view of Spawning**

“position jump” type of behavior

**Energy for Spawned Trajectories**

Energy for Spawned Trajectories

**Wigner view of Spawning**

“momentum jump” type of behavior
“Frustrated” Spawns

Steepest Descent does not always find a solution within allotted time. In this case, best solution is used if EShellOnly=False

Linear Dependence and Matrix Inversion

- When many gaussian basis functions are used, linear dependence may become an issue
- Controlled by regularization
  - Singular value decomposition of Overlap Matrix
  - Singular values below a threshold are discarded
  - Norm conservation is affected
- Overlap matrix does not have to be inverted. Solve by conjugate gradient (nice regularizing properties):

\[ \mathbf{SC} = -\mathbf{C} \left( \mathbf{H} - \mathbf{S} \right)^T \]

Cost is \( N^2 \) instead of \( N^3 \), but sparsity makes it \( O(N) \)

Diabatic vs Adiabatic Representations

- Diabatic
  - Smoother, therefore easier to integrate classical equations of motion for trajectories
  - Couplings can be large – much spawning required
  - If diabatic model is purely quadratic, benefit from exact propagation when couplings are small
  - Also, may be able to avoid integral approximations
  - Requires global information about PES – not suitable for \( \text{ab initio} \) MD
- Adiabatic
  - Nonadiabatic events are spatially/temporally localized – few spawning events lasting for short time
  - Classical mechanics is more nearly correct because electronic states are usually independent

Running a Simulation – FMS Dynamics

- FMS Dynamics
  - Widths need to be determined – these need to be tested for robustness – 25% changes should not affect amount of population transfer
  - Need to determine appropriate values for CSThresh and CFThresh – this needs to be checked for every new molecule
  - Run several trajectories without spawning, monitor nonadiabatic coupling, choose thresholds low enough to capture all population transfer but otherwise as large as possible

Running a Simulation – AIMS Dynamics

- \( \text{ab initio} \) multiple spawning
  - Need to ensure that electronic structure method is accurate
  - This involves iteration between AIMS and high-level electronic structure
  - Example with CASSCF – need to choose an active space and state-averaging
    - State ordering and S2/S1 gap at Franck-Condon point
    - Preliminary dynamics calculation
    - Calculate CASPT2 PEVs along CAS trajectories - demand consistency
    - Minimize snapshots from dynamics to find “attractor” minima or MECIs
    - Verify energetics of these points with CASPT2 / MS-CASPT2
  - If inconsistent, dynamics results are discarded – continue search for active space

Multiple Spawning

- Two Diabatic Surfaces (A+BC→AB+C collinear model)
- Triangles denote centroids of Gaussians – not all are populated!
- Linear dependence “prunes” number of Gaussians spawned
- “Back-spawning” is allowed
### Initial Conditions

- **FirstGauss=True**
  - Guarantees that the center of the Wigner is first basis function

  \[ \text{OMaxI} \rightarrow \text{if overlap between any two initial conditions} > \text{OMaxI, one is rejected. Prevents excessive linear dependence at } t=0 \]

### Absorption and Resonance Raman Spectra

- **Time-domain Formulation of Spectroscopy (Heller)**
- **Electronic Absorption Spectrum:**
  \[ \sigma_{\mu}(\omega) = C_{\mu\nu} \int \langle \psi | \mu | \psi_{\nu} \rangle \exp(i \omega \tau) d\tau \]
- **Resonance Raman Excitation Profiles:**
  \[ \sigma_{\mu+}(\omega) = C_{\mu\nu} \int \langle \psi | \mu | \psi_{\nu} \rangle \exp(i \omega \tau) d\tau \]

  - Anharmonicity and Duschinsky rotation included
  - Coordinate dependence of transition dipole can be included

### Correlation Functions

- **Correlation Function \( \verb+\rightarrow+ \) Spectrum**

### Convergence

- **Ethylene V State, Vibronic Coupling Model**
  - 1 BFxn
  - 10 BFxns
  - 20 BFxns
Pyrazine Electronic Absorption Spectra

- Structureless S₂ spectrum implying fast S₁ → S₁ internal conversion
- 3D/4D/24D vibronic coupling (Domcke/Cederbaum/Meyer/Koppel)

\[
H = \sum_{k} \left( \frac{\delta_{ik} \delta_{jk}}{2} \right) + \lambda \mathbf{Q}_{ik} + \lambda \mathbf{Q}_{jk} \]

Results for Electronic Spectra

- Prespawning used in all of these calculations
- Final number of basis functions ranges from 100-900
- Somewhat better agreement from IVR methods w/ 10⁶ trajectories
- Fewer basis functions may suffice in adiabatic representation

Saddle-Point Approximations

- Integrals which are difficult to evaluate in AIMS are treated with saddle point approximation:

\[
\langle \chi' \mid \phi \rangle \approx \langle \chi' \mid \chi \rangle \cdot \langle \chi \mid \phi \rangle
\]

Centroid of Product Gaussian
(Higher order variants possible, but require Hessian)

Minimal effect on spectrum

Effect of Nonadiabaticity on Spectrum

- C(t) limited to 150fs – still leads to significant structure w/o nonadiabaticity
- MCTDH for comparison

Results for Electronic Spectra

Dependence on Spawning Threshold

- Large spawning thresholds get basic envelope correct
- Small thresholds required to reproduce detailed structure
- Smooth convergence observed

Accuracy of FMS Method: The Spin Boson Model

- Two level system linearly coupled to a Harmonic bath:

\[
H = H_S + H_B + H_{S-B}
\]

- In the diabatic representation:

\[
H = \sum_{\alpha \beta} \langle \phi_{\alpha} \mid h_{\alpha \beta} \mid \phi_{\beta} \rangle + \sum_{\alpha} \Delta \langle \phi_{\alpha} \mid \phi_{\alpha} \rangle + c.c.
\]

\[
h_{\alpha \beta} = \hbar \omega \sum_{j} C j \Delta \omega_{j} ; \quad \hbar \omega = \frac{1}{2} \sum_{j} \left( P_{j}^{2} + X_{j}^{2} \right)
\]

- \( \omega_j \) – vibrational frequency of the jth oscillator
- \( C_j \) – electronic coupling
- \( \Delta \omega_j \) – dimensionless position and momentum

In the form of Domcke-Cederbaum-Koppel vibronic coupling models
Often used as a model for conical intersection problems
The Spin Boson Model

- Bath properties are determined by the spectral density:
  \[ J(\omega) = \frac{\pi}{2} \sum_j \delta(\omega - \omega_j) \]
- The case of an Ohmic bath:
  \[ J(\omega) = \frac{\pi}{2} \gamma \omega e^{-\omega/\gamma} \]

**Exact Results:**

- 400 dimensional model
- 4 dimensional model
  - Multiconfigurational Time-Dependent Hartree (MCTDH)

\[ \Delta\omega = \sum_j \omega_j \]

Extended Coupling Regions

- Adaptive expansion is tailored to time-space-local breakdowns of the Born-Oppenheimer approximation.
- What about cases where the BOA breaks down completely?
- Continuous spawning – ensure that basis functions always have “partners” on other electronic states when they are coupled. Why is this even practical? PESs tend to be nearly parallel in extended coupling regions?

\[ \psi = \sum_i c_i \psi_i \]

\[ \langle \hat{\mathcal{O}} \rangle_{IFG} = \sum_i \hat{c}_i \langle \hat{\mathcal{O}} \rangle_{i_F} \]

Multiple Spawning

- FMS is a hierarchy of methods
- Dynamics on a single electronic state–coupled frozen Gaussians (Heller,Metiu)
- Useful Approximations in *Ab Initio* Dynamics
  - Independent First Generation Approximation
    - Different initial Gaussian wavepackets are uncoupled
    - Includes coherences between basis function and its “children”
    - Neglects coherence between initial basis functions
  - Saddle-Point Approximation for Integrals
    - Use locality of Gaussians to evaluate integrals using local information
      \[ \int_{\mathcal{R}} |\psi_1(\mathcal{R})| \psi_2(\mathcal{R}) |\psi_3(\mathcal{R})| d\mathcal{R} \approx \text{constant of } \mathcal{R} \]

Independent First-Generation Approximation

- Spin Boson Tests – 4 DOF
- Spin Boson Tests – 400 DOF

In high dimensionality and finite T, convergence is actually faster – basis function separation is physically correct.
(See early work by Neria & Nitzan, Rossky, Bittner)
**Saddle-Point Approximations**

\[ \chi_{\lambda}(R) f(R) \chi_{\lambda}(R) dR = \int \chi_{\lambda}(R) f(R) \chi_{\lambda}(R) dR \]

- Taylor expansion of potential around maximum of product
- First-order term requires gradient at maximum of product
- Second-order term can be included if Hessian of potential available

**Photochemistry /Photophysics of Ethylene**

- Prototype for cis-trans isomerization
- Conventional Picture:
  - One-dimensional nature - emphasizing torsion
  - Chemistry and Isomerization occur on S0
  - Experimental Photoproducts: cis-trans isomers, H₂C≡CH, H₂, H₂
  - Excited State Lifetime from Absorption Spectrum: < 50 fs
  - No fluorescence

**EOM-CCSD Spectra for Ethylene**

- Rₚ and V spectra shifted to large basis
- MRSDCI vertical excitation energies

**AIMS-EOM-CCSD**

- Prototype for cis-trans isomerization
- Conventional Picture:
  - One-dimensional nature - emphasizing torsion
  - Chemistry and Isomerization occur on S0
  - Experimental Photoproducts: cis-trans isomers, H₂C≡CH, H₂, H₂
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**AIMS Excited State Dynamics of Ethylene**

- CAS(2/2)*SCI/DZV

**Do Conical Intersections Matter?**

- Regions near intersections dominate nonadiabatic events

Charge Transfer State Critical to S₁ Decay
Torsion alone is insufficient – in contrast to textbook picture
**Do Minimal Energy Conical Intersections Matter?**

Minimal energy point along seam may have little significance! Still useful in cartoon pictures of mechanisms.

**Photoinduced cis-trans Isomerization - Butadiene**

Again, charge transfer state plays key role!

SA-3-CAS(4/3)6-31G*

**Excited State Intramolecular Proton Transfer**

No H/D isotope effect!?

Experiments: Lochbrunner, Stolow, Riedle, Zewail ...

**Methyl Salicylate Energy Diagram**

No significant isotope effect!

**H-Atom Transfer in Methyl Salicylate**

H-Atom Transfer Time

Expt: 60±10 fs (Herek)
AIMS: ≈ 50 fs

**Isotope Effects in MS ESIPT**

No significant isotope effect!
Bond Alternation “Gates” H-Atom Motion

S<sub>0</sub> Keto

S<sub>1</sub> Enol

Wavepacket Dynamics on S<sub>1</sub>

Reduced densities determined by Monte Carlo integration using FMS wavefunction

Time/Energy-Resolved Fluorescence Spectra

Expt: Herek, Pedersen, Banares, and Zewail, JCP 97 9046 (1992)

Intersections from Semiempirical CASCI

- Semiempirical analog of state-averaged multi-reference ab initio methods
- Good agreement with ab initio CASSCF results
  - Qualitative interaction geometries
  - Coordinates which lift electronic degeneracy
- BUT, energetics are qualitatively incorrect
- Suggests feasibility of reparameterization

Comparison of intersection geometries and modes which lift degeneracy in retinal protonated Schiff base analog

RPSB Analog Reparameterization

- Multireference semiempirical model – Fractional Oct MO/CAS(6/6)-CI
- Combine with QM/MM model to represent solvent
- Ab initio data included in reparameterization
  - SA-2-CAS(10/10)/6-31G
  - S<sub>0</sub>/S<sub>1</sub> excitation energy at S<sub>0</sub> minimum
  - Relative energies of MECIs for 11-12 and 13-14 twisted

RPSB Analog – RPSE-CAS(6/6)
Comparisons for torsion around bonds not included in reparameterization

Solvated GFP Chromophore
Conical Intersection

RPSB Isomerization QY / Lifetime

Isomerization QY: 13%-20% (Expt)
24% (Theory, MeOH) 38% (Theory, Isolated)
Lifetime: 2-12 ps (Expt)
1:3:2 Isolation

Isolated RPSB Fluorescence

Much shorter lifetime in isolation
Dominant product 11-cis in both MeOH and gas phase

RPSB / MeOH Fluorescence

QM/MM Model
80 OPLS/AA MeOH
Kandori & Sasabe, CPL 1993
\( \tau_1 = 35 \text{ fs} \)
\( \tau_2 = 2.5 \text{ ps} \)

RPSB Isomerization Barrier

No barrier in gas phase
What causes barrier in solution?
Need free energy surfaces to understand behavior in solution!

\[ G(\theta, r) \propto -kT \ln P(\theta, r) \]

Conical intersection Topography

“Peaked”  “Sloped”

Reparameterized Semiempirical CASCI

RPSE fit to EOM-CCSD in FC region

Reparameterized SE S_1 Dynamics

100fs to reach twisted geometry
No quenching at 250fs
Initial dynamics dominated by H motion

Reparameterized SE QM/MM S_1 Dynamics

60fs to reach twisted geometry
Quenching begins at 60fs
Solvent stabilizes conical intersection
Initial dynamics similar to gas phase
150 TIP3P Water Molecules
**GFP neutral chromophore lifetime**

 ![GFP neutral chromophore lifetime graph](image)

**Solvent Effects on Conical Intersections**

 ![Solvent Effects on Conical Intersections graph](image)

**Solvent Effect on Topography**

 When one state is preferentially stabilized, intersections become
1) Peaked
2) Absolute minima

 Faster decay than in vacuum...

**Neutral in the Protein**

 ![Neutral in the Protein graph](image)

**Anion in the Protein**

 ![Anion in the Protein graph](image)

**Tunneling via Multiple Spawning Dynamics**

 Can tunneling be included in multiple spawning?
- Trivial case: Tunneling in a multi-electronic state framework
- But we do not want to include more electronic states!

**Single-Surface Spawning**
- Label atoms which may tunnel
- Label sites where atoms may tunnel
- Spawn basis functions where needed

 ![Spawned Basis Function](image)
Single-Surface Spawning Test

• 2-D Model for Proton Transfer

\[ V_s(Q) = F_s(Q) + i \omega s \left( Q - F_s(Q) \right) \]

\[ V_s(Q) = -i \omega s^2 + \xi_b s \]

• 15 Basis Functions to represent Initial State
• Wavefunction propagated for up to 4 ps
• Up to 30 final basis functions (15 spawned)

Single-Surface Spawning Results

- 15 Basis Functions to represent Initial State
- Wavefunction propagated for up to 4 ps
- Up to 30 final basis functions (15 spawned)

Note agreement for \( S(t) \) - This requires correct phase interference!

Single-Surface Spawning Spectrum

Tunneling Splitting
FMS: 91.89 cm\(^{-1}\)
Quantum: 91.90 cm\(^{-1}\)

Single-Surface Spawning for Quadratic Coupling

\[ v=0 \]

\[ v=1 \]

Agreement of Tunneling Splitting is better than absolute frequencies

Single-Surface Spawning for Linear Coupling

\[ v=0 \]

\[ v=1 \]

Agreement of Tunneling Splitting is better than absolute frequencies

Single-Surface Spawning Wavefunction
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