Can quantized vibrational effects be obtained from Ehrenfest mixed quantum classical dynamics?

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Real Time Time-Dependent electronic dynamics:

solve time dependent Schrödinger equation *explicitly* in time with frozen nuclei

Routinely used to obtain spectroscopic information

- 1. Absorption spectra (Li, Isborn, Govind, Lopata)
- 2. Circular Dichroism (Li, Rubio, Bertsch)
- 3. Correlated wave function dynamics (DePrince)
- 4. Relativistic effects (Repisky, Ruud, Li)
- 5. Spin dynamics (Li, Scuseria, Peralta)
- 6. Nonlinear properties (Li, Repisky, Ruud)
- 7. Open systems (Parkhill)

Many, many more techniques and research groups

Real time electronic dynamics for spectroscopy

$$i\hbar\frac{\partial\Phi}{\partial t} = H_{\rm el}\Phi$$

Advantages¹:

- Full band spectra
- Non-perturbative
- Scales as a Fock build (no worse than O(N⁴))
- Time domain is often more intuitive

Disadvantages:

- Large prefactor (can beat with Padé techniques²)
- Numerical stability issues more common

¹⁾ Lopata and Govind. "Modeling fast electron dynamics with real-time time-dependent density functional theory: application to small molecules and chromophores." JCTC 7.5 (2011): 1344-1355.

Bruner, LaMaster, Lopata. "Accelerated broadband spectra using transition dipole decomposition and Padé approximants." JCTC 12.8 (2016): 3741-3750.

For electronic spectroscopy, the procedure is fairly simple*



$$i\hbar\frac{\partial\Phi}{\partial t} = H_{\rm el}\Phi$$

$$\boldsymbol{\mu}(t)$$

add perturbation to molecule propagate in time

track time-dependent observable

"perturb-then-propagate" scheme

*Nice tutorial: Provorse, Makenzie R., and Christine M. Isborn. "Electron dynamics with real-time time-dependent density functional theory." IJQC (2016).

In real time time-dependent mean field methods (RT-TDSCF),





Fourier-transforming the dipole gives us an absorption spectra

 $\frac{4\pi\omega}{3c\kappa} \operatorname{Im}\left[\operatorname{Tr}\left(\mu(\omega)\right)\right]$



Dynamic polarizability α is responsible for spectra. It relates the induced dipole to the applied field.

$$\boldsymbol{\mu}(t) = \boldsymbol{\mu}(0) + (\boldsymbol{\alpha} * \boldsymbol{E})(t)$$

$$\alpha_{ij}(t) = \Theta(t) \sum_{n(\neq 0)} \langle 0|\hat{\mu}_i|n\rangle \langle n|\hat{\mu}_j|0\rangle \sin(\omega_{0n}t)$$

 α has resonances at ω_{0n} with magnitudes governed by transition dipole moment

E(t)

$$\mu_i(t) = \mu_i(0) + \alpha_{ij}(t) \cdot E_j$$

Weak "delta" field perturbation simplifies analysis by filter property

Different properties can be accessed with different perturbations and different time-dependent observables

<u>Spectroscopy</u>	Perturbation	<u>TD observable</u>
Absorption	Electric dipole	Electric dipole
Circular Dichroism	Electric dipole	Magnetic dipole
Magnetic Circular Dichroism	Electric dipole + static magnetic field	Electric dipole
X-ray Circular Dichroism	Electric dipole	Electric quadrupole

What happens to time evolving dipole when we allow nuclei to move?



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Extension to include nuclear motion: the Ehrenfest method

Electronic motion governed by TDSE, with parametric dependence on nuclear position (same at RT methods)

$$i\hbar\frac{\partial\Phi}{\partial t} = H_{\rm el}\Phi$$

Forces on nuclei governed by electronic gradient

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I \langle \Phi | H_{\rm el} | \Phi \rangle$$

Nuclei evolve on mean-field potential energy surface

...so we tried just that: H₂ molecule RHF/STO-3G

Stretched bond, zero init. velocity (order of 0.01 Angstrom) 0.0012 fs electronic time step $\gg \Delta t$ 0.0036 fs nuclear time step EPerturb with **weak** (0.0001 au) delta pulse (ground state PES) Padé transformation (Lopata 2016) after 50 fs (well converged, identical to 300 fs runs)

Bruner, LaMaster, Lopata. "Accelerated broadband spectra using transition dipole decomposition and Padé approximants." JCTC 12.8 (2016): 3741-3750.

H_2 molecule RHF/STO-3G



- Central peak corresponds to LR-TDHF energy at equilibrium geometry.
- Peaks separated by vibrational frequencies from geometric Hessian.
- Relative intensity of sidebands increases with greater initial stretch.
- No peaks at ~0.7 eV (IR dark sym. stretch)

Note that peak broadening is artificial (we add damping)

If the effects are nuclear in origin, we should see isotopic effects



Consider a diatomic molecule, moving along a vibrational normal mode *R*

$$\mu_i(t) = \mu_i(0) + \alpha_{ij}(t) \cdot E_j$$

(implied function of R, itself a function of time)

Now expand dipole about the normal mode, R_0 is equilibrium geometry



Rearrange, and (for small displacements) make *R* harmonic in time

$$\mu_i(t) - \mu_i(0) = \Delta \mu_i(t) = \alpha_{ij}(t) \cdot E_j + \frac{\partial \mu_i(0)}{\partial R} [\Delta R \cdot \cos(\omega_N t)] + \frac{\partial \alpha_{ij}(t)}{\partial R} E_j [\Delta R \cdot \cos(\omega_N t)]$$

$$R(t) - R_0 \to \Delta R \cdot \cos(\omega_N t)$$

Fourier transform resulting expansion

$$\begin{split} \Delta \mu_i(\omega) &\propto E_j \cdot \sum_{n(\neq 0)} \left[\langle 0 | \hat{\mu}_i | n \rangle \langle n | \hat{\mu}_j | 0 \rangle \right] \delta(\omega_{0n} - \omega) \\ &+ \Delta R \cdot \frac{\partial \mu_i(0)}{\partial R} \delta(\omega - \omega_N) \\ &+ \Delta R \cdot E_j \cdot \sum_{n(\neq 0)} \frac{\partial}{\partial R} \left[\langle 0 | \hat{\mu}_i | n \rangle \langle n | \hat{\mu}_j | 0 \rangle \right] \delta(\omega_{0n} \pm \omega_N - \omega) + \cdots \end{split}$$

 $+ \cdots$

Final expression, $\Delta \mu_i(\omega)$ sum of

IR modes
$$(\omega_N \text{ is vibrational frequency})$$

$$\Delta R \cdot \frac{\partial \mu_i(0)}{\partial R} \delta(\omega - \omega_N)$$

Electronic modes ω_{0n}

$$E_j \cdot \sum_{n(\neq 0)} [\langle 0|\hat{\mu}_i|n\rangle \langle n|\hat{\mu}_j|0\rangle] \delta(\omega_{0n} - \omega)$$

Raman modes
(
$$\omega_{0n} \pm \omega_N$$
) $\Delta R \cdot E_j \cdot \sum_{n(\neq 0)} \frac{\partial}{\partial R} [\langle 0|\hat{\mu}_i|n \rangle \langle n|\hat{\mu}_j|0 \rangle] \delta(\omega_{0n} \pm \omega_N - \omega)$

Slightly more realistic, stretched CO molecule RHF/6-31+G*



- Central peaks match LR-TDHF at equilibrium geometry
- IR active stretch, low energy peaks match geom. Hessian

Clearly, information about nuclear motion encoded in electric dipole response

Tempting to call it vibronic, but **no** nuclear wavefunction

Sidebands don't follow quantum (an)harmonic oscillator

We see:
$$G(n) = \omega_N \cdot n$$
 $n = 0, 1, 2, ...$
not: $G(n) = \omega_N \cdot (n + 1/2) - x \cdot \omega_N \cdot (n + 1/2)^2 + \cdots$ $n = 0, 1, 2, ...$

However, sideband peaks are *quantized* due to boundary conditions (response is periodic)

Simple way to think about it: lessons from FM radio

Frequency modulated (FM) radio



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Simple way to think about it: lessons from FM radio

Frequency modulated *dipole response*



 $cos(\omega_{0n} \cdot t + B \cdot (cos(\omega_N \cdot t)))$

Nuclear-modulated MM///MM//



Electronic density waves "ride" along nuclear motion, which governs the response (modulation always yields sidebands) Wrapping things up:

Traditionally, we think of Ehrenfest as putting electronic effects into nuclear motion

Here we showed how the flip-side can work: nuclear motion on electronic spectra

Ehrenfest probably not going to become *de facto* method for computing vibrational spectra

However, it gives important insight into how the method behaves, primarily if we are still going to use Ehrenfest for studies of electronic dephasing, etc.

Thank you!



