Time-dependent variational principles: application for quantum dynamics

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How do we calculate quantum dynamics?

Time-dependent Shrödinger equation:

$$i\hbar\frac{\partial\Phi}{\partial t} = \hat{H}\Phi$$

Let's solve it formally:

$$\Phi(t) = \Phi(0)\exp\left(-\frac{i}{\hbar}\hat{H}t\right) \Rightarrow \frac{\partial}{\partial t}\langle\Phi(t)|\Phi(t)\rangle = 0$$

We can use evolution operator to calculate dynamics of wave function — **Split operator technique**.

Pros
- accurate (Δt^3)

Cons
- slow

Is there any other way to estimate accurate quantum dynamics?

Time–dependent variational principleS(!)

Time-dependent variational principle (TDVP):

$$\delta S = \delta \left(\int_0^t W \, d\tilde{t} \right) = 0, \ W = \frac{\left\langle \Phi \left| \hat{H} - i\hbar \frac{\partial}{\partial t} \right| \Phi \right\rangle}{\langle \Phi | \Phi \rangle}$$

If $\|W\| < \infty \ \forall t$ and $\delta S = 0 \Rightarrow$ McLachlan's variational principle:

$$\delta \left(\frac{\left\langle \Phi \left| \hat{H} - i\hbar \frac{\partial}{\partial t} \right| \Phi \right\rangle}{\langle \Phi | \Phi \rangle} \right) = 0$$

If $\delta W = 0$ and $\delta \langle \Phi | \Phi \rangle = 0 \Rightarrow$ Dirac–Frenkel variational principle:

$$\left\langle \delta \Phi \left| \hat{H} - i\hbar \frac{\partial}{\partial t} \right| \Phi \right\rangle = 0$$

Wave function ansatz

Basis $\{\phi_k(\lambda_1, \ldots, \lambda_M)\}_{k=1}^N$:

$$|\Psi\rangle = \sum_{i=1}^N C_k \phi_k$$

$$|\delta\Psi\rangle = \sum_{i=1}^N \left(\delta C_k \phi_k + C_k \sum_{l=1}^M \frac{\partial \phi_k}{\partial \lambda_{kl}} \delta\lambda_{kl} \right)$$

$$\delta C_m^* \sum_{k=1}^N \left\langle \phi_m \left| \hat{H} - i\hbar\frac{\partial}{\partial t} \right| C_k \phi_k \right\rangle = 0$$

$$\delta\lambda_{mj} \sum_{k=1}^N C_m^* \left\langle \frac{\partial \phi_m}{\partial \lambda_{mj}} \left| \hat{H} - i\hbar\frac{\partial}{\partial t} \right| C_k \phi_k \right\rangle = 0$$

Equation of motions

$$\dot{\vec{C}}_n = -\frac{i}{\hbar} \sum_{k,n=1}^{N} \mathbb{S}_{nm}^{-1} \left(\mathbb{H}_{mk} - i\hbar \boldsymbol{\tau}_{mk} \right) \vec{C}_k \; - \; \text{vector of coeficients}$$

$$\dot{\lambda}_{kl} = -\frac{i}{\hbar} \sum_{m=1}^{N} \sum_{j=1}^{M} \left(\mathbb{X}^{-1} \right)_{km}^{lj} \mathbb{Y}_m^j \; - \; \text{matrix of parameters}$$

$$\mathbb{S}_{mk} = \langle \phi_m | \phi_k \rangle, \; \mathbb{H}_{mk} = \left\langle \phi_m \left| \hat{H} \right| \phi_k \right\rangle, \; \boldsymbol{\tau}_{mk} = \sum_{l=1}^{M} \left\langle \phi_m \left| \frac{\partial \phi_k}{\partial \lambda_{kl}} \right\rangle \dot{\lambda}_{kl} \right.$$

$$\mathbb{Y}_m^j = \sum_{n=1}^{N} \rho_{mn} \left(\mathbb{H}_{mn}^{(j0)} - (\mathbb{S}^{(j0)} \mathbb{S}^{-1} \mathbb{H})_{mn} \right), \; \mathbb{X}_{km}^{lj} = \rho_{km} \left(\mathbb{S}_{km}^{(lj)} - (\mathbb{S}^{(l0)} \mathbb{S}^{-1} \mathbb{S}^{(0j)})_{km} \right)$$

$$\rho_{mn} = C_m^* C_n, \; \mathbb{H}_{mn}^{(j0)} = \left\langle \frac{\partial \phi_m}{\partial \lambda_{mj}} \left| \hat{H} \right| \phi_n \right\rangle$$

$$\mathbb{S}_{mn}^{(j0)} = \left\langle \frac{\partial \phi_m}{\partial \lambda_{mj}} \middle| \phi_n \right\rangle, \; \mathbb{S}_{km}^{(0j)} = \left\langle \phi_k \left| \frac{\partial \phi_m}{\partial \lambda_{mj}} \right\rangle, \; \mathbb{S}_{km}^{(lj)} = \left\langle \frac{\partial \phi_k}{\partial \lambda_{kl}} \middle| \frac{\partial \phi_m}{\partial \lambda_{mj}} \right\rangle \right.$$

What about laws of conservation?

Conservation of norm:

$$\frac{\partial}{\partial t}\langle\Psi|\Psi\rangle = \sum_{k,m=1}^{N}\frac{\partial}{\partial t}\left(C_k^* C_m\langle\phi_k|\phi_m\rangle\right) = \frac{\partial}{\partial t}\vec{C}^\dagger \$ \vec{C} = \dot{\vec{C}}^\dagger \$ \vec{C} + \vec{C}^\dagger \$ \dot{\vec{C}} + \vec{C}^\dagger \dot{\$} \vec{C}$$

$$\dot{\vec{C}} = -\frac{i}{\hbar}\$^{-1}(\mathbb{H} - i\hbar\boldsymbol{\tau})\vec{C}$$

$$\vec{C}^\dagger \$ \dot{\vec{C}} = -\frac{i}{\hbar}\vec{C}^\dagger(\mathbb{H} - i\hbar\boldsymbol{\tau})\vec{C},$$

$$\dot{\vec{C}}^\dagger \$ \vec{C} = \left(-\frac{i}{\hbar}\$^{-1}(\mathbb{H} - i\hbar\boldsymbol{\tau})\vec{C}\right)^\dagger \$ \vec{C} = \frac{i}{\hbar}\vec{C}^\dagger(\mathbb{H} + i\hbar\boldsymbol{\tau}^\dagger)\vec{C}$$

$$\dot{\vec{C}}^\dagger \$ \vec{C} + \vec{C}^\dagger \$ \dot{\vec{C}} = -\vec{C}^\dagger(\boldsymbol{\tau} + \boldsymbol{\tau}^\dagger)\vec{C} = -\vec{C}^\dagger \dot{\$} \vec{C} \Rightarrow \frac{\partial}{\partial t}\langle\Psi|\Psi\rangle = 0$$

What about laws of conservation?

Conservation of energy:

$$\frac{\partial}{\partial t}\frac{\left\langle\psi\left|\hat{H}\right|\psi\right\rangle}{\langle\Psi|\Psi\rangle} = \frac{1}{\langle\Psi|\Psi\rangle}\frac{\partial}{\partial t}\sum_{k,m=1}^{N}C_k^*C_m\left\langle\phi_k\left|\hat{H}\right|\phi_m\right\rangle =$$

$$= \frac{1}{\langle\Psi|\Psi\rangle}\frac{\partial}{\partial t}\vec{C}^\dagger\mathbb{H}\vec{C} = \frac{\dot{\vec{C}}^\dagger\mathbb{H}\vec{C} + \vec{C}^\dagger\mathbb{H}\dot{\vec{C}}}{\langle\Psi|\Psi\rangle}$$

$$\dot{\vec{C}} = -\frac{i}{\hbar}\mathbb{S}^{-1}(\mathbb{H}-i\hbar\boldsymbol{\tau})\vec{C}$$

$$\vec{C}^\dagger\mathbb{H}\dot{\vec{C}} = -\frac{i}{\hbar}\vec{C}^\dagger\mathbb{H}\mathbb{S}^{-1}(\mathbb{H}-i\hbar\boldsymbol{\tau})\vec{C}$$

$$\dot{\vec{C}}^\dagger\mathbb{H}\vec{C} = \frac{i}{\hbar}\vec{C}^\dagger(\mathbb{H}+i\hbar\boldsymbol{\tau}^\dagger)\mathbb{S}^{-1}\mathbb{H}\vec{C}$$

$$\vec{C}^\dagger\mathbb{H}\dot{\vec{C}} + \dot{\vec{C}}^\dagger\mathbb{H}\vec{C} = -\vec{C}^\dagger(\mathbb{H}\mathbb{S}^{-1}\boldsymbol{\tau}+\boldsymbol{\tau}^\dagger\mathbb{S}^{-1}\mathbb{H})\vec{C}$$

What about laws of conservation?

Conservation of energy:

$$(\mathbb{H}\mathbb{S}^{-1}\boldsymbol{\tau})_{mk} = \sum_{n,r=1}^{N} \mathbb{H}_{mn}\mathbb{S}_{nr}^{-1}\boldsymbol{\tau}_{rk} =$$

$$= \sum_{n,r=1}^{N} \left\langle \phi_m \left| \hat{H} \right| \phi_n \right\rangle \mathbb{S}_{nr}^{-1} \sum_{l=1}^{M} \left\langle \phi_r \left| \frac{\partial \phi_k}{\partial \lambda_{kl}} \right\rangle \dot{\lambda}_{kl} =$$

$$= \sum_{l=1}^{M} \left\langle \phi_m \left| \hat{H} \left(\sum_{n,r=1}^{N} |\phi_n\rangle \mathbb{S}_{nr}^{-1} \langle \phi_r| \right) \right| \frac{\partial \phi_k}{\partial \lambda_{kl}} \right\rangle \dot{\lambda}_{kl} = \sum_{l=1}^{M} \dot{\lambda}_{kl} \left(\tilde{\mathbb{H}}_{km}^{(l0)} \right)^*$$

$$(\mathbb{H}\mathbb{S}^{-1}\boldsymbol{\tau})_{mk} + (\mathbb{H}\mathbb{S}^{-1}\boldsymbol{\tau})_{mk}^{\dagger} = 2Re \left(\sum_{l=1}^{M} \dot{\lambda}_{kl} \left(\tilde{\mathbb{H}}_{km}^{(l0)} \right)^* \right) \overset{(?)}{=} 0$$

Basis set

Frozen width gaussian wave packets:

$$|g_k\rangle = \exp\left(\frac{1}{\hbar}\sum_\alpha\left[-\frac{1}{2}\omega r_\alpha^2 + \xi_{k\alpha}r_\alpha + \eta_{k\alpha}\right]\right)$$

$$\xi_{k\alpha} = \omega q_{k\alpha} + i\frac{p_{k\alpha}}{m_k}, \ \ \eta_{k\alpha} = \frac{1}{4}\left(\ln\left[\frac{\omega}{\pi}\right] - 2\omega q_{k\alpha}^2\right) - i\frac{q_{k\alpha}p_{k\alpha}}{m_k}$$

$$|g_k\rangle = \left(\frac{\omega}{\pi}\right)^{\alpha/4}\exp\left(\frac{1}{\hbar}\sum_\alpha\left[-\frac{1}{2}\omega(r_\alpha - q_{k\alpha})^2 + i\frac{p_{k\alpha}}{m_k}(r_\alpha - q_{k\alpha})\right]\right)$$

$$\frac{\langle g_k\,|r_\alpha|\,g_k\rangle}{\langle g_k|g_k\rangle} = q_{k\alpha}, \ \ \frac{\left\langle g_k\left|-i\hbar\frac{\partial}{\partial r_\alpha}\right|g_k\right\rangle}{\langle g_k|g_k\rangle} = p_{k\alpha}$$

Trick of gaussian wave packets:

$$\dot{q}_{k\alpha} = Re(\dot{\xi}_{k\alpha})/\omega, \ \dot{p}_{k\alpha} = Im(\dot{\xi}_{k\alpha}) \ \text{— we need only quarter of } \dot{\lambda} \text{ matrix}$$

Initial conditions

Nuclear eigenstates:

$$\mathbb{H}\vec{C}_k = E_k \mathbb{S}\vec{C}_k$$

General eigenvalue problem — several ways to solve it:

1. "symmetric"
   - Lowdin orthogonalization
   - $\mathbb{S}$–matrix decomposition
2. "nonsymmetric"

"Symmetric" methods

Lowdin orthogonalization:

$$\mathbb{S} = \mathbb{U}\mathbb{S}_d\mathbb{U}^\dagger - \mathbb{S}_d \text{ is diagonal}, \mathbb{U} \text{ is unitary}$$

$$\left(\mathbb{S}_d^{-1/2}\mathbb{U}^\dagger\mathbb{H}\mathbb{U}\mathbb{S}_d^{-1/2}\right)\left(\mathbb{S}_d^{1/2}\mathbb{U}^\dagger\vec{C}_k\right) = E_k\left(\mathbb{S}_d^{1/2}\mathbb{U}^\dagger\vec{C}_k\right)$$

$$\mathbb{H}'\vec{C}_k' = E_k\vec{C}_k'$$

$\mathbb{S}$–matrix decomposition (Cholesky):

$$\mathbb{S} = \mathbb{L}\mathbb{L}^\dagger - \mathbb{L} \text{ is lower triangular}$$

$$\left(\mathbb{L}^{-1}\mathbb{H}\left(\mathbb{L}^\dagger\right)^{-1}\right)\left(\mathbb{L}^\dagger\vec{C}_k\right) = E_k\left(\mathbb{L}^\dagger\vec{C}_k\right)$$

$$\mathbb{H}''\vec{C}_k'' = E_k\vec{C}_k''$$

"Nonsymmetric" method

$\mathbb{S}$–matrix inversion

$$\mathbb{S} = \mathbb{U}\mathfrak{s}\mathbb{V}^\dagger \text{ — singular value decomposition}$$

$\mathfrak{s}$ — diagonal matrix of singular values (eigenvalues of $\mathbb{S}\mathbb{S}^\dagger$ and $\mathbb{S}^\dagger\mathbb{S}$),
$\mathbb{U}$ — unitary matrix of left–singular vectors (eigenvectors of $\mathbb{S}\mathbb{S}^\dagger$),
$\mathbb{V}$ — unitary matrix of right–singular vectors (eigenvectors of $\mathbb{S}^\dagger\mathbb{S}$).

$$\mathbb{S}^{-1} = \mathbb{V}\mathfrak{s}^{-1}\mathbb{U}^\dagger$$

Types of singular values decompositions:

1. Full SVD — consider all singular values
2. Truncated SVD — consider all singular values greater then ε, all other assume equal to zero
3. Regularized SVD — consider all singular values with certain weights: $s_i' = w_i s_i$

$$w_i = (s_i^2 + \varepsilon^2)/s_i^2 \text{ or } w_i = 1 + \varepsilon \cdot \exp\left(-\varepsilon s_i\right)/s_i, \text{ where } \varepsilon \text{ is small}$$