Time-dependent variational principles: application to quantum dynamics

Student of group 515
Paramonov Nikita

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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 propagator 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 $\{\phi_k(\vec{R}|\lambda_{k1},\ldots,\lambda_{kM})\}_{k=1}^N$:

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

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

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

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

Equation of motions

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

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

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

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

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

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

What about laws of conservation?

Conservation of norm:

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

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

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

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

What about laws of conservation?

Conservation of energy:

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

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

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

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

$$\vec{C}^\dagger \dot{\mathbb{H}} \vec{C} = \sum_{m,k=1}^{N} C_m^* C_k \sum_{l=1}^{M} \left(\mathbb{H}_{mk}^{(0l)} \dot{\lambda}_{kl} + \mathbb{H}_{mk}^{(l0)} \dot{\lambda}_{ml}^* \right)$$

What about laws of conservation?

Conservation of energy:

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

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

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

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

$$\frac{\partial}{\partial t} \frac{\left\langle \Psi \left| \hat{H} \right| \Psi \right\rangle}{\langle \Psi | \Psi \rangle} = 2Re(\mathbb{Y}\dot{\Lambda}), \;\; Re(\mathbb{Y}\dot{\Lambda}) \overset{(?)}{=} 0$$

Any other drawbacks?

$\mathbb{H}$–matrix:

$$\left\langle \phi_m \middle| \hat{H} \middle| \phi_k \right\rangle = \left\langle \phi_m \middle| -\frac{\hbar^2}{2M}\Delta \middle| \phi_k \right\rangle + \left\langle \phi_m \middle| V(\vec{R}) \middle| \phi_k \right\rangle$$

We need to know full potential energy surface to calculate $\langle \phi_m | V | \phi_k \rangle$!

Solution: harmonic approximation

Let's expand potential energy:

$$V(\vec{R}) = V(\vec{R}_0) + \sum_{\alpha=1}^{M} \left(\frac{\partial V}{\partial R_\alpha} \right)\Bigg|_{R_\alpha = R_{\alpha\mathbf{0}}} (R_\alpha - R_{\alpha 0}) +$$

$$+ \sum_{\alpha,\beta=1}^{M} \left(\frac{\partial^2 V}{\partial R_\alpha \partial R_\beta} \right)\Bigg|_{\substack{R_\alpha = R_{\alpha\mathbf{0}} \\ R_\beta = R_{\beta\mathbf{0}}}} (R_\alpha - R_{\alpha 0})(R_\beta - R_{\beta 0}) + \ldots$$

Basis set

Frozen width gaussian wave packets:

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

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

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

$$\langle g_k | g_k\rangle = 1,\ \ \langle g_k \left| R_\alpha \right| g_k\rangle = q_{k\alpha},\ \ \left\langle g_k \left| -i\frac{\partial}{\partial R_\alpha} \right| g_k \right\rangle = p_{k\alpha}$$

Trick of gaussian wave packets:

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

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

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

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

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

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

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

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

"Nonsymmetric" method

$\mathbb{S}$–matrix inversion

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

$\mathbb{s}$ — 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 $\mathbb{S}^{\dagger}\mathbb{S}$).

$$\mathbb{S}^{-1} = \mathbb{V}\mathbb{s}^{-1}\mathbb{U}^{\dagger}, \; \left(\mathbb{S}^{-1}\mathbb{H}\right)\vec{C}_k = E_k\vec{C}_k$$

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 $s_i' = w_i s_i$: $w_i = (s_i^2 + \varepsilon^2)/s_i^2$ or $w_i = 1 + \varepsilon \cdot \exp\left(-\varepsilon s_i\right)/s_i$, where ε is small