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):

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

McLachlan's variational principle:

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

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

$$\dot{\vec{C}} = -\frac{i}{\hbar}\mathbb{S}^{-1}\left(\mathbb{H} - i\hbar\boldsymbol{\tau}\right)\vec{C} \text{ — vector of coeficients}$$

$$\dot{\Lambda} = -\frac{i}{\hbar}\mathbb{X}^{-1}\mathbb{Y} \text{ — matrix of parameters}$$

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

$$\mathbb{Y}_m^j = \sum_{k=1}^{N}\rho_{mk}\left(\mathbb{H}_{mk}^{(j0)} - (\mathbb{S}^{(j0)}\mathbb{S}^{-1}\mathbb{H})_{mk}\right),\ \mathbb{X}_{mk}^{jl} = \rho_{mk}\left(\mathbb{S}_{mk}^{(jl)} - (\mathbb{S}^{(j0)}\mathbb{S}^{-1}\mathbb{S}^{(0l)})_{mk}\right)$$

$$\rho_{mk} = C_m^* C_k,\ \mathbb{H}_{mk}^{(j0)} = \left\langle\frac{\partial\phi_m}{\partial\lambda_{mj}}\left|\hat{H}\right|\phi_k\right\rangle$$

$$\mathbb{S}_{mk}^{(j0)} = \left\langle\frac{\partial\phi_m}{\partial\lambda_{mj}}\right|\left.\phi_k\right\rangle,\ \mathbb{S}_{mk}^{(0l)} = \left\langle\phi_m\left|\frac{\partial\phi_k}{\partial\lambda_{kl}}\right.\right\rangle,\ \mathbb{S}_{mk}^{(jl)} = \left\langle\frac{\partial\phi_m}{\partial\lambda_{mj}}\left|\frac{\partial\phi_k}{\partial\lambda_{kl}}\right.\right\rangle$$

Basis set

Frozen width gaussian wave packets:

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

$$\begin{cases}\xi_{k\alpha} = \omega q_{k\alpha} + ip_{k\alpha}\\ \eta_{k\alpha} = \frac{1}{4}\left(\ln\left[\frac{\omega}{\pi}\right] - 2\omega q_{k\alpha}^2\right) - iq_{k\alpha}p_{k\alpha}\end{cases}$$

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

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