Trajectory guided gaussian basis method

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1 Gaussian Basis

One possible way to solve time-dependent Schrödinger equation is to expand the initial wavepacket as a linear combination of gaussian basis.

$$g_m(x,t) = \sqrt[4]{\frac{a}{\pi}} \exp\left(-\frac{\alpha}{2}(x-q_m(t))^2 + \imath p_m(t)(x-q_m(t)\right) \tag{1}$$

$$|\psi_0\rangle = \sum_{n=1,\ldots,N} c_n(t=0)|g_n(q_n,p_n,t=0)\rangle \tag{2}$$

$$\langle g_m|\psi_0\rangle = \sum_n c_n \langle g_m|g_n\rangle, \quad m = 1,...,N. \tag{3}$$

where N is the number of basis used to project the initial wavepacket.

Initial coefficients $c_n(0)$ can be obtained by solving the matrix equation

$$\mathbf{Mc} = \mathbf{b} \tag{4}$$

where

$$\mathbf{M}_{mn} = \langle g_m|g_n\rangle, \quad \mathbf{b} = \{\langle g_1|\psi_0\rangle, \ldots, \langle g_n|\psi_0\rangle\}. \tag{5}$$

Normalization of the wavepacket is conversed in the propagation.

$$N = \langle\psi|\psi\rangle = \sum_{mn} \boldsymbol{c}_m^* \mathbf{M}_{mn} \boldsymbol{c}_n, \tag{6}$$

$$\frac{dN}{dt} = 0 \tag{7}$$

Define

$$\boldsymbol{c} = \{c_1, c_2, \ldots, c_N\} \tag{8}$$

and

$$\boldsymbol{\phi} = \{g_1(q_1,p_1), \ldots, g_N(q_N,p_N)\}, \tag{9}$$

Wavefunction at time t can be written as

$$\psi(x,t) = \boldsymbol{c}^T(t)\boldsymbol{\phi}(t) \tag{10}$$

if we substitute Eq. (10) into time-dependent Schrödinger equation , propagation of the initial wavepacket can be transformed into the evolution of the coefficients $c_n(t)$ and the motion of $(p_n(t), q_n(t))$ of gaussian wave packets. The equations for evolution of $\boldsymbol{c}$ will be

$$\imath \mathbf{M}\dot{c} = (\mathbf{H} - \imath\dot{\mathbf{M}})\boldsymbol{c}, \tag{11}$$

where

$$\dot{\mathbf{M}}_{mn} = \langle g_m|\dot{g_n}\rangle \tag{12}$$

and $\mathbf{H}$ is the hamiltonian matrix,

$$\mathbf{H}_{mn} = \langle g_m| - \frac{\hbar^2}{2m}\nabla^2 + V(x)|g_n\rangle. \tag{13}$$

Potential energy is expanded into second-order Taylor series at position of each trajectory

$$V(x) = V(q_n) + \nabla V(q_n)(x-q_n) + \frac{\nabla^2 V(q_n)}{2}(x-q_n)^2 + O((x-q_n)^3) \tag{14}$$

Substituting Eq. (14) to Eq. (11) and ignore the third-order term, we will obtain

$$\mathbf{H}_{mn} = \langle g_m|d_0 + d_1(x-q_n) + d_2(x-q_n)^2|g_n\rangle. \tag{15}$$

$$d_0 = V(x_n) - \frac{p_n^2 - \alpha}{2m}, \quad d_1 = -\nabla U(x_n), \quad d_2 = \frac{1}{2}\left(\nabla^2 V(x_n) - \frac{\alpha^2}{m}\right) \tag{16}$$