Correlation function

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I. QM CORRELATION

Quantum mechanical correlation is defined as

$$C_{AB} = Tr[\hat{\rho} A U^{\dagger}(t) B U(t)] \tag{1}$$

where $U(t)$ is the propagation operator for time-independent Hamiltonian,

$$U(t) = \exp(-\imath \hat{H} t/\hbar) \tag{2}$$

At absolute zero,

$$\hat{\rho} = |\psi_0\rangle\langle\psi_0|, \tag{3}$$

then correlation becomes

$$C_{AB} = \langle\psi_0|\hat{A}U^{\dagger}(t)\hat{B}U(t)|\psi_0\rangle \tag{4}$$

$$= \langle\psi_0|AU^{\dagger}(t)B|\psi_t\rangle \tag{5}$$

$$= \langle U(t)A^{\dagger}\psi_0|B|\psi_t\rangle \tag{6}$$

Assume $\hat{A} = \sum_i \hat{x}_i$ and define $\phi(\boldsymbol{x}, 0) = \sum_i x_i \psi(\boldsymbol{x}, 0)$, $\phi(\boldsymbol{x}, t)$ is a wavefunction with nodes, at least one node at $\boldsymbol{x} = 0$ at starting point, then $U(t)A^{\dagger}\psi_0$ is equivalent to propagate wavefunction $\phi(\boldsymbol{x}, t)$.

A wavefunction with nodes can be described by product of a nodeless wavepacket and a polynomial function

$$\phi(\boldsymbol{x}, t) = \psi(\boldsymbol{x}, t)\chi(\boldsymbol{x}, t), \tag{7}$$

where $\chi(\boldsymbol{x}, t)$ is represented by a polynomial basis $f(\boldsymbol{x})$,

$$\chi(\boldsymbol{x}, t) = \boldsymbol{f}^T \boldsymbol{c} = \sum_i f_i c_i \tag{8}$$

For linear basis, $f(\boldsymbol{x}) = (1, x_1, x_2, \ldots, x_{N_{dim}})$, N_{dim} is the number of degree of freedom, usually taken as $3 \times N_{atom}$ in Cartesian space. Substitute Eq. (7) into time-dependent Schrödinger equation , after some algebraic manipulations, one obtain

$$\dot{\boldsymbol{c}} = -\frac{\hbar}{2m}\mathbf{M^{-1}}(\mathbf{2\Pi} + \imath\mathbf{D})\mathbf{c}. \tag{9}$$

where

$$\Pi_{ij} = \sum_{\alpha=1}^{N_{dim}} \langle p_\alpha f_i | \nabla_\alpha f_j \rangle, \tag{10}$$

$$D_{ij} = \sum_{\alpha=1}^{N_{dim}} \langle \nabla_\alpha f_i | \nabla_\alpha f_j \rangle \tag{11}$$

$$M_{ij} = \langle f_i | f_j \rangle \tag{12}$$

Here $\langle \cdots \rangle$ represents average over ensemble of quantum trajectories. Substitute Eq. (7) back into Eq. (6), we obtain

$$C_{AB}(t) = \langle \psi(\boldsymbol{x}, t) \chi(\boldsymbol{x}, t) | \hat{B} | \psi(\boldsymbol{x}, t) \rangle \tag{13}$$

Assume $\hat{B}$ is a multiplicative operator, most commonly is position-dependent operators, $\hat{B}(\boldsymbol{x})$,

$$C_{AB}(t) = \int d\boldsymbol{x} \rho(\boldsymbol{x}, t) \chi^*(\boldsymbol{x}, t) B(\boldsymbol{x}) \tag{14}$$

$$\approx \int d\boldsymbol{x} \rho(\boldsymbol{x}, t) [\boldsymbol{c}^*(t) \cdot \boldsymbol{f}(\boldsymbol{x})] B(\boldsymbol{x}) \tag{15}$$

$$= \sum_{k=1}^{N_{traj}} w^{(k)} [\boldsymbol{c}^*(t) \cdot \boldsymbol{f}(\boldsymbol{x}^{(k)})] B(\boldsymbol{x}^{(k)}) \tag{16}$$