精确解：薛定谔方程与刘维尔方程

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1　绝热表象展开

在绝热表象下,

$$\hat{H} = \hat{T}_R + \hat{V}_b(\mathbf{R}) + \hat{T}_r + \hat{V}_s(\mathbf{r}) + \hat{V}_C(\mathbf{r}, \mathbf{R}) = \hat{T}_R + \hat{H}_0(\mathbf{r}; \mathbf{R}) \tag{1}$$

并假设薛定谔方程的解可以写作

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_i \psi_i(\mathbf{r}; \mathbf{R}) \chi_i(\mathbf{R}, t) \tag{2}$$

其中ψ_i是由$\hat{H}_0$本征函数构成的完备基.

定义

$$\begin{cases} \langle \psi_i | \hat{H}_0 | \psi_j \rangle = \int \mathrm{d}\mathbf{r}\, \psi_i^*(\mathbf{r}; \mathbf{R}) \hat{H}_0(\mathbf{r}; \mathbf{R}) \psi_j(\mathbf{r}; \mathbf{R}) = V_{ij}(\mathbf{R}) \\ \langle \psi_i | \psi_j \rangle = \int \mathrm{d}\mathbf{r}\, \psi_i^*(\mathbf{r}; \mathbf{R}) \psi_j(\mathbf{r}; \mathbf{R}) = S_{ij}(\mathbf{R}) \\ \langle \psi_i | \boldsymbol{\nabla}_k | \psi_j \rangle = \int \mathrm{d}\mathbf{r}\, \psi_i^*(\mathbf{r}; \mathbf{R}) \boldsymbol{\nabla}_k \psi_j(\mathbf{r}; \mathbf{R}) = \mathbf{d}_{ij}^k(\mathbf{R}) \end{cases} \tag{3}$$

对于含时薛定谔方程(Time-Dependent Schrödinger Equation, TDSE)，我们有

$$\mathrm{i}\hbar \sum_j \psi_j(\mathbf{r}; \mathbf{R}) \frac{\partial \chi_j(\mathbf{R}, t)}{\partial t} = \hat{T}_R \sum_j \psi_j(\mathbf{r}; \mathbf{R}) \chi_j(\mathbf{R}, t) + \hat{H}_0 \sum_j \psi_j(\mathbf{r}; \mathbf{R}) \chi_j(\mathbf{R}, t) \tag{4}$$

$$\Rightarrow \mathrm{i}\hbar \sum_j S_{ij}(\mathbf{R}) \frac{\partial \chi_j(\mathbf{R}, t)}{\partial t} = \sum_j V_{ij}(\mathbf{R}) \chi_j(\mathbf{R}, t) - \int \mathrm{d}\mathbf{r} \psi_i^*(\mathbf{r}; \mathbf{R}) \sum_{j,k} \frac{\hbar^2 \boldsymbol{\nabla}_k^2}{2M_k} \psi_j(\mathbf{r}; \mathbf{R}) \chi_j(\mathbf{R}, t) \tag{5}$$

$$= \sum_j V_{ij}(\mathbf{R}) \chi_j(\mathbf{R}, t)$$

$$-\sum_k \frac{\hbar^2}{2M_k}\sum_j \left[\langle\psi_i|\boldsymbol{\nabla}_k^2|\psi_j\rangle \chi_j(\mathbf{R},t) + 2\langle\psi_i|\boldsymbol{\nabla}_k|\psi_j\rangle \boldsymbol{\nabla}_k\chi_j(\mathbf{R},t) + S_{ij}(\mathbf{R})\boldsymbol{\nabla}_k^2\chi_j(\mathbf{R},t)\right] \tag{6}$$

$$=\sum_j \left(V_{ij}(\mathbf{R}) - \sum_{k,l}\frac{\hbar^2\mathbf{d}_{il}^k(\mathbf{R})\mathbf{d}_{lj}^k(\mathbf{R})}{2M_k}\right)\chi_j(\mathbf{R},t) - \sum_{j,k}\left[\frac{\hbar^2\mathbf{d}_{ij}^k}{M_k}\boldsymbol{\nabla}_k\chi_j(\mathbf{R},t) + \frac{\hbar^2 S_{ij}(\mathbf{R})}{2M_k}\boldsymbol{\nabla}_k^2\chi_j(\mathbf{R},t)\right] \tag{7}$$

如果我们假设环境的自由度是一(（即k只有一种取值，因此$\mathbf{R}$是一维的，M_k也退化为环境的质量M_b)，那么，对于满足重叠矩阵$S_{ij}(R)=\delta_{ij}$是单位矩阵且势能函数$V_{ij}(R)=\varepsilon_i(R)\delta_{ij}$是对角矩阵的绝热表象而言，

$$\mathrm{i}\hbar\frac{\partial\chi_i(R,t)}{\partial t} = \varepsilon_i(R)\chi_i(R,t) - \sum_{j,k}\frac{\hbar^2 d_{ik}(R)d_{kj}(R)}{2M_b}\chi_j(R,t) - \sum_j \frac{\hbar^2 d_{ij}(R)}{M_b}\frac{\partial\chi_j(R,t)}{\partial R} - \frac{\hbar^2}{2M_b}\frac{\partial^2\chi_i(R,t)}{\partial R^2} \tag{8}$$

对于满足重叠矩阵$S_{ij}(R)=\delta_{ij}$也是单位矩阵而非绝热耦合$d_{ij}(R)=0$为零的透热表象而言，

$$\mathrm{i}\hbar\frac{\partial\chi_i(R,t)}{\partial t} = \sum_j V_{ij}(R)\chi_j(R,t) - \frac{\hbar^2}{2M_b}\frac{\partial^2\chi_i(R,t)}{\partial R^2} \tag{9}$$

而对于仅满足重叠矩阵$S_{ij}(R)=\delta_{ij}$是单位矩阵的力基而言，

$$\mathrm{i}\hbar\frac{\partial\chi_i(R,t)}{\partial t} = \sum_j\left(V_{ij}(R) - \sum_k\frac{\hbar^2 d_{ik}(R)d_{kj}(R)}{2M_b}\right)\chi_j(R,t) - \sum_j \frac{\hbar^2 d_{ij}(R)}{M_b}\frac{\partial\chi_j(R,t)}{\partial R} - \frac{\hbar^2}{2M_b}\frac{\partial^2\chi_i(R,t)}{\partial R^2} \tag{10}$$

这里的哈密顿量为

$$H_{ij} = V_{ij} - \frac{\hbar^2}{2M_b}\left(\sum_k d_{ik}d_{kj} + 2d_{ij}\frac{\partial}{\partial R} + \delta_{ij}\frac{\partial^2}{\partial R^2}\right) \tag{11}$$

且对于不同的基，势能V_{ij}和非绝热耦合d_{ij}的形式也可能不同。

为了证明哈密顿量的厄密性，我们需要考虑其中对空间的偏导数部分。因为χ_i是完备基，故而有

$$\frac{\partial\chi_j(R,t)}{\partial R} = \sum_k |\chi_k\rangle\langle\chi_k|\frac{\partial}{\partial R}|\chi_j\rangle = \sum_k C_{jk}(t)\chi_k(R,t) \tag{12}$$

其中

$$C_{jk}(t) = \langle\chi_k|\frac{\partial}{\partial R}|\chi_j\rangle = \int \mathrm{d}R\,\chi_k^*(R,t)\frac{\partial}{\partial R}\chi_j(R,t) \tag{13}$$

$$= \chi_k^*(R,t)\chi_j(R,t)\Big|_{-\infty}^{+\infty} - \int \mathrm{d}R\,\frac{\partial\chi_k^*(R,t)}{\partial R}\chi_j(R,t) \tag{14}$$

$$=0 - \left(\int \mathrm{d}R\,\chi_j^*(R,t)\frac{\partial}{\partial R}\chi_k(R,t)\right)^* = -C_{kj}^* \tag{15}$$

可以看到，C是反厄米的。这里我们利用了

$$\chi_k^*(R,t)\chi_j(R,t)\Big|_{-\infty}^{+\infty} = 0 \tag{16}$$

这是因为$\chi_i \in \mathcal{L}^2$是平方可积的。此外我们把非绝热耦合矩阵记为D，即$D_{ij} = d_{ij}$。因此，哈密顿量为

$$H = V(R) - \frac{\hbar^2}{2M_b}\big(D^2(R) + 2D(R)C(t) + C(t)^2\big) \tag{17}$$

但是，厄密性要求$[D,C] = 0$，而这不是平凡的。只有在透热表象下才能保证这一点。

2　离散变量表象：有限差分方法

我们想要计算离散变量表象(Discrete Variable Representation, DVR)下的导数，其中一种方法是有限差分。假设我们知道了格点上的函数值，

$$f_k = f(x_k), \quad x_k = k\Delta x, \quad k \in \mathbb{Z} \quad \text{and} \quad |k| \leqslant N \tag{18}$$

这里，如果N是有限值，那么下述结果就是有限差分，例如$N = 1$就给出了求导的三点公式。但如果$N \to \infty$且引入周期性边界条件我们可以得到与离散傅里叶变换（Discrete Fourier Transformation (DFT)）一样的结果。

使用拉格朗日插值多项式，

$$f(x) = \sum_{-N\leqslant k\leqslant N} f_k \prod_{\substack{-N\leqslant l\leqslant N \\ l\neq k}} \frac{x - x_l}{x_k - x_l} \tag{19}$$

原点处的一阶导为

$$f'(0) = \frac{\partial}{\partial x}\,|0\rangle = \sum_k |k\rangle\,\langle k|\frac{\partial}{\partial x}|0\rangle = \sum_k \langle k|\frac{\partial}{\partial x}|0\rangle\, f_k \tag{20}$$

$$f'(0) = \sum_{-N\leqslant k\leqslant N} f_k \sum_{\substack{-N\leqslant l_1\leqslant N\\ l_1\neq k}} \frac{1}{x_k - x_{l_1}} \prod_{\substack{-N\leqslant l\leqslant N\\ l\neq k,l_1}} \frac{0-x_l}{x_k-x_l} \tag{21}$$

$$= \frac{f_0}{\Delta x} \sum_{\substack{-N\leqslant l\leqslant N\\ l\neq 0}} \frac{1}{l} + \sum_{\substack{-N\leqslant k\leqslant N\\ k\neq 0}} \frac{f_k}{\Delta x} \sum_{\substack{-N\leqslant l_1\leqslant N\\ l_1\neq k}} \frac{1}{k-l_1} \prod_{\substack{-N\leqslant l\leqslant N\\ l\neq k,l_1}} \frac{l}{l-k} \tag{22}$$

$$= \sum_{\substack{-N\leqslant k\leqslant N\\ k\neq 0}} \frac{f_k}{2k\Delta x} \prod_{\substack{-N\leqslant l\leqslant N\\ l\neq k,0,-k}} \frac{l}{l-k} \tag{23}$$

$$= \sum_{\substack{-N\leqslant k\leqslant N\\ k\neq 0}} \frac{f_k}{2k\Delta x} \prod_{\substack{1\leqslant l\leqslant N\\ l\neq k}} \frac{l^2}{l^2-k^2} \tag{24}$$

$$\tag{25}$$

由于

$$\prod_{l=1}^{+\infty} \frac{l^2}{l^2-x^2} = \frac{\pi x}{\sin(\pi x)} \tag{26}$$

$$\Rightarrow \prod_{\substack{l=1\\ l\neq k}}^{+\infty} \frac{l^2}{l^2-k^2} = \lim_{x\to k} \frac{k^2-x^2}{k^2} \prod_{l=1}^{+\infty} \frac{l^2}{l^2-x^2} \tag{27}$$

$$= \lim_{x\to k} \frac{\pi x}{\sin(\pi x)} \frac{k^2-x^2}{k^2} = -2(-1)^k \tag{28}$$

我们有

$$\langle k|\frac{\partial}{\partial x}|0\rangle = -\frac{(-1)^k}{k\Delta x}(1-\delta_{k0}) \Rightarrow \langle m|\frac{\partial}{\partial x}|n\rangle = -\frac{(-1)^{m-n}}{(m-n)\Delta x}(1-\delta_{mn}) \tag{29}$$

以及

$$\left.\frac{\partial \chi_i(R,t)}{\partial R}\right|_{R=R_n,t=t_0} = \sum_{-N\leqslant m\leqslant N} \chi_i(R_m,t_0)\,\langle m|\frac{\partial}{\partial x}|n\rangle = -\sum_{\substack{-N\leqslant m\leqslant N\\ m\neq n}} \frac{(-1)^{m-n}}{(m-n)\Delta x}\chi_i(R_m,t_0) \tag{30}$$

原点处的二阶导为

$$f''(0) = \frac{\partial^2}{\partial x^2}|0\rangle = \sum_k |k\rangle\,\langle k|\frac{\partial^2}{\partial x^2}|0\rangle = \sum_k \langle k|\frac{\partial^2}{\partial x^2}|0\rangle\, f_k \tag{31}$$

$$f''(0) = \sum_{-N\leqslant k\leqslant N} f_k \sum_{\substack{-N\leqslant l_1\leqslant N\\ l_1\neq k}} \frac{1}{x_k-x_{l_1}} \sum_{\substack{-N\leqslant l_2\leqslant N\\ l_2\neq k,l_1}} \frac{1}{x_k-x_{l_2}} \prod_{\substack{-N\leqslant l\leqslant N\\ l\neq k,l_1,l_2}} \frac{0-x_l}{x_k-x_l} \tag{32}$$

$$=\frac{f_0}{\Delta x^2}\sum_{\substack{-N\leqslant l_1,l_2\leqslant N\\ l_1,l_2\neq 0\\ l_1\neq l_2}}\frac{1}{l_1 l_2}+\sum_{\substack{-N\leqslant k\leqslant N\\ k\neq 0}}\frac{f_k}{\Delta x^2}\sum_{\substack{-N\leqslant l_1,l_2\leqslant N\\ l_1,l_2\neq k\\ l_1\neq l_2}}\frac{1}{(k-l_1)(k-l_2)}\prod_{\substack{-N\leqslant l\leqslant N\\ l\neq k,l_1,l_2}}\frac{l}{l-k} \tag{33}$$

$$=-\frac{2f_0}{\Delta x^2}\sum_{1\leqslant l\leqslant N}\frac{1}{l^2}+\sum_{\substack{-N\leqslant k\leqslant N\\ k\neq 0}}\frac{f_k}{\Delta x^2}\sum_{\substack{-N\leqslant l_1\leqslant N\\ l_1\neq k,0}}\frac{2}{k(k-l_1)}\prod_{\substack{-N\leqslant l\leqslant N\\ l\neq k,l_1,0}}\frac{l}{l-k} \tag{34}$$

$$=-\frac{2f_0}{\Delta x^2}\sum_{1\leqslant l\leqslant N}\frac{1}{l^2}-\sum_{\substack{-N\leqslant k\leqslant N\\ k\neq 0}}\frac{f_k}{k\Delta x^2}\sum_{\substack{-N\leqslant l_1\leqslant N\\ l_1\neq k,0}}\frac{1}{l_1}\prod_{\substack{-N\leqslant l\leqslant N\\ l\neq k,-k,0}}\frac{l}{l-k} \tag{35}$$

$$=\sum_{\substack{-N\leqslant k\leqslant N\\ k\neq 0}}\frac{f_k}{k^2\Delta x^2}\prod_{\substack{1\leqslant l\leqslant N\\ l\neq k}}\frac{l^2}{l^2-k^2}-\frac{2f_0}{\Delta x^2}\sum_{1\leqslant l\leqslant N}\frac{1}{l^2} \tag{36}$$

因为$\sum\limits_{n=1}^{+\infty}\frac{1}{n^2}=\frac{\pi^2}{6}$，

$$D^2_{0k}=-\frac{1}{\Delta x^2}\left[\frac{\pi^2}{3}\delta_{k0}+\frac{2(-1)^k}{k^2}(1-\delta_{k0})\right] \tag{37}$$

$$\Rightarrow D^2_{mn}=-\frac{1}{\Delta x^2}\left[\frac{\pi^2}{3}\delta_{mn}+\frac{2(-1)^{m-n}}{(m-n)^2}(1-\delta_{mn})\right] \tag{38}$$

且

$$\langle k|\frac{\partial^2}{\partial x^2}|0\rangle=-\frac{1}{\Delta x^2}\left[\frac{\pi^2}{3}\delta_{k0}+\frac{2(-1)^k}{k^2}(1-\delta_{k0})\right] \tag{39}$$

$$\Rightarrow\langle m|\frac{\partial^2}{\partial x^2}|n\rangle=-\frac{1}{\Delta x^2}\left[\frac{\pi^2}{3}\delta_{mn}+\frac{2(-1)^{m-n}}{(m-n)^2}(1-\delta_{mn})\right] \tag{40}$$

注意这里$D^2\neq(D^1)^2$。

3 离散变量表象：箱中粒子本征函数

在这部分我们希望用一种不同的方式推导出导数的形式。由于体系可以看作是一个有限长范围内的一个粒子，我们可以考虑利用一维势箱的哈密顿量本征函数来作为基组展开。假设格点为x_0到x_N，由于边界条件我们有$f_0=f_N=0$，那么我们需要$N-1$个函数，对应$N-1$个自由格点，它们满足

$$\begin{cases} x_i=x_0+i\Delta x\\ \psi_n(x)=\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi(x-x0)}{L}\right)\\ \psi_n(x_i)=\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi i}{N}\right)\end{cases} \tag{41}$$

其中$L = x_N - x_0$是势箱的长度，$\Delta x \Delta x = L/N$是格点间距。

对于动能项，我们有

$$
\begin{aligned}
T_{ij} =& -\frac{\hbar^2}{2m}\Delta x\sum_{n=1}^{N-1}\psi_n(x_i)\psi_n''(x_j) && (42)\\
=&\frac{\hbar^2}{2m}\frac{2}{N}\frac{\pi^2}{L^2}\sum_{n=1}^{N-1}n^2\sin\left(\frac{n\pi i}{N}\right)\sin\left(\frac{n\pi j}{N}\right) && (43)\\
=&\frac{\pi^2\hbar^2}{2NmL^2}\left[\sum_{n=0}^{N-1}n^2\cos\left(\frac{n\pi(i-j)}{N}\right)-\sum_{n=0}^{N-1}n^2\cos\left(\frac{n\pi(i+j)}{N}\right)\right] && (44)\\
=&\frac{\pi^2\hbar^2}{4mL^2}\begin{cases}(2N^2+1)/3-\csc^2(i\pi/N), & \text{if} \quad i=j\\ \csc^2((i-j)\pi/2N)-\csc^2((i+j)\pi/2N), & \text{if} \quad i\neq j\end{cases} && (45)
\end{aligned}
$$

因为有$Nk\pi = (i \pm j)\pi \Rightarrow \sin(Nk\pi) = 0, \cos(Nk\pi) = (-1)^{i+j}$，

$$
\sum_{n=1}^{N-1}n^2\cos(nk\pi) = \frac{(-1)^{i+j}N}{2}\left(\csc^2\left(\frac{k\pi}{2}\right)-N\right) \tag{46}
$$

现在，如果我们将盒子展开到$\mathbb{R}$，由于$x_i = x_0 + i\Delta x$和$x_0 \to -\infty$以及Δx是有限值，$i+j$是无穷而$i-j$是有限的，所以

$$
T_{ij} = \frac{\hbar^2}{2m\Delta x}\begin{cases}\pi^2/3, & \text{if} \quad i=j\\ 2/(i-j)^2, & \text{if} \quad i\neq j\end{cases} \tag{47}
$$

对于动量，类似地，有

$$
\begin{aligned}
p_{ij} =& -\mathrm{i}\hbar\Delta x\sum_{n=1}^{N-1}\psi_n(x_i)\psi_n'(x_j) && (48)\\
=& -\mathrm{i}\hbar\frac{2}{N}\frac{\pi}{L}\sum_{n=1}^{N-1}n\sin\left(\frac{n\pi i}{N}\right)\cos\left(\frac{n\pi j}{N}\right) && (49)\\
=&\frac{\pi\hbar}{\mathrm{i}NL}\left[\sum_{n=1}^{N-1}n\sin\left(\frac{n\pi(i+j)}{N}\right)+\sum_{n=1}^{N-1}n\sin\left(\frac{n\pi(i-j)}{N}\right)\right] && (50)\\
=&\frac{\mathrm{i}\pi\hbar}{2L}\begin{cases}\cot(i\pi/N), & \text{if} \quad i=j\\ \cot((i+j)\pi/2N)+\cot((i-j)\pi/2N), & \text{if} \quad i\neq j\end{cases} && (51)
\end{aligned}
$$

因为

$$
\sum_{n=1}^{N-1}n\sin(n\pi k) = -\frac{(-1)^{i+j}N\cot k\pi/2}{2} \tag{52}
$$

类似地，将其扩展到$\mathbb{R}$后，$i+j$和i变成无穷大,

$$p_{ij} = \frac{(-1)^{i+j}\mathrm{i}\hbar}{(i-j)\Delta x} \tag{53}$$

因此。箱中粒子本征函数的求导结果为

$$\langle m|\frac{\partial}{\partial x}|n\rangle = -\frac{(-1)^{m+n}}{(m-n)\Delta x}(1-\delta_{mn}) \tag{54}$$

$$\langle m|\frac{\partial^2}{\partial x^2}|n\rangle = -\frac{1}{\Delta x^2}\frac{\pi^2}{3}\delta_{mn} + \frac{2(-1)^{m+n}}{(m-n)^2}(1-\delta_{mn}) \tag{55}$$

这与无穷阶有限差分是一致的。

但是上述过程对动量的导数不是严格的。严格推导如下：在DVR下，

$$\langle x_i|\psi_m\rangle = \sqrt{\Delta x}\psi_m(x_i) \tag{56}$$

因此，

$$\langle x_i|x_j\rangle = \sum_{m,n} \langle x_i|\psi_m\rangle \langle \psi_m|\psi_n\rangle \langle \psi_n|x_j\rangle \tag{57}$$

$$= \frac{2}{N}\sum_{m,n} \sin\left(\frac{m\pi i}{N}\right)\sin\left(\frac{n\pi j}{N}\right)\delta_{mn} \tag{58}$$

$$= \frac{1}{N}\sum_{n} \cos\left(\frac{n\pi(i-j)}{N}\right) - \cos\left(\frac{n\pi(i+j)}{N}\right) = \delta_{ij} \tag{59}$$

$$\langle x_i|\hat{T}|x_j\rangle = \sum_{m,n} \langle x_i|\psi_m\rangle \langle \psi_m|\hat{T}|\psi_n\rangle \langle \psi_n|x_j\rangle \tag{60}$$

$$= \frac{2\Delta x}{L}\sum_{m,n} \sin\left(\frac{m\pi i}{N}\right)\frac{n^2\pi^2\hbar^2}{2mL^2}\delta_{mn}\sin\left(\frac{n\pi j}{N}\right) \tag{61}$$

$$= \frac{\pi^2\hbar^2}{NmL^2}\sum_{n} n^2\sin\left(\frac{n\pi i}{N}\right)\sin\left(\frac{n\pi j}{N}\right) \tag{62}$$

$$= \frac{\pi^2\hbar^2}{4mL^2}\begin{cases}(2N^2+1)/3 - \csc^2(i\pi/N), & \text{if} \quad i=j \\ \csc^2((i-j)\pi/2N) - \csc^2((i+j)\pi/2N), & \text{if} \quad i\neq j\end{cases} \tag{63}$$

但是，这个推导是有问题的，例如我们无法得到$\langle x_i|f(\hat{x})|x_j\rangle = f(x_i)\delta_{ij}$，比如$f=V$的情况。对于动量（或者说一阶导）也有类似的问题

$$\langle x_i|\frac{\partial}{\partial x}|x_j\rangle = \sum_{m,n} \langle x_i|\psi_m\rangle \langle \psi_m|\frac{\partial}{\partial x}|\psi_n\rangle \langle \psi_n|x_j\rangle \tag{64}$$

$$=\frac{2}{N}\sum_{m,n}\sin\left(\frac{m\pi i}{N}\right)\sin\left(\frac{n\pi j}{N}\right)\frac{4mn(1-(-1)^{m+n})}{L(m^2-n^2)} \tag{65}$$

$$=-\frac{4}{NL}\sum_{m} m\sin\left(\frac{m\pi i}{N}\right)\sum_{n\neq m(\mathrm{mod}2)}\left(\frac{1}{n+m}+\frac{1}{n-m}\right)\sin\left(\frac{j\pi n}{N}\right) \tag{66}$$

4 绝热表象展开的TDSE与DVR的结合

接下来的问题是把TDSE写成DVR矩阵的形式，即

$$\mathrm{i}\hbar\frac{\partial\chi}{\partial t}=H\chi \tag{67}$$

或者

$$\mathrm{i}\hbar\frac{\partial\chi_{mn}}{\partial t}=\sum_{m',n'}H_{mn,m'n'}\chi_{m'n'} \tag{68}$$

其中

$$\chi=\left[\chi_0(R_0)\ \chi_0(R_1)\ \cdots\ \chi_0(R_n)\ \chi_1(R_0)\ \cdots\ \chi_1(R_{N-1})\ \cdots\ \chi_{M-1}(R_{N-1})\right]^T \tag{69}$$

$$\chi_{mn}=\chi_m(R_n)=\chi_m(R_0+n\Delta x) \tag{70}$$

N是格点数，M是势能面数。

由于我们无法确认非透热表象下的哈密顿量是否厄米。我们在这里只构建透热表象哈密顿量，

$$\sum_{m',n'}H_{mn,m'n'}\chi_{m'n'}=\mathrm{i}\hbar\left.\frac{\partial\chi_m(R,t)}{\partial t}\right|_{R=R_n} \tag{71}$$

$$=\sum_{m'}V_{mm'}(R_n)\chi_{m'}(R_n)-\frac{\hbar^2}{2M_b}\left.\frac{\partial^2\chi_{m'}}{\partial R^2}\right|_{R=R_n} \tag{72}$$

$$=\sum_{m'}V_{mm'n}\chi_{m'n'}\delta_{nn'}+\frac{\hbar^2\delta_{mm'}}{2M_b\Delta x^2}\sum_{m'n'}\left[\frac{\pi^2}{3}\chi_{m'n'}\delta_{nn'}+\frac{2(-1)^{n'-n}}{(n'-n)^2}(1-\delta_{nn'})\right] \tag{73}$$

因此,

$$H_{mn,m'n'}=V_{mm'n}\delta_{nn'}+\frac{\pi^2\hbar^2}{6M_b\Delta x^2}\delta_{mm'}\delta_{nn'}+\frac{(-1)^{n'-n}\hbar^2}{M_b(n'-n)^2\Delta x^2}(1-\delta_{nn'})\delta_{mm'} \tag{74}$$

其中三指标的V和d是指在对应位置上的矩阵元，例如$V_{mkn}=V_{mk}(R_n)$。我们可以看到，如果V是厄米的（在没有通过吸收势对对角元引入虚数项的情况下），哈密顿量确实是厄米的。

对于非透热表象则无需考虑厄密性，哈密顿量可以写作

$$\begin{aligned}\sum_{m',n'} H_{mn,m'n'}\chi_{m'n'} =& \mathrm{i}\hbar \left.\frac{\partial\chi_m(R,t)}{\partial t}\right|_{R=R_n} \qquad (75)\\
=& \sum_{m'} V_{mm'}(R_n)\chi_{m'}(R_n) - \frac{\hbar^2}{2M_b}\sum_{m',k} d_{mk}(R_n)d_{km'}(R_n)\chi_{m'}(R_n)\\
&- \frac{\hbar^2}{M_b}\sum_{m'} d_{mm'}(R_n)\left.\frac{\partial\chi_{m'}}{\partial R}\right|_{R=R_n} - \frac{\hbar^2}{2M_b}\left.\frac{\partial^2\chi_{m'}}{\partial R^2}\right|_{R=R_n} \qquad (76)\\
=& \sum_{m'}\left(V_{mm'n} - \frac{\hbar^2}{2M_b}\sum_k d_{mkn}d_{km'n}\right)\chi_{m'n'}\delta_{nn'}\\
&+ \frac{\hbar^2}{M_b\Delta x}\sum_{m',n'} d_{mm'n}\frac{(-1)^{n+n'}}{n'-n}\chi_{m'n'}(1-\delta_{nn'})\\
&+ \frac{\hbar^2\delta_{mm'}}{2M_b\Delta x^2}\sum_{m'n'}\left[\frac{\pi^2}{3}\delta_{nn'} + \frac{2(-1)^{n'-n}}{(n'-n)^2}(1-\delta_{nn'})\right]\chi_{m'n'} \qquad (77)
\end{aligned}$$

因此

$$\begin{aligned}H_{mn,m'n'} =& \left(V_{mm'n} - \frac{\hbar^2}{2M_b}\sum_k d_{mkn}d_{km'n}\right)\delta_{nn'} + \frac{(-1)^{n+n'}\hbar^2}{(n'-n)M_b\Delta x}d_{mm'n}(1-\delta_{nn'})\\
&+ \left[\frac{\pi^2\hbar^2}{6M_b\Delta x^2}\delta_{nn'} + \frac{(-1)^{n'-n}\hbar^2}{M_b(n'-n)^2\Delta x^2}(1-\delta_{nn'})\right]\delta_{mm'} \qquad (78)
\end{aligned}$$

只有**没有**吸收势的透热表象哈密顿量是厄米的并且可以对角化来演化动力学，其它情况下则需要RK4或者类似的方法。

5 离散傅里叶变换

对于一般的傅里叶变换，我们只在意$f(x)$在$[0,L]$上的行为

$$f(x) = \sum_k \gamma_k \exp\left(\frac{2k\pi\mathrm{i}}{L}x\right) \qquad (79)$$

$$\gamma_k = \frac{1}{L}\int_0^L \mathrm{d}x\, f(x)\exp\left(-\frac{2k\pi\mathrm{i}}{L}x\right) \qquad (80)$$

定义$\Delta x = \frac{L}{N}$以及$x_n = n\Delta x$，那么如果我们知道所有的格点上的函数值$f(x_n) = f_n$，

$$\gamma_k = \frac{\Delta x}{L}\sum_{n=0}^{N-1} f(x_n)\exp\left(-\frac{2k\pi\mathrm{i}}{L}x_n\right) = \frac{1}{N}\sum_{n=0}^{N-1} f(x_n)\exp\left(-\frac{2nk\pi\mathrm{i}}{N}\right), \quad k=0,1,\ldots,N-1 \qquad (81)$$

如果记$c_k = N\gamma_k$，

$$c_k = \sum_{n=0}^{N-1} f(x_n) \exp\left(-\frac{2nk\pi\mathrm{i}}{N}\right), \quad f_n = \frac{1}{N}\sum_{k=0}^{N-1} c_k \exp\left(\frac{2nk\pi\mathrm{i}}{N}\right) \tag{82}$$

现在，如果区间变为$[a,b]$，并记$x_n' = x_n + a$和$f_n = f(x_n')$，那么

$$f(x) = \sum_k \gamma_k \exp\left(\frac{2k\pi\mathrm{i}}{L}x\right) \tag{83}$$

以及

$$\gamma_k = \frac{1}{L}\int_a^b \mathrm{d}x\, f(x) \exp\left(-\frac{2k\pi\mathrm{i}}{L}x\right) \tag{84}$$

$$= \frac{1}{L}\int_0^L \mathrm{d}x\, f(x+a) \exp\left(-\frac{2k\pi\mathrm{i}}{L}(x+a)\right) \tag{85}$$

$$= \exp\left(-\frac{2k\pi\mathrm{i}a}{L}\right)\frac{\Delta x}{L}\sum_{n=0}^{N-1} f(x_n+a) \exp\left(-\frac{2k\pi\mathrm{i}}{L}x_n\right) \tag{86}$$

$$= \exp\left(-\frac{2k\pi\mathrm{i}a}{L}\right)\frac{1}{N}\sum_{n=0}^{N-1} f_n \exp\left(-\frac{2nk\pi\mathrm{i}}{N}\right) \tag{87}$$

如果

$$c_k' = N\exp\left(\frac{2k\pi\mathrm{i}a}{L}\right)\gamma_k = \sum_{n=0}^{N-1} f_n \exp\left(-\frac{2nk\pi\mathrm{i}}{N}\right) \tag{88}$$

那么

$$f(x) = \frac{1}{N}\sum_{k=0}^{N-1} c_k' \exp\left(-\frac{2k\pi\mathrm{i}a}{L}\right)\exp\left(\frac{2k\pi\mathrm{i}}{L}x\right) = \frac{1}{N}\sum_{k=0}^{N-1} c_k' \exp\left(\frac{2k\pi\mathrm{i}}{L}(x-a)\right) \tag{89}$$

对于格点，我们有

$$f_n = \frac{1}{N}\sum_{k=0}^{N-1} \exp\left(\frac{2k\pi\mathrm{i}}{L}(x_n+a-a)\right) = \frac{1}{N}\sum_{k=0}^{N-1} c_k' \exp\left(\frac{2nk\pi\mathrm{i}}{N}\right) \tag{90}$$

且对于r阶导数，我们需要将k从$[0,N-1]$移到$[-N/2,N/2]$，即

$$\begin{aligned}\frac{\mathrm{d}^{2a}f}{\mathrm{d}x^{2a}} =& \frac{1}{N}\sum_{0\leqslant k\leqslant \frac{N}{2}} c_k'\left(\frac{2k\pi\mathrm{i}}{L}\right)^{2a}\exp\left(\frac{2k\pi\mathrm{i}}{L}(x-a)\right)\\ &+\frac{1}{N}\sum_{\frac{N}{2}<k\leqslant N} c_k'\left(\frac{2(k-N)\pi\mathrm{i}}{L}\right)^{2a}\exp\left(\frac{2k\pi\mathrm{i}}{L}(x-a)\right)\end{aligned} \tag{91}$$

$$
\begin{aligned}
\frac{\mathrm{d}^{2a+1}f}{\mathrm{d}x^{2a+1}} =& \frac{1}{N}\sum_{0\leqslant k<\frac{N}{2}} c_k'\left(\frac{2k\pi\mathrm{i}}{L}\right)^{2a+1}\exp\left(\frac{2k\pi\mathrm{i}}{L}(x-a)\right) \\
&+\frac{1}{N}\sum_{\frac{N}{2}<k\leqslant N} c_k'\left(\frac{2(k-N)\pi\mathrm{i}}{L}\right)^{2a+1}\exp\left(\frac{2k\pi\mathrm{i}}{L}(x-a)\right)
\end{aligned}
\tag{92}
$$

在格点上则有

$$
\begin{aligned}
\left.\frac{\mathrm{d}^{2a}f}{\mathrm{d}x^{2a}}\right|_{x=x_n'} =& \frac{1}{N}\sum_{0\leqslant k\leqslant\frac{N}{2}} c_k'\left(\frac{2k\pi\mathrm{i}}{L}\right)^{2a}\exp\left(\frac{2nk\pi\mathrm{i}}{N}\right) \\
&+\frac{1}{N}\sum_{\frac{N}{2}<k\leqslant N} c_k'\left(\frac{2(k-N)\pi\mathrm{i}}{L}\right)^{2a}\exp\left(\frac{2nk\pi\mathrm{i}}{N}\right)
\end{aligned}
\tag{93}
$$

$$
\begin{aligned}
\left.\frac{\mathrm{d}^{2a+1}f}{\mathrm{d}x^{2a+1}}\right|_{x=x_n'} =& \frac{1}{N}\sum_{0\leqslant k<\frac{N}{2}} c_k'\left(\frac{2k\pi\mathrm{i}}{L}\right)^{2a+1}\exp\left(\frac{2nk\pi\mathrm{i}}{N}\right) \\
&+\frac{1}{N}\sum_{\frac{N}{2}<k\leqslant N} c_k'\left(\frac{2(k-N)\pi\mathrm{i}}{L}\right)^{2a+1}\exp\left(\frac{2nk\pi\mathrm{i}}{N}\right)
\end{aligned}
\tag{94}
$$

6 刘维尔方程中的有限差分

混合量子经典刘维尔方程(Mixed Quantum-Classical Liouville Equation, MQCLE)为

$$
\begin{aligned}
\frac{\partial\hat{\rho}_W(R,P,t)}{\partial t} =& -\frac{\mathrm{i}}{\hbar}\left[\hat{H}_W(R,P),\hat{\rho}_W(R,P,t)\right] \\
&+\frac{1}{2}\left(\left\{\hat{H}_W(R,P),\hat{\rho}_W(R,P,t)\right\}-\left\{\hat{\rho}_W(R,P,t),\hat{H}_W(R,P)\right\}\right)
\end{aligned}
\tag{95}
$$

其中的对易子可以直接计算，而泊松括号可以用类似上文的方法计算。

对于一般基$|\alpha(R)\rangle$,

$$
\begin{aligned}
&\frac{\partial\rho_W^{\alpha\beta}(R,P,t)}{\partial t} \\
=&\langle\alpha|-\frac{\mathrm{i}}{\hbar}\left[\hat{H}_W,\hat{\rho}_W\right]+\frac{1}{2}\left(\left\{\hat{H}_W,\hat{\rho}_W\right\}-\left\{\hat{\rho}_W,\hat{H}_W\right\}\right)|\beta\rangle && (96)\\
=&\sum_\gamma\left(-\frac{\mathrm{i}}{\hbar}H_W^{\alpha\gamma}\rho_W^{\gamma\beta}+\frac{\mathrm{i}}{\hbar}\rho_W^{\alpha\gamma}H_W^{\gamma\beta}\right)-\frac{1}{2}\sum_\gamma\left(F_W^{\alpha\gamma}\frac{\partial\rho_W^{\gamma\beta}}{\partial P}+\frac{\partial\rho_W^{\alpha\gamma}}{\partial P}F_W^{\gamma\beta}\right) \\
&+\sum_\gamma\left(\frac{P}{M}\rho_W^{\alpha\gamma}d_{\gamma\beta}-\frac{P}{M}d_{\alpha\gamma}\rho_W^{\gamma\beta}\right)-\frac{P}{M}\frac{\partial\rho_W^{\alpha\beta}}{\partial R} && (97)
\end{aligned}
$$

$$
\begin{aligned}
=&-\frac{1}{2}\sum_{\gamma}\left[F_W^{\alpha\gamma}(R)\frac{\partial\rho_W^{\gamma\beta}(R,P,t)}{\partial P}+\frac{\partial\rho_W^{\alpha\gamma}(R,P,t)}{\partial P}F_W^{\gamma\beta}(R)\right]-\frac{P}{M}\frac{\partial\rho_W^{\alpha\beta}(R,P,t)}{\partial R}\\
&+\sum_{\gamma}\rho_W^{\alpha\gamma}(R,P,t)\left[\frac{\mathrm{i}}{\hbar}H_W^{\gamma\beta}(R,P)+\frac{P}{M}d_{\gamma\beta}(R)\right]\\
&-\sum_{\gamma}\left[\frac{\mathrm{i}}{\hbar}H_W^{\alpha\gamma}(R,P)+\frac{P}{M}d_{\alpha\gamma}(R)\right]\rho_W^{\gamma\beta}(R,P,t)
\end{aligned}
\tag{98}
$$

其中$\hat{F}_W=-\frac{\partial\hat{H}_W}{\partial R}$.

对于哈密顿量$H_W^{\alpha\beta}(R,P)=\varepsilon_\alpha(R,P)\delta_{\alpha\beta}$是对角的绝热表象而言，

$$
\begin{aligned}
\frac{\partial\rho_W^{\alpha\beta}(R,P,t)}{\partial t}=&-\left(\frac{\mathrm{i}[\varepsilon_\alpha(R,P)-\varepsilon_\beta(R,P)]}{\hbar}+\frac{P}{M}\frac{\partial}{\partial R}+\frac{F_W^{\alpha\alpha}(R)+F_W^{\beta\beta}(R)}{2}\frac{\partial}{\partial P}\right)\rho_W^{\alpha\beta}\\
&-\sum_{\gamma}d_{\alpha\gamma}(R)\left(\frac{P}{M}+\frac{\varepsilon_\alpha(R,P)-\varepsilon_\gamma(R,P)}{2}\frac{\partial}{\partial P}\right)\rho_W^{\gamma\beta}(R,P,t)\\
&+\sum_{\gamma}d_{\gamma\beta}(R)\left(\frac{P}{M}+\frac{\varepsilon_\beta(R,P)-\varepsilon_\gamma(R,P)}{2}\frac{\partial}{\partial P}\right)\rho_W^{\alpha\gamma}(R,P,t)
\end{aligned}
\tag{99}
$$

对于非绝热耦合$d_{\alpha\beta}(R)=0$始终为零的透热表象而言，

$$
\begin{aligned}
\frac{\partial\rho_W^{\alpha\beta}(R,P,t)}{\partial t}=&-\frac{1}{2}\sum_{\gamma}\left[F_W^{\alpha\gamma}(R)\frac{\partial\rho_W^{\gamma\beta}(R,P,t)}{\partial P}+\frac{\partial\rho_W^{\alpha\gamma}(R,P,t)}{\partial P}F_W^{\gamma\beta}(R)\right]-\frac{P}{M}\frac{\partial\rho_W^{\alpha\beta}(R,P,t)}{\partial R}\\
&+\frac{\mathrm{i}}{\hbar}\sum_{\gamma}\left[\rho_W^{\alpha\gamma}(R,P,t)H_W^{\gamma\beta}(R,P)-H_W^{\alpha\gamma}\rho_W^{\gamma\beta}\right]
\end{aligned}
\tag{100}
$$

对于“力”$F_W^{\alpha\beta}(R)=-\langle\alpha;R|\frac{\partial\hat{H}_W(R,P)}{\partial R}|\beta;R\rangle=f_\alpha(R)\delta_{\alpha\beta}$是对角的力基而言，

$$
\begin{aligned}
\frac{\partial\rho_W^{\alpha\beta}(R,P,t)}{\partial t}=&-\frac{f_\alpha(R)+f_\beta(R)}{2}\frac{\partial\rho_W^{\alpha\beta}(R,P,t)}{\partial P}-\frac{P}{M}\frac{\partial\rho_W^{\alpha\beta}(R,P,t)}{\partial R}\\
&+\sum_{\gamma}\rho_W^{\alpha\gamma}(R,P,t)\left[\frac{\mathrm{i}}{\hbar}H_W^{\gamma\beta}(R,P)+\frac{P}{M}d_{\gamma\beta}(R)\right]\\
&-\sum_{\gamma}\left[\frac{\mathrm{i}}{\hbar}H_W^{\alpha\gamma}(R,P)+\frac{P}{M}d_{\alpha\gamma}(R)\right]\rho_W^{\gamma\beta}(R,P,t)
\end{aligned}
\tag{101}
$$

为了计算对R和对P的导数，我们可以利用类似的格点方法。由于我们只需要处理一阶导，拉格朗日插值就足够处理。因此

$$
\left.\frac{\partial\rho_W^{\alpha\beta}(R,P,t)}{\partial R}\right|_{R_i,P_j,t}=-\sum_{k\neq i}\frac{(-1)^{k-i}}{(k-i)\Delta x}\rho_W^{\alpha\beta}(R_k,P_j,t)
\tag{102}
$$

$$\left.\frac{\partial \rho_W^{\alpha\beta}(R,P,t)}{\partial P}\right|_{R_i,P_j,t} = -\sum_{k\neq i}\frac{(-1)^{k-j}}{(k-j)\Delta p}\rho_W^{\alpha\beta}(R_i,P_k,t) \tag{103}$$

其中$\Delta x = \frac{x_{\max}-x_{\min}}{N}$, $p \in \left[-\frac{\pi\hbar}{\Delta x}, \frac{\pi\hbar}{\Delta x}\right)$，$\Delta p = \frac{\pi\hbar}{N\Delta x} = \frac{\pi\hbar}{x_{\max}-x_{\min}}$。这里的$N$是其中一个方向（$x$或者$p$）上的格点数；换句话说，相空间中共有$N^2$个格点。

基于这些方程，我们可以推导出不同基下的刘维尔超算符的形式，

$$\begin{aligned}
\left.\frac{\partial \rho_W^{\alpha\beta}(R,P,t)}{\partial t}\right|_{R_i,P_j,t} =& -\frac{1}{2}\sum_{\gamma} F_W^{\alpha\gamma}(R_i)\left.\frac{\partial \rho_W^{\gamma\beta}(R,P,t)}{\partial P}\right|_{R_i,P_j,t} \\
&-\frac{1}{2}\sum_{\gamma}\left.\frac{\partial \rho_W^{\alpha\gamma}(R,P,t)}{\partial P}\right|_{R_i,P_j,t} F_W^{\gamma\beta}(R_i) - \frac{P_j}{M}\left.\frac{\partial \rho_W^{\alpha\beta}(R,P,t)}{\partial R}\right|_{R_i,P_j,t} \\
&+\sum_{\gamma}\rho_W^{\alpha\gamma}(R_i,P_j,t)\left[\frac{\mathrm{i}}{\hbar}H_W^{\gamma\beta}(R_i,P_j)+\frac{P_j}{M}d_{\gamma\beta}(R_i)\right] \\
&-\sum_{\gamma}\left[\frac{\mathrm{i}}{\hbar}H_W^{\alpha\gamma}(R_i,P_j)+\frac{P_j}{M}d_{\alpha\gamma}(R_i)\right]\rho_W^{\gamma\beta}(R_i,P_j,t) \qquad (104)\\
=&\sum_{\alpha',j'\neq j}\frac{(-1)^{j'-j}}{2(j'-j)\Delta p}F_W^{\alpha\alpha'}(R_i)\rho_W^{\alpha'\beta}(R_i,P_{j'},t) \\
&+\sum_{\beta',j'\neq j}\frac{(-1)^{j'-j}}{2(j'-j)\Delta p}F_W^{\beta'\beta}(R_i)\rho_W^{\alpha\beta'}(R_i,P_{j'},t) \\
&+\sum_{i'\neq i}\frac{(-1)^{i'-i}P_j}{(i'-i)M\Delta x}\rho_W^{\alpha\beta}(R_{i'},P_j,t) \\
&+\sum_{\beta'}\left[\frac{\mathrm{i}}{\hbar}H_W^{\beta'\beta}(R_i,P_j)+\frac{P_j}{M}d_{\beta'\beta}(R_i)\right]\rho_W^{\alpha\beta'}(R_i,P_j,t) \\
&-\sum_{\alpha'}\left[\frac{\mathrm{i}}{\hbar}H_W^{\alpha\alpha'}(R_i,P_j)+\frac{P_j}{M}d_{\alpha\alpha'}(R_i)\right]\rho_W^{\alpha'\beta}(R_i,P_j,t) \qquad (105)\\
=&-\mathrm{i}\sum_{\alpha'\beta'i'j'}\hat{\mathcal{L}}_{\alpha\beta ij,\alpha'\beta'i'j'}\rho_W^{\alpha'\beta'}(R_{i'},P_{j'},t) \qquad (106)\\
\Rightarrow \hat{\mathcal{L}}_{\alpha\beta ij,\alpha'\beta'i'j'} =& \frac{\mathrm{i}(-1)^{j'-j}}{2(j'-j)\Delta p}[F_W^{\alpha\alpha'}(R_i)\delta_{\beta\beta'}+F_W^{\beta'\beta}(R_i)\delta_{\alpha\alpha'}]\delta_{ii'}(1-\delta_{jj'}) \\
&+\frac{\mathrm{i}(-1)^{i'-i}P_j}{(i'-i)M\Delta x}\delta_{\alpha\alpha'}\delta_{\beta\beta'}(1-\delta_{ii'})\delta_{jj'} \\
&+\frac{1}{\hbar}[H_W^{\alpha\alpha'}(R_i,P_j)\delta_{\beta\beta'}-H_W^{\beta'\beta}(R_i,P_j)\delta_{\alpha\alpha'}]\delta_{ii'}\delta_{jj'} \\
&+\frac{\mathrm{i}P_j}{M}[d_{\beta'\beta}(R_i)\delta_{\alpha\alpha'}-d_{\alpha\alpha'}(R_i)\delta_{\beta\beta'}]\delta_{ii'}\delta_{jj'} \qquad (107)
\end{aligned}$$

可以看出，刘维尔超算符在各个基下都是厄米的。

对于$d_{\alpha\beta}(R)=0$的透热表象，

$$\begin{aligned}\hat{\mathcal{L}}_{\alpha\beta ij,\alpha'\beta'i'j'}=&\frac{\mathrm{i}(-1)^{j'-j}}{2(j'-j)\Delta p}[F_W^{\alpha\alpha'}(R_i)\delta_{\beta\beta'}+F_W^{\beta'\beta}(R_i)\delta_{\alpha\alpha'}]\delta_{ii'}(1-\delta_{jj'})\\&+\frac{\mathrm{i}(-1)^{i'-i}P_j}{(i'-i)M\Delta x}\delta_{\alpha\alpha'}\delta_{\beta\beta'}(1-\delta_{ii'})\delta_{jj'}\\&+\frac{1}{\hbar}[H_W^{\alpha\alpha'}(R_i,P_j)\delta_{\beta\beta'}-H_W^{\beta'\beta}(R_i,P_j)\delta_{\alpha\alpha'}]\delta_{ii'}\delta_{jj'}\end{aligned}\tag{108}$$

对于$H_W^{\alpha\beta}(R,P)=\varepsilon_\alpha(R,P)\delta_{\alpha\beta}$的绝热表象，

$$\begin{aligned}\hat{\mathcal{L}}_{\alpha\beta ij,\alpha'\beta'i'j'}=&\frac{\mathrm{i}(-1)^{j'-j}}{2(j'-j)\Delta p}[F_W^{\alpha\alpha'}(R_i)\delta_{\beta\beta'}+F_W^{\beta'\beta}(R_i)\delta_{\alpha\alpha'}]\delta_{ii'}(1-\delta_{jj'})\\&+\frac{\mathrm{i}(-1)^{i'-i}P_j}{(i'-i)M\Delta x}\delta_{\alpha\alpha'}\delta_{\beta\beta'}(1-\delta_{ii'})\delta_{jj'}\\&+\frac{\varepsilon_\alpha(R_i,P_j)-\varepsilon_\beta(R_i,P_j)}{\hbar}\delta_{\alpha\alpha'}\delta_{\beta\beta'}\delta_{ii'}\delta_{jj'}\\&+\frac{\mathrm{i}P_j}{M}[d_{\beta'\beta}(R_i)\delta_{\alpha\alpha'}-d_{\alpha\alpha'}(R_i)\delta_{\beta\beta'}]\delta_{ii'}\delta_{jj'}\end{aligned}\tag{109}$$

对于$F_W^{\alpha\beta}(R)=f_\alpha(R)\delta_{\alpha\beta}$的力基，

$$\begin{aligned}\hat{\mathcal{L}}_{\alpha\beta ij,\alpha'\beta'i'j'}=&\frac{\mathrm{i}(-1)^{j'-j}}{2(j'-j)\Delta p}[f_\alpha(R_i)+f_\beta(R_i)]\delta_{\alpha\alpha'}\delta_{\beta\beta'}\delta_{ii'}(1-\delta_{jj'})\\&+\frac{\mathrm{i}(-1)^{i'-i}P_j}{(i'-i)M\Delta x}\delta_{\alpha\alpha'}\delta_{\beta\beta'}(1-\delta_{ii'})\delta_{jj'}\\&+\frac{1}{\hbar}[H_W^{\alpha\alpha'}(R_i,P_j)\delta_{\beta\beta'}-H_W^{\beta'\beta}(R_i,P_j)\delta_{\alpha\alpha'}]\delta_{ii'}\delta_{jj'}\\&+\frac{\mathrm{i}P_j}{M}[d_{\beta'\beta}(R_i)\delta_{\alpha\alpha'}-d_{\alpha\alpha'}(R_i)\delta_{\beta\beta'}]\delta_{ii'}\delta_{jj'}\end{aligned}\tag{110}$$

如果要进行基变换的话，假定

$$\hat{\rho}^{\mathrm{adia}}(R,t)=C^\dagger(R)\hat{\rho}^{\mathrm{dia}}(R,t)C(R)\tag{111}$$

在部分维格纳变换下，

$$\hat{\rho}_W^{\mathrm{adia}}(R,P,t)=C^\dagger(R)\hat{\rho}_W^{\mathrm{dia}}(R,P,t)C(R)\tag{112}$$

即

$$(\hat{\rho}_W^{\mathrm{adia}})_{\alpha\beta}(R_i,P_j,t)=\sum_{\alpha',\beta'}C^\dagger_{\alpha\alpha'}(R_i)(\hat{\rho}_W^{\mathrm{dia}})_{\alpha'\beta'}(R_i,P_j,t)C_{\beta'\beta}(R_i)\tag{113}$$

$$
\begin{aligned}
&= \sum_{\alpha',\beta',i',j'} C^{\dagger}_{\alpha\alpha'}(R_i) C_{\beta'\beta}(R_i) \delta_{ii'} \delta_{jj'} (\hat{\rho}^{\text{dia}}_W)_{\alpha'\beta'}(R_{i'}, P_{j'}, t) && (114)\\
&= \sum_{\alpha',\beta',i',j'} \mathcal{C}_{\alpha\beta ij,\alpha'\beta' i'j'} (\hat{\rho}^{\text{dia}}_W)_{\alpha'\beta'}(R_{i'}, P_{j'}, t) && (115)\\
\Rightarrow \hat{\rho}^{\text{adia}}_W &= \mathcal{C} \hat{\rho}^{\text{dia}}_W && (116)
\end{aligned}
$$

其中

$$
\begin{aligned}
\mathcal{C} &= C^{\dagger}_{\alpha\alpha'}(R_i) C_{\beta'\beta}(R_i) \delta_{ii'} \delta_{jj'} && (117)\\
&= C^{*}_{\alpha'\alpha}(R_i) C_{\beta'\beta}(R_i) \delta_{ii'} \delta_{jj'} && (118)
\end{aligned}
$$

一方面

$$
\begin{aligned}
\hat{\rho}^{\text{dia}}_W &= C \hat{\rho}^{\text{adia}}_W C^{\dagger} && (119)\\
\Rightarrow (\hat{\rho}^{\text{dia}}_W)_{\alpha\beta}(R_i, P_j, t) &= \sum_{\alpha',\beta',i',j'} C_{\alpha\alpha'}(R_i) C^{\dagger}_{\beta'\beta}(R_i) \delta_{ii'} \delta_{jj'} (\hat{\rho}^{\text{adia}}_W)_{\alpha'\beta'}(R_{i'}, P_{j'}, t) && (120)\\
\Rightarrow \hat{\rho}^{\text{dia}}_W &= \mathcal{C}' \hat{\rho}^{\text{adia}}_W && (121)
\end{aligned}
$$

其中密度矩阵的基变换

$$
\mathcal{C}' = C_{\alpha\alpha'}(R_i) C^{*}_{\beta\beta'}(R_i) \delta_{ii'} \delta_{jj'} = \mathcal{C}^{\dagger} \tag{122}
$$

与矢量的基变换相同。

然而，用这种方法所构建的刘维尔超算符矩阵太过巨大以至于耗尽了内存，这意味着实际上该方法不可行。因此，我们需要引入特罗特展开。如果我们将其展开为三项，

$$
\hat{\mathcal{L}} = \hat{\mathcal{L}}^Q + \hat{\mathcal{L}}^R + \hat{\mathcal{L}}^P \tag{123}
$$

其中

$$
\begin{aligned}
-\mathrm{i}\hat{\mathcal{L}}^Q \hat{\rho}_W &= -\frac{\mathrm{i}}{\hbar} \left[\hat{H}_W - \frac{\mathrm{i}\hbar P}{M} D, \hat{\rho_W} \right] && (124)\\
-\mathrm{i}\hat{\mathcal{L}}^R \hat{\rho}_W &= -\frac{P}{M} \frac{\partial \hat{\rho}_W}{\partial R} && (125)\\
-\mathrm{i}\hat{\mathcal{L}}^P \hat{\rho}_W &= -\frac{1}{2} \left(\hat{F}_W \frac{\partial \hat{\rho}_W}{\partial P} + \frac{\partial \hat{\rho}_W}{\partial P} \hat{F}_W \right) && (126)
\end{aligned}
$$

那么传播子可以写成

$$
\exp\left(-\mathrm{i}\hat{\mathcal{L}}t\right) = \lim_{t\to 0} \exp\left(-\frac{\mathrm{i}\hat{\mathcal{L}}^Q t}{2}\right) \exp\left(-\frac{\mathrm{i}\hat{\mathcal{L}}^R t}{2}\right) \exp\left(-\mathrm{i}\hat{\mathcal{L}}^P t\right) \exp\left(-\frac{\mathrm{i}\hat{\mathcal{L}}^R t}{2}\right) \exp\left(-\frac{\mathrm{i}\hat{\mathcal{L}}^Q t}{2}\right) \tag{127}
$$

其中

- 对于量子刘维尔$\hat{\mathcal{L}}^Q$，它可以在每个格点上单独进行。由于动能项在部分维格纳变换后成为常数不影响对易子的结果，我们记

$$\hat{V}'(R_i,P_j)=\hat{V}_W(R_i)-\frac{\mathrm{i}\hbar P_j}{M}D(R_i) \tag{128}$$

其中D是非绝热耦合矩阵，故而

$$\exp\left(-\mathrm{i}\hat{\mathcal{L}}^Q t\right)\hat{\rho}_W(R_i,P_j)=\exp\left(-\frac{\mathrm{i}\hat{V}'(R_i,P_j)t}{\hbar}\right)\hat{\rho}_W(R_i,P_j)\exp\left(\frac{\mathrm{i}\hat{V}'(R_i,P_j)t}{\hbar}\right) \tag{129}$$

- 对于经典位置刘维尔$\hat{\mathcal{L}}^R$，它可以在密度矩阵中一个矩阵元的所有相同动量的格点上演化，即分解为密度矩阵的不同矩阵元（相对于势能面而言）和不同的动量。由于，

$$\left.\frac{\partial\rho_W^{\alpha\beta}(R,P_j)}{\partial R}\right|_{R=R_i}=-\sum_{k\neq i}\frac{(-1)^{k-i}}{(k-i)\Delta x}\rho_W^{\alpha\beta}(R_k,P_j)=D_R\rho_W^{\alpha\beta}(\cdot,P_j) \tag{130}$$

其中

$$(D_R)_{ik}=\begin{cases}0, & \text{if}\quad i=k\\ -\frac{(-1)^{k-i}}{(k-i)\Delta x}, & \text{if}\quad i\neq k\end{cases} \tag{131}$$

是不依赖相空间坐标的反厄米矩阵，那么

$$\exp\left(-\mathrm{i}\hat{\mathcal{L}}^R t\right)\rho_W^{\alpha\beta}(\cdot,P_j)=\exp\left(-\frac{P_jD_Rt}{M}\right)\rho_W^{\alpha\beta}(\cdot,P_j)=\exp\left(-\mathrm{i}\frac{-\mathrm{i}P_jD_R}{M}t\right)\rho_W^{\alpha\beta}(\cdot,P_j) \tag{132}$$

- 对于经典动量刘维尔，类似地，

$$\left.\frac{\partial\rho_W^{\alpha\beta}(R_i,P)}{\partial P}\right|_{P=P_j}=-\sum_{k\neq i}\frac{(-1)^{k-j}}{(k-j)\Delta p}\rho_W^{\alpha\beta}(R_i,P_k)=D_P\rho_W^{\alpha\beta}(R_i,\cdot) \tag{133}$$

其中

$$(D_P)_{jk}=\begin{cases}0, & \text{if}\quad j=k\\ -\frac{(-1)^{k-j}}{(k-j)\Delta p}, & \text{if}\quad j\neq k\end{cases} \tag{134}$$

也是不依赖相空间坐标的反厄米矩阵。值得注意的是，除非是在力算符（或者力矩阵$\hat{F}_W$）对角的表象中，否则这个传播子的形式相对前两者而言更加复杂。对于一般的情况，

$$-\mathrm{i}\hat{\mathcal{L}}^P\hat{\rho}_W(R_i,P_j)=-\frac{1}{2}\left[\sum_{\alpha'}F_W^{\alpha\alpha'}(R_i)\frac{\partial\rho_W^{\alpha'\beta}(R_i,P_j)}{\partial P}+\sum_{\beta'}\frac{\partial\rho_W^{\alpha\beta'}(R_i,P_j)}{\partial P}F_W^{\beta'\beta}(R_i)\right] \tag{135}$$

$$
\begin{aligned}
=&\frac{1}{2}\left[\sum_{\alpha',j'\neq j}F_W^{\alpha\alpha'}(R_i)\frac{(-1)^{j'-j}}{(j'-j)\Delta p}\rho_W^{\alpha'\beta}(R_i,P_{j'})\right.\\
&\left.+\sum_{\beta',j'\neq j}\frac{(-1)^{j'-j}}{(j'-j)\Delta p}\rho_W^{\alpha\beta'}(R_i,P_{j'})F_W^{\beta'\beta}(R_i)\right] \qquad (136)\\
=&\sum_{\alpha',\beta',j'}\frac{(-1)^{j'-j}(1-\delta_{jj'})}{2(j'-j)\Delta p}(F_W^{\alpha\alpha'}(R_i)\delta_{\beta\beta'}+F_W^{\beta'\beta}(R_i)\delta_{\alpha\alpha'})\rho_W^{\alpha'\beta'}(R_i,P_{j'}) \qquad (137)
\end{aligned}
$$

这可以导出一个六指标的刘维尔。这个超算符是厄米的，但是仍然过于复杂以至于在实际运算中可能耗尽内存。但是在力基下，传播子变为

$$
\begin{aligned}
\exp\left(-\mathrm{i}\hat{\mathcal{L}}^P t\right)\rho_W^{\alpha\beta}(R_i,\cdot)&=\exp\left(-\frac{[F^d_{\alpha\alpha}(R_i)+F^d_{\beta\beta}(R_i)]D_P t}{2}\right)\rho_W^{\alpha\beta}(R_i,\cdot) \qquad (138)\\
&=\exp\left(-\mathrm{i}\frac{-\mathrm{i}[F^d_{\alpha\alpha}(R_i)+F^d_{\beta\beta}(R_i)]D_P}{2}t\right)\rho_W^{\alpha\beta}(R_i,\cdot) \qquad (139)
\end{aligned}
$$

故而演化可以在力基下的密度矩阵某一矩阵元的某一相同位置的所有不同动量格点上进行。

7 周期性边界条件下的导数

如果边界条件是周期性的，并且我们假定格点区域关于原点对称，即$x_i=i\Delta x,\quad i=0,\pm1,\dots,\pm N$，那么

$$
f(x)=\frac{1}{2N+1}\sum_{k=-N}^{N}c'_k\exp\left(\frac{2k\pi\mathrm{i}}{L}(x+N\Delta x)\right) \qquad (140)
$$

其中

$$
c'_k=\sum_{n=-N}^{N}f_n\exp\left(-\frac{2nk\pi\mathrm{i}}{2N+1}\right) \qquad (141)
$$

这与上文离散傅里叶变换(Discrete Fourier Transformation, DFT)的结果是类似的，此外有$L=(2N+1)\Delta x$。

那么对于一阶导，有

$$
\left.\frac{\mathrm{d}f}{\mathrm{d}x}\right|_{x=x_m}=\frac{1}{2N+1}\sum_{k=-N}^{N}c'_k\left(\frac{2k\pi\mathrm{i}}{L}\right)\exp\left(\frac{2mk\pi\mathrm{i}}{2N+1}\right) \qquad (142)
$$

$$=\frac{2\pi\mathrm{i}}{(2N+1)L}\sum_{k=-N}^{N}\left[\sum_{n=-N}^{N}f_n\exp\left(-\frac{2nk\pi\mathrm{i}}{2N+1}\right)\right]k\exp\left(\frac{2mk\pi\mathrm{i}}{2N+1}\right) \tag{143}$$

$$=\frac{2\pi\mathrm{i}}{(2N+1)L}\sum_{n=-N}^{N}f_n\left[\sum_{k=-N}^{N}\exp\left(-\frac{2nk\pi\mathrm{i}}{2N+1}\right)k\exp\left(\frac{2mk\pi\mathrm{i}}{2N+1}\right)\right] \tag{144}$$

$$=\frac{2\pi\mathrm{i}}{(2N+1)L}\sum_{n=-N}^{N}f_n\left[\sum_{k=-N}^{N}k\exp\left(\frac{2(m-n)k\pi\mathrm{i}}{2N+1}\right)\right] \tag{145}$$

对于内层的求和，当$m\neq n$时，令

$$a=\frac{2(m-n)\pi\mathrm{i}}{2N+1} \tag{146}$$

所以$\exp[(2N+1)a]=1$，则

$$\sum_{k=-N}^{N}k\exp\left(\frac{2(m-n)k\pi\mathrm{i}}{2N+1}\right)=\sum_{k=-N}^{N}k\exp(ak) \tag{147}$$

$$=\frac{\partial}{\partial a}\left[\sum_{k=-N}^{N}\exp(ak)\right] \tag{148}$$

$$=\frac{\partial}{\partial a}\left[\frac{\mathrm{e}^{a(N+1)}-\mathrm{e}^{-aN}}{\mathrm{e}^{a}-1}\right] \tag{149}$$

$$=\frac{[(N+1)\mathrm{e}^{a(N+1)}+N\mathrm{e}^{-aN}](\mathrm{e}^{a}-1)-(\mathrm{e}^{a(N+1)}-\mathrm{e}^{-aN})\mathrm{e}^{a}}{(\mathrm{e}^{a}-1)^2} \tag{150}$$

$$=\frac{(2N+1)\mathrm{e}^{-aN}}{\mathrm{e}^{a}-1} \tag{151}$$

而当$m=n$时，

$$\sum_{k=-N}^{N}k=0 \tag{152}$$

因此，

$$\left.\frac{\mathrm{d}f}{\mathrm{d}x}\right|_{x=x_m}=\frac{2\pi\mathrm{i}}{(2N+1)L}\sum_{\substack{n=-N\\n\neq m}}^{N}f_n\frac{(2N+1)\mathrm{e}^{-aN}}{\mathrm{e}^{a}-1} \tag{153}$$

$$=\frac{\pi}{L}\sum_{\substack{n=-N\\n\neq m}}^{N}f_n\frac{\exp\left[-\frac{2(m-n)\pi\mathrm{i}}{2N+1}\left(N+\frac{1}{2}\right)\right]}{\frac{1}{2\mathrm{i}}\left[\exp\left(\frac{(m-n)\pi\mathrm{i}}{2N+1}\right)-\exp\left(-\frac{(m-n)\pi\mathrm{i}}{2N+1}\right)\right]} \tag{154}$$

$$=\sum_{\substack{n=-N\\n\neq m}}^{N} f_n \frac{(-1)^{m-n}\pi}{L\sin\left(\frac{(m-n)\pi}{2N+1}\right)} \tag{155}$$

$$=\sum_{\substack{n=-N\\n\neq m}}^{N} D_{mn} f_n \tag{156}$$

故而周期性边界条件下的一阶导矩阵元为

$$D_{ij}=\begin{cases}0, \quad \text{if} \quad i=j\\ \frac{(-1)^{i-j}\pi}{L\sin\left(\frac{(i-j)\pi}{2N+1}\right)}, \quad \text{otherwise}\end{cases} \tag{157}$$

可以看出，这个矩阵是反厄米的。

对于二阶导，

$$\left.\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}\right|_{x=x_m} =-\frac{1}{2N+1}\sum_{k=-N}^{N} c'_k \frac{4k^2\pi^2}{L^2}\exp\left(\frac{2mk\pi\mathrm{i}}{2N+1}\right) \tag{158}$$

$$=-\frac{4\pi^2}{(2N+1)L^2}\sum_{k=-N}^{N}\left[\sum_{n=-N}^{N} f_n \exp\left(-\frac{2nk\pi\mathrm{i}}{2N+1}\right)\right]k^2\exp\left(\frac{2mk\pi\mathrm{i}}{2N+1}\right) \tag{159}$$

$$=-\frac{4\pi^2}{(2N+1)L^2}\sum_{n=-N}^{N} f_n\left[\sum_{k=-N}^{N} k^2\exp\left(\frac{2(m-n)k\pi\mathrm{i}}{2N+1}\right)\right] \tag{160}$$

对于内层的求和，当$m\neq n$时，同样令

$$a=\frac{2(m-n)\pi\mathrm{i}}{2N+1} \tag{161}$$

所以$\exp[(2N+1)a]=1$，则

$$\sum_{k=-N}^{N} k^2\exp\left(\frac{2(m-n)k\pi\mathrm{i}}{2N+1}\right)=\frac{\partial^2}{\partial a^2}\left[\frac{\mathrm{e}^{a(N+1)}-\mathrm{e}^{-aN}}{\mathrm{e}^a-1}\right] \tag{162}$$

$$\begin{aligned}=&\frac{\mathrm{e}^{-aN}}{(\mathrm{e}^a-1)^3}[N^2\mathrm{e}^{(2N+3)a}+(1-2N-2N^2)\mathrm{e}^{(2N+2)a}\\&+(N+1)^2\mathrm{e}^{(2N+1)a}-(N+1)^2\mathrm{e}^{2x}+(2N^2+2N-1)\mathrm{e}^{x}-N^2]\end{aligned} \tag{163}$$

$$=-\frac{(2N+1)\mathrm{e}^{-aN}(\mathrm{e}^a+1)}{(\mathrm{e}^a-1)^2} \tag{164}$$

而当$m=n$时，显然有

$$\sum_{k=-N}^{N} k^2 = \frac{N(N+1)(2N+1)}{3} \tag{165}$$

因此，

$$\begin{aligned}
-\frac{\hbar^2}{2m}\left.\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}\right|_{x=x_m} &= -\frac{2\pi^2\hbar^2}{(2N+1)mL^2}\sum_{\substack{n=-N\\ n\neq m}}^{N} f_n \frac{(2N+1)\mathrm{e}^{-aN}(\mathrm{e}^a+1)}{(\mathrm{e}^a-1)^2} \\
&\quad + f_m \frac{2\pi^2\hbar^2}{(2N+1)mL^2}\frac{N(N+1)(2N+1)}{3} && (166) \\
&= \frac{\pi^2\hbar^2}{mL^2}\sum_{\substack{n=-N\\ n\neq m}}^{N} f_n \frac{\exp\left[-\frac{(m-n)(2N+1)\pi\mathrm{i}}{2N+1}\right]\frac{1}{2}\left[\exp\left(\frac{(m-n)\pi\mathrm{i}}{2N+1}\right)+\exp\left(-\frac{(m-n)\pi\mathrm{i}}{2N+1}\right)\right]}{\left(\frac{1}{2\mathrm{i}}\left[\exp\left(\frac{(m-n)\pi\mathrm{i}}{2N+1}\right)-\exp\left(-\frac{(m-n)\pi\mathrm{i}}{2N+1}\right)\right]\right)^2} \\
&\quad + f_m \frac{2N(N+1)\pi^2\hbar^2}{3mL^2} && (167) \\
&= \sum_{n=-N}^{N} f_n \left[\frac{(-1)^{m-n}\pi^2\hbar^2\cos\left(\frac{(m-n)\pi}{2N+1}\right)}{mL^2\sin^2\left(\frac{(m-n)\pi}{2N+1}\right)}(1-\delta_{mn}) + \frac{[(2N+1)^2-1]\pi^2\hbar^2}{6mL^2}\delta_{mn}\right] && (168) \\
&= \sum_{n=-N}^{N} T_{mn} f_n && (169)
\end{aligned}$$

即周期性边界条件下的动能矩阵元为

$$T_{ij} = \frac{\pi^2\hbar^2}{mL^2} \times \begin{cases} \frac{(2N+1)^2-1}{6}, & \text{if} \quad i=j \\ \frac{(-1)^{i-j}\cos\left(\frac{(i-j)\pi}{2N+1}\right)}{\sin^2\left(\frac{(i-j)\pi}{2N+1}\right)}, & \text{otherwise} \end{cases} \tag{170}$$