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，

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

$$-\sum_j \frac{\hbar^2 d_{ij}(R)}{M_b}\frac{\partial\chi_j(R,t)}{\partial R} - \frac{\hbar^2}{2M_b}\frac{\partial^2\chi_i(R,t)}{\partial R^2} \tag{8}$$

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，

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

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，

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

$$-\sum_j \frac{\hbar^2 d_{ij}(R)}{M_b}\frac{\partial\chi_j(R,t)}{\partial R} - \frac{\hbar^2}{2M_b}\frac{\partial^2\chi_i(R,t)}{\partial R^2} \tag{10}$$

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

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

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

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

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

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

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

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

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

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

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

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

且

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

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

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

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

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

$$T_{ij} = -\frac{\hbar^2}{2m}\Delta x \sum_{n=1}^{N-1} \psi_n(x_i)\psi_n''(x_j) \tag{42}$$

$$= \frac{\hbar^2}{2m}\frac{2}{N}\frac{\pi^2}{L^2} \sum_{n=1}^{N-1} n^2 \sin\left(\frac{n\pi i}{N}\right)\sin\left(\frac{n\pi j}{N}\right) \tag{43}$$

$$= \frac{\pi^2\hbar^2}{2NmL^2}\left[\sum_{n=0}^{N-1} n^2 \cos\left(\frac{n\pi(i-j)}{N}\right) - \sum_{n=0}^{N-1} n^2 \cos\left(\frac{n\pi(i+j)}{N}\right)\right] \tag{44}$$

$$= \frac{\pi^2\hbar^2}{4mL^2}\begin{cases} (2N^2+1)/3 - \csc^2\left(i\pi/N\right), & \text{if} \quad i = j \\ \csc^2\left((i-j)\pi/2N\right) - \csc^2\left((i+j)\pi/2N\right), & \text{if} \quad i \neq j \end{cases} \tag{45}$$

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

$$p_{ij} = -\mathrm{i}\hbar\Delta x \sum_{n=1}^{N-1} \psi_n(x_i)\psi_n'(x_j) \tag{48}$$

$$= -\mathrm{i}\hbar\frac{2}{N}\frac{\pi}{L} \sum_{n=1}^{N-1} n \sin\left(\frac{n\pi i}{N}\right)\cos\left(\frac{n\pi j}{N}\right) \tag{49}$$

$$= \frac{\pi\hbar}{\mathrm{i}NL}\left[\sum_{n=1}^{N-1} n \sin\left(\frac{n\pi(i+j)}{N}\right) + \sum_{n=1}^{N-1} n \sin\left(\frac{n\pi(i-j)}{N}\right)\right] \tag{50}$$

$$= \frac{\mathrm{i}\pi\hbar}{2L}\begin{cases} \cot(i\pi/N), & \text{if} \quad i = j \\ \cot((i+j)\pi/2N) + \cot((i-j)\pi/2N), & \text{if} \quad i \neq j \end{cases} \tag{51}$$

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，

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

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

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

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

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

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

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

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

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

或者

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

其中

$$\chi = \begin{bmatrix} \chi_0(R_0) & \chi_0(R_1) & \cdots & \chi_0(R_n) & \chi_1(R_0) & \cdots & \chi_1(R_{N-1}) & \cdots & \chi_{M-1}(R_{N-1}) \end{bmatrix}^T \tag{69}$$

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

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，

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

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

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

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。

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对于非透热表象则无需考虑厄密性，哈密顿量可以写作

$$\sum_{m',n'} H_{mn,m'n'}\chi_{m'n'} = i\hbar \left. \frac{\partial \chi_m(R,t)}{\partial t}\right|_{R=R_n} \tag{75}$$

$$= \sum_{m'} V_{mm'}(R_n)\chi_{m'}(R_n) - \frac{\hbar^2}{2M_b}\sum_{m',k} d_{mk}(R_n)d_{km'}(R_n)\chi_{m'}(R_n)$$

$$- \frac{\hbar^2}{M_b}\sum_{m'} d_{mm'}(R_n)\left.\frac{\partial \chi_{m'}}{\partial R}\right|_{R=R_n} - \frac{\hbar^2}{2M_b}\left.\frac{\partial^2 \chi_{m'}}{\partial R^2}\right|_{R=R_n} \tag{76}$$

$$= \sum_{m'}\left(V_{mm'n} - \frac{\hbar^2}{2M_b}\sum_k d_{mkn}d_{km'n}\right)\chi_{m'n'}\delta_{nn'}$$

$$+ \frac{\hbar^2}{M_b\Delta x}\sum_{m',n'} d_{mm'n}\frac{(-1)^{n+n'}}{n'-n}\chi_{m'n'}(1-\delta_{nn'})$$

$$+ \frac{\hbar^2\delta_{mm'}}{2M_b\Delta x^2}\sum_{m'n'}\left[\frac{\pi^2}{3}\delta_{nn'} + \frac{2(-1)^{n'-n}}{(n'-n)^2}(1-\delta_{nn'})\right]\chi_{m'n'} \tag{77}$$

因此

$$H_{mn,m'n'} = \left(V_{mm'n} - \frac{\hbar^2}{2M_b}\sum_k d_{mkn}d_{km'n}\right)\delta_{nn'} + \frac{(-1)^{n+n'}\hbar^2}{(n'-n)M_b\Delta x}d_{mm'n}(1-\delta_{nn'})$$

$$+ \left[\frac{\pi^2\hbar^2}{6M_b\Delta x^2}\delta_{nn'} + \frac{(-1)^{n'-n}\hbar^2}{M_b(n'-n)^2\Delta x^2}(1-\delta_{nn'})\right]\delta_{mm'} \tag{78}$$

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

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

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

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$f(x_n) = f_n$,

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

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

$$\frac{\mathrm{d}^{2a}f}{\mathrm{d}x^{2a}} = \frac{1}{N}\sum_{0\leqslant k\leqslant\frac{N}{2}} c'_k\left(\frac{2k\pi\mathrm{i}}{L}\right)^{2a}\exp\left(\frac{2k\pi\mathrm{i}}{L}(x-a)\right)$$

$$+ \frac{1}{N}\sum_{\frac{N}{2}<k\leqslant N} c'_k\left(\frac{2(k-N)\pi\mathrm{i}}{L}\right)^{2a}\exp\left(\frac{2k\pi\mathrm{i}}{L}(x-a)\right) \tag{91}$$

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

在格点上则有

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

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

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

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

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$|\alpha(R)\rangle$,

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

$$= -\frac{1}{2}\sum_\gamma \left[F_W^{\alpha\gamma}(R)\frac{\partial \rho_W^{\gamma\beta}(R,P,t)}{\partial P} + \frac{\partial \rho_W^{\alpha\gamma}(R,P,t)}{\partial P}F_W^{\gamma\beta}(R) \right] - \frac{P}{M}\frac{\partial \rho_W^{\alpha\beta}(R,P,t)}{\partial R}$$

$$+ \sum_\gamma \rho_W^{\alpha\gamma}(R,P,t)\left[\frac{\mathrm{i}}{\hbar}H_W^{\gamma\beta}(R,P) + \frac{P}{M}d_{\gamma\beta}(R) \right]$$

$$- \sum_\gamma \left[\frac{\mathrm{i}}{\hbar}H_W^{\alpha\gamma}(R,P) + \frac{P}{M}d_{\alpha\gamma}(R) \right]\rho_W^{\gamma\beta}(R,P,t) \tag{98}$$

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，

$$\frac{\partial \rho_W^{\alpha\beta}(R,P,t)}{\partial t} = -\left(\frac{\mathrm{i}[\varepsilon_\alpha(R,P) - \varepsilon_\beta(R,P)]}{\hbar} + \frac{P}{M}\frac{\partial}{\partial R} + \frac{F_W^{\alpha\alpha}(R) + F_W^{\beta\beta}(R)}{2}\frac{\partial}{\partial P} \right)\rho_W^{\alpha\beta}$$

$$- \sum_\gamma d_{\alpha\gamma}(R)\left(\frac{P}{M} + \frac{\varepsilon_\alpha(R,P) - \varepsilon_\gamma(R,P)}{2}\frac{\partial}{\partial P} \right)\rho_W^{\gamma\beta}(R,P,t)$$

$$+ \sum_\gamma d_{\gamma\beta}(R)\left(\frac{P}{M} + \frac{\varepsilon_\beta(R,P) - \varepsilon_\gamma(R,P)}{2}\frac{\partial}{\partial P} \right)\rho_W^{\alpha\gamma}(R,P,t) \tag{99}$$

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

$$\frac{\partial \rho_W^{\alpha\beta}(R,P,t)}{\partial t} = -\frac{1}{2}\sum_\gamma \left[F_W^{\alpha\gamma}(R)\frac{\partial \rho_W^{\gamma\beta}(R,P,t)}{\partial P} + \frac{\partial \rho_W^{\alpha\gamma}(R,P,t)}{\partial P}F_W^{\gamma\beta}(R) \right] - \frac{P}{M}\frac{\partial \rho_W^{\alpha\beta}(R,P,t)}{\partial R}$$

$$+ \frac{\mathrm{i}}{\hbar}\sum_\gamma \left[\rho_W^{\alpha\gamma}(R,P,t)H_W^{\gamma\beta}(R,P) - H_W^{\alpha\gamma}\rho_W^{\gamma\beta} \right] \tag{100}$$

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，

$$\frac{\partial \rho_W^{\alpha\beta}(R,P,t)}{\partial t} = -\frac{f_\alpha(R) + f_\beta(R)}{2}\frac{\partial \rho_W^{\alpha\beta}(R,P,t)}{\partial P} - \frac{P}{M}\frac{\partial \rho_W^{\alpha\beta}(R,P,t)}{\partial R}$$

$$+ \sum_\gamma \rho_W^{\alpha\gamma}(R,P,t)\left[\frac{\mathrm{i}}{\hbar}H_W^{\gamma\beta}(R,P) + \frac{P}{M}d_{\gamma\beta}(R) \right]$$

$$- \sum_\gamma \left[\frac{\mathrm{i}}{\hbar}H_W^{\alpha\gamma}(R,P) + \frac{P}{M}d_{\alpha\gamma}(R) \right]\rho_W^{\gamma\beta}(R,P,t) \tag{101}$$

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

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

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

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，

$$\left.\frac{\partial \rho_W^{\alpha\beta}(R,P,t)}{\partial t}\right|_{R_i,P_j,t} = -\frac{1}{2}\sum_{\gamma}F_W^{\alpha\gamma}(R_i)\left.\frac{\partial \rho_W^{\gamma\beta}(R,P,t)}{\partial P}\right|_{R_i,P_j,t}$$

$$-\frac{1}{2}\sum_{\gamma}\left.\frac{\partial \rho_W^{\alpha\gamma}(R,P,t)}{\partial P}\right|_{R_i,P_j,t}F_W^{\gamma\beta}(R_i) - \frac{P_j}{M}\left.\frac{\partial \rho_W^{\alpha\beta}(R,P,t)}{\partial R}\right|_{R_i,P_j,t}$$

$$+\sum_{\gamma}\rho_W^{\alpha\gamma}(R_i,P_j,t)\left[\frac{\mathrm{i}}{\hbar}H_W^{\gamma\beta}(R_i,P_j) + \frac{P_j}{M}d_{\gamma\beta}(R_i)\right]$$

$$-\sum_{\gamma}\left[\frac{\mathrm{i}}{\hbar}H_W^{\alpha\gamma}(R_i,P_j) + \frac{P_j}{M}d_{\alpha\gamma}(R_i)\right]\rho_W^{\gamma\beta}(R_i,P_j,t) \tag{104}$$

$$= \sum_{\alpha',j'\neq j}\frac{(-1)^{j'-j}}{2(j'-j)\Delta p}F_W^{\alpha\alpha'}(R_i)\rho_W^{\alpha'\beta}(R_i,P_{j'},t)$$

$$+\sum_{\beta',j'\neq j}\frac{(-1)^{j'-j}}{2(j'-j)\Delta p}F_W^{\beta'\beta}(R_i)\rho_W^{\alpha\beta'}(R_i,P_{j'},t)$$

$$+\sum_{i'\neq i}\frac{(-1)^{i'-i}P_j}{(i'-i)M\Delta x}\rho_W^{\alpha\beta}(R_{i'},P_j,t)$$

$$+\sum_{\beta'}\left[\frac{\mathrm{i}}{\hbar}H_W^{\beta'\beta}(R_i,P_j) + \frac{P_j}{M}d_{\beta'\beta}(R_i)\right]\rho_W^{\alpha\beta'}(R_i,P_j,t)$$

$$-\sum_{\alpha'}\left[\frac{\mathrm{i}}{\hbar}H_W^{\alpha\alpha'}(R_i,P_j) + \frac{P_j}{M}d_{\alpha\alpha'}(R_i)\right]\rho_W^{\alpha'\beta}(R_i,P_j,t) \tag{105}$$

$$= -\mathrm{i}\sum_{\alpha'\beta'i'j'}\hat{\mathcal{L}}_{\alpha\beta ij,\alpha'\beta'i'j'}\rho_W^{\alpha'\beta'}(R_{i'},P_{j'},t) \tag{106}$$

$$\Rightarrow \hat{\mathcal{L}}_{\alpha\beta ij,\alpha'\beta'i'j'} = \frac{\mathrm{i}(-1)^{j'-j}}{2(j'-j)\Delta p}[F_W^{\alpha\alpha'}(R_i)\delta_{\beta\beta'} + F_W^{\beta'\beta}(R_i)\delta_{\alpha\alpha'}]\delta_{ii'}(1-\delta_{jj'})$$

$$+\frac{\mathrm{i}(-1)^{i'-i}P_j}{(i'-i)M\Delta x}\delta_{\alpha\alpha'}\delta_{\beta\beta'}(1-\delta_{ii'})\delta_{jj'}$$

$$+\frac{1}{\hbar}[H_W^{\alpha\alpha'}(R_i,P_j)\delta_{\beta\beta'} - H_W^{\beta'\beta}(R_i,P_j)\delta_{\alpha\alpha'}]\delta_{ii'}\delta_{jj'}$$

$$+\frac{\mathrm{i}P_j}{M}[d_{\beta'\beta}(R_i)\delta_{\alpha\alpha'} - d_{\alpha\alpha'}(R_i)\delta_{\beta\beta'}]\delta_{ii'}\delta_{jj'} \tag{107}$$

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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

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

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$$= \sum_{\alpha',\beta',i',j'} C^{\dagger}_{\alpha\alpha'}(R_i) C_{\beta'\beta}(R_i) \delta_{ii'} \delta_{jj'} (\hat{\rho}^{\text{dia}}_W)_{\alpha'\beta'}(R_{i'}, P_{j'}, t) \tag{114}$$

$$= \sum_{\alpha',\beta',i',j'} \mathcal{C}_{\alpha\beta ij,\alpha'\beta'i'j'} (\hat{\rho}^{\text{dia}}_W)_{\alpha'\beta'}(R_{i'}, P_{j'}, t) \tag{115}$$

$$\Rightarrow \hat{\rho}^{\text{adia}}_W = \mathcal{C} \hat{\rho}^{\text{dia}}_W \tag{116}$$

其中

$$\mathcal{C} = C^{\dagger}_{\alpha\alpha'}(R_i) C_{\beta'\beta}(R_i) \delta_{ii'} \delta_{jj'} \tag{117}$$

$$= C^{*}_{\alpha'\alpha}(R_i) C_{\beta'\beta}(R_i) \delta_{ii'} \delta_{jj'} \tag{118}$$

一方面

$$\hat{\rho}^{\text{dia}}_W = C \hat{\rho}^{\text{adia}}_W C^{\dagger} \tag{119}$$

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

$$\Rightarrow \hat{\rho}^{\text{dia}}_W = \mathcal{C}' \hat{\rho}^{\text{adia}}_W \tag{121}$$

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

$$-\mathrm{i}\hat{\mathcal{L}}^Q \hat{\rho}_W = -\frac{\mathrm{i}}{\hbar} \left[\hat{H}_W - \frac{\mathrm{i}\hbar P}{M} D, \hat{\rho}_W \right] \tag{124}$$

$$-\mathrm{i}\hat{\mathcal{L}}^R \hat{\rho}_W = -\frac{P}{M} \frac{\partial \hat{\rho}_W}{\partial R} \tag{125}$$

$$-\mathrm{i}\hat{\mathcal{L}}^P \hat{\rho}_W = -\frac{1}{2} \left(\hat{F}_W \frac{\partial \hat{\rho}_W}{\partial P} + \frac{\partial \hat{\rho}_W}{\partial P} \hat{F}_W \right) \tag{126}$$

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

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

是不依赖相空间坐标的反厄米矩阵，那么

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

- 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

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

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，

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

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$$= \frac{1}{2} \left[\sum_{\alpha', j' \neq j} F_W^{\alpha\alpha'}(R_i) \frac{(-1)^{j'-j}}{(j'-j)\Delta p} \rho_W^{\alpha'\beta}(R_i, P_{j'}) \right.$$

$$\left. + \sum_{\beta', j' \neq j} \frac{(-1)^{j'-j}}{(j'-j)\Delta p} \rho_W^{\alpha\beta'}(R_i, P_{j'}) F_W^{\beta'\beta}(R_i) \right] \tag{136}$$

$$= \sum_{\alpha', \beta', j'} \frac{(-1)^{j'-j}(1 - \delta_{jj'})}{2(j'-j)\Delta p} (F_W^{\alpha\alpha'}(R_i)\delta_{\beta\beta'} + F_W^{\beta'\beta}(R_i)\delta_{\alpha\alpha'}) \rho_W^{\alpha'\beta'}(R_i, P_{j'}) \tag{137}$$

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

$$\exp\left(-\mathrm{i}\hat{\mathcal{L}}^P t\right) \rho_W^{\alpha\beta}(R_i, \cdot) = \exp\left(-\frac{[F_{\alpha\alpha}^d(R_i) + F_{\beta\beta}^d(R_i)]D_P t}{2}\right) \rho_W^{\alpha\beta}(R_i, \cdot) \tag{138}$$

$$= \exp\left(-\mathrm{i}\frac{-\mathrm{i}[F_{\alpha\alpha}^d(R_i) + F_{\beta\beta}^d(R_i)]D_P}{2} t\right) \rho_W^{\alpha\beta}(R_i, \cdot) \tag{139}$$

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$x_i = i\Delta x$，$i = 0, \pm 1, \ldots, \pm N$，那么

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

其中

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

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$L = 2N\Delta x$。

那么对于一阶导，有

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

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

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

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

对于内层的求和，令

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

所以$\exp[(2N+1)a]=1$，则

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

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

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

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

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

因此，

$$\left.\frac{\mathrm{d}f}{\mathrm{d}x}\right|_{x=x_m}=\frac{2\pi i}{(2N+1)L}\sum_{n=-N}^{N}f_n\frac{(2N+1)e^{-aN}}{e^a-1} \tag{152}$$

$$=\frac{\pi}{L}\sum_{n=-N}^{N}f_n\frac{\exp\left[-\frac{2(m-n)\pi i}{2N+1}\left(N+\frac{1}{2}\right)\right]}{\frac{1}{2i}\left[\exp\left(\frac{(m-n)\pi i}{2N+1}\right)-\exp\left(-\frac{(m-n)\pi i}{2N+1}\right)\right]} \tag{153}$$

$$=\sum_{n=-N}^{N}f_n\frac{(-1)^{m-n}\pi}{L\sin\left(\frac{(m-n)\pi}{2N+1}\right)} \tag{154}$$

$$=\sum_{n=-N}^{N}D_{mn}f_n \tag{155}$$

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故而周期性边界条件下的一阶导矩阵元为

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

(156)

可以看出，这个矩阵是反厄米的。二阶及更高阶导数的推导也是类似的。